J Surfact Deterg (2011) 14:37–41
DOI 10.1007/s11743-010-1199-2

ORIGINAL ARTICLE

Synthesis and Characterization of a Novel Series of Cationic Fumaric Polymerizable Emulsifiers

Weihong Qiao · Cui Cao · Yingli Sun · Hongzhu Liu · Xingshun Zhao · Xinmei Fu

Received: 18 September 2009 / Accepted: 2 April 2010 / Published online: 29 April 2010

Abstract A series of novel cationic fumaric polymerizable emulsifiers (named as *F* series emulsifiers) were synthesized. The chemical structures of these emulsifiers were confirmed by ^{1}H NMR and MS and their minimal inhibitory concentrations to *Escherichia coli* were determined. Antibacterial tests of latex films showed that [2-(*N*-benzyl-*N*,*N*-dimethylamino)ethyl]dodecyl fumaric ammonium bromide, [2-(*N*-benzyl-*N*,*N*-dimethylamino)ethyl]decyl fumaric ammonium chloride and [2-(*N*-benzyl-*N*,*N*-dimethylamino) ethyl]dodecyl fumaric ammonium chloride can possibly be used as a polymerizable bactericides.

Keywords Cationic fumaric polymerizable emulsifiers · Synthesis · Characterization · Minimal inhibitory concentrations

Abbreviations

MIC	Minimal inhibitory concentration
CTAB	Cetyl or hexadecyltrimethyl ammonium bromide

Introduction

Emulsifiers play important roles in emulsion polymerization. Traditional emulsifiers are adsorbed onto the surface of latex particles by physical adsorption. The weak physical adsorption of traditional emulsifiers may cause the destabilization of the latex and water sensitivity of the film. However, polymerizable emulsifiers can improve the stability of the lattices against electrolytes [1, 2], shear forces [3] and freezing/thawing [4], as well as affecting the water sensitivity of the film formed [2, 5–7].

The polymer emulsion which is polymerized by an antimicrobial cationic emulsifier has antibacterial properties, and it can overcome the shortcoming of high toxicity and poor security of the low molecular weight antimicrobial agent [8–15]. When this polymer emulsion is applied to the preparation of coatings, the coatings have lasting antibacterial properties, and other additive antibacterial agents are not needed.

Usually anionic and non-ionic emulsifiers are used in the preparation of coatings, while cationic emulsifiers are seldom used in the preparation of coatings. In this paper, a series of fumaric cationic polymerizable emulsifiers (*F* series emulsifiers) were synthesized and used in the emulsion polymerization of vinyl acetate–butyl acrylate–vinyl versatate–hexafluorobutyl methacrylate, the antimicrobial activity of *F* series emulsifiers and the latex film was tested. The results indicate an excellent degree of antimicrobial activity and good application prospects of the *F* series polymerizable emulsifiers.

Experimental

Materials

Maleic anhydride (analytical grade, Tianjin Fuyu Fine Chemical Co. Ltd), *n*-decanol, *n*-dodecanol and *n*-tetradecyl alcohol (analytical grade, Tianjin Damao Chemical

W. Qiao (✉) · C. Cao · Y. Sun · X. Fu
State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, People Republic of China
e-mail: qiaoweihong2001@sina.com

H. Liu · X. Zhao
Dalian Zebon Fluorocarbon Paint Stock Co. Ltd., Yingtai Road, Dalian 116036, People Republic of China

Reagent Factory), phosphorus trichloride (analytical grade, Tianji No. 1 Chemical Reagent Factory), dimethylethanolamine (analytical grade, Feixiang Chemicals Co. Ltd), benzyl chloride (analytical grade, Beijing Xingjin Chemical Factory), benzyl bromide (analytical grade, Shanghai Nuotai Chem Co. Ltd), Hexadecyltrimethyl ammonium bromide (CTAB, analytical grade, Xiamen Pioneer Technology Co. Ltd).

Synthesis of Polymerizable Emulsifiers

The series of polymerizable emulsifiers, with the length of the carbon chain 10, 12, or 14, were synthesized according to the reaction scheme shown in Fig. 1.

Synthesis of **1** was carried out according to reference [16].

Alkyloxyacrylyl chloride-2-butenoic acid alkyl ester (**2**). Compound **1** (0.05 mol) was placed in a three-necked flask, stirred and heated. When the solid had turned to liquid, PCl_3 (0.025 mol) was added dropwise, then allowed to react for 2 h at 60 °C. After standing at ambient temperature for 2 h, the surplus PCl_3 was removed by vacuum distillation. The crude product was obtained by filtering to remove H_3PO_3, which was used in the following reaction without purification.

(2*E*)-alkyl-(dimethylaminoethyl) butenedionate 2-(dimethylamino)ethyl alkyl ester (**4**). Dimethyl-ethanolamine (0.05 mol), K_2CO_3 (0.05 mol) and butanone in sequence were placed in a three-necked flask. Then compound **2** was added dropwise to the reaction mixture and stirred for 2 to 4 h at 70 to 80 °C. The solution was filtered when it had cooled to room temperature and then washed with acetone. Compound **3** was obtained by drying in a vacuum for 4 h. Compound **3** was dissolved in water, using sodium hydroxide solution to control the pH of the solution to weak alkaline, and compound **4** was extracted using chloroform.

[2-(*N*-benzyl-*N*,*N*-dimethylamino)ethyl]alkyl fumaric quaternary ammonium salt (**5**). The compound **4** (0.05 mol), benzyl chloride (or benzyl bromide; 0.05 mol) and butanone were placed in a reactor and stirred for 16 to 24 h at 60 to 70 °C. Removing solvent butanone by rotary evaporator, compound **5** was obtained. A typical ^1H NMR (CD_3OD, 400 MHz) for *F* series product: δ 0.86–0.90 (t, 3H, CH_2–**CH_3**), 1.26–1.35 (m, 18H, –**$(CH_2)_9$**–), 1.65–1.70 (m, 2H, –$(CH_2)_9$–**CH_2**–CH_2–), 3.16–3.27 (s, 6H, –**$N(CH_3)_2$**–), 3.84–3.91 (t, 2H, –$(CH_2)_9$–CH_2–**CH_2**–O–), 4.15–4.20 (t, 2H, –O–**CH_2**–CH_2–$N(CH_3)_2$–), 4.68–4.76 (t, 2H, –CH_2–**CH_2**–$N(CH_3)_2$–), 4.76–4.86 (s, 2H, –$N(CH_3)_2$–**CH_2**–C_6H_5–), 6.85–6.90 (s, 2H, –CO–**CH=CH**–CO–),

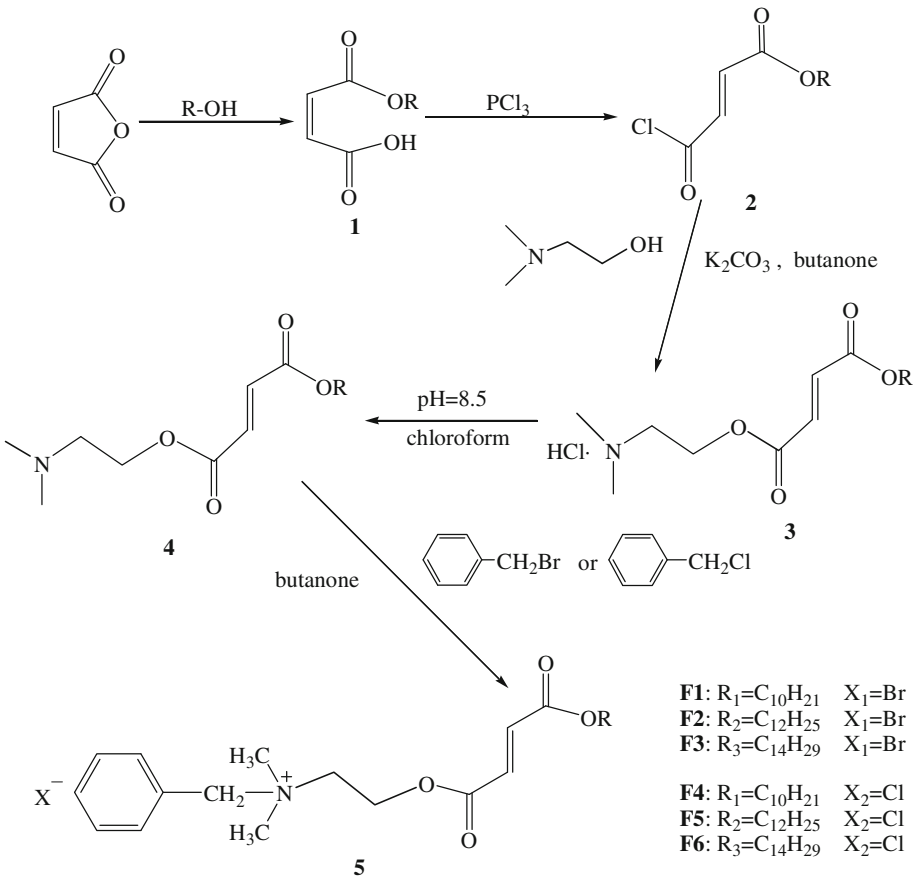

Fig. 1 Synthesis of fumaric cationic polymerizable emulsifiers

7.61–7.63 (m, 5H, $-CH_2-\mathbf{C_6H_5}-$). MSD: **F1**: *m/z* 418.3 (M^+-Br^-). **F2**: *m/z* 446.3 (M^+-Br^-). **F3**: *m/z* 474.3 (M^+-Br^-). **F4**: *m/z* 418.3 (M^+-Cl^-). **F5**: *m/z* 446.3 (M^+-Cl^-). **F6**: *m/z* 474.3 (M^+-Cl^-).

Measurement of Minimal Inhibitory Concentration (MIC)

(1) A suspension of *Escherichia coli* with a concentration range of 5.0×10^5 to 10.0×10^6 cfu/mL was prepared.
(2) A culture medium was prepared containing the antibacterial agent: the antibacterial agent solution was doubly diluted with distilled water to different concentrations as the test solutions. The test solutions with different concentrations (5 mL in each case) were added to a test-tube which contained 5 mL Luria–Bertani medium (its concentration two times that of the test solution).
(3) The bacterial suspension 0.1 mL was inoculated into the above antibacterial culture medium. The concentration of the *Escherichia coli* suspension was 3.55×10^6 cfu/mL. This group was used as experimental samples.
(4) A positive control sample was prepared by inoculating the bacterial suspension into the culture medium without any antibacterial agent by the method mentioned above.
(5) Negative control samples were prepared by placing the culture medium in two test tubes.
(6) The experimental samples, positive control and negative control were all put into an incubator for culturing for 24 h at 37 °C.
(7) The number of living bacteria in the experimental samples was calculated.

Preparation of Latex Films

The emulsifiers and CTAB were used with the same technique for the emulsion polymerization of vinyl acetate–butyl acrylate–vinyl versatate–hexafluorobutyl methacrylate, recipes were presented in Table 1.

Table 1 Recipes for emulsion polymerization

	VAc	BA	VEOVA 10	HFBMMA	SF	V50	H_2O
Charge (g)	1.86	0.62	0.62	0.93	0.18	0.07	37.93
Feed (g)	28.14	9.38	9.38	14.07	2.69	0.28	42.30
Total (g)	30	10	10	15	2.87	0.35	80.23

Vac vinyl acetate, *BA* butyl acrylate, *VeoVa 10* vinyl versatate, *HFBMMA* hexafluorobutyl methacrylate, *SF* emulsifier, *V50* 2, 2′-azobis (2-amidinopropane) hydrochloride

Latex films were prepared by placing the required amount of latexes on polyester sheets and then drying them at 30 °C under static air in a temperature-controlled chamber for 24 h. After the film formation, a representative and uniform piece (3 cm × 3 cm) was cut from each sheet, and the square samples were prepared and dried at 40 °C in vacuo for another 24 h.

Antibacterial Test of Latex Film

The antibacterial activity of the synthesized latex film was evaluated according to the method of viable plate count against *Escherichia coli* BL21(DE3) [17–20]. A certain amount of the bacterial suspension was inoculated to negative control samples, blank control sample and latex film samples. This was done five times at the same time on 3 different samples. When the humidity was greater than 90%, these 3 kinds of samples were covered with a cover glass and cultured for 24 h at 37 °C in sterilized petri dishes by the sticking membrane method. Then these samples and cover glass were eluted with 20 mL of washing liquid for many times. Then, 200 μL washer liquid was taken and inoculated into the Luria–Bertani medium. The numbers of live bacteria were calculated after being cultured for 24–48 h in an incubator.

Results and Discussion

Structural Characterization

The *trans*-structure of the *F* series product was observed by coupling constants from ^{1}H-NMR. The J of the H on the unsaturated carbon of the *F* series product is 15.6 Hz, which is higher than that of the similar *trans*-alkene (structure of fumaric monoester monoacidamide) 14 Hz [19] and *cis*-isomer monododecyl maleate 12.8 Hz. The fact is that J of the H on the unsaturated carbon of the *trans*-alkene is higher than that of the *cis*-isomer.

By analyzing this five steps reaction, only the second step reaction has the possibility to cause the isomerization. Usually, when the temperature is higher than about 100 °C or the existence of some acids (HCl and H_3PO_3 etc.), it is easily to bring about the isomerization of the maleate [20]. During the second step reaction, H_3PO_3 produced as a byproduct acid in this reaction, can catalyze the isomerization of *cis*-isomers to *trans*-isomers in the process of acylchlorination. For other four step reactions, neither a high temperature nor the existence of any acid can cause the isomerization of alkene. The possible reaction mechanism is shown in Fig. 2.

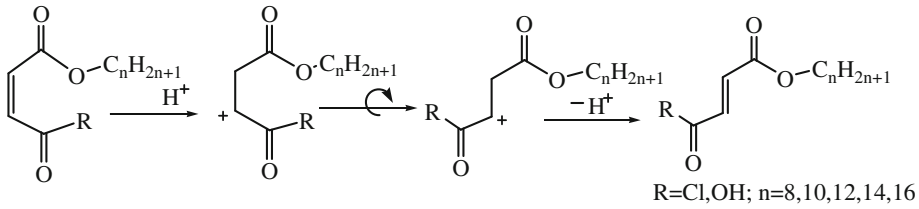

Fig. 2 Mechanism of the acid catalyzed transformation of the hemiesters of maleic acid and their chlorides to *trans*-isomers

Table 2 The minimal inhibitory concentration of the polymerizable surfactants

Emulsifiers	CTAB	F1	F2	F3	F4	F5	F6
MIC (10^{-5} mol/L)	2.44	4.88	2.44	625	9.77	4.88	625

Minimal Inhibitory Concentration (MIC) of the Polymerizable Emulsifiers

The designed quaternary ammonium salt polymerizable emulsifiers with an ester bond and double bonds, not only possess polymerizable ability, but also show antibacterial properties, and they adsorb by covalent bonds to the surface of latex particles during emulsion polymerization. The latex itself has antibacterial properties after formation of the latex film. If the latex is used in paint, the paint may be endowed with antibacterial properties without the need of an additional antibacterial agent. In order to test the antibacterial property of the polymerizable emulsifiers synthesized, it was necessary to study their MIC and antibacterial activity of their latex film.

The MIC values of the polymerizable emulsifiers with regard to *Escherichia coli* were studied and are shown in Table 2. The results show that the traditional cationic emulsifier CTAB gives lower MIC values and presents good antibacterial properties. The MIC values of F1, F2, F4 and F5 belong to an identical concentration gradient as CTABs, therefore F1, F2, F4 and F5 also possess these good antibacterial properties. In contrast, the MIC values of F3 and F6 are higher and they do not show good antibacterial properties. When the carbon chain length of the aliphatic group of the quaternary ammonium bromide and quaternary ammonium chloride is the same, such as in F1 and F4, F2 and F5, F3 and F6, the MIC values of the former are lower than that of the later. This indicates that the antibacterial effect of quaternary ammonium bromide is better than quaternary ammonium chloride. With both quaternary ammonium bromide or quaternary ammonium chloride, the MIC of the compounds with chains twelve carbon long is lower than those with chains of ten and fourteen carbons. This also shows that the length of the carbon chain has an influence on the MIC.

Table 3 The anti-bacterial test of latex films with regard to the numbers of viable bacteria

Number of the parallel experiment	Emulsifier					
	CTAB	F2	F3	F4	F5	F6
1	0	0	520	0	0	610
2	0	0	460	0	0	570
3	0	0	430	*6*	0	430
4	0	0	390	0	*1*	540
5	0	0	455	0	0	455

Antibacterial Activity of Latex Film

The antimicrobial activity of the latex film was tested and the antibacterial data are shown in Table 3. According to Table 3, latex films of CTAB, F2, F4 and F5 can inhibit *Escherichia coli*, latex films of F3 and F6 have a certain germicidal action but the effect was limited. After polymerization, the polymerizable emulsifiers still had antibacterial activity and the antibacterial activity was related to the carbon chain length. The antibacterial activity of the latex films of the polymerizable emulsifiers with chains twelve carbons long was better than those with chains with ten and fourteen carbons and this was confirmed by the MIC.

From Table 3, the latex film of the traditional emulsifier CTAB also showed favorable germicidal action. This is because CTAB, itself a favorable bactericide, remained in the latex after emulsion polymerization and gathered on the surface of the latex film after film formation. However, the synthesized cationic emulsifiers, with a polymerizable group and antibacterial properties, were bonded on the surface of the latex particles by covalent bonds. Therefore, the polymerizable emulsifiers cannot be washed out of the surface of the latex film by water and could show abiding antibacterial properties, but the traditional emulsifier CTAB may be washed out of the surface of the latex film.

Then the latex film of CTAB was washed ultrasonically for 24 h, then the amount which had been washed out of the surface of the latex film was measured by titration. The strength of ultrasonic elution was enough to isolate the emulsifier that was not bonded to the latex film surface completely, and the titration analysis methods were accurate to 5 ppm. As the mass of emulsifier, latex films and

monomer in the emulsion polymerization was known, it was calculated that CTAB, 3.97% of the whole mass of latex film, was washed out of the latex film by ultrasonic washing. The concentration of the CTAB on the surface of the latex film was 1.53×10^{-2} mol/L when the volume of bacteria vaccinated on the surface of latex film was 0.2 mL in the antibacterial test, this concentration was far more than the MIC (2.44×10^{-5} mol/L). This is the reason the latex film of CTAB also has antibacterial properties. Using the same methods of washing, F5 could be washed away because of its being water-soluble, but the amount of F5 which was washed out of the latex film was near to zero. This indicated that F5 was bonded onto the surface of latex film, and the antibacterial property of the latex film was caused by F5. This experiment showed that the traditional emulsifier did not have long-lasting antibacterial properties but that polymerizable bactericides can be developed successfully.

Acknowledgments We thank Professor Lingyun Jia of School of Environmental and Biological Science and Technology in Dalian University of Technology for supporting the testing of MIC. The financial support granted by Dalian Science and Technology Programme (China, No. 2007A10GX124) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT0711) is gratefully appreciated.

References

1. Greene BW, Saunders FL (1970) In situ polymerization of surface-active agents on latex particles: the electrolyte stability of styrene/butadiene latexes. J Colloid Interface Sci 33:393–404
2. Unzue MJ, Schoonbrood HAS, Asua JM, Goni AM, Sherrington DC, Stahler K, Goebel KH, Tauer K, Sjoberg M, Holmberg K (1997) 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
3. Soula O, Guyot A, Williams N, Grade J, Blease T (1999) Styrenic surfmer in emulsion copolymerization of acrylic monomers. II. Copolymerization and film properties. J Polym Sci Part A Polym Chem 37:4205–4217
4. Sindt O, Gauthier C, Hamaide T, Guyot A (2000) Reactive surfactants in heterophase polymerization. XVI. Emulsion copolymerization of styrene-butyl acrylate-acrylic acid in the presence of simple maleate reactive surfactants. J Appl Polym Sci 77:2768–2776
5. Asua JM, Schoonbrood HAS (1998) Reactive surfactants in heterophase polymerization. Acta Polymerica 49:671–686
6. Abele S, Gauthier C, Graillat C, Guyot A (1999) Films from styrene–butyl acrylate lattices using maleic or succinic surfactants: mechanical properties, water rebound and grafting of the surfactants. Polymer 41:1147–1155
7. Amalvy JI, Unzue MJ, Schoonbrood HAS, Asua JM (2002) Reactive emulsifiers in heterophase polymerization: colloidal properties, film-water absorption, and emulsifier exudation. J Polym Sci Part A Polym Chem 40:2994–3000
8. Sun H, Xia Y, Chen L, Tan ZY, Meng LY (2006) Present situation and development trend of research on antibacterial agent at home and abroad. China Plastics Industry 34:1–4
9. Ikeda T, Tazuke S, Suzuki Y (1984) Biologically active polycations, 4. Synthesis and antimicrobial activity of poly(trialkylvinylbenzylammonium chloride)s. Makromolekulare Chemie 185:869–876
10. Nudel R, Gilbert E, Schrier EE (1982) Water insoluble disinfectant composition. U.S. Patent 4,349,646
11. Hiroki K, Yoshio Y (1987) Antibacterial polymer. U.S. Patent 4,826,924
12. Jesse AM, Abdelmoula N, Hwang-Hsing C, Anura PD, Brian D, John C (2006) Quaternary ammonium substituted thieno[3, 2-e]-1, 2-thiazine-6-sulfonamide-1,1-dioxides: potential membrane impermeable inhibitors of carbonic anhydrase. Bioorg Med Chem 14:2052–2059
13. Guthrie C, Walter G, Qureshi H, Shoaib S (2001) Multiple choice: new microbial control option for paint and coating. Mod Paint Coat 91:21–23
14. Kourai H, Manabe Y, Matsutani E, Hasegawa Y, Nakagawa K (1995) Antimicrobial activities of alkylallyldimethylammonium iodides and alkylallyldiethylammonium iodides. Bokin bobia 23:271–280
15. Wang RX, Guo JF, Gao BJ (2006) Antibacterial property and mechanism of macromolecular quaternary pyridine salt. Chinese J Appl Chem 23:184–187
16. Hamaide T, Ziicmanis A, Monnet C, Guyot A (1994) Synthesis and NMR characterization of new poly(ethoxyalkyl) maleates. Polymer Bull 33:133–139
17. Wang M, Ding XG, Cao XD, Yang H (2003) Preparation of Ag^{+}/TiO2 antibacterial film on the stainless steel. Cailiao Kexue Yu Gongcheng Xuebao 21:379–382
18. Ni H, Dan Z, Xu B, Xiong J, Xiong PY (2005) Antibacterial property of stainless steel implanted by Cu ions. Gongneng Cailiao 36:1906–1908
19. Nelson WL, Freeman DS, Sankar R (1975) Bicyclic amino alcohols. Isomeric 2-dimethylaminomethyl-3-hydroxymethylbicyclo[2.2.1] hept-5-enes. J Org Chem 40:3658–3664
20. Dymicky M (1983) Preparation of monomethyl fumarate. Org Prep Proced Int 15:233–238

Author Biographies

Weihong Qiao obtained an M.Sc. in 1994 and a Ph.D. in 2000 from Dalian University of Technology. Since 1994, she has been teaching and working at Dalian University of Technology, and her main field of research is the synthesis and physical chemistry of emulsifiers.

Cui Cao is a master's student at Dalian University of Technology. Her main field of research is synthesis and properties of emulsifiers.

Yingli Sun obtained an M.Sc. from Dalian University of Technology in 2008. His main field of research is the synthesis and physical chemistry of emulsifiers.

Hongzhu Liu is a senior engineer, and his main field of research is the exploration of waterborne fluorine-containing polymers and waterborne coatings.

Xingshun Zhao is an engineer, and his main field of research is the exploration of waterborne fluorine-containing polymers and waterborne coatings.

Xinmei Fu is an engineer, and her main field of research is organic mass spectrometry and high performance liquid chromatography.