Synthesis and Characterization of a Novel Multibranched Block Polyether Demulsifier by Polymerization

Lixin Wei, Meng Chao, Xuanrui Dai, Xinlei Jia, Xiaoheng Geng, and Haiying Guo

ABSTRACT: Various flooding technologies were applied in the middle and late stages of the oilfield, which made the heavy oil emulsion receive much concern because of its high stability and separation difficulty. In our paper, alcohol molecules were used as initiators and multibranched block copolymers were synthesized through open-loop polymerization technology. A variety of novel modified block polyether demulsifiers with demulsification activity were finally synthesized through water-soluble modification and oil-soluble modification, which achieved efficient demulsification of heavy oil emulsions. Hydrophile–lipophile balance (HLB) values and surface tension were used to characterize demulsifiers. In addition, their demulsification efficiency was evaluated by measuring the amount of dehydration in the separated heavy oil emulsion experiments. The experimental results showed that within 5 h, the demulsification effect of the water-soluble demulsifier is better than that of the oil-soluble demulsifier. When the HLB value of the demulsifier reaches a certain value, the dehydration rate and the demulsification effect reach the highest point. When the amount of demulsifier is 50 μg/g and the demulsification temperature is 85 °C, the dehydration rate of the water-soluble demulsifier X-6 reached 91%, the water quality was clear, and the demulsification effect reached its peak. This work will provide a novel and efficient demulsifier for demulsification and dehydration of heavy oil emulsions.

INTRODUCTION

Oil is the most important energy and strategic material in the world and its demand has increased rapidly with the growing global economy. In the process of oil exploitation, due to the composition of the crude oil, the flooding process, and even the distribution of underground crude oil, water is always produced during the processing and refining of crude oil.1−3 The presence of water in crude oil and natural surface-active substances in petroleum causes emulsification of crude oil under conditions of temperature and shear.4−5 At present, about 80% of the crude oil in the world is recovered in the form of an emulsion.6

With the large-scale exploitation of conventional oil resources in various countries, heavy oil has attracted much attention because of its huge reserves.7 Canada, the United States, China, Venezuela, Indonesia, and other countries are all rich in heavy oil resources. In recent years, thermal oil recovery technology has gradually been replaced by thermochemical oil recovery technology; the main method is to increase the recovery of heavy oil using surfactants or polymers as oil displacement agents.8−10 However, surfactants and polymers will aggregate on the oil–water surface to form a rigid, stable, viscoelastic interface film, which will further improve the stability of the heavy oil emulsion and destroy the continuity of demulsification technology of the heavy oil emulsion.10−12 The demulsification technology for heavy oil emulsions can be divided into three categories: mechanical, chemical, and biological, of which chemical is the most economical and commonly used method of demulsification. The demulsification rate of the heavy oil emulsion can be increased by adding a small amount of the demulsifier. At the same time, factors such as the demulsification temperature and the amount of the demulsifier affect the demulsification rate. The above factors can be optimized by further research.13−15 Novel demulsifiers such as ionic liquid demulsifiers or magnetic demulsifiers are currently being researched. Ezzat et al.16 synthesized a novel amphiphilic ionic liquid demulsifier using dialkyl-substituted imidazoles as the head group and combining with acetate and 4-(trifluoromethoxy) phenyl borate anion, Abdullah et al.17 synthesized amphiphilic ionic liquids (AILs) and formed the corresponding IL (GEB-CL). The chloride ion was replaced by a trifluoroacetic acid (TFA) ion to form the second IL (GEB-TFA), which had a strong ability to reduce the surface tension and IFT. Atta et al.18 prepared a new type of an ionic surfactant using cashew nut oil as a raw material and put forward a viewpoint that the single surfactant as a heavy oil
dispersant and a demulsifier had a good effect through experimental analysis. Al-Lohedan et al.19 prepared a new amphiphilic Gemini ionic liquid (GILs) using poly(ethylene terephthalate) (PET). The results of characterization and performance evaluation showed that the demulsification efficiency increases with the increase in the water content. Alves et al.20 synthesized five different chemical surfactants based on castor oil and determined that the demulsification effect of MACO1 was better at 60 °C through characterization of the synthesized surfactants and the demulsification experiment of the bottle test method. Ali et al.21 synthesized a novel demulsifier P (MMA-AA-DVB)/Fe3O4 magnetic submicron ion and studied the demulsification performance of the demulsifier in a heavy oil–water emulsion. Although the research on novel demulsifiers for heavy oil emulsions has broad application prospects, further research is needed, and the existing technologies cannot comprehensively surpass traditional chemical demulsifiers in terms of the synthesis process, application scope, and demulsification effect. The demulsifying ability is manifested by controlling the hydrophilic–lipophilic balance values and destroying the stable and rigid interface film formed by the surfactant, polymer, and the like at the oil–water interface.22−24 Block polyether demulsifiers were gradually applied to crude oil demulsification in the 1940s. The block polyether demulsifier mainly consists of a polymerization reaction between an initiator and propylene oxide (PO) and ethylene oxide (EO) under the action of a catalyst and forms a hydrophobic block of poly(propylene oxide) (PPO) and a hydrophilic block of poly(ethylene oxide) (PEO).25−27 Demulsifier compounding, chain extension, and cross-linking are common modification methods for demulsifiers.28 Water-soluble modification and oil-soluble modification use active hydrogen groups in the demulsifier to react with other active molecules, which can change the hydrophilic and lipophilic properties, increase the molecular weight and the number of branches of the demulsifier molecule, and improve the demulsification effect.29

The purpose of this work is to study the synthesis of a novel modified polyether demulsifier for heavy oil emulsions. In our paper, a series of block-modified polyether demulsifiers were synthesized by changing the ratio of propylene oxide (PO) and ethylene oxide (EO). Demulsifiers were characterized by surface activity and hydrophilic–lipophilic balance (HLB) values. Through bottle test analysis and determination of the optimal block-modified polyether demulsifier, the purpose of improving the efficient demulsification of heavy oil demulsifiers at this stage was achieved and it provided a reference for the synthesis of polyether demulsifiers.

■ RESULTS AND DISCUSSION

Determination of the Content of a Cross-Linker. Oil-soluble demulsifiers modified with 10% PM-200 solutions of different qualities were synthesized, and demulsification dehydration experiments were carried out by the bottle test method, and the demulsification rates of different oil-soluble modified demulsifiers in 5 h were recorded. The amount of the demulsifier added was 50 μg/g and the demulsification temperature in the water bath was set at 85 °C. The demulsification dehydration experiment results are shown in Figure 1. It can be seen that as the amount of modified cross-linking agent increases, the demulsification rate of the oil-soluble demulsifier increases first and then decreases after 5 h. When the dosage is 4% of the mass of the polyether demulsifier, the demulsification rate reaches the highest. This is because when the amount of the cross-linking agent is small, appropriately increasing the amount of the cross-linking agent can improve the demulsification rate. When the concentration of the cross-linking agent is too high, the diffusion speed of the demulsifier in the process of demulsification is reduced and the demulsification rate is reduced at the same demulsification time.

Hydrophilic–Lipophilic Balance (HLB) Values of a Polyether Demulsifier. The above experimental method is used to determine the hydrophilic–lipophilic balance (HLB) values, and the measurement results are shown in Figure 2, where D is a polyether demulsifier, W is a water-soluble modified polyether demulsifier, and O is an oil-soluble modified polyether demulsifier. As shown in Figure 2 that in the same series, the water-soluble modified polyether demulsifier has the highest HLB value and high hydrophilicity, the polyether demulsifier itself is second, and the oil-soluble...
modified polyether demulsifier has the lowest HLB value. For different series of HLB values, as the proportion of EO and PO in the molecular weight in the X-1 to X-8 series increases, the HLB values and hydrophilicity of polyether demulsifiers and water-soluble polyether demulsifiers increase. The oil-soluble modified polyether demulsifier has a relatively stable overall HLB value in the X-3 to X-6 series, and the HLB value of other series decreases significantly.

**Surface Tension of a Polyether Demulsifier Solution.**
The surface tension of the polyether demulsifier and the modified polyether demulsifier aqueous solution was measured by the pendant drop method. The measurement results are shown in Figure 3. The surface tension of a polyether demulsifier aqueous solution and water-soluble modified and oil-soluble modified polyether demulsifiers has the same tendency. When the concentration is 1–50 mg/L, the surface tension decreases rapidly; after 50 mg/L, it decreases slowly and finally stabilizes at about 37.2 mN/m. The surface tension—concentration curve of the water-soluble polyether aqueous solution is slightly lower than that of the polyether aqueous solution, and both the polyether and water-soluble modified polyether curves are lower than the oil-soluble modified polyether curve. This showed that the water-soluble modified polyether aqueous solution was slightly better than the polyether aqueous solution in its ability to reduce surface tension. The ability of oil-soluble modified polyether aqueous solution to reduce surface tension was lower than that of polyether and water-soluble modified polyether aqueous solutions. From the perspective of the final effect, all three polyethers could effectively reduce surface tension, and at the same time had better displacement and replacement capabilities and higher surfactivity.

**Demulsification Mechanism Analysis.** After the demulsifier was added to the heavy oil emulsion, the high surface activity of the demulsifier could pass through the external phase of the emulsion to reach the oil—water interface, and the demulsifier with higher hydrophilic properties reached the oil—water interface faster. The block polyether demulsifier synthesized in this experiment has high surface activity, can reduce the interfacial tension, preferentially adsorbs on the oil—water interface, and replaces the asphaltene molecules at the oil—water interface. A large number of demulsifier molecules are adsorbed on the oil—water interface in this way, and an interface film with lower stability is formed. Under the action of heating or shaking, the macromolecules in the emulsion made irregular Brownian motions and collided with other macromolecules, causing the interface film to rupture, and the water in the internal phase broke through the interface film and entered the external phase to agglomerate to achieve the purpose of oil—water separation. Figure 4 shows the demulsification mechanism of the demulsifier.

**Demulsification Experiment.** A series of modified block polyether demulsifiers were tested for demulsification using the bottle test method. The demulsifier addition amount and the water bath demulsification temperature were 50 μg/g and 85 °C. The demulsification test results are shown in Figures 5–7. As shown in Figure 5, the overall demulsification rate of the water-soluble modified polyether demulsifier is above 80%, while the maximum demulsification rate of the oil-soluble modified polyether demulsifier reaches 70% and the minimum demulsification rate is less than 5%. The overall demulsification rate of the oil-soluble demulsifier is significantly lower than that of the water-soluble modified demulsifier. As the molecular weight of the X-series demulsifier increases, the demulsification rate of the water-soluble modified demulsifier gradually increases, and the X-6 series has the highest demulsification rate, reaching 91%. When the molecular weight increases again, the demulsification rate decreases slightly and remains stable. The larger the proportion of EO and PO added to the molecules of the modified demulsifier, the higher the molecular weight and hydrophilicity of the water-soluble modified demulsifier. Before the hydrophilicity reached a proper value, as the hydrophilicity increased, the oil—water interface adsorbed by the demulsifier increased, the oil—water interface tension was weakened, the interface film strength was reduced, and the demulsification rate increased. When the hydrophilicity was too large, the number of demulsifiers dissolved in water increased, which caused the reduction of the oil—water interface of the remaining demulsifiers, and the demulsification rate decreased slightly. Before the demulsifier dissolved in water reached saturation, the demulsification rate was stable.

Figure 6 shows that the demulsification speed of the X-6 series is higher than that of other series of water-soluble modified demulsifiers, reaching the highest point of the demulsification rate. With the increase of the proportion of polyether demulsifiers by EO and PO, the demulsification rate and demulsification speed of demulsifiers also increased. However, the demulsification speeds of X-7 and X-8 series polyether demulsifiers between 2 and 3 h are lower than other X series. The demulsification speed increased again between 3 and 5 h and reached the average demulsification rate. This phenomenon indicated that the demulsification speed was related to the proportion of EO and PO in the polyether demulsifier. The effect of the proportion of EO and PO on the demulsification rate was relatively small. When the proportion of EO and PO approached a certain value, the demulsification efficiency and demulsification rate reached the maximum. Figure 7 shows the amount of dehydration per hour of a water-soluble modified polyether demulsifier. The X-6 series water-soluble modified block polyether demulsifier has a higher dehydration volume and dehydration speed than other series before 3 h. Although X-7 and X-8 series polyether demulsifiers

![Figure 3](image-url)
have the highest dehydration volumes and dehydration speeds in the 4th hour, the overall dehydration volumes and dehydration speeds are lower than X-6 series water-soluble modified polyether demulsifiers.

■ CONCLUSIONS
High-efficiency demulsifier is an inevitable trend in the development of demulsifiers in the future and plays an important role in the demulsification of crude oil emulsions. In our paper, a series of modified block polyether demulsifiers were synthesized and used for demulsification of heavy oil emulsions. Both polyether demulsifiers and modified polyether demulsifiers could effectively reduce surface tension. Among them, water-soluble modification had the strongest ability to reduce surface tension. When the appropriate hydrophilic–hydrophobic HLB value was reached, the breaking rate and breaking rate of the demulsifier reached the highest point. The dehydration test of the block polyether demulsifier was carried out through the bottle test method, which confirmed that for the Liaohe heavy oil, the water-soluble modification of the
demulsifier was better than the oil-soluble modification. The
demulsification speed and demulsification rate were related to
the proportion of EO and PO in the polyether demulsifier.
Finally, the X-6 series demulsifier was optimal. The X-6 series
demulsifier could reach the 91% dehydration rate at a
dehydrating temperature of 85 °C and a demulsifier dosage of
50 μg/g.

EXPETIMENTAL SECTION

Materials. Ethylene oxide (EO) and propylene oxide (PO)
were provided by the laboratory. Formaldehyde (40 wt %),
nonylphenol, xylene, methanol, 2-phenylmethane disocyanate
（MDI）, and potassium hydroxide were purchased from the
Tianjin Tianti Chemical Reagent Co., Ltd. Triethylenetetra-
amine was purchased from the Tianjin Comeo Chemical
Reagent Co., Ltd. Epichlorohydrin was purchased from the
Shanghai Zhanyun Chemical Co., Ltd. The oil-in-
water oil emulsion used for demulsification evaluation
was obtained from the Liaoh Oilfield. The physicochemical
characteristics of Liaoha heavy oil are shown in Table 1.

Synthesis of a Novel Modified Polyether Demulsifier.
Nonylphenol (82.3 g) and triethylenetetramine (158.4 g) were
put into a three-necked flask. The three-necked flask was put
in an oil bath, which was heated to 50 °C under stirring at 330
rpm for 30 min. Xylene (223.6 mL) was introduced dropwise
into a three-necked flask, and the oil bath was heated to 70 °C
to completely dissolve nonylphenol and was then cooled to 35
°C. The formaldehyde solution (82 g) was added dropwise
using a separatory funnel within 1.5 h. The molar ratio
between nonylphenol, triethylenetetramine, and formaldehyde
was 1:2.2. The condenser tube was connected to a three-
necked flask, and the temperature of the reflux water was
increased at 105 °C for 1 h, and then the oil bath was gradually
heated at 120 °C until bubbles were seen inside the solution.

Xylene was recovered after 2 h of heat preservation and reflux.
The temperature was increased to 150 °C for 3 h and the reflux
water was observed for 1 h. Finally, the temperature of the oil
bath was gradually increased to 200 °C, and the temperature
was maintained for 0.5 h. The three-necked flask was cooled to
155 °C and the initiator was obtained.

The initiators and a small amount of potassium hydroxide as
a catalyst were added to the autoclave. N2 was used to replace
the air in the autoclave and then the vacuum pump was used to
pump out the gas in the autoclave, and the operation was
stopped after the pressure indication reached the negative
pressure. Propylene oxide (PO) was slowly introduced from
the open feed port. The mass ratios of the initiator to the
propylene oxide (PO) were 1:69, 1:99, 1: 139, and 1: 199.
After the completion of the feed, the feeding valve was closed
and the temperature was increased to 110 °C to perform the
polymerization reaction. The reaction ended when the pressure
reading returned to negative pressure and remained stable. A
small amount of potassium hydroxide was added to the
autoclave again; ethylene oxide (EO) was introduced into the
autoclave in a second polymerization reaction. After
the reaction was completed, the polyether demulsifier was formed.
The mass ratios of ethylene oxide (EO) to propylene oxide
(PO) were 1:3.7 and 1:2.7. The final polyether demulsifiers X-
1 to X-8 were formed. The molecular weights of X-1 to X-8
increase as the ratio of ethylene oxide (EO) to propylene oxide
(PO) increases. The reaction formula is shown in Figure 8.
Table 2 shows the synthesis ratio of the polyether demulsifier.

Modification of a Novel Modified Polyether Demulsi-
 fier. Epichlorohydrin was used for water-soluble modification
demulsifiers. The generated polyether (100 g) was put into a
four-necked flask, heated to 55 °C in a water bath, and stirred
at a speed of 300 rpm. When the temperature reached 55 °C,
kuposium hydroxide (1.2 g) was put into a four-necked flask
and stirred for 20 min. After increasing the temperature to 70
°C, epichlorohydrin was dropped into the four-necked flask
using a separatory funnel. After the dropwise addition was
completed, the temperature was increased to 85 °C and was
maintained for 2 h. The temperature was lowered to 60 °C,
and methanol (70 g) and water (30 g) were added to obtain a
water-soluble block polyether demulsifier (50 wt %). Figure 9
shows the synthetic reaction formula of the water-soluble
modified demulsifier.

The oil-soluble modification adopted the modification method of adding an appropriate cross-linking agent. The
generated polyether (100 g) and xylene (50 g) were put into a
four-necked flask and heated in a water bath to 60 °C. A 10%
PM-200 xylene solution was slowly dropped into the four-
necked bottle using a separatory funnel. At the same time,
a glass rod was used to dip the solution in a four-necked flask
and test the drawing length. When the length of the drawn wire
reached 3–4 cm, dropwise addition of the 10% PM-200 xylene
solution was stopped. Finally, xylene (46.8 g) was added to
obtain an oil-soluble block polyether demulsifier (50 wt %).
Figure 10 shows the schematic diagram of chemical synthesis
of modified polyether. Figure 11 shows the structural formula
of the demulsifier after cross-linking.

Table 1. Physicochemical Characteristics of Liaoh Heavy Oil

| property          | value     |
|-------------------|-----------|
| density (kg·m⁻³)  | 957.6     |
| dynamic viscosity (mPa·s) | 893.1  |
| gum (%)           | 15.69     |
| asphaltene (%)    | 9.57      |
| acid value (mgKOH·g⁻¹) | 2.07   |
| pour point (°C)   | 18        |
| sulfur content (%) | 0.158    |

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Figure 7. Dehydrated volume of water-soluble modified demulsifier per hour.
Cross-Linking Agent Content Determination Experiment. X-3 synthesized above was selected for the oil-soluble modification experiment. PM-200 solutions (10%) of different qualities, such as 2, 4, 6, 8, and 10% of the mass of polyether demulsifier, were added to the oil-soluble modification experiment. The demulsification and dehydration experiments of five oil-soluble modified demulsifiers in the bottle test method were carried out.

Hydrophile−Lipophile Balance (HLB) Value Determination. The cloud point method was used to measure the HLB value of the synthesized X-series demulsifier. A 10% aqueous solution of the synthesized X-series demulsifier was placed in a test tube equipped with a thermometer, and the liquid level was controlled at 50 mm. The test tube was heated in an oil bath, and the temperature was gradually increased to observe the transparency of the solution. After the solution appeared turbid, the value was read and recorded on the thermometer immediately. After the experiment, the HLB value was calculated according to the formula. The calculation formula is as follows:

$$HLB = 0.0980X + 4.02$$  \hspace{1cm} (1)

where $X$ is the cloud point of a 10% block polyether demulsifier aqueous solution.

Surface Tension Measurement. The Kruss DSA100 contact-angle measuring instrument was used for measuring polyether demulsifiers and modified polyether demulsifiers. Polyether aqueous solutions with different concentrations were prepared, including concentrations of 0.01, 0.1, 1, 10, 50, 100, 300, 500, 103, and 104 mg/L. The prepared polyether demulsifier aqueous solution was heated in a water bath and the temperature was set at 80 °C. The surface tension measurements of a polyether aqueous solution with different concentrations were carried out using the pendant drop method and a 1 mL disposable syringe.

Determination of the Water Content in Heavy Oil. Heavy oil was heated to a flowing state in a water bath at 80 °C; the diesel oil was used as a solvent, poured into a round bottom flask, and a few pieces of shard were added. The cleaned and dried receiving bottle and a straight tube

### Table 2. Synthetic Ratio of the Polyether Demulsifier

| Demulsifier samples | Molecular weight | Initiator:PO | PO:EO |
|---------------------|------------------|--------------|-------|
| X-1                 | $0.845 \times 10^5$ | 1.69         | 3.7:1 |
| X-2                 | $0.967 \times 10^5$ | 1.69         | 2.7:1 |
| X-3                 | $1.071 \times 10^5$ | 1.99         | 3.7:1 |
| X-4                 | $1.117 \times 10^5$ | 1.99         | 2.7:1 |
| X-5                 | $1.327 \times 10^5$ | 1.139        | 3.7:1 |
| X-6                 | $1.448 \times 10^5$ | 1.139        | 2.7:1 |
| X-7                 | $1.879 \times 10^5$ | 1.199        | 3.7:1 |
| X-8                 | $1.956 \times 10^5$ | 1.199        | 2.7:1 |

Figure 8. Polymerization formula of demulsifiers.

Figure 9. Synthetic reaction formula of the water-soluble modified demulsifier.
condenser were connected to a round bottom flask and then the round bottom flask was heated. The experiment ended when the volume of the liquid in the receiver no longer changed; the volume of the liquid in the receiver was read and recorded. Finally, the instrument was disassembled and cleaned.

Demulsification Test. A series of block polyether demulsifiers were tested for demulsification using the bottle test method. The heavy oil emulsion was heated to a flowing state using a water bath, and the upper emulsion of the heavy oil was taken and stirred in a beaker. The taken emulsion was poured into a test bottle and 50 μg/g demulsifier was added to the test bottle using a micropipette. The test bottle was shaken by hand until the demulsifier and emulsion were completely mixed, and then the test bottle was placed in the designated water bath. Each group of test bottles retained a set of blank control measurements. The volume of water released at different times was observed and recorded. The demulsification rate of each demulsifier was measured according to the proportion of the volume of separated water, and the calculation formula is as follows:

\[ W(\%) = \frac{V_T}{V_O} \times 100 \]  

where \( W \) is the demulsification rate of the heavy oil emulsion by the demulsifier, \( V_T \) is the volume of water separated from the heavy oil emulsion, and \( V_O \) is the volume of water contained in the heavy oil emulsion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00949.

The schematic diagram of water-soluble modification and oil-soluble modification (PDF)

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Notes
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