

Synthesis and Properties of Novel Cationic Maleic Diester Polymerizable Surfactants

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Abstract: Three new cationic polymerizable surfactants are synthesized by the reaction of alkylmaleic hemiester with glycidyltrimethylammonium chloride. Their structures are confirmed by ^1H NMR, IR and elements analysis. The values of CMC and γ_{CMC} of these surfactants have been measured. One can obtain nearly monodisperse polystyrene latex by emulsion polymerization using the polymerizable surfactant.

Keywords: Polymerizable surfactant, maleic diester, surface active monomer, surfmer.

The surfactants used in the emulsion polymerization can be thereafter the source of many problems for the application, such as adhesives and coatings. To overcome these negative aspects essentially related to their mobility in the final polymer, surfactants can be covalently linked to the particle surface through incorporation into the polymer chains. Recent years, polymerizable surfactants (surface active monomer or surfmer) are widely reported and used in the emulsion polymerization, many polymerizable groups have been used such as substituted styrene and acrylic or methacrylic esters^{1,2}. However, owing to their high reactivity, early incorporation might occur and lead to the loss of the surfactant which can be buried inside the particles during their growth. In contrast, a too low reactivity of the surfmer (such as crotonic ester)² can be the cause of incomplete conversion and poor covalent incorporation. Therefore, polymerizable groups with intermediate reactivity should be used and the reactivity ratios for copolymerization of the surfmer with the main monomer have been reported to be of major importance³. Actually, the surfmer should be unable to homopolymerize ($r_{\text{surfmer}} \approx 0$) and the reactivity ratio of the comonomer should be comprised between 0.5 and 10^3 . The use of non-homopolymerizable maleate group was proposed^{1,4,5} and shown to be suited since it has good incorporation of the corresponding surfmers.

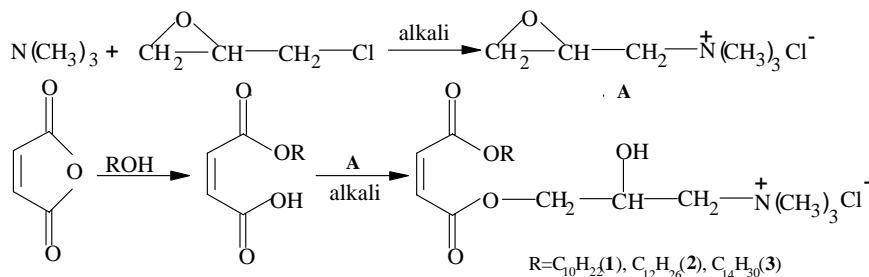
In the present work, we introduce hydroxypropyl and maleate group into alkyltrimethylammonium halide to obtain three new cationic polymerizable surfactants. Synthesis route and the structures of polymerizable surfactants are shown in **Scheme 1**.

Surface tension and CMC

The maleic diesters polymerizable surfactants were three times recrystallized from a

mixture of acetone and ethanol. The surfactants obtained are white substances with rather good solubility in water.

Scheme 1



The surface tension and the CMC are determined by using the method of the plate of Willehmy. The apparatus is a Krüss K122 equipped with a Dosimat Krüss 665 and the temperature is maintained precisely at 30°C. **Figure 1** gives the dependence of surface tension on the surfactant concentration. The break points give CMC values of each surfactant (see **Table 1**). The CMC decreases with increasing length of the alkyl group, due to the increased hydrophobic character of the molecule. The plot of logCMC vs. the carbon number in the alkyl group is linear (shown in **Figure 2**).

Table 1 CMC values and surface tension of polymerizable surfactants

R	1 (C ₁₀ H ₂₂)	2 (C ₁₂ H ₂₆)	3 (C ₁₄ H ₃₀)
CMC (mM)	5.54	3.68	2.15
γ (mN/m)	25.2	23.55	22.54

Batch emulsion polymerization

Batch emulsion polymerization was carried out at 70°C using a conventional 100 ml thermostated reactor and K₂S₂O₈ as initiator. The results of the emulsion polymerization are shown in **Table 2** (with surfactant **2** as an example). The surface tension of the final latices is observed to be very high and close to that of water, indicating a low concentration of surfmer in the aqueous phase (lower than CMC). The reason for this low concentration may be the chemical anchoring of the surfmer to the particles. Latices synthesized with a related maleate surfmer reported in the literature showed similarly high surface tension⁶. The particle diameter D is measured by dynamic light scattering with an Auto Sizer LO-C (Malvern Instruments). The polydispersity of the particle diameters is calculated automatically. It is considered that emulsion is monodisperse when the polydispersity index (PDI) is lower than 0.1⁴. We can obtain nearly monodisperse latex particles with diameters ranging from about 60 nm to 80 nm (shown in **Table 2** and **Figure 3**). The polymerization mechanics and seeded polymerization using polymerizable surfactants will be studied in latter work.

Table 2 Results of batch emulsion polymerization using maleate surfactant

Monomer (wt.% in the latex)	Surfmer (wt.% with respect to monomer)	D_p (nm)	PDI	γ (mN/m)
10	2	72.5	0.0542	71.23
15	2	67.5	0.0581	71.01

Figure 1 Plot of surface tension vs. the concentration of surfactants in water

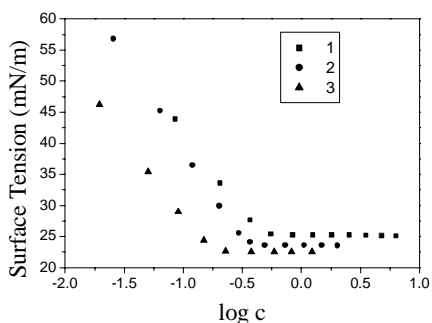


Figure 2 Linear correlation of log CMC and C atoms number in alkyl groups

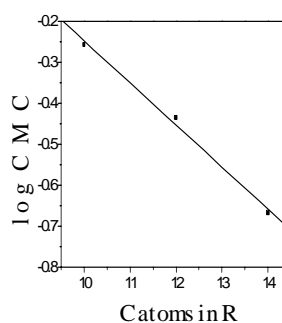
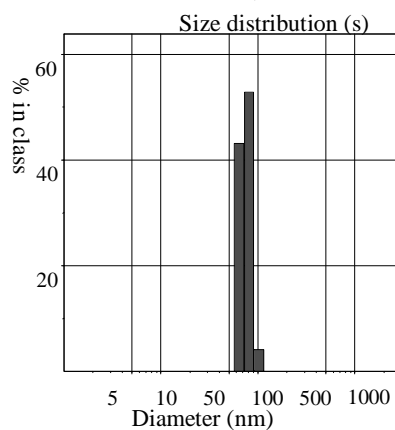


Figure 3 Particle size distribution (monomer content 10wt.%)



Latex stability

The experiment results of latex stability are shown in **Table 3**. One can find the particle sizes of latex have no evident increase, it means the particles do not coagulate. Meanwhile, the polydispersity index has a little increase. The distribution of particles is still nearly monodispersity.

Table 3 The stability of latex

Test item	After polymerization (10% solid content)	After 5 freeze-thawing cycles*	After 3 months storage**
Dp (nm)	72.5	73.8	72.9
PDI	0.0542	0.092	0.078

*A small amount of latex was cooled at -20°C during 30 min and then reheated at room temperature, 10% solid content.

** storage at room temperature

Acknowledgment

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References and notes

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7. **1** ($\text{R} = \text{C}_{10}\text{H}_{22}$): IR (KBr, cm^{-1}): 3447, 1736, 1636, 1603, 1577, 1434, 1180, 817, 612. $^1\text{H-NMR}$ (300MHz, CDCl_3 , ppm): δ 0.88 (t, 3H, $\text{J} = 6.6\text{Hz}$, CH_3), 1.26 (s, 14H, $(\text{CH}_2)_7$), 1.68 (t, 2H, $\text{J} = 6.9\text{Hz}$, $\text{CH}_2\text{-CH}_2\text{-OOC-}$), 3.34 (s, 9H, $\text{N}(\text{CH}_3)_3$), 3.65-3.88 (m, 5H, $\text{OCH}_2\text{CHCH}_2$), 4.03 (t, 2H, $\text{J} = 6.6\text{Hz}$, CH_2COO), 6.3-6.5 (d, 2H, $\text{J} = 13\text{Hz}$, $\text{HC} = \text{CH}$). Anal. Calcd. for $\text{C}_{20}\text{H}_{38}\text{ClNO}_5$ (%): C, 58.97; H, 9.34; N, 3.44. Found: C, 58.94; H, 9.18; N, 3.38.
2 ($\text{R} = \text{C}_{12}\text{H}_{26}$): IR (KBr, cm^{-1}): 3446, 1736, 1636, 1603, 1578, 1431, 1184, 809, 611. $^1\text{H-NMR}$ (300MHz, CDCl_3 , ppm): δ 0.86 (t, 3H, $\text{J} = 6.6\text{Hz}$, CH_3), 1.26 (s, 14H, $(\text{CH}_2)_7$), 1.69 (t, 2H, $\text{J} = 6.9\text{Hz}$, $\text{CH}_2\text{-CH}_2\text{-OOC-}$), 3.36 (9H, s, $\text{N}(\text{CH}_3)_3$), 3.65-3.88 (5H, m, $\text{OCH}_2\text{CHCH}_2$), 4.05 (t, 2H, $\text{J} = 6.6\text{Hz}$, CH_2COO), 6.3-6.5 (d, 2H, $\text{J} = 13\text{Hz}$, $\text{HC} = \text{CH}$). Anal. Calcd. for $\text{C}_{22}\text{H}_{42}\text{ClNO}_5$ (%): C, 60.69; H, 9.65; N, 3.22. Found: C, 60.65; H, 9.58; N, 3.20.
3 ($\text{R} = \text{C}_{14}\text{H}_{22}$): IR (KBr, cm^{-1}): 3447, 1736, 1636, 1603, 1577, 1432, 1184, 809, 612. $^1\text{H-NMR}$ (300MHz, CDCl_3 , ppm): δ 0.88 (t, 3H, $\text{J} = 6.6\text{Hz}$, CH_3), 1.27 (s, 14H, $(\text{CH}_2)_7$), 1.70 (t, 2H, $\text{J} = 6.9\text{Hz}$, $\text{CH}_2\text{-CH}_2\text{-OOC-}$), 3.38 (s, 9H, $\text{N}(\text{CH}_3)_3$), 3.65-3.88 (m, 5H, $\text{OCH}_2\text{CHCH}_2$), 4.06 (t, 2H, $\text{J} = 6.6\text{Hz}$, CH_2COO), 6.3-6.5 (d, 2H, $\text{J} = 13\text{Hz}$, $\text{HC} = \text{CH}$). Anal. Calcd. for $\text{C}_{24}\text{H}_{46}\text{ClNO}_5$ (%): C, 62.20; H, 9.94; N, 2.16. Found: C, 62.18; H, 9.90; N, 2.14.

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