

# 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

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**ABSTRACT:** Several polymerizable surfactants (surfmers) have been used in the semi-continuous emulsion copolymerization of styrene, butyl acrylate, and acrylic acid. Three of the (anionic) surfmers (sodium 11-crotonoyl undecan-1-yl sulfate, sodium 11-methacryloyl undecan-1-sulfate, and sodium sulfopropyl tetradecyl maleate) were prepared in house with purities between 53 and 82%. Physicochemical properties such as the critical micelle concentration, the adsorption isotherm, and the specific adsorption area were determined. The surfmers were then used with constant addition profiles in semi-continuous reactions, and the instantaneous conversions of the main monomers determined. The particle size, amount of coagulum, surface tension, and stability against electrolyte solutions of the latices were evaluated. Films were cast of some of the latices, and the visual appearance and water adsorption were assessed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1803–1820, 1997

**Key words:** polymerizable surfactant (surfmer); synthesis; emulsion copolymerization; latex stability; film properties

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## INTRODUCTION

In the process and products of emulsion polymerization, surfactants play a very significant role. They are very important for fast nucleation of latex particles, emulsification of monomer droplets, and stabilization of the latex particles during the polymerization and during the shelf life of the la-

tex. However, when the latex is exploited, for example, in films and coatings, the presence of surfactant can have adverse effects. Once the film has been formed, the surfactant can migrate through it and concentrate in pockets, which increases percolation by water and, in general, increases water sensitivity. The surfactant can also migrate to the surface of the film and affect gloss or other surface properties. It can affect film formation and, once at the surface, it can also leak out, causing environmental problems. Additionally, in the latex production and storage stage, the physically bound surfactant can desorb from the latex particles and, thus, cause destabilization. Also, in polymer recovery via coagulation, the surfactant can have negative effects, for example, in wastewater treatment. An expensive and time-consuming solution to these problems is to opt for the removal of the surfactant after the polymerization by washing with water,<sup>1</sup> but this is obviously not practical. Another solution, and widely applied, involves the use of hydrophilic comonomers, such as (meth)acrylic acid; (meth)acrylamide and derivatives thereof; sulfonated monomers, such as 2-sulfoethyl methacrylate; and styrene sulfonate. However, relatively large amounts of these comonomers are needed to obtain sufficient stabilization effects, and this can lead to a considerable change of the overall polymer properties, although sometimes advantageously. A more promising way forward is the use of reactive surfactants. Applications of these ensures that the surfactant moiety is bound covalently to the polymer material so that desorption from the latex particle surface or migration in the polymer film are impeded. These reactive surfactants can be a combination of a surfactant and an initiator (inisurf),<sup>2,3,4</sup> a combination of a surfactant with a transfer agent (transurf),<sup>5</sup> or a combination of a surfactant and a monomer, referred to as a surfmer.<sup>6</sup> The latter have been described in the literature before as polymerizable surfactants.

With respect to the use of normal surfactants, improvements through the use of surfmers have been obtained in the following areas: mechanical stability of the latex<sup>7</sup>; electrolyte stability of the latex<sup>8</sup>; very high solids contents<sup>9</sup>; control of surface charge density<sup>10</sup>; and in applications in films, which indicated a decrease of surfactant migration<sup>11</sup>; an improvement of water resistance,<sup>12–16</sup> and adhesivity.<sup>13,15,16</sup> Syntheses of surfmers with differing polar head groups and their homopoly-

merization above and below their critical micelle concentration (CMC) have been broadly reported. Examples include anionic surfmers with sulfate or sulfonate head groups,<sup>1,10–12,17–19</sup> cationic surfmers,<sup>20,21</sup> and nonionic surfmers.<sup>13,22</sup> Also, a wide range of reactive groups can be found; for example, allylics,<sup>23,24</sup> acrylamides,<sup>18</sup> (meth)acrylates,<sup>9,22</sup> styrenics,<sup>10,13</sup> and maleates.<sup>19</sup> Surfmers such as these have been studied in homopolymerizations in water above and below their CMC; for overviews, refer to the literature.<sup>25,26</sup> There are also many examples of their use in emulsion copolymerizations (refer to the literature<sup>7,8,10,11,27–30</sup>).

A general requirement for a good surfmer to be applied in emulsion polymerization is a limited solubility in water, expressed in its CMC. If the surfmer has a high water solubility, the partitioning of the surfactant could be shifted too much towards the aqueous phase. On the one hand, this can lead to a decreased stabilization of the polymer particles; and, on the other hand, it could enhance the probability of unfavorable reactions in the aqueous phase, such as polyelectrolyte formation. A low CMC can be obtained by making sure the apolar (alkyl) chain has a sufficient length (say at least C<sub>10</sub>). Furthermore, its polar component should have a relatively large volume and charge; for example, a sulfate or sulfonate group, whose charge is independent of pH in the range of values normally encountered in emulsion polymerization. Naturally, the hydrophilic–hydrophobic balance of the surfmer should provide sufficient stabilization of an oil-in-water emulsion and the resultant polymer latex. In terms of polymerizability, the polymerizable component of the surfmer should allow copolymerization with other (main) monomers. Guillaume et al.<sup>27</sup> has shown that when the surfmer is relatively reactive and can readily homopolymerize, part of the surfmer forms polyelectrolyte in the aqueous phase. Minimalization of the tendency to homopolymerize is therefore advantageous, especially if the CMC has a relatively high value. In addition to the structure of the polymerizable group (acrylate, methacrylate, styrenic, acrylamide, vinyl ester, maleic etc.), its exact location within the molecule could also be a parameter of importance, as was suggested to be the case with a series of cationic maleates, where the maleate group was moved along the alkyl hydrophobe.<sup>31</sup> Another example of this effect can be found in surfmers derived from alkene acids, where allylics react better than 9-alkenes (oleics).<sup>14</sup>

**Table I** Surfmer Name, Code, Chemical Structure, and Origin

Surfmers	Code	Chemical Structure	Origin
Maleate sulfonate	M14	$C_{14}H_{29}OOC-CH=CH-COOC_3-$ $H_6SO_3Na$	This work
Maleate nonionic	MALPEO	$C_{12}H_{25}OOC-CH=CH-COO-$ $(C_2H_4O)_{42}-H$	Hamaide et al. <sup>40</sup>
Crotonate sulfate	CRO	$NaSO_4C_{11}H_{22}OOC-CH=CH(CH_3)$	This work
Methacrylate sulfate	MET	$NaSO_4C_{11}H_{22}OOC-C(CH_3)=CH_2$	This work
Methacrylate nonionic <sup>a</sup>	METPEO	—	Sipomer Bem, Rhône-Poulenc, Bilbao (Spain)
Allyl sulfonate <sup>b</sup>	ALL	$C_{12}H_{25}OOC-CH_2-CH(SO_3Na)-$ $COOCH_2CH=CH_2$	TREM LF-40, Henkel, Barcelona (Spain)
Sodium dodecyl sulfate	SDS	$C_{12}H_{25}SO_4Na$	Texapon 12-96, Henkel

<sup>a</sup> In a solution with 25% water and 25% methacrylic acid. This solution was dried in vacuum before use.

<sup>b</sup> In a 40% aqueous solution, which was dried before use.

Reactive surfactants in general have been the subject of an extensive study undertaken within a network, "Reactive Surfactants in Heterophase Polymerization," sponsored by the European Union (Human Capital and Mobility Programme). Within this network, reactive surfactants have been prepared, analyzed, and used in heterophase polymerizations, and the resulting polymer latices characterized. This article is part of a series,<sup>32-34</sup> in which a limited number of surfmers with strongly varying reactivity in copolymerization have been investigated both with respect to their applicability in a given emulsion copolymerization, as well as with respect to their incorporation mechanism. The results of these two issues have been combined and used to draw more general conclusions regarding the optimal choice of surfmer type for a given comonomer system.<sup>34</sup>

In this article, we present the synthesis and screening of three anionic surfmers, mainly differing in the nature of the polymerizable group. One is an ester of methacrylic acid (sodium 11-methacryloyl undecan-1-sulfate, MET), the second is an ester of crotonic acid (sodium 11-crotonoyl undecan-1-yl sulfate, CRO), and the third is a diester of maleic acid (sodium 3-sulfopropyl tetradecyl maleate, M14). The methacrylic derivative is an example of a very reactive surfmer; the crotonic derivative, an example of a generally nonreactive surfmer. The maleic derivative was chosen for its intermediate reactivity and for the fact that it cannot homopolymerize (in the aqueous phase), a feature all maleic diesters share.<sup>35,36</sup> The maleic acid derivative has been described in literature before,<sup>19,37-39</sup> but its use according to

literature has been limited to low solid content styrene emulsion polymerizations. Kozuka et al.<sup>19</sup> applied this maleate derivative and others in a number of emulsion copolymerizations and generally found a significant decrease of the chemical oxygen demand of the filter water they used to wash the latices and an improvement in properties such as transparency, heat stability, and processing heat flowability. In addition to these surfmers, we have now also used other surfmers for comparison: an allylic sulfonate (commercial, TREM LF-40); and two nonionic surfmers, a poly(ethyleneoxide) maleate (prepared within the context of the network<sup>40</sup>) and a poly(ethyleneoxide) methacrylate (commercial, Sipomer Bem). Sodium dodecyl sulfate (SDS) was used as a reference, nonpolymerizable surfactant. The purity and physicochemical properties of the surfmers have been examined (CMC, adsorption isotherm, and specific adsorption area  $a_s$ ). All the surfmers used in this work are tabulated in Table I.

These surfmers have been used in unseeded high solids emulsion copolymerizations of styrene (S), butyl acrylate (BA), and acrylic acid (AA) with the surfactant concentrations such that the systems would be close to the stability limit, in order to observe a maximum effect. The reactions were analyzed with respect to formation of coagulum, particle size, and evolution of surface tension with overall conversion. In these experiments, also, mixtures of the anionic surfmers with the nonionic surfmers were used. Also, the stability against electrolyte solutions was assessed. With M14, CRO, and SDS, the effect of surfmer on the overall rate of polymerization was checked in

**Table II Molecular Weight, Purity, and Surface Properties of Surfmers**

Surfmer	Molecular Weight (g mol)	Purity (%)	CMC Tensiometry (g L)	$\sigma_{cmc}$ (mN m)	CMC Conductimetry (g L)	$\alpha_s$ (Å <sup>2</sup> )
M14	456	75	0.08	35	0.39 : 0.2 <sup>37</sup>	38
MALPEO	2132	—	0.095	35	—	53 <sup>b</sup>
CRO	358	65	4.9	36	—	—
MET	358	53	2.5	36	—	—
METPEO	1494	—	0.024	43	—	—
ALL	428	—	0.51 <sup>a</sup>	—	—	55 <sup>a,c</sup>
SDS	288	91	1.15	31	—	42

<sup>a</sup> Urquiola.<sup>41</sup><sup>b</sup> Surface area calculated from surface tension air–water surface.<sup>c</sup> Measurement performed with a polystyrene latex.

seeded experiments. From these latices, films were cast and visually inspected. Their water absorption during extended periods of immersion in water was determined.

## EXPERIMENTAL

### Materials

The following chemicals were used. Bromoundecan-1-ol (Aldrich Chem. Co., London, UK), methacrylic acid (Aldrich Chem. Co.), 2,6-di-*t*-butyl-4-methyl phenol (Aldrich Chem. Co.), *n*-tetrabutylammonium bromide (Aldrich Chem. Co.), magnesium sulfate (Aldrich Chem. Co.), crotonic acid (B.D.H., London, UK), sodium carbonate (B.D.H.), sodium hydroxide (B.D.H.), and chlorosulfonic acid (B.D.H.) were used as supplied. Styrene (S) and butyl acrylate (BA) were distilled before use and stored at  $-18^{\circ}\text{C}$ . Acrylic acid (AA, with 10 ppm *p*-methoxyphenol), potassium persulfate (KPS, Fluka, Madrid, Spain, 99%),  $\alpha,\alpha'$ -azobisisobutyronitril (AIBN, Fluka), sodium bicarbonate (99.5%, Merck, Bilbao, Spain), sodium

dodecyl sulfate (SDS), sodium chloride (99.5%, Panreac, Barcelona, Spain), and calcium chloride (Panreac, 98%) were used as received. SDS was applied as a reference surfactant (also see Results and Discussion section). Other reagents and solvents were general purpose species and were used as supplied, unless otherwise specified. Details of the surfmers (molecular weight, purity, physicochemical properties, and reactivity in copolymerization) are given in Tables II and III. Where the reactivity ratios of the surfmers themselves have not been determined, a corresponding monomer has been taken.

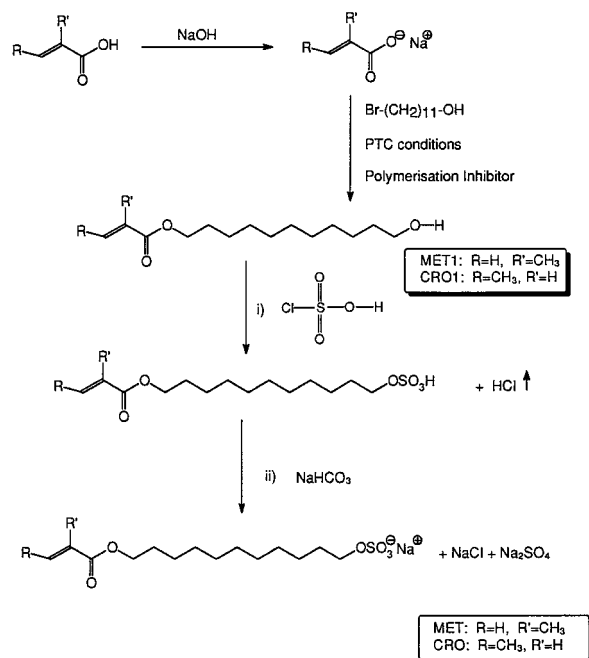
### Synthesis of Sodium 11-Methacryloyloxy Undecan-1-yl Sulfate (MET) and Sodium 11-Crotonoyloxy Undecan-1-yl Sulfate (CRO)

Both surfmers were synthesized according to reaction Scheme 1. The procedure is exemplified by the synthesis of MET surfmer. CRO surfmer was produced starting from crotonic acid. <sup>1</sup>H-NMR assignments are summarized in Table IV and microanalytical data in Table V. <sup>1</sup>H-NMR spectra were

**Table III Reactivity Ratios of Surfmers (or Corresponding Monomers) with Main Monomers**

Surfmer or Equivalent Monomer	Styrene ( $r_s, r_{\text{surfmer}}$ )	Butyl Acrylate ( $r_{\text{BA}}, r_{\text{surfmer}}$ )	Methyl Methacrylate ( $r_{\text{MMA}}, r_{\text{surfmer}}$ )
Diethyl maleate (M14)	8–10, 0 <sup>42-A</sup>	—	354, 0 <sup>43</sup>
Methyl crotonate (CRO)	26, 0.01 <sup>44</sup>	—	—
Dodecyl–methyl methacrylate (MET)	0.53, 0.30 <sup>42-B</sup>	0.32, 2.6 <sup>45</sup>	—
Allyl sulfonate (ALL)	13, 0.5 <sup>41</sup>	9, 0.37 <sup>41</sup>	—

42-A: N. Toyoda, M. Yoshida, and T. Otsu, *Polym. J.* (Tokyo) **15**, 225 (1983).42-B: T. Otsu, T. Ito, and M. Isoto, *Kogyo Kagaku Zasshi*, **69**, 986 (1966).



**Scheme 1** Synthesis of MET and CRO.

obtained on a Bruker AMX250 instrument. Elemental microanalyses were performed on a Perkin–Elmer Series II Elemental Analyser. Melting points were recorded using a Gallenkamp Digital Melting Point Apparatus.

#### Sodium Methacrylate Salt (1)

Sodium hydroxide (27.6 g, 0.69 mol) dissolved in deionized water was placed in a round-bottomed

flask and kept in an ice bath for 10 minutes. Methacrylic acid (59.75 g, 0.69 mol) was added dropwise under stirring to the above solution. After 30 minutes, the reaction mixture was freeze-dried. The product was then dissolved in methanol and precipitated with diethyl ether. After filtering, a white powder (71.14 g, 0.65 mol) was obtained in 95% yield.

#### Preparation of 11-methacryloyloxy undecan-1-ol (MET1)

Sodium methacrylate (70 g, 0.65 mol), 11-bromoundecan-1-ol (36.95 g, 0.148 mol), *n*-tetrabutylammonium bromide (13.86 g, 0.04 mol), 2,6-di-*t*-butyl-4-methyl phenol (75 mg, 0.34 mmol) dissolved in deionized water (130 mL) and chloroform (70 mL) were placed in a round-bottomed flask. The reaction vessel was placed in an oil bath at 100°C, and vigorous magnetic stirring was applied for three days. After that time, the chloroform layer was washed with 2% sodium hydroxide solution (4 × 250 mL) and distilled water (4 × 250 mL). The organic layer was dried over magnesium sulfate, and the solvent evaporated. A yellowish viscous liquid (29.42 g, 0.11 mol) was obtained. The latter was distilled in a Kugelrohr under vacuum (0.01 mm Hg) at 190°C, yielding a viscous clear liquid (23.63 g, 0.09 mol) in 62% yield.

#### Synthesis of Sodium 11-methacryloyloxy undecan-1-yl sulfate (MET)

Chlorosulfonic acid (8.65 g, 0.074 mol) was placed in a three-necked round bottom flask, which was

**Table IV** <sup>1</sup>H-NMR Assignments for MET and CRO Surfmers

Compound	<sup>1</sup> H-NMR Resonances
Sodium methacrylate salt	(D <sub>2</sub> O) <i>d</i> = 1.8 (s, 3H, CH <sub>3</sub> —), 5.3 (s, 1H, —CH <sub>trans</sub> —), 5.6 (m, 1H, —CH <sub>cis</sub> —).
Sodium crotonate salt	(D <sub>2</sub> O) <i>d</i> = 1.7 ( <i>d</i> , 3H, CH <sub>3</sub> —), 5.75 ( <i>d</i> , 1H, =CH—CO <sub>2</sub> ), 6.6 (m, 1H, C(CH <sub>3</sub> )H=CH—).
11-Methacryloyloxy undecan-1-ol (MET1)	(CDCl <sub>3</sub> ) <i>d</i> = 1.18–1.76 (m, 18H, —CH <sub>2</sub> —), 1.93 (s, 3H, CH <sub>3</sub> —), 3.65 ( <i>t</i> , 2H, —CH <sub>2</sub> —OH), 4.1 ( <i>t</i> , 2H, —COOCH <sub>2</sub> —), 5.54 (s, 1H, —CH <sub>trans</sub> —), 6.2 (m, 1H, H—CH <sub>cis</sub> —).
11-Crotonoyloxy undecan-1-ol (CRO1)	(CDCl <sub>3</sub> ) <i>d</i> = 1.18–1.76 (m, 18H, —CH <sub>2</sub> —), 1.83 ( <i>d</i> , 3H, CH <sub>3</sub> —), 3.65 ( <i>t</i> , 2H, CH <sub>2</sub> —OH), 4.11 ( <i>t</i> , 2H, —COOCH <sub>2</sub> —), 5.88 ( <i>d</i> , 1H, CH=CHCO <sub>2</sub> ), 7.01 (m, 1H, —CH=CH—).
Sodium 11-methacryloyloxy undecan-1-yl sulfate (MET)	(CDCl <sub>3</sub> ) <i>d</i> = 1.18–1.76 (m, 18H, —CH <sub>2</sub> —), 1.96 (s, 3H, CH <sub>3</sub> —), 3.98 ( <i>t</i> , 2H, —CH <sub>2</sub> —OSO <sub>3</sub> <sup>−</sup> ), 4.10 ( <i>t</i> , 2H, —COOCH <sub>2</sub> —), 5.66 (m, 1H, —CH <sub>trans</sub> —), 6.2 (m, 1H, —CH <sub>cis</sub> —).
Sodium 11-crotonoyloxy undecan-1-yl sulfate (CRO)	(CDCl <sub>3</sub> ) <i>d</i> = 1.18–1.76 (m, 18H, —CH <sub>2</sub> —), 1.96 (s, 3H, CH <sub>3</sub> —), 3.98 ( <i>t</i> , 2H, —CH <sub>2</sub> —OSO <sub>3</sub> <sup>−</sup> ), 4.10 ( <i>t</i> , 2H, —COO—CH <sub>2</sub> —), 5.88 ( <i>d</i> , 1H, —CH=CH <sub>2</sub> CO—), 7.01 (m, 1H, —CH=CH—).

**Table V** Microanalytical Data for MET and CRO Surfmers

Compound	Microanalytical Data	
	Calculated (%)	Found (%)
Sodium methacrylate salt	C, 44.4; H, 4.7	C, 44.3; H, 4.9
Sodium cotonate salt	C, 44.4, H, 4.7	C, 44.3, H, 4.3
11-Methacryloyl undecan-1-ol (MET1)	C, 70.2; H, 11	C, 69.4; H, 10.9
11-Crotonoyl undecan-1-ol (CRO1)	C, 70.2; H, 11	C, 69.7, H, 11.2
Sodium 11-methacryloyl undecan-1-yl sulfate (MET)	C, 50.2, H, 7.6, S, 8.9	C, 31.6; H, 3.7, S, 7.6 Cl 0.65
Sodium 11-crotonoyl undecan-1-yl sulfate (CRO)	C, 50.2, H, 7.6, S, 8.9	C, 34.8, H, 5.8, S, 6.2

fitted with a mechanical stirrer, a dropping funnel, and a nitrogen inlet. 11-Methacryloyloxy undecan-1-ol (MET1) (19 g, 0.074 mol) was added dropwise over one hour with vigorous stirring. The reaction mixture was then stirred for two hours and purged with nitrogen for two hours more. The mixture at this point was a brown viscous liquid, which was added dropwise to a saturated sodium hydrogen carbonate ice solution (20 mL) with vigorous stirring. During the addition process, the mixture was kept basic by adding the sodium hydrogen carbonate, as required. Isopropanol (56 mL) and water (90 mL) were then added. A white precipitate appeared, which was filtered off, and the filtrate washed with petroleum ether of 40–60°C (2 × 40 mL). The sample was freeze-dried, yielding a light yellow solid (35 g), in 130% yield. This means that a relatively low purity surfmer (53%; see below and Table II) was obtained.

### Emulsion Polymerizations

The surfmers have been applied first in a series of *ab initio* (nonseeded) reactions. In a second series, seeded experiments were carried out to ensure similar particle sizes and particle surface areas so that the effect of the surfmer on stability and film properties can be properly examined relative to other surfmers and the reference surfactant SDS. The recipes for the nonseeded reactions are given in Table VI. For the second series, a seed latex was prepared (Table VII), and the recipe for the seeded reactions is given in Table VIII. In this series, only M14, CRO, and SDS have been used as surfactants. The amount of SDS introduced via the seed latex in the seeded reaction constitutes 2.5% of the total amount of emulsifier, which is

considered not to be significant because it represents 0.35 g L of water in the final latex, which, without considering any adsorption on the latex particles, is well below the CMC (1.15 g L; see Table II). The reactions were carried out in glass reactors with a water jacket for temperature control. A heat exchanger fed with tap water was placed between the reactor and the water bath to control any sudden heat production and to keep the reactor at the set temperature (80°C). In the nonseeded reactions, the charge was reacted for 30 minutes before the feeding was started. Two separate feeds were used: one with the neat monomers; the second an aqueous feed with initiator, buffer, and surfactant. The feed flow rates were computer-controlled using an algorithm of proportional integral control. The pumps (Pro-Minent Gamma/4-RS, feed range 0.1–50 mL min) pumped the two feed streams from bottles (placed on balances, Sartorius Universal U 4100 S, ±0.01 g), whose decrease in weight was monitored online by the computer. After the feeding period (four hours), the systems were left to react further for another one to two hours.

### Analysis of Emulsion Polymerizations, Coagulum Formation, Latex Stability, and Film Properties

During the reactions, samples were taken to determine the conversion of the main monomers, the residual monomer composition, particle size, and surface tension of the latex. The conversion of the main monomers was determined with gravimetry. This results in values for the fractional weight-average conversion (weight of polymer formed divided by weight of monomers added until that time), which will be referred to as fractional conversion. Gas chromatography (Shimadzu GC 14-

**Table VI Recipe for Nonseeded, Semicontinuous Reactions at 80°C with 50% Solids**

Compound	Initial Charge (g)	Feed (g)	Partitioning Charge to Feed	Total (g)
S	14.85	133.65	10/90	148.5
BA	14.85	133.65	10/90	148.5
AA	0.3	2.7	10/90	3.0
KPS <sup>a</sup>	0.225 : 0.45	0.225/0	50/50, 100/0	0.45
NaHCO <sub>3</sub>	0.225 : 0.45	0.225/0	50/50, 100/0	0.45
H <sub>2</sub> O	195	105	65/35	300
Surfmer <sup>b,c</sup>	0.9	2.1	30/70	3.0

<sup>a</sup> In some cases, all the initiator and buffer were in the initial charge; while in the other, half were in the initial charge, and half were fed.

<sup>b</sup> For those surfmers for which a purity is given in Table II, this amount refers to pure surfmer.

<sup>c</sup> With M14, 6.0 and 15.0 g of total surfactant were also used.

A, column: SGE-25QC5/BP20 110) was used to determine the ratio of residual S and BA, from which, in combination with the conversion data, the copolymer composition can be calculated. Particle size was determined with light scattering (LS) with a Malvern System 4700c. This technique gives a *z*-average particle size [ $d_z = \Sigma(n_i d_i^5) / \Sigma(n_i d_i^4)$ ]. In some cases, transmission electron microscopy (TEM) was used. TEM was performed with an Hitachi H-7000 FA. The samples were treated beforehand by drying the latex under ultraviolet (UV) light in order to crosslink the polymer (by way of the acrylate units) and by negative staining with phosphotungstic acid. Counting 800–1000 particles afforded the particle size distribution and the polydispersity (ratio of weight-average diameter and number-average diameter). Surface tension was measured with a programmable tensiometer KSV Sigma 70 with a du Nouy ring at 22°C.

The amount of coagulum was measured by collecting coagulum on reactor wall and stirrer, and

by filtering the latex (mesh 63). It is presented as weight of coagulum per total weight of monomer added. The latex stability against electrolytes was determined by adding 10 mL of an electrolyte solution to 10 g of latex. After 24 hours, the particle size was measured again with LS; and the amount of coagulum, if any, was weighed. Films were prepared from some of the latices by casting on a glass plate with a rubber rim, giving a film of 140 × 70 × 2–3 mm<sup>3</sup>. The latex was left to dry at 35°C for five days under a cover that allowed gentle ventilation. The water sensitivity of the films was determined by submerging a piece of the film in water (1 g in 50 g of water) and determining the relative weight increase.

## RESULTS AND DISCUSSION

### Synthesis of MET, CRO, and M14

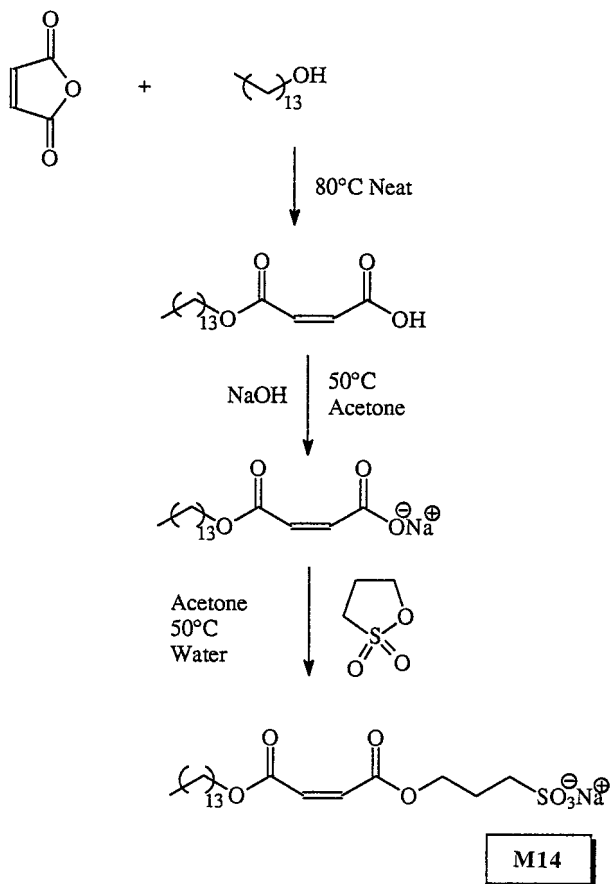
Three different anionic surfmers were synthesized with polymerizable groups of different reactivity,

**Table VII Recipe for Seed Latex Prepared in Batch Mode at 80–90°C**

Compound	Charge (g)
S	30
BA	30
AA	—
KPS	6.69
NaHCO <sub>3</sub>	2.32
H <sub>2</sub> O	1940
SDS	2.33

**Table VIII Recipe for Seeded, Semicontinuous Reactions at 80°C with 55% Solids Content**

Compounds	Initial Charge (g)	Feed (g)	Total (g)
S	—	146.25	148.5
BA	—	146.25	148.5
AA	—	3.0	3.0
KPS	0.225	0.225	0.45
NaHCO <sub>3</sub>	0.225	0.225	0.45
H <sub>2</sub> O	—	111	255
Surfactant	—	6	6
SDS	—	—	0.18
Seed latex	150	—	—



**Scheme 2** Synthesis of M14.

i.e., a maleate sulfonate (M14), a methacrylate sulfonate (MET), and a crotonate sulfonate (CRO).

The more convenient approach to the synthesis of a polymerizable surface-active molecule is to attach the polymerizable group to the hydrophobic tail in a first step, leaving the insertion of the head group to the end of the reaction sequence. In this manner, working with intermediates, which are surface-active, is avoided; thus, problems with isolation and purification are minimized. Another important consideration in the design of the synthesis of a surfmer is the mildness of the various steps in order to avoid spontaneous polymerization.

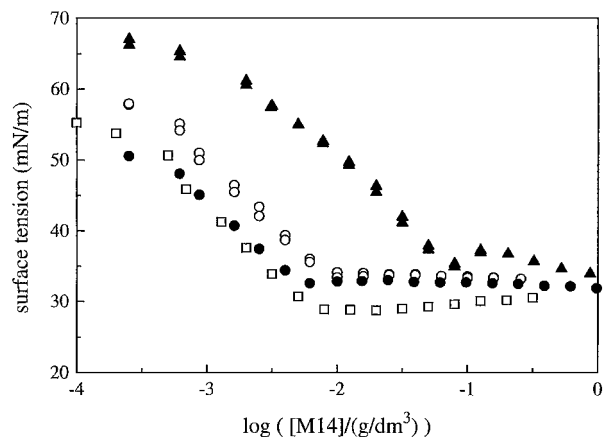
Sulfate surfmers (MET and CRO) were synthesized following reaction Scheme 1. Firstly, the hydrophobic tail and the polymerizable function were attached via a phase-transfer-catalyzed reaction.<sup>46</sup> The sodium salt of the corresponding carboxylic acid, methacrylic acid, or crotonic acid was used to displace the bromide ion from 11-bromoundecan-1-ol to yield the methacryloyl or croto-

noyl alkyl alcohol (MET1, CRO1). A polymerization inhibitor was added in order to avoid polymerization during this step and was removed in the work-up. Pure alkyl alcohol monomers were obtained after vacuum distillation.

The sulfation reaction is the crucial step in the synthesis. The sulfation of these reactive alcohols is based on a BP patent<sup>47</sup> using chlorosulfonic acid as sulfating agent. The methacrylic or crotonic alkyl alcohol was added to neat chlorosulfonic acid, in excess, maintained below 5°C. The addition of alcohol was carried out under vigorous stirring to allow the diffusion of hydrochloric acid that was formed. However, the system inevitably became highly viscous. The reaction was quenched with sodium carbonate in order to obtain the desired sodium salt (MET, CRO); and, in addition, inorganic salts were produced, arising from the neutralization of hydrochloric acid and the excess of chlorosulfonic acid. Although the <sup>1</sup>H-NMR spectra of the products (Table IV) confirmed that the monomers were successfully sulfated, the corresponding microanalytical data were very poor, as shown in Table V. The presence of chloride and the low carbon content confirms the contamination by inorganic salts. Typical mild methods of purification of organic sulfates were used; however, the purity of the organic products was not improved significantly. Since it is well known that commercially produced surface active species are often contaminated with inorganic salts to varying extent, and since the final aim of this work was to screen surfmers in emulsion polymerization, the synthesized surfmers were used in polymerizations despite the salt contamination. Their purity was measured using a two-phase titration method<sup>48,49</sup> and is indicated in Table II.

The maleate sulfonate (M14) was synthesized following the procedure reported before.<sup>19,37,39</sup> The synthesis was carried out in three steps, as shown in Scheme 2. Firstly, the maleic anhydride was opened with tetradecyl alcohol to give maleic acid *n*-tetradecyl monoester. Then, the sodium salt of this acid was produced by neutralization with sodium hydroxide and was then reacted with propanesultone to yield the desired surfmer. When this last step was performed in pure acetone, as reported by Kozuka et al.,<sup>19</sup> the yield was only ~ 30%. However, Goebel et al.<sup>37,39</sup> found that the presence of water during the reaction considerably enhanced the yield. Both <sup>1</sup>H- and <sup>13</sup>C-NMR spectra show small shoulders on the main peaks as a result of some hydrolysis of the esters.





**Figure 1** Surface tension versus M14 concentration in various aqueous solutions at 22°C: ( $\blacktriangle$ ) pure water (replicate runs); ( $\circ$ ) 0.15%  $\text{Na}_2\text{S}_2\text{O}_8$  + 0.15%  $\text{NaHCO}_3$  (replicate runs); ( $\bullet$ ) 0.30%  $\text{Na}_2\text{S}_2\text{O}_8$  + 0.30%  $\text{NaHCO}_3$ ; ( $\square$ ) 0.15%  $\text{Na}_2\text{S}_2\text{O}_8$  + 0.15%  $\text{NaHCO}_3$  + 1.0% acrylic acid.

### Purity and Physicochemical Properties of the Surfmers

All the surfmers used in this work are tabulated in Table I. The purity of some of the surfactants was assessed using a two-phase titration procedure (see Table II). This is a method with which anionic surface-active species can be titrated in a two-phase medium of water and  $\text{CHCl}_3$ . Although the use of this method requires calibration, the deviations at higher concentrations are normally within 5%. At low concentrations of the sample surfactant, the deviations are very large, and calibration is absolutely necessary.<sup>32</sup> As can be seen, the purity of CRO and MET is not very high (the impurities are mainly  $\text{NaCl}$  and undecylenic alcohol), and this may affect the surface properties.

One of the physicochemical properties that has been determined is the critical micelle concentration, CMC. At the CMC, several properties of the aqueous surfactant solution show a discontinuity, for example, surface tension, conductivity (in case of ionic surfactants), density, and turbidity. We have chosen to monitor surface tension as a function of surfactant concentration in order to determine the CMC. The measurements were performed with a programmable tensiometer KSV Sigma 70 with a du Nouy ring. All measurements were carried out at 22°C. Figure 1 shows the surface tension of M14 as a function of surfactant concentration. At low surfactant concentration, the surface tension decreases with increasing con-

centration. The break of the curve is indicative of the CMC; above this concentration, the surface tension remains constant. One can see that addition of salts (in this case, the initiator and buffer in quantities corresponding to the basic emulsion polymerization recipe; see below) and acrylic acid decreases the CMC by one order of magnitude as a result of decreased repulsion between the anionic head groups. The CMC of each surfactant is given in Table II. The CMC of M14 is relatively low compared with CRO, MET, and SDS. This is due to its longer apolar tail, which is a tetradecyl chain. The nonionic surfactants also show a low CMC, and this is due to the absence of electrostatic repulsion between the polar groups in the micelle.

When a surfmer is used in emulsion polymerization for stabilization of a latex, most surfactant should adsorb onto the surface of the latex particles. This is partly determined by the CMC; in general, the higher the CMC, the more surfactant will be dissolved in the bulk aqueous phase. The distribution of the surfmer between the surface of the polymer particles, the aqueous phase, and the micelles is partly determined by the CMC. The lower the CMC, the lower the amount of surfmer in the aqueous phase; hence, the less likely its polymerization in the continuous phase. On the other hand, there is not a general rule for the effect of the CMC on the competition between adsorption and micellization. Thus, in ionic surfactants, an increase of the length of the alkyl chain of the hydrophobic group decreases the CMC, and the adsorption is facilitated slightly more than micellization; whereas an increase of branching gives a higher CMC, and adsorption is also facilitated more than micellization.<sup>50</sup> In many semicontinuous emulsion polymerizations, once the polymer particles are present in the reactor (either formed by polymerization of the initial charge or because they were added as a seed), the process is conducted without micelles to avoid secondary nucleations. Under these conditions, low CMC values increase the ratio of the surfmer adsorbed to the surfmer in the aqueous phase. The equilibrium between surface and bulk is also determined by specific interactions between the surfactant and the latex particle surface. If the driving force for adsorption is strong, as for a nonionic surfactant on a totally hydrophobic particle surface, a surface monolayer will form already at concentrations below the CMC. If, on the other hand, there is electrostatic repulsion between the surface and

the surfactant head-groups, the surface will not be covered by surfactant molecules at the CMC. The amount of surfactant adsorbed at the particle surface will continue to increase also far beyond the CMC.

The adsorbed amount of an emulsifier on the surface of a latex particle as a function of the equilibrium concentration in the aqueous phase is called adsorption isotherm. The maximum amount of surfmer that can be adsorbed onto a given surface area corresponds to the specific area ( $a_s$ ) of the surfmer, assuming a monolayer adsorption. This value can be determined using a cleaned latex sample with a known total surface area. If the surface tension of the latex is measured as a function of the total amount of added surfmer, and the same is done for a solution without the latex particles present, the amount of surfmer adsorbed can be calculated assuming that equal surface tensions correspond to equal surfmer concentrations in the aqueous phase. An example of this experiment is given in Figure 2(a), where the surface tension is plotted versus the total concentration of M14 in the presence and absence of a S-BA-AA latex prepared with SDS (the SDS has been removed by washing the latex); the corresponding adsorption isotherm is given in Figure 2(b). It can be seen that the adsorption isotherm is not linear. The initial part of the curve is steeper, indicating a driving force of adsorption. It was assumed that this isotherm was of the Langmuir-type, as follows:

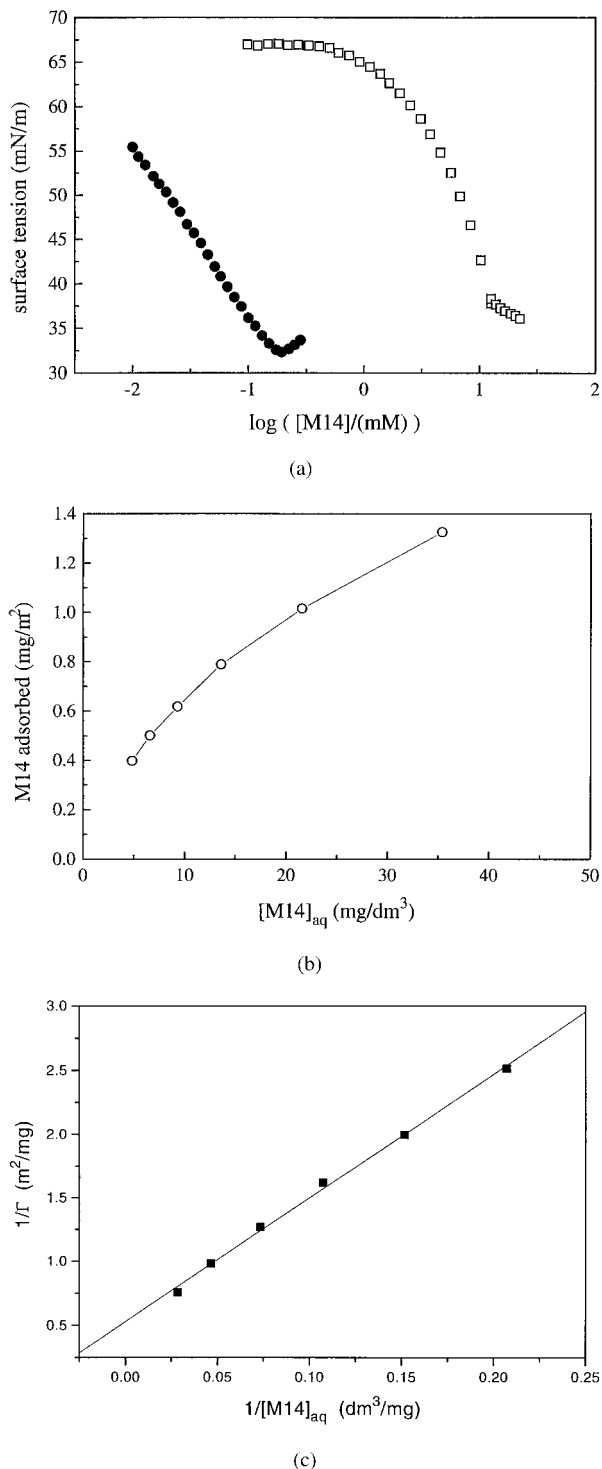
$$\Gamma = \frac{\Gamma_m [E]_{\text{aq}}}{k + [E]_{\text{aq}}} \quad (1)$$

where  $\Gamma$  is the surface concentration of the surfmer in equilibrium with an aqueous solution of surfmer of concentration  $[E]_{\text{aq}}$ ;  $\Gamma_m$  is the surface concentration of the surfactant at monolayer adsorption; and  $k$  a constant.

Equation (1) can be rearranged as follows:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{k}{\Gamma_m} \frac{1}{[E]_{\text{aq}}} \quad (2)$$

If the surfmer adsorption follows the Langmuir equation, a plot of  $1/\Gamma$  versus  $1/[E]_{\text{aq}}$  should be a straight line with slope  $k/\Gamma_m$  and intercept equal to  $1/\Gamma_m$ . Figure 2(c) shows that this is the case. From the intercept, the value of  $a_s$  is calculated (see Table II). No value is given for MET due to



**Figure 2** (a) Surface tension versus overall M14 concentration in pure water ( $\bullet$ ), and in the presence of a S-BA-AA latex prepared with SDS ( $\square$ ). (b) Adsorption isotherm of M14 calculated from data of Figure 2(a). (c) Inverse of the surface concentration of M14 versus inverse of M14 concentration in the aqueous phase, calculated from data in Figure 2(b).

the low purity of this surfactant. Also, for the CRO surfactant, no  $\alpha_s$  value is given. This is due to the fact that at higher concentration, crystals started to precipitate out of the CRO solution, a fact which makes the surface tension versus concentration plot unreliable.

### High Solids Content Emulsion Polymerizations

With the surfmers reported in the previous sections, a series of emulsion copolymerizations of S, BA, and AA were carried out. The main objective was to assess whether the surfmers that were prepared in this work (M14, CRO, and MET) could be used in emulsion polymerizations under industrial conditions (semicontinuous, high solids content, high temperature), what the effect of different kinds of polymerizable groups is, whether the kinetics of the copolymerization would be affected or not by the presence of a copolymerizable surfactant, and whether there would be an improvement in latex or film properties. Also, the effect of using mixtures of anionic surfmers with nonionic surfmers was investigated. To do so, the reactions were carried out with only 1 wt % of surfmer so that the latex system would be in the stability limit. This enables a better comparison of the surfmer performance. A standard recipe, commonly used in industrial applications in coatings, was chosen. It involves the emulsion copolymerization of styrene (S), butyl acrylate (BA), and acrylic acid (AA) with a weight ratio of 49.5 : 49.5 : 1. At this composition, the terpolymer has a  $T_g$  of about 2°C. This enables films to be made from the latices

to study the film properties. In this basic recipe (which can be seeded or nonseeded), the main monomers (S, B, AA) are added at a constant, low flow rate to ensure a homogeneous copolymer composition. The solid content is such (50–55%) that it can be compared to industrial conditions. The initiator concentration that is applied is such that the rate of polymerization ensures a fractional conversion of about 80%. The adequate amount of initiator was determined by trial and error.

The intrinsic reactivity of the polymerizable groups in the surfmers can provide a basic idea about the suitability of the surfmer. For example, the surfmer has to copolymerize, and so the reactivity ratio between the main monomers and the surfmer ( $r_{\text{monomer}}$ ) should not be too large. In Table III, the reactivity ratios between some common monomers and the surfmers are given. One can see that on the basis of reactivity with S, the MET surfmer can be expected to be the most reactive, and the CRO surfmer the least reactive. Also, the range of reactivities is quite broad. In the following sections, we will discuss the nonseeded reactions and the seeded reactions.

### Nonseeded Reactions (Anionic Surfmers, 1%)

In these reactions carried out at 50% solids according to the procedure given in Table VI, 1% of anionic surfmer (on monomer basis) was used (except in two cases with M14). It can be seen that, in some cases, all the initiator was charged (100 : 0); while in others, half was charged and

**Table IX** Amount of Coagulum<sup>a</sup> and Diameter<sup>b</sup> of Latex in Reactions with Various Anionic Surfmers at 1% on Total Monomer Basis

Reaction	Initiator	Initiator Charge to Feed	Surfactant	Coagulum (%)	Diameter (nm)
SDS	KPS	50 : 50	SDS	1.1	99
M141	KPS	50 : 50	M14 (1%)	2.5	152 <sup>c</sup>
M142	KPS	50 : 50	M14 (2%)	0.5	130 <sup>c</sup>
M145	KPS	50 : 50	M14 (5%)	0.6	102 <sup>c</sup>
MET	KPS	50 : 50	MET	24	—
M14B1	KPS	100 : 0	M14	5.6	129
CRO	KPS	100 : 0	CRO	1.5	186
M14C1	AIBN	100 : 0	M14	8.5	159
ALL1	AIBN	100 : 0	ALL	5.7	153

<sup>a</sup> Percentage on total monomer.

<sup>b</sup> From LS.

<sup>c</sup> From TEM.

**Table X Latex Mechanical Stability<sup>a</sup> and Stability Against Electrolytes**

Reaction	$t_{\text{coag}}$ (s) <sup>b</sup>	NaCl (0.1M)	NaCl (0.2M)	NaCl (0.5M)	CaCl <sub>2</sub> (0.1M)
SDS	30	4.3 <sup>c</sup>	6.1 <sup>c</sup>	100 <sup>c</sup>	100 <sup>c</sup>
M141	30	1.4 <sup>c</sup>	5.1 <sup>c</sup>	83 <sup>c</sup>	100 <sup>c</sup>

<sup>a</sup> 12,000 rpm; ASTM D 1076-88, 4287-88, 2196-86.

<sup>b</sup> Time before total coagulation.

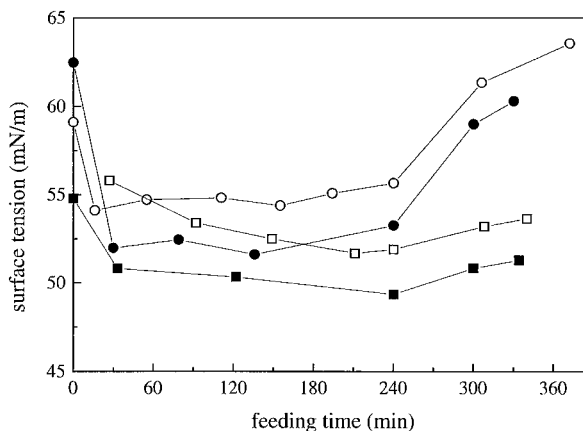
<sup>c</sup> Percentage of coagulum after 24 h.

half was fed (50 : 50). In Table IX, the amounts of coagulum obtained in each reaction are given, together with the particle diameter, as determined with LS.

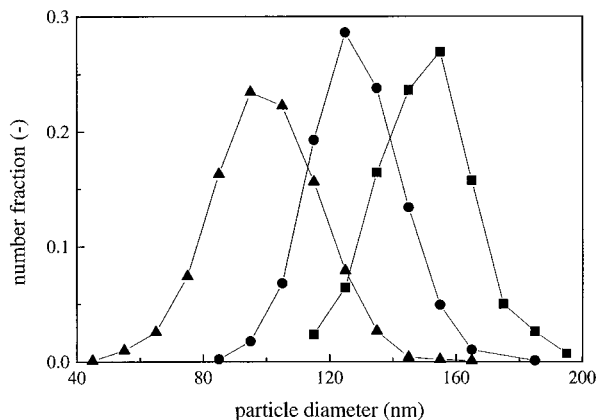
Stability tests were performed for the latexes SDS and M141. The results are presented in Table X. It can be seen that there are no major improvements when replacing a nonreactive surfactant with the reactive M14. Also, in the evolution of fractional conversion versus time (not shown here), no differences were observed. The only variation that could be detected was a difference in the amount of coagulum formed, 1% with SDS, and 2.5% with M14 (see Table IX).

When MET is used as the surfmer, however, the amount of coagulum increases significantly and reaches unacceptable levels (24%, Table IX). This could be due to the fact that this surfmer, in contrast to M14, can homopolymerize and is quite reactive with the main monomers (see Table III). This behavior could give rise to polyelectrolyte formation in the aqueous phase (the CMC of MET is also significantly higher than that of M14). This polyelectrolyte could destabilize existing particles by bridging flocculation; or, if the amount of polyelectrolyte is significant with respect to the amount available for adsorption on the latex particle surface, the latter could be diminished to such an extent that coagulation is induced. As can be seen in Figure 3, where the evolution of surface tension is plotted as a function of reaction time for several reactions, the surface tension of latex MET is at all times lower than that of M141, which may indicate that indeed there are more water-soluble species present in the case of MET. This is even more the case if we compare the reactions M14B1 and CRO, in which the initiator was charged completely at the beginning. Here the surface tension is lower in the case of CRO, which also has less coagulum, as can be appreciated from Table IX. This may be caused by two of the following effects.

1. The fact that CRO is less reactive than M14, so that by charging all M14 in the beginning, more of this surfmer may become interred in the particle interiors; whereas the less reactive CRO may reach a lower level of conversion and remain available for stabilization. The level of conversion of the surfmers will be addressed in another article.<sup>32</sup> It must be noted that the fractional conversion of the main monomers was slightly higher in the case of M14B1, which may also have led to a higher M14 conversion. This difference in fractional conversion, and therefore the rate of polymerization, is probably due to a higher particle concentration in the case of M14B1, which, in turn, may be due to the much lower CMC of M14.
2. The very fact that the CMC of CRO is so much higher than that of M14 means that the equilibrium between surfmer adsorbed onto the particle surface and the surfmer dissolved in the aqueous phase is shifted



**Figure 3** Surface tension versus reaction time for reactions with various surfmers: (○) M141, (●) MET, (□) M14B1, and (■) CRO.



**Figure 4** Particle size distributions, measured with transmission electron microscopy, for three reactions with varying amounts of M14: (M141, ■) 1%, (M142, ●) 2%, and (M145, ▲) 5%.

much more to the aqueous phase in the case of CRO, and its higher concentration in the aqueous phase has a direct effect on the surface tension.

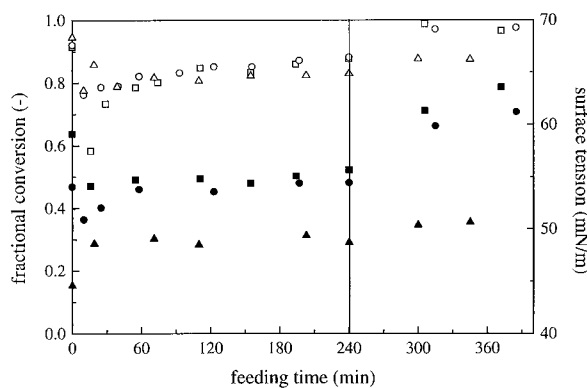
If one compares reactions M141 and M14B1, one can observe the effect of the partitioning of the initiator over charge and feed. If all of the KPS is charged in the beginning, the final amount of coagulum is significantly higher. This can be attributed to the fact that the more KPS is present in the beginning, the more particles are formed, leading to a larger surface area to be covered by the same amount of surfmer. It is also possible that this leads to a higher rate of polymerization of M14 in the beginning, leading to a higher amount being buried in the particle interior. Comparing reactions M14B1 and M14C1, one can see the effect of the type of initiator. When the oil-soluble AIBN is used, the amount of coagulum is somewhat higher, despite the fact that the particle size is higher and the total surface area to be covered smaller. This may be attributed to the fact that part of the sulfate groups afforded by the decomposition of KPS contribute to the electrostatic stabilization, something which is impossible with AIBN, of course. The number of moles of KPS that decomposed during the reaction constitute more than a third of the number of moles of M14 (taking  $k_d$  of KPS as  $5.8 \times 10^{-5} \text{ s}^{-1} 42^\circ\text{C}$ ).

The use of ALL instead of M14 in reactions initiated with AIBN gives somewhat less coagulum, and this may be due to the fact that ALL is less reactive than M14 and therefore has less

tendency to remain buried in the particle interior. This is the same effect as found with CRO, where it is even more pronounced. This may be caused also by the fact that the particles formed with CRO are larger; therefore, the surface charge density is higher.

With the M14 surfmer, two more reactions were carried out where the amount of M14 was increased to 2 and 5% (M142/5). One can see that the amount of coagulum formed is considerably less when going from 1 to 2%, but a further increase gives no significant improvement. The particle size decreases with an increase in surfmer content, as expected; and the distributions are unimodal (see Fig. 4). The polydispersity of the latex M145 was somewhat higher than in the other two reactions (1.08 versus 1.03). Apparently, the period of nucleation in this reaction lasted longer than in the other two reactions. Analyzing the number of particles formed as a function of surfmer concentration gives the following dependence:  $Np \sim [\text{M14}]^{0.7}$ .

The following surface tensions of the final lattices are different and show an expected decrease with an increasing amount of surfmer in the reaction: 63.6, 61.2 and 50.6 mN/m, respectively, which can be attributed to the presence of more surface active species at the end. All other things being equal, this means that the conversion of the surfmer is not 100%, at least not in the reactions with 2 and 5% M14. This is confirmed if we look at the evolution of the surface tension and conversion as a function of time in Figure 5. One can see that the instantaneous conversion in the cases of 1 and 2% M14 is very similar, with a gradual



**Figure 5** Fractional conversion (open symbols) and surface tension (closed symbols) versus time for three reactions with varying amounts of M14: (M141, □, ■) 1%, (M142, ○, ●) 2%, and (M145, △, ▲) 5%.

increase during the feeding period from about 76 to 87%. During the additional batch period, the conversion increases further to high conversion. However, in the reaction with 5% M14, the conversion behavior is different; here, the instantaneous conversion does not show a large increase at the end of the feeding period. The surface tension in the case of 1 and 2% M14 shows a decrease in the beginning, probably indicating the start of the reaction. The surface tension then reaches a constant level, which is maintained during the feeding period. At the end of that period, it shows an increase, indicating polymerization of the remaining M14. In the reaction with 5%, this increase is absent, in parallel with the evolution of the conversion in this reaction. It is not clear what causes this, but perhaps it can be attributed to the presence of the relatively high level of the maleate monomer, which may decrease the rate of polymerization, for example, by decreasing the rate of propagation.

Films were cast of these three latices, and these showed better visual appearance the higher the surfmer content. With 1%, the film is opaque with veins and bubbles; with 2%, the film looks more homogeneous, and the veins have disappeared; with 5%, the film starts the look a bit bluish and is quite homogeneous. This can be partly ascribed to a better film formation with the smaller particle size of M145. However, the adsorption of water increases significantly with an increase in the amount of surfmer: after 14 days of immersion in water, M145 had absorbed 28% of its weight in water; whereas M142 had absorbed 18%; and M141, 8%, as expected from the increase in concentration of polar components.

#### Combinations of Anionic and Nonionic Surfmers

In Table XI are shown some of the results obtained with semi-continuous reactions, where a combination of an anionic surfmer with a nonionic surfmer was used. In these reactions, KPS was used as the initiator, and it was partitioned 50 : 50 over charge and feed.

Comparing the first two reactions of this series (M14D and MIXA), one can see that replacing part of the M14 with the nonionic MALPEO increased the amount of coagulum significantly from 2 to 11%, whilst the fractional conversion of the main monomers during the reaction decreased from being higher than 75% to being between 60 and 30%. Analysis of the purity of MALPEO

**Table XI** Amount of Coagulum in Reactions with Combinations of Various Anionic and Nonionic Surfmers

Reaction	Surfactants <sup>b</sup>	Coagulum (%) <sup>b</sup>
M14D <sup>a</sup>	M14 (1%)	2
MIXA <sup>a</sup>	M14 (0.75%)–MALPEO (0.25%)	11
MIXB	M14 (0.75%)–METPEO (0.25%)	16
MIXC	M14 (1%)–METPEO (1%)	23
MIXD	MET (1%)–METPEO (1%)	32
MIXE	M14 (1%)–METPEO (1%)	> 60

<sup>a</sup> Carried out at 70°C with initiator partitioning of 100 : 0.

<sup>b</sup> Percentage on total monomer.

showed that this surfmer contained remains of the silica catalyst that was used in its synthesis, and perhaps this can account for the instability.

Replacing 0.25% of the M14 with a nonionic methacrylate surfmer (MIXB) was also detrimental in terms of stability, with the coagulum increasing from 2.5 to 16%. Also, the addition of 1% of METPEO to 1% of M14 (MIXC) increased the amount of coagulum to 23%. This kind of instability was also observed in reaction MET and reaction MIXD, where the anionic MET is combined with the METPEO, and can perhaps be ascribed to polymerization in the aqueous phase, leading to bridging flocculation. It was attempted to reduce the amount of coagulum by changing the addition strategy of the surfmer. For example, in reaction MIXE, the METPEO was added after 225 minutes of the feeding period (240 minutes), during which the M14 was being fed. This resulted after a few minutes in complete coagulation of the latex, which previously had been completely stable.

From these unseeded reactions, it can be concluded that the latex instability and coagulum formation increase when the intrinsic reactivity of the surfmer increases; the observed order is roughly as follows: SDS ~ CRO < ALL < M14 < MALPEO ~ MET < METPEO.

The reason for this destabilization could be that the more reactive the surfmer, the more it can be buried in the particle interior at the end of the reaction, leaving part of the surfmer unavailable

for stabilization at the particle surface. The M14 seems to follow this behavior, while CRO and ALL, which are much less reactive, remain at the surface for stabilization. This could be checked by measuring the conversion of the surfmers as a function of reaction time, and this is reported in another article.<sup>32</sup> The use of methacrylic surfmers in the S–BA–AA system results in a high amount of coagulum, both in the case of an anionic and nonionic surfmer. This could be ascribed to formation of polymer soluble in the aqueous phase, which leaves less surfactant available for stabilization. In the case of the nonionic methacrylate, this formation could give rise to bridging flocculation. The higher the CMC and the higher the tendency to copolymerize and homopolymerize, the higher the possibility of formation of such a polymer.

Furthermore, it can be seen that if larger amounts of M14 are used (1, 2, and 5%), there might be an effect on the rate of polymerization of the main monomers. However, it is difficult to assess this, as the number of particles in that series of reactions was not the same. For the same reason, the comparison of the film properties was hampered. Hence, in the following section, the results of three seeded reactions are reported. In these, the particle diameter and number are constant, and this allows a fair comparison of reaction rate and film properties for different surfactants.

#### Seeded Reactions (Anionic Surfmers, 2%)

Three seeded reactions using SDS, M14, and CRO were carried out at a solids content of 55% with 2% of surfactant on a monomer basis. Table VIII gives the recipe for these reactions, and Table VII for the seed latex. The particle diameter of the seed was 39 nm (light scattering). Some of the results are given in Table XII. It can be seen that final particle diameters ranged from 163 to 178 nm (light scattering). The particle numbers ranged from 4.1 to  $4.9 \times 10^{17} \text{ dm}^{-3}$ . Comparison of these sizes with that calculated from the seed diameter by assuming that neither coagulations nor secondary nucleations occurred during the process ( $dp = 159 \text{ nm}$ ) suggests that a limited coagulation occurred during the polymerization. However, these results should be considered with caution because the particle diameter measured by light scattering is not the volume average, which is the one needed to carry out the calcula-

**Table XII** Amount of Coagulum,<sup>a</sup> Particle Size (LS), Final Surface Tension, Final pH, and Stability Against Electrolytes<sup>b</sup> of Seeded Reactions with SDS M14, and CRO

Reaction	55SDS2	55M142	55CRO2
Coagulum (%)	0.9	1.0	1.3
Diameter (nm)	163	171	178
$\sigma$ (mN m)	42	53	50
pH	4.4	3.8	4.7
NaCl (0.2M)	172	174	182
NaCl (0.5M)	237	168	243
NaCl (1M)	total coag	188	260
CaCl <sub>2</sub> (0.05M)	total coag	total coag	total coag

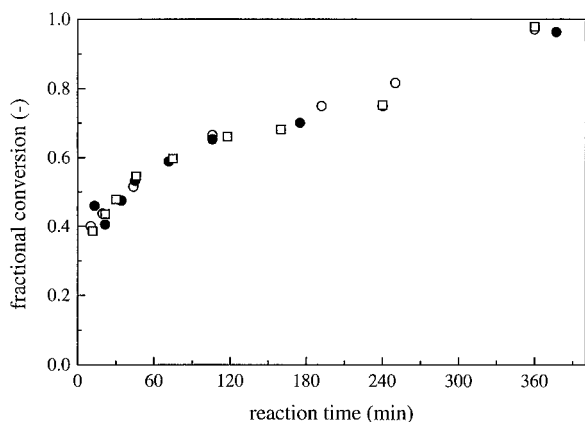
<sup>a</sup> Percentage on monomer.

<sup>b</sup> Diameter of latex particles 24 hours after adding the electrolyte solution.

tion described above. In addition, the error associated with light scattering measurements of polydisperse latexes is at least of the same order of magnitude of the variation of the diameters reported in Table XII.

The amount of coagulum is quite low, and it should be noted that the main source for coagulum formation seems to be the drying up of latex on the reactor wall. As it could be expected, the final surface tension is the lowest for the nonreactive SDS and the highest for the most reactive surfmer, M14. The latex 55M142 showed the lowest pH, and this probably results from the acid by-products caused by hydrolysis. As far as stability against electrolyte is concerned, one can see that the 55M142 latex is the most stable. It showed the smallest variation of the diameter, which is constant within experimental error. The 55CRO2 latex is less stable than the 55M142 latex but more stable than the 55SDS2 latex.

The fact that the particle numbers are almost the same makes it possible to judge the conversion versus time results more realistically. The results are shown in Figure 6. It can be seen that the evolution of the fractional conversion in the three reaction is practically identical. This means that substitution of the 2% of SDS with either CRO or M14 does not affect the rate of polymerization. Urquiola et al.<sup>29</sup> observed a strong decrease of the rate of polymerization when using ALL as a surfactant in emulsion polymerizations of vinyl acetate. Based on our results, it seems impossible to conclude whether the lower instantaneous conversion observed in reaction M145 compared with



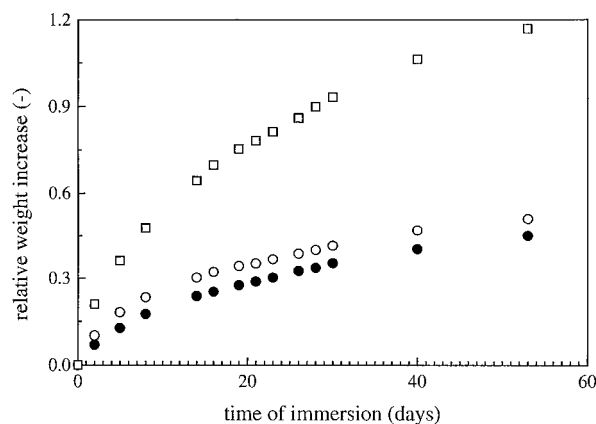
**Figure 6** Fractional conversion versus time for three seeded reactions: (○) 55SDS2, (●) 55M142, and (□) 55CRO2.

M141 and M142 is a result of a kinetic effect brought about by the high concentration of M14 or whether it was an artifact, perhaps caused by oxygen leaking into the system. As far as kinetic effects are concerned, one could think of enhanced chain transfer, followed by desorption (as was the case of ALL with vinyl acetate), or even a decreased rate of propagation (the M14 radical and monomer being much more bulky than S, BA, or AA). However, 5% of surfactant can be considered an unusually high concentration, so the conclusion could be that for practical concentrations there is no effect on the kinetics.

From these three latices, films were cast with a thickness of  $0.3 \pm 0.1$  mm. The appearance of the films is described in Table XIII. The absence of veins and occluded bubbles (air, water) and the relatively high transparency, homogeneity, and gloss of the film 55CRO2 are possibly caused by the high content of impurities of the CRO; the

**Table XIII** Appearance of the Films Cast from the Latices of the Seeded Reactions

Physical Property	55SDS2	55M142	55CRO2
Diameter (nm)	163	171	178
Surface tension (mN m)	42	53	50
Veins	+++	+	—
Occluded bubbles	yes	yes	no
Transparency	low	good	good
Homogeneity	+	+++	+++
Gloss	+	++	+++



**Figure 7** Fractional weight increase through water absorption of the latex films: (○) 55SDS2, (●) 55M142, and (□) 55CRO2.

undecyl alcohol could act as a plasticizer and aid the film formation. In comparison, the 55SDS2 film shows the highest level of veins, inhomogeneities, and opacity. This surfactant is the purest of the three, and there would be little reason to expect plasticization. The 55M142 film shows intermediate properties. Here also, an alcohol is left, but to a lower extent. The contact angle of water on the films was also visually assessed, but no difference was seen in the three films; the contact angles were all quite low, indicating a relatively high degree of wetting, which is not a good sign if the latex is to be applied in a coating. The water sensitivity was further studied in water absorption experiments, the results of which are shown in Figure 7. It can be seen that the 55CRO2 film has a very high degree of water absorption, which could be a result of the high degree of impurities or because it has not reacted to a high degree. The 55M142 films show much less water absorption, and even less than 55SDS2. This can be due to a higher degree of conversion than CRO or to the fact that the 55M142 film has the lowest number of polar groups (lower than both 55CRO2 and 55SDS2) because M14 has the highest molecular weight.

From the results of these seeded reactions, one can conclude that the CRO surfmer is not the optimum surfmer for the present monomer system (S-BA-AA), as its film shows a high water sensitivity, and the idea behind the surfmers is that they should decrease the water sensitivity. It also shows a low resistance to electrolyte solutions. The M14 shows more promising results, its water sensitivity is slightly better than SDS, and the



resistance against electrolyte solutions significantly better.

A final remark is that in this type of screening of surfmers, the latter are fed into the reactor with a profile that is rather arbitrary; for the main monomers, such a profile works quite well, and the polymer that is formed will have a nearly constant composition. However, the question is whether a constant fraction of surfmer built into the copolymer results in a proper use of the stabilizing properties of the surfmer units. One can imagine that a relatively reactive surfmer, such as the methacrylics, and perhaps also the maleates, remains buried within the particle if indeed it is incorporated to the same extent as the other monomers. This is unknown for the present systems, which makes it tricky to come to final conclusions. Therefore, as we do not know whether the surfmers have been used optimally, we can really only assess the surfmers' applicability with respect to the way it is used here (i.e., with constant addition profile) and with the monomer system used here (S-BA-AA). More work needs to be done to see whether the surfmers could be used in a better way.<sup>34</sup>

## CONCLUSIONS

It has been shown that a range of polymerizable surfactants with varying copolymerization reactivities could be prepared with relatively straightforward syntheses. The purities of the surfmers prepared, however, were not high in some cases. These surfmers have been used in nonseeded, semicontinuous emulsion copolymerizations of styrene, butyl acrylate, and acrylic acid at high solids content, resulting in relatively stable latices with polymerizable surfactants, such as the crotonate and the allylic surfactants, which are quite unreactive. More reactive polymerizable surfactants, such as the maleates, give latices with stabilities comparable with, or even better than, similar latices with SDS, a reference surfactant. The very reactive methacrylic surfactants give very unstable latices with large amounts of coagulum, irrespective of whether they were added continuously or at the end of a reaction carried out with another surfmer. This can probably be ascribed to formation of polyelectrolytes soluble in the aqueous phase (depriving the latex particle surface from a stabilizing groups) or even to bridging flocculation in the case of nonionic

methacrylic surfactants. Of some of the anionic surfactants which give stable latices in the nonseeded reactions (crotonate and maleate derivatives), it was observed in seeded reactions that they do not affect the kinetics of the emulsion polymerization. Of the ensuing latices, it can be said that the maleate latex had a better stability against electrolytes. The films cast from these latices showed that the crotonate caused a large water sensitivity, whereas the maleate latex had a water sensitivity slightly better than the SDS latex. It can be concluded that the methacrylate is not a suitable polymerizable surfactant for the S-BA-AA system. Of the other surfactants, it can be said that the maleate derivative is the most promising; but the kinetics of the incorporation of the surfactants needs to be studied to be able to be conclusive about their applicability in the S-BA-AA system.

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