

Carbon Dioxide Switchable Polymer Surfactant Copolymerized with 2-(dimethylamino)ethyl Methacrylate and Butyl Methacrylate as a Heavy-Oil Emulsifier

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ABSTRACT: A CO₂-switchable polymer surfactant was synthesized with 2-(dimethylamino)ethyl methacrylate and butyl methacrylate. The conductivity, ζ potential, and particle size change illustrated the switchability of the surfactant, and this change could be repeated. Its surface tension decreased sharply when the sample was bubbled with CO₂; this indicated the enhancement of the surface activity. In the heavy-oil emulsion with a surfactant concentration of 8 g/L, the viscosity almost reached the highest stability. When CO₂ overflowed the emulsion, it became unstable when the temperature beyond 40°C. The emulsion had a nice resistance to inorganic salt, which was maintained stably even when the concentration of NaCl was as high as 90,000 ppm. The emulsion could later be broken by the removal of CO₂. Its hydration rate was over 22 times faster than that in the presence of CO₂. The amount of residual oil in water was only about 53.84 ppm; this showed a good demulsification ability. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41307.

KEYWORDS: copolymers; recycling; stimuli-sensitive polymers; surfaces and interfaces; surfactants

Received 28 May 2014; accepted 19 July 2014

DOI: 10.1002/app.41307

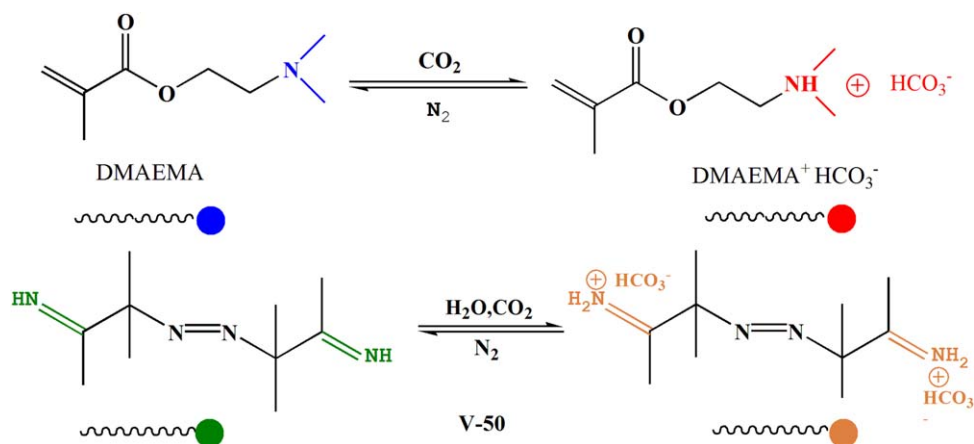
INTRODUCTION

The yield of conventional petroleum has not been able to support its daily requirements in recent years. In contrast, some unconventional oils have attracted our attention. Heavy oil, which has a great reserve and comparative concentrated distribution, is regarded as one of the most important resources in the world.^{1,2} However, the high viscosity of heavy oil restricts its exploitation and pipelining; thus, the lowering of the heavy-oil viscosity is quite significant.

The viscosity of heavy oil can be decreased by heating, the addition of thin oil, and chemical methods. However, heating and the addition of thin oil are usually required for high energy consumption and increase the transportation volume.^{3,4} In contrast, emulsification is a kind of chemical viscosity reduction approach, which we usually prefer to use in oil viscosity reduction because of its low cost and lower energy consumption.^{5,6} The surfactant plays a crucial role in this method, but the emulsion is difficult to break if conventional surfactants are adopted. Therefore, a switchable surfactant that could allow heavy oil be emulsified and demulsified promptly is preferable in oil exploitation and pipelining.

There are a great many kinds of switchable surfactants available, including pH, light, temperature, redox, and CO₂-triggered categories.⁷ However, pH-, light-, temperature-, and redox-responding surfactants have many restrictions and may not be used in oil fields. In our previous works, we studied some CO₂-switchable low-molecular-weight surfactants: those with environmentally friendly and recyclable properties have received great attention.⁸

In recent years, CO₂-switchable emulsions have been reported frequently. Jessop and coworkers^{9,10} first proposed amidine-based emulsions that could be triggered by CO₂.^{9,10} They found out that emulsions that were emulsified by amidine-based surfactants could be easily broken through the removal of CO₂.¹¹ However, the synthesis of amidine is very difficult. In the year 2011, Zhao and coworkers^{12,13} first synthesized an array of hydrogels with a gel-to-sol transition with amine-based thermal monomers. They indicated that repeated cycles of formation and dissociation of these hydrogels could be switched by CO₂ without temperature and pH changes. Later, Jessop's group^{14,15} prepared CO₂ stimuli-responsive polystyrene latexes. In his experiment, the CO₂-switchable monomer DEAEEMA and styrene were used. The products, which were quite stable at room



Scheme 1. Protonated and deprotonated morphologies of DMAEMA and V-50 with and without CO_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature, could be destabilized by the bubbling of air through the sample.

There have been hardly any reports recently about the use of CO_2 -switchable polymer surfactants to decrease the viscosity of heavy oil. They may better affect the decrease of the viscosity of heavy oil. The size and position of hydrophilic and hydrophobic groups included in polymer surfactants can be modified easily; this permits them to form surfactants with different constructions. On the other hand, the petroleum industry could provide a great many superior and cheap monomers, and this would make CO_2 -switchable polymer surfactants have superb practical value and prospects.

In this study, an amine-functionalized polymer surfactant was prepared through the combination of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with butyl acrylate, and this, with both advantages of a CO_2 -switchable tertiary amine and a polymer surfactant, was used in heavy-oil emulsification. The switchability of the polymer was proven by changes in the conductivity, ζ potential, and particle size. The interfacial tension, viscosity value, and dehydration rate indicated its emulsion characteristics for polymer surfactant use in heavy oil.

EXPERIMENTAL

Materials

DMAEMA, butyl methacrylate (BMA), and 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) were purchased from Aldrich Co. All of the chemical reagents were in analytical grade. Heavy oil was provided by the Number 114 Oil Well in Fengcheng Oilfield in Xinjiang Province.

Synthesis of the Polymer Surfactant

The synthesis was carried out in a three-necked flask equipped with a condenser and a stirrer. BMA and distilled water were

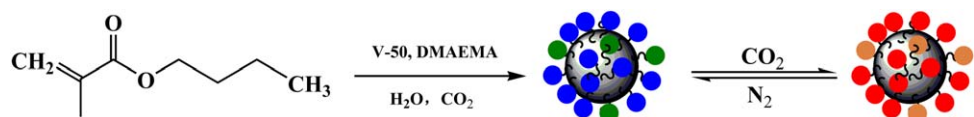
added to the flask and bubbled with CO_2 for 30 min at room temperature (20°C). DMAEMA and V-50 were dissolved in pure water separately and then bubbled with CO_2 to obtain their protonated morphologies (Scheme 1). The DMAEMA solution was added to the flask and followed by the V-50 solution when DMAEMA and V-50 were entirely dissolved in water. The reaction took place at room temperature (20°C) with stirring at 300 rpm for 30 min and then heating to 65°C for 15 h (Scheme 2). CO_2 was continually bubbled through the system during the whole process.

Measurement of the Switchability

Conductivity. The CO_2 -switchable polymer surfactant was added to pure water until it was well dispersed to prepare a solution with a concentration (C) of 0.4 g/L. A DDS-11A conductometer (Shanghai Rex Xinjing Instrument Co., Ltd., China) with a DJS-1C platinum electrode (cell constant = 1.052) was used to measure the conductivity of the solution. CO_2 was bubbled through the solution at a flow rate of 0.1 L/min (as confirmed by an LZB-3 flowmeter) with a needle. The measurement was performed at room temperature (20°C) until the conductivity change over time reached a constant value. Then, N_2 was bubbled into the solution with a needle until there was no variation in the conductivity value; the flow rate was still 0.1 L/min. The whole process was repeated for two cycles.^{16,17}

ζ Potential and Particle Size

ζ potential and particle size measurements were used to measure the molecular morphological changes of the polymer surfactant. A higher absolute value of the ζ potential and a lower value of the particle size indicated that the colloidal dispersion became more stable. Two different C s of the polymer solutions (0.4 and 0.8 g/L) were prepared, and their statistics were



Scheme 2. Synthesis of the CO_2 -triggered switchable polymer surfactant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table I. Viscosity (η) of the Emulsion After the Use of Surfactants with a Ratio Series of Monomers at 50°C

[BMA]/[DMAEMA] (mol %)	37.5	50.0	62.5	75.0	87.5	100.0	112.5
η (mPa s)	No emulsion	416	133	31	199	392	No emulsion

determined with Zeta PALS 190 PLUS according to the manufacturer's recommendations. The measurements, after CO₂ was bubbled through the solutions, were performed at room temperature (20°C) three times, and we obtained the average number as their final value. Then, the solutions were bubbled with N₂ until the CO₂ was entirely removed from the system, and the measurements of their ζ potential and particle size were performed as described previously.^{18,19}

Surface Tension (γ). The CO₂-switchable polymer surfactant was entirely dissolved in pure water after bubbling with sufficient CO₂ to form aqueous solutions with a series of Cs. A JZHY-180 tensiometer (Hebei Chengde Lab Instruments Co., Ltd., China) with a Pt-Ir-20 ring was used to measure its γ at room temperature (20°C). The γ of deionized water was regulated to 74.2 ± 0.2 mN/m at the beginning to adjust the apparatus.^{20–22} γ decreased with increasing surfactant C. At each C point, we recorded five measurements and used the average number as the final value. Then, the critical micelle concentration (cmc) was determined from the breakpoint of the curve of γ versus the logarithm of C.²³

Measurement of the Emulsification

Interfacial Tension. A spinning drop ultralow interfacial tension meter was used in this measurement. Oil drops were placed in sample cell, which contained different Cs of the surfactant solutions. Each sample was measured five times when the interfacial tension value reached a nearly constant number, and we used the average number as the final value.^{24,25} The density of oil was 1.028 g/mL, and the temperature was 30°C.

Preparation of the Emulsion. An amount of surfactant was dissolved in the pure water to form a solution with a certain C. Heavy-oil and surfactant solutions were preheated in a GKC-11-2 digital intelligent thermostatic water bath (Nantong Jinshi Test Instrument Co., Ltd., China) at a temperature of 60°C for 1 h, and CO₂ was continually bubbled through the surfactant solution during this process. Heavy oil was gradually added to the surfactant solution, and the system was stirred at a speed of 5000 rpm for 30 min to form the emulsion.

Emulsion Stability. The stability of heavy-oil emulsion under different situations was measured through a graduated cylinder. Heavy-oil emulsions with different Cs of surfactant were prepared first. The experiment was performed in a water bath at room temperature (20°C) for 50 h, and the dehydration rate was recorded. Then, the C that showed the best emulsion stability and viscosity reduction in the surfactant solution was adopted in the following experiments. The following emulsion stability measurements, including different ratios of water and oil, a variety of Cs of sodium chloride, and a series of temperatures, were performed as described previously.

Emulsion Viscosity. An NDJ-8SN rotational viscometer (Shanghai Precision & Scientific Instrument Co., Ltd., China) was used to measure the viscosity of the emulsion. We first measured the viscosity of the emulsion with different Cs of the surfactant at room temperature (20°C), and then, a certain C of the surfactant solution that showed the best emulsion stability and viscosity reduction was used to emulsify heavy oil under other conditions, including different ratios of water contents, a variety of Cs of sodium chloride, and a series of temperatures.

Measurement of Demulsification

Residual Oil in the Water Phase. Residual oil was extracted by the addition of petroleum ether into the water phase three times after demulsification. A series of Cs (from 10 to 90 ppm) of standard solutions, which were prepared by the mixture of heavy oil with petroleum ether according to the transmittance of the residual oil sample, were adopted to obtain the standard line with a UV spectrophotometer (UV-1800, Shimadzu Co., Ltd.). Then, the residual oil sample's absorbance value was also measured, and its C in the water phase was calculated from a linear equation that was derived from the standard line referred to previously.

Residual Water in the Oil Phase. A distilling apparatus with a condenser was used in this measurement. Toluene was mixed with the oil phase to carry out the residual water measurements. The temperature of distillation was maintained at 120°C for 3 h, and then the distillation was left standing at room temperature over 10 h until the distilled water and toluene were entirely separated.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymer Surfactant

Synthesis of the Surfactant. Different ratios of DMAEMA to BMA (from 8:9 to 8:3) were adopted in this experiment. Each of these was applied to decrease the viscosity of heavy oil. Polymer surfactant solutions with Cs of 10 g/L were prepared. The ratio of heavy oil to the solution was 1 to 1. The experiment was performed at a temperature of 50°C, and the viscosity of heavy oil was 15,000 mPa s. The results indicate that the ratio of 75 mol % BMA/DMAEMA had the best viscosity reduction ability (Table I).

Fourier Transform Infrared (FTIR) Spectrum of the Polymer Surfactant

The IR spectra of DMAEMA as a CO₂-switchable polymer was obtained by a Nicolet Nexus 470 spectrometer (on KBr tablets) in the range 4500–500 cm⁻¹.^{26,27} The stretching vibration peak of N—H in the quaternary ammonium structure [(CH₃)₂NC—H⁺] appeared at 3418.2 cm⁻¹; this indicated that the polymer contained a quaternary ammonium salt structure. The peak at 1616.0 cm⁻¹ corresponded to C=O bonding in the

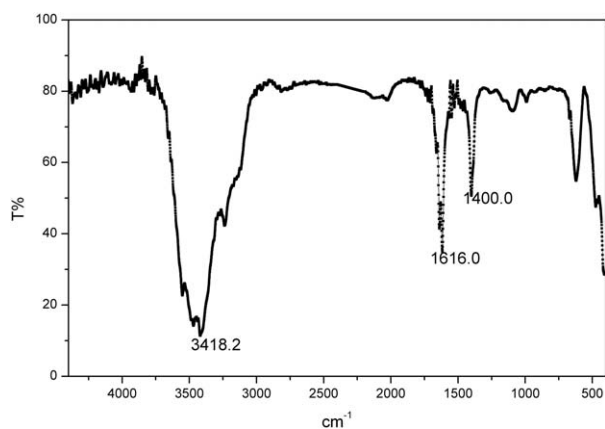


Figure 1. FTIR spectrum of the amine-based polymer surfactant.

—CO—O—C— group and showed that the structure of BMA was included. The stretching vibration peak of the C—H bonds of methyl and methylene in DMAEMA and BMA was at 1400.0 cm^{-1} . In conclusion, the polymer contained the structures of DMAEMA and BMA (Figure 1).

Measurement of the Switchability

Conductivity. The switchability and repeatability of the polymer surfactant were examined through its conductivity during alternate bubbling with CO_2 and N_2 . The solution with a C of 0.4 g/L was adopted in this process, and the flow rate of the gases (CO_2 and N_2) was 0.1 L/min . The original conductivity of the solution was $0.034\text{ }\mu\text{S/cm}$. Then, it increased sharply when during bubbling with CO_2 and was unchanged when it reached a value of $0.059\text{ }\mu\text{S/cm}$ 7 min later. N_2 was then bubbled through the solution. The conductivity of the solution recovered smoothly at the beginning of this process and remained at a low, nearly constant, value between 0.037 and $0.035\text{ }\mu\text{S/cm}$ 20 min later (Figure 2). The experiment referred to previously was performed at room temperature (20°C) and was repeated twice.

ζ Potential and Particle Size. The switchability of the polymer was also proven by the ζ potential and effective diameter changes. Two different C s (0.4 and 0.8 g/L) of the polymer

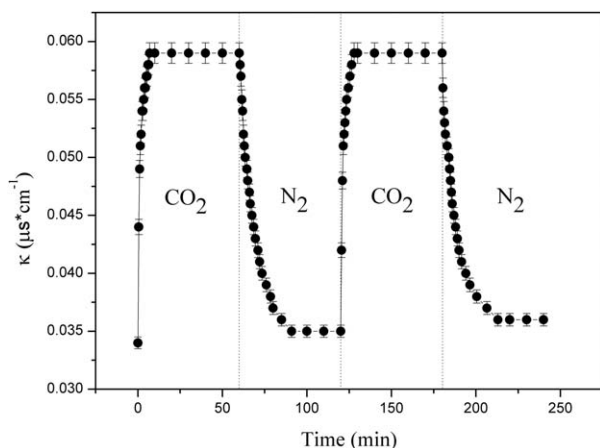


Figure 2. Conductivity curve of the amine-based polymer surfactant solution (0.4 g/L) at 20°C . (K is the conductivity value of the surfactant solution).

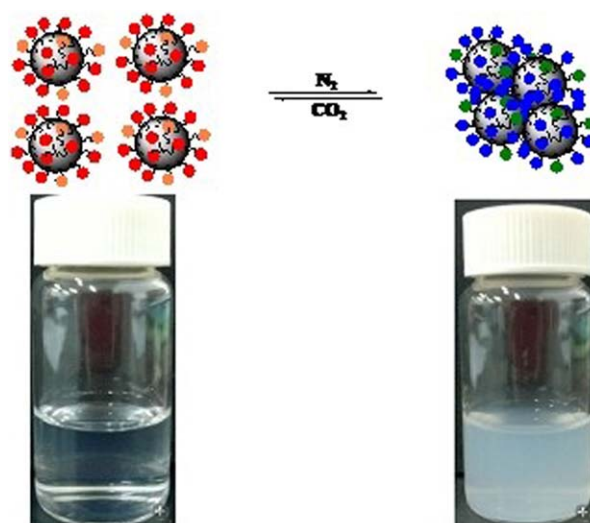
Table II. Variation of the ζ Potential and the Effective Diameter for the Polymer Solution (with C s of 0.4 and 0.8 g/L) During Bubbling with CO_2 and N_2 , Respectively

Sample		0.8 g/L	0.4 g/L
ζ potential (mV)	After CO_2	64.25	69.15
	After N_2	-46.60	-47.12
Effective diameter (nm)	After CO_2	2531.9	2378.1
	After N_2	9490.7	8472.8

surfactant solution were adopted in this experiment. The results indicate that the absolute value of the ζ potential increased in the presence of CO_2 and decreased during bubbling with N_2 (Table II). When the value of the ζ potential increased, the polymer particles, which were protonated by CO_2 , were well dispersed in water, forming a solution with a higher transmittance (Scheme 3). This phenomenon could also be demonstrated by the changes in the effective diameter. The particles with comparatively smaller diameters dispersed into water in the presence of CO_2 . When the CO_2 was removed by bubbling with N_2 , those particles with a deprotonated morphology coagulated together and formed masses with bigger diameters (Table II). The scanning electron microscopy (SEM) micrographs are shown in Figure 3.

γ . The cmc and surface tension at the critical micelle concentration (γ_{cmc}) were obtained from the curve of γ versus C . The Du Nouy ring method was adopted to measure γ at 20°C .

In its neutral morphology, the polymer could not decrease γ of water because it was unable to dissolve in water. However, when the solution was bubbled with CO_2 , the tertiary amine was protonated, and this allowed it to dissolve in water and form a solution with a comparatively low γ (Figure 4). The result indicates that γ changed very slowly with C s of 0.3 to 0.7 g/L and remained nearly constant (at 34.5 mN/m) when C was greater



Scheme 3. Coagulation and dispersion of the polymer solution by bubbling with CO_2/N_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

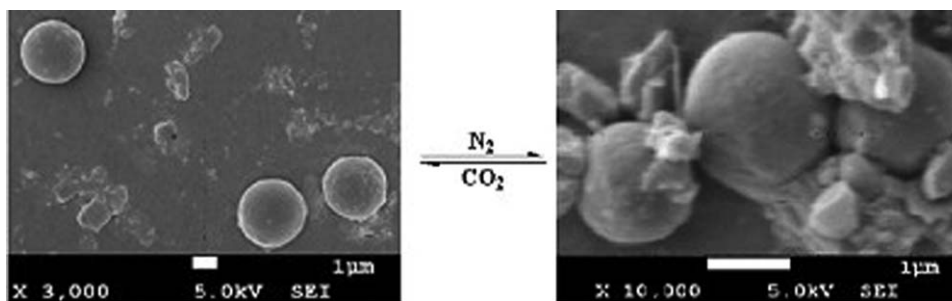


Figure 3. SEM micrographs of the polymer in the presence of CO₂ (left) and aggregation without CO₂ (right).

than 0.7 g/L. In contrast, γ increased sharply when C was lower than 0.3 g/L. So, obviously, when the cmc was 0.3 g/L, γ_{cmc} was 34.2 mN/m.

Measurement of the Emulsification

Interfacial Tension. The oil phase and water phase could be mixed more easily with decreasing interfacial tension; this contributed to the formation of an oil-in-water (O/W) heavy-oil emulsion. The surface activity of the surfactant increased when the C of surfactant increased; this helped to reduce its interfacial tension. We could clearly see that the interfacial tension decreased sharply at a comparatively lower C (from 4 to 8 g/L) and changed very slowly at C s over 10 g/L; this illustrated that the extra surfactant could not enhance the ability of the interfacial tension to decrease when a specific value of surfactant C was reached (Figure 5).

Effect of the Surfactant C on the Emulsion Stability. Six different C s of surfactant solution were prepared in this experiment. The dehydration volume of the emulsions were measured in graduated cylinders at room temperature (20°C) for 50 h, and the ratio of oil to water was 1 to 1. The result is shown in Figure 6. Heavy oil could be emulsified when the C of the surfactant was over 4 g/L, and a volume of 63.0% of water was separated out after 50 h, whereas it was unable to form emulsion when the C was less than 2 g/L. This was because the activity of the surfactant was not sufficient under the lower C . As the C of surfactant increased, the emulsion became more stable.

The separated volume of water after 50 h decreased to 30.4 and 4% when the C s of the surfactant reached 6 and 8 g/L, respectively. However, the stability of the emulsion increased slowly when the C of surfactant was over 8 g/L. Their stability (10 and 12 g/L) were very close to 8 g/L and separated volumes of water of only 3.6 and 2.2% after 50 h.

The viscosities of the emulsions were quite similar because their type was O/W, in which the viscosity was closer to that of the external phase. At the same temperature (20°C), the viscosity of heavy oil was greater than 10⁵ mPa (Table III).

In conclusion, the surfactant with a C of 8 g/L was the most valuable one because it was the lowest C surfactant that maintained a very good stability and a viscosity reduction ability. In the following context, this C surfactant was adopted to measure the other statistics.

Effect of the Water Content on the Emulsion Stability. The water content strongly affected the stability of the emulsion. The surfactant with a C of 8 g/L was adopted; and the measurement was performed at room temperature (20°C). The measuring method was referred to previously (Figure 7). Emulsions with low water contents (40 and 45%) had similar stabilities, only separating out 3.0 and 3.3% volumes of water, respectively. As the water content increased, the emulsion became unstable, separating a 13.8% volume of water when the value reached 60%. The stabilities of the emulsions with 50 and 55% water contents were placed in the middle.

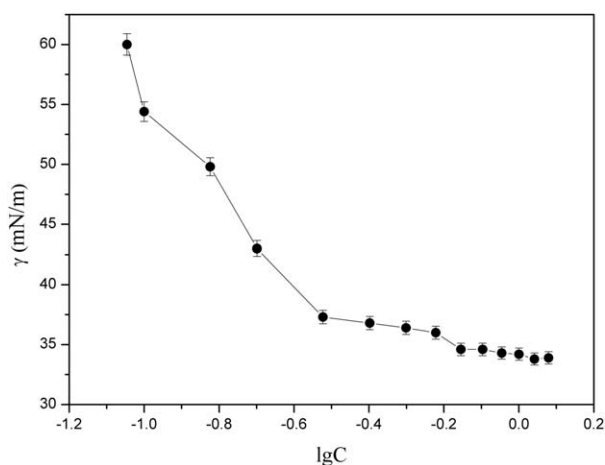


Figure 4. Curve of γ versus C after bubbling with CO₂.

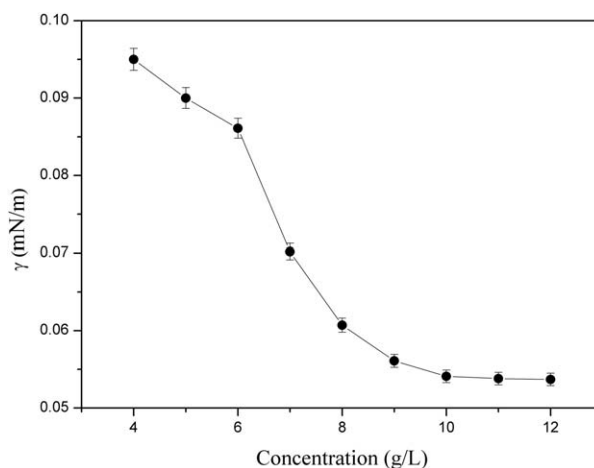


Figure 5. Curve of γ versus C of the surfactant.

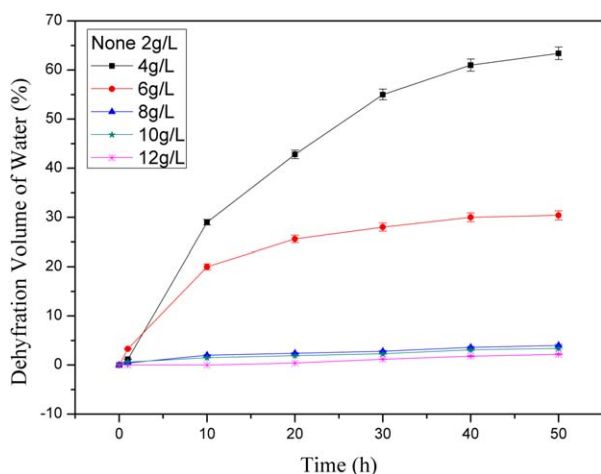


Figure 6. Dehydration volume of water under different Cs of surfactant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table III. Viscosity (η) of the Emulsions with Different Cs of Surfactant

C (g/L)	2	4	6	8	10	12
η (mPa s)	No emulsion	148	136	120	78	80

Viscosities of the emulsions with different water contents are shown in Table IV. The viscosity of the heavy oil was greater than 10^5 mPa s at the same temperature (20°C).

Effect of the Temperature on the Emulsion Stability. The stability of the emulsion decreased sharply with increasing temperature (Figure 8). Two reasons accounted for this phenomenon. For one thing, a higher temperature decreased the thermodynamic stability of the emulsion and made the drop more likely to aggregate. This contributed to the breakage of the emulsion. In addition, the increased temperature stimulated CO_2 to spill out of the system, and this deprotonated the surfactant and

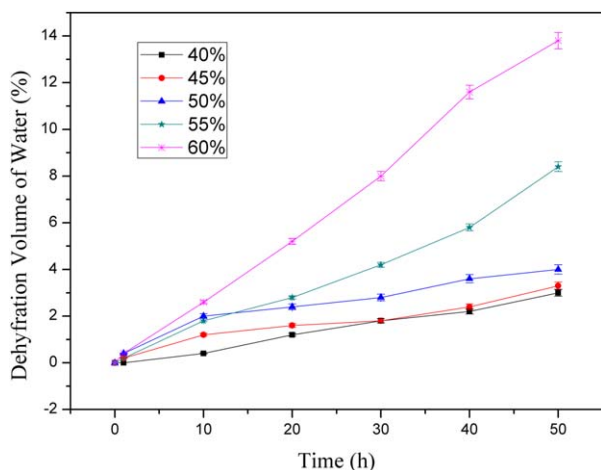


Figure 7. Dehydration volume of water under different water contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table IV. Viscosity (η) of the Emulsions with Different Water Contents

Water Content (%)	40	45	50	55	60
η (mPa s)	334	198	120	58	33

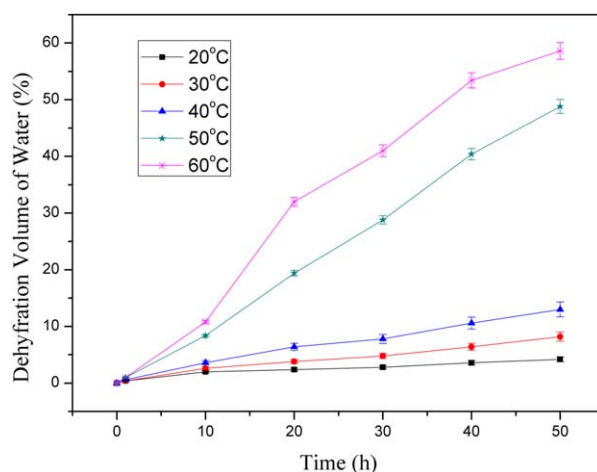


Figure 8. Dehydration volume of water at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

made the emulsion unstable. As a result, the activity of the polymer surfactant was lowered. In this measurement, a surfactant with a C of 8 g/L was adopted, the ratio of oil to water was 1 to 1.

The viscosity of the emulsion at each temperature is shown in Table V. The viscosity of the heavy oil was greater than 10^5 mPa s at the same temperature (20°C).

Effect of Sodium Chloride on the Emulsion Stability. The existence of sodium chloride affected the surface activity of the surfactant. Its ζ potential was compressed by the opposite electron (Cl^-); this led to worse depression of the surfactant in the emulsion and reduced its surface activity. The emulsion without NaCl was the most stable one, and dehydration was higher and similar volumes of water were released when the existence of NaCl increased to 50,000 and 70,000 ppm. The emulsion, which included approximate 90,000 ppm sodium chloride, was more inclined to destabilize and was unable to emulsify when the C of NaCl was greater than 110,000 ppm (Figure 9).

Demulsification of the Heavy-Oil Emulsion

Phase-Separation Rate. The polymer surfactant was deprotonated when CO_2 was entirely removed from the heavy-oil emulsion by bubbling with N_2 until its conductivity was not

Table V. Viscosity (η) of the Emulsion at Different Temperatures

Temperature	20°C	30°C	40°C	50°C	60°C
η (mPa s)	120	99	68	47	33

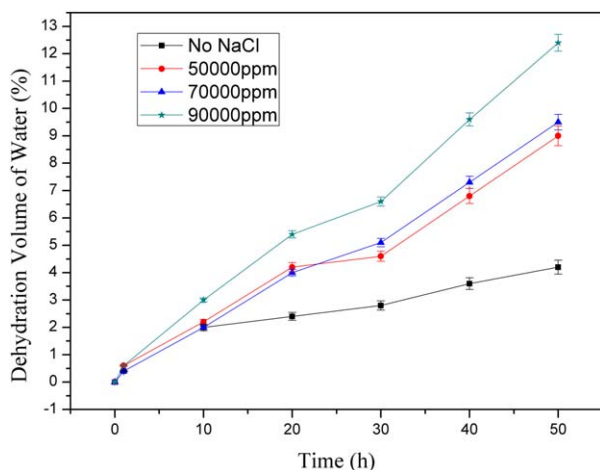


Figure 9. Dehydration volume of water under different C_s of NaCl. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

changed; this removed the surface activity of the surfactant and contributed to demulsification. The dehydration volume of water (which was 61.2% after 50 h) was extremely high. In sharp contrast, the emulsion that was saturated with CO_2 was very stable, dehydrating a 4% volume of water after only 50 h under the same conditions (Figure 10). We chose 20 h as the comparison point for the dehydration rate of emulsion, which was bubbled with N_2 , because it became smooth after 20 h. The result indicates that the speed of demulsification, after N_2 bubbling, was over 22 times faster than that in the presence of CO_2 at the time point of 20 h.

Residual Oil in the Water Phase and Residual Water in Oil. A standard line was fitted by C versus the absorbance of a series of standard solutions. The absorbance value of the oil sample was 3.749, and the C of the residual oil was 53.84 ppm; this was calculated from the standard equation (Figure 11).

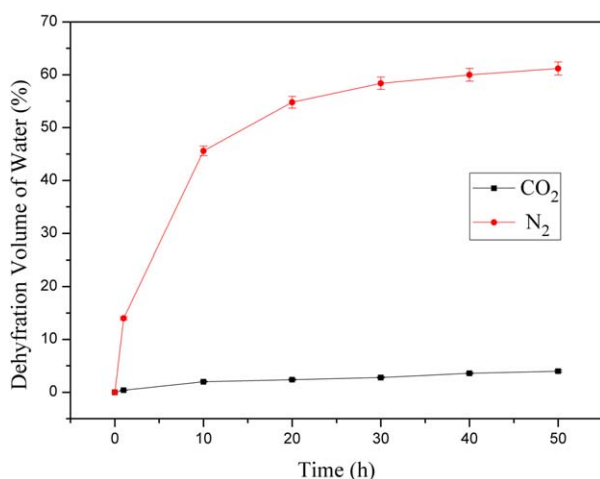


Figure 10. Dehydration volume of water when bubbled with CO_2/N_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

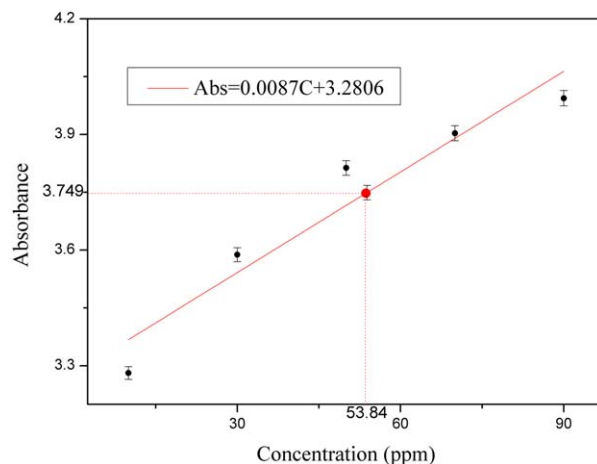


Figure 11. Residual O/W calculated from a UV standard line of C versus absorbance. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The oil phase was mixed with toluene to distill the residual water. The system dehydrated an 8.125% volume of water after 3 h of distillation and 10 h of separation.

CONCLUSIONS

The polymer surfactant that was synthesized from the CO_2 -switchable monomer DMAEMA and BMA at a molar ratio of 8:6 showed the best ability in viscosity reduction. The tertiary amine group in DMAEMA was protonated by bubbling with CO_2 , and this increased its surface activity. The quaternary ammonium was deprotonated and could be changed back into a tertiary amine morphology when CO_2 was removed through bubbling with N_2 . The stability of the heavy-oil emulsion increased obviously when the C of the surfactant increased from a lower value to 8 g/L, whereas it changes very slowly under a comparatively high C (>8 g/L). The heavy-oil emulsion under high temperature was unstable because of the decreased thermodynamic stability and the overflow of CO_2 . However, the dispersion of the surfactant under a high C of inorganic salt (NaCl) was very nice because the positive ion (Na^+) had limited influence on the ζ potential of quaternary ammonium; this contributed to the maintenance of its stability. The heavy-oil emulsion became unstable when it was bubbled with N_2 . It was clear that the dehydration rate increased over 22 times compared with that in the presence of CO_2 ; this indicated that the emulsion could be easily demulsified by the removal of CO_2 . The separation of oil from water after pipelining is a complicated problem; the introduction of a CO_2 -switchable polymer surfactant may solve this issue in a low-cost and environmentally friendly way.

ACKNOWLEDGMENTS

The authors declare no competing financial interest. The authors thank the Opening Fund Project from the State Key Laboratory of Polymer Materials Engineering (Sichuan, China) for financial support (contract grant number KF201305). This project was also supported by the Sichuan Youth Science & Technology Foundation (China; contract grant number 2010JG0051).

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