Preparation of Acrylic/Acrylate Copolymeric Surfactants by Emulsion Polymerization Used in Pesticide Oil-in-Water Emulsions

Yongli Shi,[1,2] Ting Zheng,[1] Qing Shang[1]

[1]*School of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, People's Republic of China*
[2]*School of Materials Science and Engineering, Tianjin University, 300072 Tianjin, China*

Received 21 February 2011; accepted 18 May 2011
DOI 10.1002/app.34974
Published online 2 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this work, acrylic/acrylate copolymeric surfactants, which can be used in the preparation of pesticide oil-in-water emulsions (EW), were synthesized by emulsion polymerization, using potassium persulfate ($K_2S_2O_8$) as an initiator, dodecyl mercaptan (DDM) as a chain transfer agent at the temperature range of 82–85°C. When the weight ratio of monomers was m(butyl acrylate) : m(methyl methacrylate) : m(acrylic acid) = 4 : 4 : 1.6 and the dosage of DDM was 2% (percentage of monomer mass), the prepared acrylic/acrylate copolymeric surfactants had a number-average molecular weight of 2.5×10^4 and exhibited good stability for pesticide EW. The carboxylic group distribution studies show that only the surface carboxylic groups make dispersed pesticide oil droplets more stable. The acrylic/acrylate copolymeric surfactants prepared by shot-monomer had the most surface carboxylic group distribution (46.6%). To obtain greater surface carboxylic group distribution, maleic anhydride (MA) was used to modify the polymer system. Adding 2% MA (percentage of monomer mass) to the polymerization system, the surface carboxylic groups were increased 12% over unmodified acrylic/acrylate copolymeric surfactants. Compared with traditional pesticide EW, the avermectin EW prepared with acrylic/acrylate polymeric surfactant had much better stability. Meanwhile, its pesticide effect was similar to that of a control (1.8% abamectin emulsifiable solution). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3117–3127, 2012

Key words: surfactants; emulsion polymerization; carboxylic group distribution; pesticide EW; monomers

INTRODUCTION

An oil-in-water emulsion (EW) is an environmentally friendly pesticide formulation. It uses water rather than organic solvents as a continuous phase, which reduces the environmental pollution and decreases production costs. Moreover, it has great significance in the exploration of new pesticide formulations. Usually, traditional pesticide EW preparation involves direct mixing of the pesticide oil and water in the presence of appropriate surfactants. The pesticide EW is an unstable multiphase thermodynamic system,[1,2] Its poor stability has no very effective solution as yet. This problem has become a major factor that limits the further development of pesticide EW. The stability of pesticide EW depends on the surfactants used in formulation. The ideal surfactants have the remarkable capacity of efficiently reducing the interfacial tension between the immiscible fluids (as long as the surfactant system is properly chosen).[3] At present, some traditional commercially available surfactants used in pesticide EW preparation are micromolecular chemicals, such as alkylphenol ethoxylates (OP), sodium alcohol ether sulfate (AES), and sodium alpha-olefin sulfonate (AOS). Also, the use of some novel macro-molecular surfactants such as Pluronic and Agrimer types in pesticide formulations have been reported.[4] But, none of these commercially available surfactants were able to improve the stability of pesticide EW efficiently. Moreover, there are no surfactants designed specifically for pesticide EW preparation. These drawbacks of traditional surfactants have become a serious obstacle to further applications of pesticide EW.

Considering these problems, we prepared a novel acrylic/acrylate amphiphilic copolymer which can be used as a polymeric surfactant to improve the stability of pesticide EW. Compared with conventional surfactants, our acrylic/acrylate copolymeric surfactants have an enhanced oil-loving (hydrophobic) portion and a large water-loving (hydrophilic)

Correspondence to: Q. Shang (shangqingyl@163.com).
Contract grant sponsor: 10th Five Years Plan (Foundation of the 10th Five Years Key Programs for Science and Technology Development of China).

part. This makes them become promising polymeric surfactants for stabilizing pesticide EW, because they possess a stronger adsorption power and an enhanced dispersing ability. Thus, they have many advantages. To begin with, in contrast to conventional micromolecular surfactants, the acrylic/acrylate copolymeric surfactants chains can wind around the oil droplets to produce steric hindrance between the dispersed droplets and prevent them from reuniting.[5] Second, compared with other polymeric surfactants, their hydrophobic portions are adsorbed in pesticide oil droplets, and they can form a layer of negative charges (entropy layer). Therefore, when separated oil droplets approach each other, these negative charge layers will prevent them from coming together. Third, by changing the functional monomer concentration ratio, their hydrophilic and hydrophobic portions are easily adjusted to suit the needs of different pesticide EW. Finally, the acrylic/acrylate copolymeric surfactants prepared by emulsion polymerization do not need further segregation before being used in pesticide EW preparations, thus improving manufacturing efficiency.

According to reports in the literature, in the resulting acrylic/acrylate copolymeric surfactants, part of carboxylic groups were distributed on the surface of polymers (particle surface) and another part was wrapped up by polymer chains and encapsulated in the polymers (buried). In addition, a small portion of the acrylic acid (AA) did not react with other monomers but self-polymerized in the aqueous phase, and these carboxylic groups were distributed in water (serum).[6–10] Experiments showed that in pesticide EW, only the surface carboxylic group generated electric double layers to improve pesticide EW stability. To get more surface carboxylic group distribution, maleic anhydride (MA) was used to modify the polymeric system. Finally, the modified acrylic/acylate copolymeric surfactant exhibited an enhanced dispersing power.

The acrylic/acylate copolymeric surfactants can be used in many pesticide EW preparations such as abamectin EW, beta cypermethrin EW, and acetochlor EW. In this work, a novel abamectin EW was prepared with the acrylic/acrylate copolymeric surfactants. The resulting abamectin EW showed enhanced stability. Laboratory toxicity tests were also performed, and the results were satisfactory.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, monomer), butyl acrylate (BA, monomer), and AA (functional monomer) were distilled under vacuum to remove any traces of inhibitor and were stored at −4°C before use. MA (functional monomer), dodecyl mercaptan (DDM, chain transfer agent), and potassium persulfate ($K_2S_2O_8$, initiator) of chemically pure grade were purchased from Tianjin Damao Chemical Reagent Factory, China. Alkylphenol ether sulfosuccinate sodium salt (MS-1), alkylphenol polyoxyethylene (OP-10), and sodium dodecyl sulfate (SDS) of commercially pure grade were used directly without any further treatment. Abamectin, AR grade (95% pure), was purchased from Hebei Veyong Bio-Chemical Co., China.

Preparation of acrylic/acrylate copolymeric surfactants

The acrylic/acrylate copolymeric surfactant emulsion was prepared by emulsion polymerization in a 250 mL four-neck flask equipped with a mechanical stirrer, a thermometer, and a condenser. A mixture (a) of 4 g MMA, 4 g BA, 1.6 g AA, 0.2 g MA, and 0.2 g DDM was dispersed in another mixture (b) of 10 g distilled water, 6 g OP-10, 2 g MS-1, and 0.5 g SDS with mechanical stirring for 40 min to obtain mixture (c). $K_2S_2O_8$ (0.5 g) was dissolved in 25 mL of distilled water to give mixture (d). The four-neck flask, pretreated with 40 mL distilled water, was heated to 82°C using a controllable water bath and then mixtures (c) and (d) were added to the four-neck flask in droplets for 3 h. After feeding the monomers, the flask was maintained at 82–84°C for 30 min to guarantee that the residual monomers reacted completely. Then, the four-neck flask was cooled to 25°C. The acrylic/acrylate copolymeric surfactant emulsion was adjusted to pH 7.0–7.1 with 10% aqueous NaOH solution, and the acrylic/acrylate copolymeric surfactant emulsion was prepared.

To separate the acrylic/acrylate copolymeric surfactants from the emulsion, 0.12 mol L^{-1} hydrochloric acid solution was added to the prepared acrylic/acrylate copolymeric surfactant emulsion in droplets with mechanical stirring. The acrylic/acrylate copolymeric surfactants demulsified and deposited quickly with the addition of the hydrochloric acid solution. The precipitates were separated, and the emulsifiers and unreacted monomers were washed away with large amounts of 95% methanol solution several times. Then, the precipitated polymers were dried in a vacuum freeze dryer (LGJ-10, China) under −25°C for 24 h. The dried acrylic/acrylate copolymeric surfactants were used for Fourier transform infrared spectroscopy (FTIR) characterization. The acrylic/acrylate copolymeric surfactants were used in the preparation of pesticide EW directly without any further treatment.

Preparation of pesticide EW

A novel pesticide EW was prepared with the acrylic/acrylate copolymeric surfactant emulsion,

and abamectin was selected as a model pesticide. The formulation was prepared in a 100 mL three-neck flask equipped with a mechanical stirrer and a thermometer. The specific preparation process is as follows: 50 g of acrylic/acrylate copolymeric surfactant emulsion pretreated in a three-neck flask was maintained at 45°C using a controlled temperature water bath. A total of 1.4 g (95%) of abamectin was dissolved in 5 g of cyclohexanone, and the solution was added to the three-neck flask with mechanical stirring for 10 min. A total of 1.5 g of antifreeze and 0.25 g of silicone antifoam were added to the above solution. Then, the three-neck flask was cooled to 25°C. The active ingredient content of abamectin EW was about 2%.

CHARACTERIZATION

Structure characterization of copolymer

FTIR (Bio-Rad FTS-135, Ameirica) was used to study the structure of the acrylic/acrylate copolymer surfactants. The FTIR samples were prepared with KBr powder under a hydraulic pressure of 400 kg. The infrared spectra of the samples were obtained from an FTIR spectrophotometer and recorded in the absorption mode, covering a range from 500 to 4000 cm^{-1}. ^{1}H-NMR experiments were performed using a probe for the liquid state on powdered samples in 5 mm diameter tubes, with a recycle time of 5 s, 90° pulse lengths (6.9 ms) and a 200 kHz bandwidth.

Atomic force microscope

The atomic force microscope (AFM) system used here is a set of a Seiko Instrument SPI-3800N probe station. The acrylic/acrylate copolymeric surfactant surface was conducted with a gold-coated AFM probe (Seiko Instrument: SI-AF01-A, Japan) in contact mode. The injection voltage used was 7 V, and the scanning speed was 0.1 mm s^{-1}.

Particle size distribution

The average particle size distribution of the acrylic/acrylate copolymeric surfactants was characterized by the light scattering technique, using a Zetasizer 2000 instrument (Malvern, Britain). To prepare the sample, 1 mL of polymer emulsion was diluted in 200 mL of distilled water.

Gel permeation chromatography

The acrylic/acrylate copolymeric surfactants were analyzed using gel permeation chromatography (GPC) to measure the molecular weight. Waters GPC equipment was used for chromatographic analysis, a differential refractive index meter (Waters 410 detector, America) as a detector, and a series of two columns (Waters HR 4E and HR 3, America) for separating constituents of the acrylic/acrylate copolymeric surfactants by molecular size were used. For the validity of the results, the sample must be kept at a constant temperature, achieved by keeping the columns constant at 35°C in a column oven. All processed data collections were controlled by computer software.

Carboxylic group distribution

The distribution of carboxylic groups was measured by conductivity-titration method. The detailed experimental process is as follows: Acrylic/acrylate copolymeric surfactant emulsion (5 mL) was diluted in 30 mL of distilled water. The solids content of diluted acrylic/acrylate copolymeric surfactant emulsions was calculated by the gravity method. Adjusting the pH of diluted acrylic/acrylate copolymeric surfactant emulsion to 11.50 ± 0.02 with 0.385 mol L^{-1} NaOH solution, the pH of acrylic/acrylate copolymeric surfactants emulsion was monitored using a digital pH meter (PHS-25, China). Finally, the resulting emulsion was allowed to stand for about 30 min. Then, the treated emulsion was titrated with 0.0242 mol L^{-1} H_2SO_4 solution, and the electric conductivity of the titrated emulsion was detected with a conductivity meter (DDS-307, China). The contents of carboxyl groups were calculated according to the following formulas:

$$S_a(\%) = \frac{V_{sb} \times 2c \times 72.06}{W \times S} \times 10^{-3} \quad (1)$$

$$F_a(\%) = \frac{V_f \times 2c \times 72.06}{W \times S} \times 10^{-3} \quad (2)$$

$$B_a(\%) = (1 - S_a - F_a) \times 100\% \quad (3)$$

where S_a is the content of surface carboxyl groups (%), F_a is the content of serum carboxyl groups (%), B_a is the content of buried carboxyl groups (%), V_{sb} is the volume of H_2SO_4 solution that titrated the surface carboxyl groups (mL), V_f is the volume of H_2SO_4 solution that titrated the serum carboxyl groups (mL), c is the concentration of H_2SO_4 solution (mol L^{-1}), W is the quantity of acrylic/acrylate copolymeric surfactant emulsion, and S is the solids content of acrylic/acrylate copolymeric surfactant emulsion (%).

Mechanical properties

Certain acrylic/acrylate copolymeric surfactant emulsion was sprayed on a polytetrafluoroethylene board. And the emulsion was dried in a 101A-2

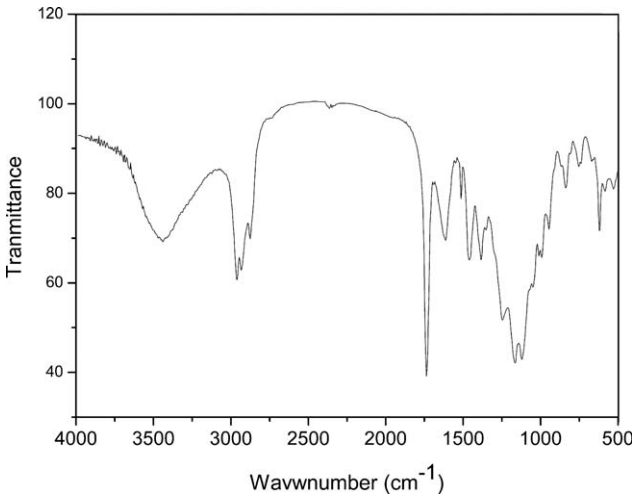

Figure 1 FTIR spectrum of acrylic/acrylate copolymeric surfactants.

electrothermal blowing dry box (Shanghai Experimental Instrument, China) for 24 h to obtain an acrylic/acrylate copolymeric surfactant polymer membrane (about 20 μm in thickness). Then the membrane was cut into strips of 50 mm in length by 20 mm in width. The drawing behavior of acrylic/acrylate copolymeric surfactant belts were test on a Testometric AX Universal Material Testing Machine.

Testing for a stable pesticide EW

The storage stability of abamectin EW was studied following the methods described by the Collaborative International Pesticides Analytical Council. Abamectin EW samples were put into several 10 mL ampoule bottles at 25°C, adding pure nitrogen for 15 s and sealed by ampere glass melting. Three ampoule bottles were stored in a 101A-2 electrothermal blowing dry box (Shanghai Experimental Instrument, China). After storage at (54 ± 2)°C for 14 days, the determined average active ingredient content must not be lower than 95% relative to the determined average content found before storage; in addition, the abamectin EW must be free of "oil" and/or "cream." Another three ampoule bottles were stored in a DLAB-5/20 low-temperature cooling liquid circulating pump (Greatwall Scientific Industrial and Trading Co., China) at (0 ± 2)°C for 7 days. The abamectin EW should be free of "oil" and/or "cream," and the abamectin EW active ingredient content must not be lower than 95% relative to the average content before storage. A total of 5 mL of abamectin EW was diluted with 100 mL of standard water (342 ppm), and the sample was allowed to stand for 24 h at (30 ± 2)°C; after standing it should be free of "oil" and/or "cream." Other samples were stored at 25°C for a year to determine their long-term stability.

Laboratory toxicity tests

Laboratory toxicity tests of abamectin EW were performed at the Plant Protection Institute of Hebei Academy of Agricultural and Forestry Sciences. All tests were performed using *Plutella maculipennis Curtis* (1st–3rd instar larva) as a potential target. This species was selected, because it was specified for acute toxicity testing. Sample concentrations suitable for toxicity testing were obtained by diluting samples with distilled water. A total of 2.0% abamectin emulsifiable solution (EC) was used as a control pesticide.

RESULTS AND DISCUSSION

Characterization of acrylic/acrylate copolymeric surfactants

FTIR spectra of refined acrylic/acrylate copolymer surfactants were obtained and are presented in Figure 1. In the spectrum, the peak observed at 1731.25 cm^{-1} is due to the conjugated ester carbonyl stretching of acrylic/acrylate copolymers. The asymmetry stretching vibration of methyl was observed at 2962.45 cm^{-1}. The characteristic absorption peaks appearing at 2853.65 and 1465.42 cm^{-1} are due to the carbonyl stretching and the bending vibration of —CH—. The peaks observed at 1725.64, 1400.67, and 920.32 cm^{-1} were typical stretching of —COOH. No absorption peaks of carbon double bonds were observed. These results confirmed that the acrylic/acrylate copolymers had been prepared. To fully elucidate the structure of acrylic/acrylate copolymeric surfactants, ^{1}H-NMR studies have been undertaken (Fig. 2). Notably, the signals of the methylic protons (0.5-1.5 ppm) can be seen after the copolymerization. The absorptions for the protons (3.5–4.5 ppm) of —$COCH_2$— groups were plainly visible. Preliminary results indicate that the complete conversion of all monomers and the acrylic/acrylate copolymeric surfactants were prepared.

For acrylic/acrylate copolymeric surfactants, molecular weight has some effect on their properties. The main influences are the following: on one hand, the acrylic/acrylate copolymeric surfactants with lower molecular weight form micelles easily. Because of the increase in micelles and association numbers, their dispersing power is greatly decreased. On the other hand, acrylic/acrylate copolymeric surfactants with higher molecular weights will wind together and lose their surface activities. Only the acrylic/acrylate copolymer surfactants with moderate molecular weights have much better stabilization and dispersing power, which makes them suitable for use as polymeric surfactants. In emulsion copolymerization, the dosage

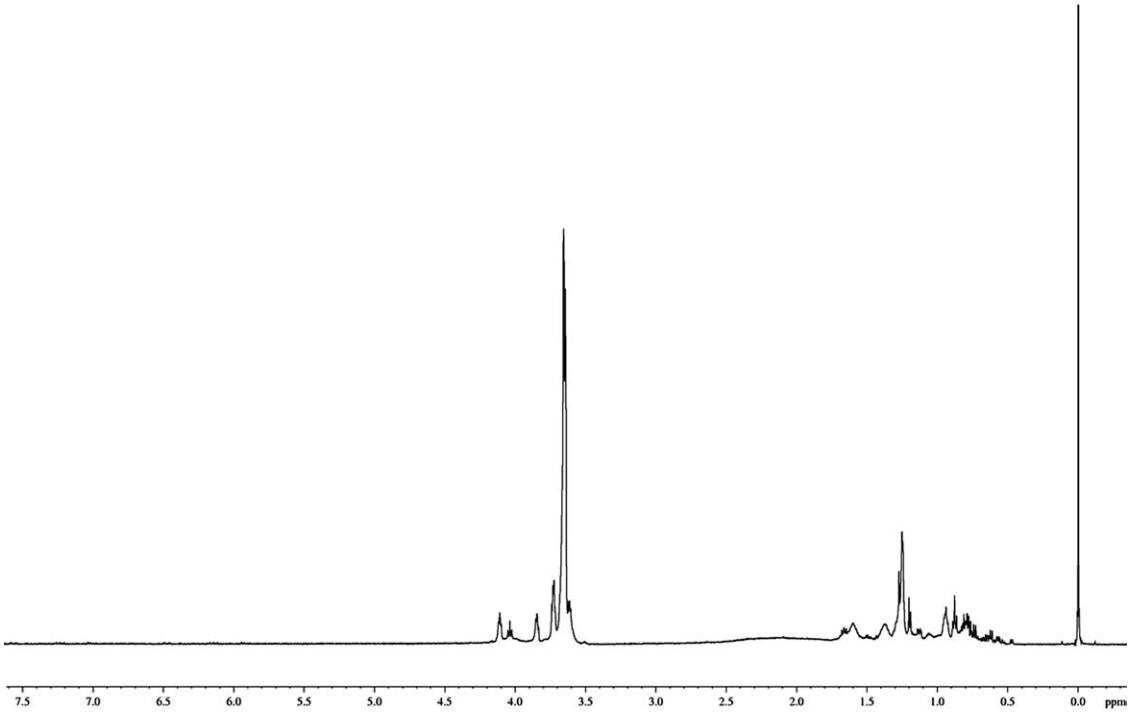

Figure 2 ^{1}H-NMR spectrum of acrylic/acrylate copolymeric surfactants.

of emulsifiers has an effect on copolymeric surfactant molecular weight.

Under the same experimental conditions but with changing dosages of emulsifiers, we discovered that the number-average molecular weights of acrylic/acrylate copolymeric surfactants decreased gradually with increased percent of emulsifiers (see Table I), and the smallest number-average molecular weight was about 3.3×10^4. To prepare copolymeric surfactants with much smaller molecular weights, dodecyl thioalcohol (DDM) was used as a chain transfer agent to control the copolymers molecular weight. With the DDM increasing, the molecular weight of the copolymers decreased accordingly. The reason for this is as follows: in emulsion copolymerization, with DDM added, the increasing active chains were transferred to DDM molecules; when the increase in active chains ceased, the molecular weight decreased. The relationship between DDM dosage and polymer molecular weight is shown in Figure 3. The molecular weights of acrylic/acrylate copolymeric surfactants could be limited to a small range by adjusting the quantities of DDM. Investigations concerning the relationship between the molecular weight of the copolymeric surfactants and their dispersing ability were studied as follows: a series of abamectin EW were prepared with different acrylic/acrylate copolymeric surfactants which have various molecular weights. The resulting pesticides EW were divided into three groups and stored at 25°C, 0°C, and 55°C for 14 days. After storage, the particle size distributions of pesticides EW were determined. When the molecular weight was around 2.5×10^4, the particle size of pesticide EW had the smallest increase (see Fig. 4), which indicated that this abamectin EW may have better stability. The moderate molecular weight of 2.5×10^4 was determined initially, and the proper dosage of DDM was 2% (percentage of monomers mass). The influences of different molecular weight of conventional and the acrylic/acrylate copolymeric surfactants on their dispersing powers were also discussed. From Figure 4, we can see that the emulsifier dispersing powers presented the trend of first decrease then increase with the increase of molecular weight. The dispersing powers of acrylic/acrylate copolymeric surfactants were better than conventional emulsifiers. And the acrylic/acrylate copolymeric surfactants with moderate molecular weight (2.5×10^4) had more perfect emulsifier dispersing powers.

TABLE I
The Variation of Acrylic/Acrylate Copolymeric Surfactants Average Molecular Weight with Different Emulsifier Mass

Emulsifier (%)	Mw (weight-average molecular weight)	Mn (number-average molecular weight)	Mv (viscosity-average molecular weight)
4	62,207	36,178	50,838
6	40,372	34,307	36,730
8	35,565	32,950	34,528

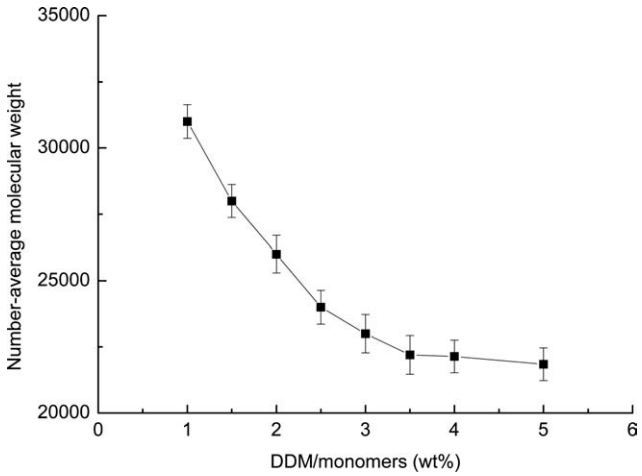

Figure 3 The relationship between DDM mass and polymer molecular weight.

The size distributions are monomodal, as seen from the histograms in Figure 5. And the morphologies of acrylic/acrylate copolymeric surfactants with and without SDS were shown in Figure 6. The average particle sizes of acrylic/acrylate copolymeric surfactants with different emulsifiers are summarized. The use of SDS as an emulsifier leads to the formation of relatively small nanoparticles (~ 40 nm). Larger particles are obtained in the case of the absence of SDS as an emulsifier (approximately 98 nm). The size distribution of the latter particles is slightly broader in comparison with the former ones, which indicated that the former copolymer particles have uniform particle size and stable performance. This property is very important to the dispersing power of acrylic/acrylate copolymeric surfactants.

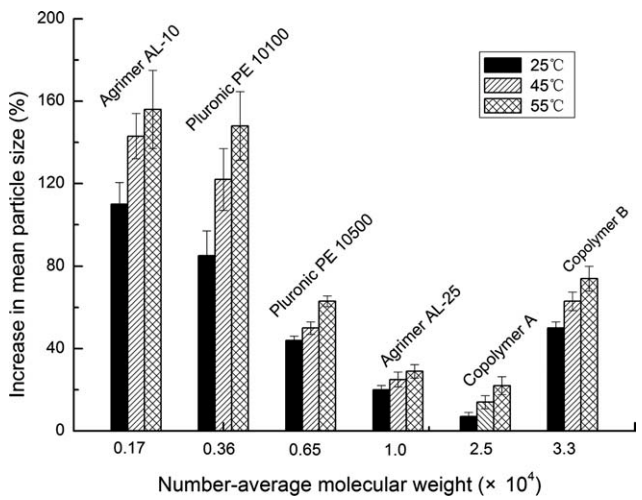

Figure 4 The influnces of different molecular weight of conventional and the acrylic/acrylate copolymeric surfactants on their dispersing powers.

Carboxylic group distribution

AA was typically used as a functional monomer in emulsion polymerization to increase the hydrophilic power of polymers. It can improve the adhesion and mechanical properties of the acrylic/acrylate copolymers.[11–14] In the preparation of acrylic/acrylate copolymeric surfactants, when AA increased from 0.6 g to 1.2 g, the average tension of acrylic/acrylate copolymers belts increased from 1.72 ± 0.21 N mm^{-1} to 2.95 ± 0.40 N mm^{-1} (see Fig. 7). And these data supported that AA improved the mechanical properties of acrylic/acrylate copolymeric surfactants. In emulsion copolymerization, the carboxyl groups are distributed in three phases (buried, particle surface, and serum). The small quantity of serum carboxylic groups can be explained by the high water solubility of AA and the different reactivity ratios associated with MMA (r_{AA} = 1.73, r_{MMA} = 0.418) and BA (r_{AA} =1.31, r_{BA} = 0.91).[15,16] The AA dissolved in water will self-polymerize in the aqueous phase to form serum carboxylic groups.[17,18] Another portion of the carboxylic groups is distributed on the acrylic/acrylate copolymers surface. According to K.L Hoy's theory, these surface —COO^- groups repel one another via their electrostatic interactions to extend and form an electric double layer which Kenneth called the entropy layer. The entropy layer improved the mechanical properties of the acrylic/acrylate copolymers surfactants. In pesticide EW, the hydrophobic portion of polymeric surfactants is anchored in pesticide oil droplets, and the —COO^- groups are distributed on the droplets surface. The electrostatic repulsion of electric layers prevents the dispersed oil droplets from reuniting again. However, the buried carboxylic groups have difficulty in forming an entropy layer, so they make no contributions to the stability of pesticide EW. Therefore, it was necessary to make more carboxyl groups on the acrylic/acrylate copolymer surfaces.

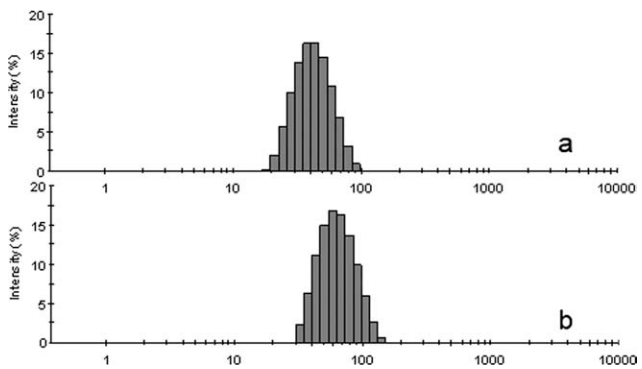

Figure 5 Average particle diameters of samples: (a) acrylic/acrylate copolymeric surfactants prepared with SDS as an emulsifier, (b) acrylic/acrylate copolymeric surfactants prepared without SDS.

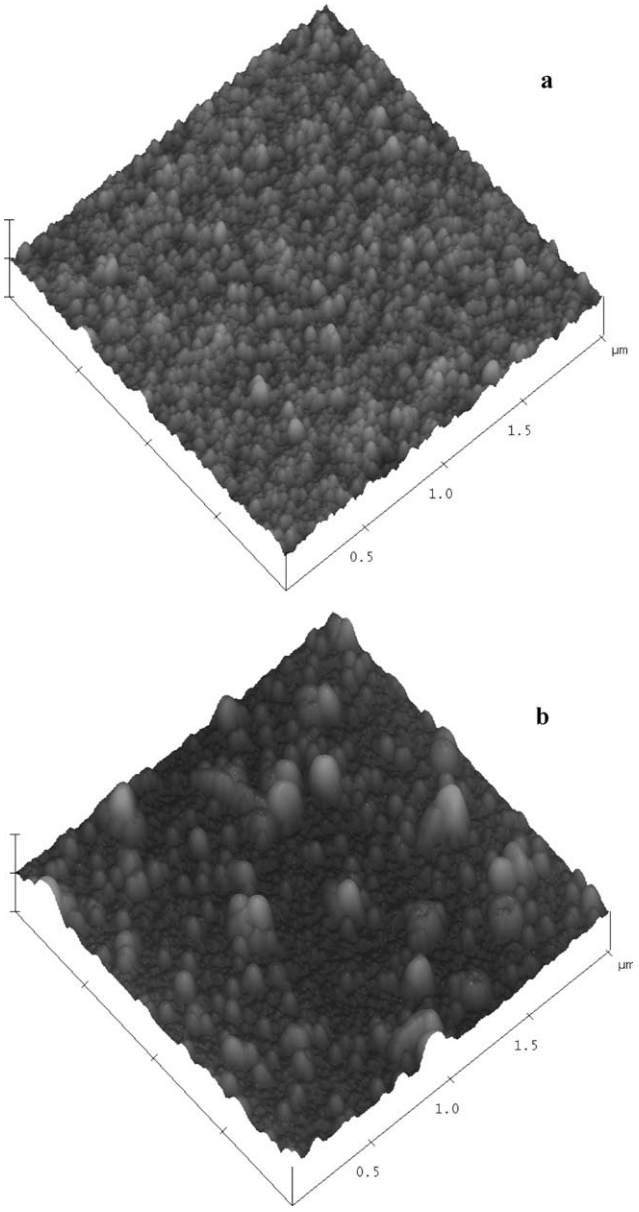

Figure 6 AFM of acrylic/acrylate copolymeric surfactants: (a) acrylic/acrylate copolymeric surfactants prepared with SDS as an emulsifier, (b) acrylic/acrylate copolymeric surfactants prepared without SDS.

The influences of functional monomer mass on carboxylic group distribution were studied. The experimental data indicated that the carboxylic groups distributed in three phases all increased with rising AA mass. The contents of carboxylic groups distribution was calculated and the results (see Fig. 8) showed that serum carboxyl groups (F_a) and surface carboxyl groups (S_a) increased slightly, but the buried carboxylic groups increased visibly. This is because the amount of free radicals and nucleation increased with AA addition, which resulted in the particles and carboxylic groups increasing. Meanwhile, specific surface areas of the acrylic/acrylate copolymers enlarged with diminishing particle size, and then more free radicals diffused into the colloidal particles and were buried in them. Consequently, the buried carboxylic groups increased sharply.

The carboxylic group distribution also depends on different AA feeding methods (batch, semibatch, or shot-monomer) in emulsion polymerization.[19–21] For batch addition, the results indicated that over 10 % of carboxylic groups were distributed in the aqueous phase [see Fig. 9(a)]. That can be explained by the high water solubility of AA. That part of AA self-polymerized in water instead of reacting with other monomers. As for semibatch, a large amount of carboxylic groups was buried in the acrylic/acrylate copolymers [see Fig. 9(b)]. A possible reason for this is that much AA dispersed into colloidal nuclei and was buried in acrylic/acrylate copolymers during emulsion copolymerization. In shot-monomer, most of the carboxylic groups appear on the polymer surfaces [see Fig. 9(c)]. The functional monomers

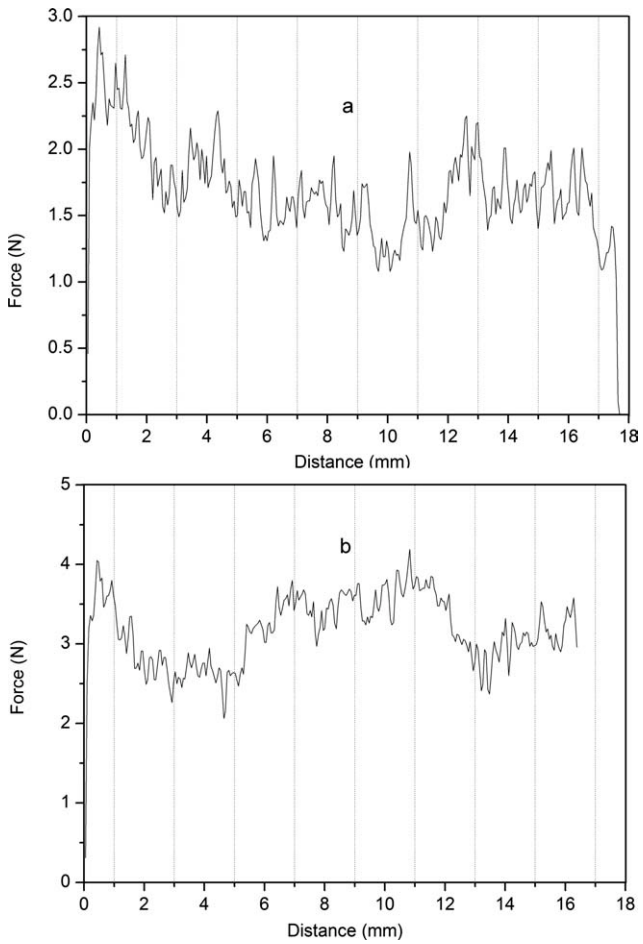

Figure 7 The average tension of acrylic/acrylate copolymers belts: (a) acrylic/acrylate copolymeric surfactants prepared with 0.6 g AA, (b) acrylic/acrylate copolymeric surfactants prepared with 1.2 g SDS.

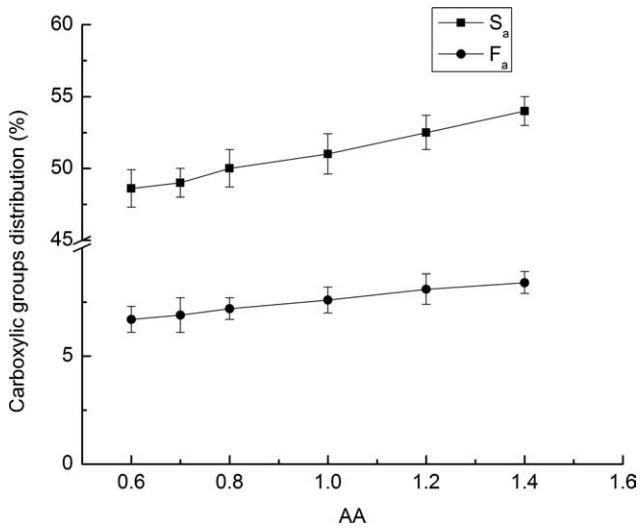

Figure 8 Different carboxylic group distribution at different dosages of AA.

added in droplets were dispersed in oil and aqueous phase in a certain proportion. The AA dissolved in the oil phase copolymerized with other monomers and this part of the carboxyl groups was buried in acrylic/acrylate copolymeric surfactants. Another part of AA dissolved in the aqueous phase and diffused into the polymer particles to supplement the reacted AA; it copolymerized with other monomers during the on-going diffusion. The carboxylic groups formed certain graded distributions from acrylic/acrylate copolymeric surfactant surfaces to their cores, which caused most carboxylic groups to distribute on the surface of acrylic/acrylate copolymeric surfactants.[22] Only a small portion of AA self-polymerized in the aqueous phase and dissolved in water or absorbed on the surface of acrylic/acrylate copolymeric surfactants.[23] Thus, shot-monomer was determined to be the optimum monomer feeding method.

To increase surface carboxylic group distribution, MA was used to modify the acrylic/acrylate copolymers. Under the same experimental conditions but increasing the mass of MA, the carboxylic group distribution was calculated and is shown in Figure 10. Experimental results showed that the acrylic/acrylate copolymers produced more surface carboxylic groups distribution because a MA molecule can generate two carboxylic groups, so it has better hydrophilic power than AA. Also, its reactivity ratio is small when copolymerized with MMA and BA. These properties make it difficult for MA to self-polymerize in water, which decreases the serum carboxylic group distribution. Meanwhile, S_a increases with increase in MA mass.

Investigations of the influence of carboxylic group distribution on the stability of pesticide EW were performed as follows: different abamectin EW were prepared using different acrylic/acrylate copolymeric surfactants with various surface carboxylic groups. The resulting abamectin EW was then sealed in 10 mL ampoule bottles. These ampoule bottles were stored at 25°C, 0°C, and 55°C. After 2 weeks storage, the average particle size and the particle size distribution of the samples were redetermined (results are shown in Fig. 11). Figure 11 illustrates that the particle sizes of abamectin EW changed after storage, but the variation trend was opposite. With the surface carboxylic groups increasing, the change in particle size is decreased. When the S_a was 60%, the abamectin EW had the smallest variation. These results indicated that the abamectin EW with smaller variation may have better stability. Meanwhile, they also demonstrated that S_a improved the stability of pesticide EW.

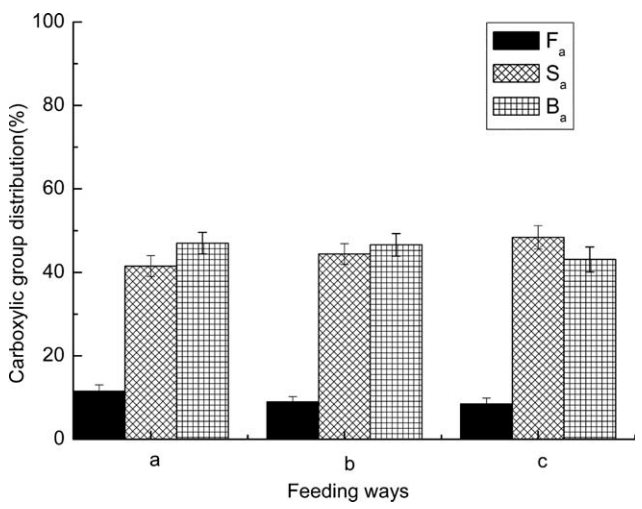

Figure 9 Carboxyl group distribution of different feed methods: (a) batch, (b) semi-batch, and (c) shot-member.

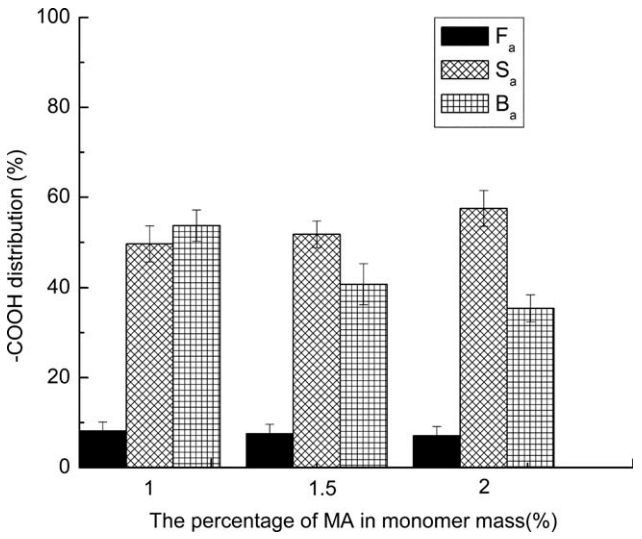

Figure 10 The contents of surface carboxylic groups with increasing MA mass.

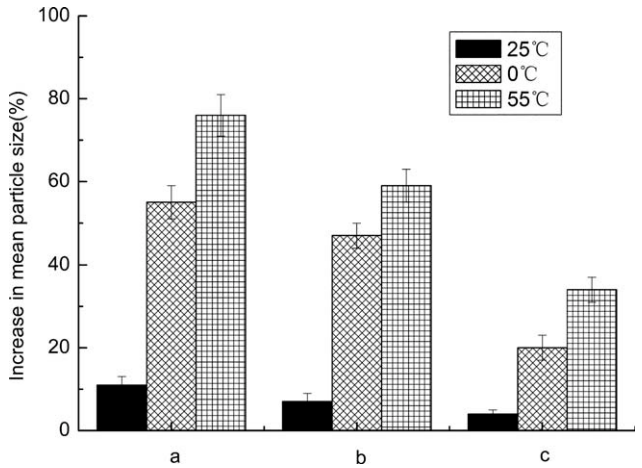

Figure 11 The influence of surface carboxylic group distribution on their dispersing powers: (a) containing 34.5% Sa, (b) containing 43.6% Sa, (c) containing 57.81% Sa.

The dispersing powers of different polymeric surfactants

Investigations concerning the dispersing ability of the acrylic/acrylate copolymeric surfactants were performed with several commercially available polymeric surfactants used as control surfactants (Table II). The studies were performed in the same way: 200 g L^{-1} of the active ingredient of abamectin (20 g) were suspended in a solution (30 g) of 2 wt % commercially available polymeric surfactants, 2 wt % OP-10, 0.5 wt % MS-1, 0.125 wt % SDS, and the final solutions were used as controls. The acrylic/acrylate surfactant emulsion had the same concentration as the commercially available polymeric surfactant solution and was used directly without further treatment, which guaranteed that the control experiments were performed under the same conditions. A series of abamectin EW was prepared, and the resulting EW was then divided into

TABLE II
Trade Names of the used Polymeric Surfactants

Group 1	Group 2
Pluronic PE10100	Agrimer AL25
Pluronic PE10500	Agrimer AL10
Pluronic PE12200	Agrimer VA03E
Acrylic/acrylate copolymeric surfactants	Acrylic/acrylate copolymeric surfactants

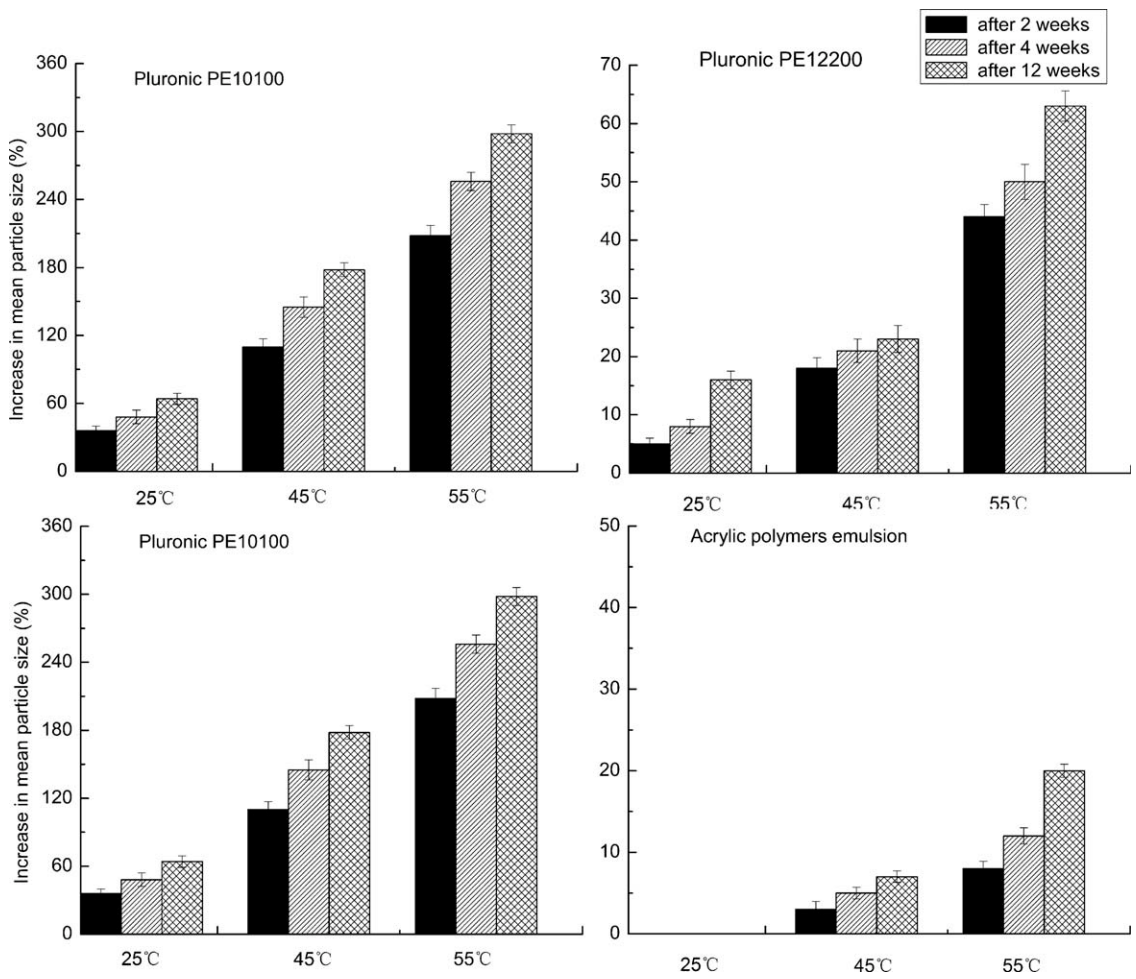

Figure 12 Relative particle size increase of abamectin EW prepared with acrylic/acrylate copolymeric surfactants and different Pluronic polymeric surfactants.

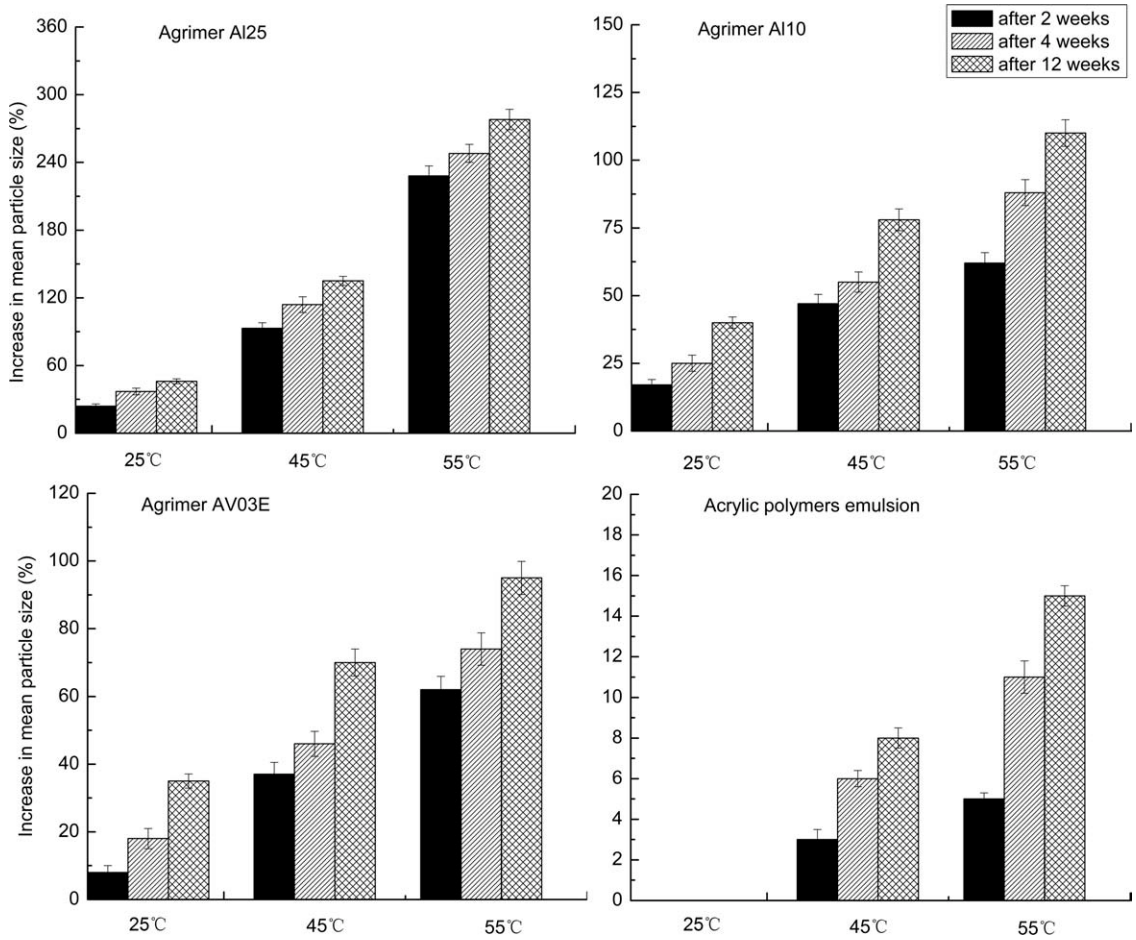

Figure 13 Relative particle size increase of abamectin EW prepared with acrylic/acrylate copolymeric surfactants and different Agrimer polymeric surfactants.

three samples that were stored under different conditions: 25°C, 45°C, and 55°C. After 2, 4, and 12 weeks of storage under these conditions, the mean particle size and the particle size distribution of the samples were redetermined. Figures 12 and 13 show the increase in particle size after storage.

TABLE III
The Emulsion Stability Results of Acrylic/Acrylate Copolymeric Surfactants

Method	Time	Particle size (nm)	Qualities
0°C	0 day	640 ± 5	Free of foam
	3 days	642 ± 5	and cream
	6 days	644 ± 6	
	9 days	643 ± 5	
	12 days	644 ± 7	
54°C	0 day	640 ± 5	Free of foam
	3 days	645 ± 6	and cream
	6 days	648 ± 6	
	9 days	650 ± 5	
	12 days	653 ± 5	
25°C	0 month	640 ± 5	Free of foam
	4 months	644 ± 6	and cream
	8 months	647 ± 5	
	12 months	649 ± 4	

All the data indicated that the acrylic/acrylate copolymeric surfactants we prepared had much better dispersing power than other control surfactants. There may be three reasons for this different dispersing behavior of polymeric surfactants: First, and most importantly, the control surfactants cannot form the entropy layer on the surface of oil droplets. Without the protection of electrostatic repulsion between the entropy layers, the dispersed oil droplets reunite quickly, and the dispersing power of control surfactants is decreased. Second, the physicochemical parameters of the model pesticide will lead to different dispersing abilities of the used polymeric surfactants.[4] Overall, the acrylic/acrylate copolymeric surfactants

TABLE IV
Results of Laboratory Toxicity Tests

		Corrective mortalities/%		
Pesticide formulations	Ratio	1 day	3 days	7 days
1.8% abamectin EW	1000	71.3	80.6	86.7
	3000	72.2	81.4	89.9
1.8% Abamectin EC	1000	70.5	79.8	85.6
	3000	71.7	80.2	88.5

exhibited much better dispersing power than did the control commercially available polymeric surfactants.

Tests of abamectin EW

The stability of abamectin EW was evaluated in a classical way by measuring the particle size against storage time over 12 days at 0°C, 55°C, and a year at 25°C (see Table III). The storage stability of the abamectin EW completely met specified standard requirements. The particle size did not significantly change over the storage periods. The abamectin EW showed excellent stability.

The mortality of *Plutella maculipennis Curtis* is shown in Table IV. The results showed that the mortality of *Plutella maculipennis Curtis* was over 70%, 80%, and 85% after the 1st, 2nd, and 3rd days of observation, respectively. The effect of abamectin EW was similar to that of the control medicament (2.0% abamectin EC).

CONCLUSION

Acrylic/acrylate copolymeric surfactants with moderate molecular weight were prepared by emulsion polymerization in the aqueous phase. The structure of acrylic/acrylate copolymeric surfactants contains a hydrophilic portion and a hydrophobic portion, and the properties of each portion were enhanced. The hydrophilic portion has much greater solubility in water than do other classical surfactants, and the hydrophobic part has more oil adsorption power. This structure is beneficial to the dispersing power of acrylic/acrylate copolymeric surfactants. The carboxylic groups distributed on the surface of acrylic/acrylate copolymeric surfactants were able to readily form the electric double layer, which improved the mechanical properties and the dispersing power of the acrylic/acrylate copolymeric surfactants. To cause more carboxyl groups to be distributed on the surface of acrylic/acrylate copolymeric surfactants, the optimum monomer feeding method and the dosage of AA were determined. MA was also used to modify the acrylic/acrylate copolymeric surfactants. The dispersing power of the acrylic/acrylate copolymeric surfactants exceeded that of other commercially available polymeric surfactants. A novel abamectin EW was prepared with acrylic/acrylate copolymeric surfactants. Studies showed that abamectin was homogeneously dispersed in the aqueous phase, and the novel abamectin EW exhibited excellent stability. The laboratory toxicity tests of emamectin EW showed that the effects of abamectin EW in prevention and cure were similar to that of the control formulation (2.0 % abamectin EC).

The authors thank Cory Berkland for providing language help.

References

1. Texter, J. J Disper Sci Technol 2001, 22, 499.
2. Meller, A.; Stavans, J. Langmuir 1996, 12, 301.
3. Ait-Kadi, A.; Marchal, P.; Choplin, L. Can J Chem Eng 2002, 80, 1166.
4. Haas, S.; Hässlin, H.-W.; Schlatter, C. Colloid Surf A 2001, 183/185, 785.
5. Rajot, I.; Bone, S.; Graillat, C.; Hamaide, T. Macromolecules 2003, 36, 7484.
6. Vijayendran, B. R. J Appl Polym Sci 1979, 23, 893.
7. Maurcio, P. O.; Domingos, S.; Giordaniand, A. M. Eur Polym J 2006, 42, 1196.
8. Wang, P. H.; Pan, C. Y. Colloid Polym Sci 2001, 279, 171.
9. Glenn, L.; Shoaf; Poehlein G. W. J Appl Polym Sci 1991, 42, 1213.
10. Guillaume, J. L; Pichot Cand J. J.; Guillot. Polym Sci Part A 1988, 26, 1937.
11. Blackley, D. Polymer Latices, 2nd ed.; Chapman & Hall: London, 1997; Vol. 2.
12. Ceska, G. J Appl Polym Sci 1974, 18, 2493.
13. Okaya, T.; Sakota, K. J Appl Polym Sci 1977, 20, 2583.
14. Slawinski, M., PhD Thesis, University of Eindhoven, Holland, 1999.
15. Karlsson, O. J.; Hassander, H.; Wesslen, B. J Appl Polym Sci, 2000, 77:297.
16. Vollmert, B. Angew Macromol Chem 1968, 3, 1.
17. Emelie, B, PhD Thesis, University Claude Bernard, LYON I, France, 1984.
18. Santos, A. M.; McKenna, T.; Guillot, J. J Appl Polym Sci 1997, 65, 2343.
19. Sakota, K.; Okaya, T. J Appl Polym Sci 1997, 21, 1035.
20. Santos, AM, PhD Thesis, University Claude Bernard, LYON I, France, 1996.
21. Vorwerg, L.; Gilbert, R. Macromolecules 2000, 33, 6693.
22. Smith, C. C.; Anderson, W. F.; Freewood, R. J. Eng Geol 2001, 60, 253.
23. Gunasekara, A. S.; Donovan, J. A.; Baoshan, X. Chemosphere 2000, 41, 115.