RESEARCH ARTICLE

Synthesis and laboratory evaluation of iso-tridecyloxypolyethylene glycol acrylate copolymers as potential viscosity reducers for heavy oil

Fusheng Zhang$^1$ | Qun Lei$^2$ | Guoliang Liu$^1$ | Gongqing Liao$^3$ | Xiaofang Xu$^3$ | Weidong Meng$^3$

$^1$Key Laboratory of Oilfield Chemicals, China National Petroleum Corporation, Beijing, China
$^2$Research Institute of Petroleum Exploration and Development, PetroChina, Beijing, China
$^3$Key Laboratory of Science and Technology of Eco-textile, Ministry of Education, Donghua University, Shanghai, China

Correspondence
Weidong Meng, Key Laboratory of Science and Technology of Eco-textile, Ministry of Education, Donghua University, Shanghai 201620, China.
Email: wdmeng@dhu.edu.cn

Funding information
the National Science and Technology Major Project, Grant/Award Number: 2016ZX05010-004-002; PetroChina Company Limited, Grant/Award Number: Science and Technology Major Project, 2019B-1410

Abstract
As driven by the increase in global fuel demand and decrease in worldwide reserves of conventional oil, it is important to develop new production technologies for heavy oil. In this work, copolymers PAAI$_7$, PAAI$_{10}$, and PAAI$_{15}$ were synthesized and evaluated as potential viscosity reducers for heavy oil. iso-Tridecyloxypolyethylene glycol acrylates (I13C$_x$AA, $x = 7, 10, 15$), acrylic amide (AM), and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were polymerized to give the copolymers PAAI$_x$, respectively. Copolymers PAAI$_x$ were characterized by FTIR, $^1$H NMR spectroscopy, and TGA and showed good thermal stabilities as the decomposition temperature was above 350°C. Their viscosity-average molecular weights were measured as in the range between $6.53 \times 10^6$ and $10.58 \times 10^6$ g/mol. The effects of temperature, shear rate, and salinity on the viscosity of polymer solutions were studied, and PAAI$_x$ had reasonable rheological properties. The solutions of PAAI$_x$ in formation water could emulsify heavy oil sample to form oil-in-water emulsion when mass ratio of oil:water was in the range of 6:4-2:8, respectively. The rates of reduction in viscosity of emulsions compared with that of original oil sample were 53.5%-97.5% at 50°C under shear rate of 20 s$^{-1}$. The effects of oil:water ratio, emulsifying temperature, and shear rate on the viscosities of emulsions were extensively studied, and the effect of the polymer structure on the emulsification and viscosity reduction of heavy oil was also discussed. Among three copolymers, PAAI$_{15}$ formed the most stable emulsion with heavy oil and the emulsion had the lowest viscosity. PAAI$_{15}$ had the potential for further study.

KEYWORDS
acrylates, emulsification, heavy oil, iso-tridecyloxypolyethylene glycol, viscosity reduction
INTRODUCTION

After the conventional water-flooding process, the residual oil in the field remains as a discontinuous phase in the form of oil drops and turns heavier. The heavy oil contains thousands of compounds; most of them have large molecular weights and aggregations of interlocked network structures. These complicated network structures are responsible for the high density and viscosity of the heavy oil and resulting in the decline of mobility. Enhanced oil recovery (EOR) methods are therefore essential for application to recover the major fraction of the residue heavy oil. Polymer flooding is a common EOR technique, in which a solution of water-soluble high molecular weight polymer is pumped into the reservoir. Polymers enhance the viscosity of displacing fluid and decrease the water/oil mobility ratio. Reduction in the mobility ratio leads to an increase in the macroscopic displacement efficiency. One of the most widely used polymers in polymer flooding is the commercially available partially hydrolyzed polyacrylamide; however, this conventional polymer needs to be in very high molecular weight to achieve sufficiently high viscosity and suffers poor adaptability to harsh reservoirs. Surfactants are also used alone or in combination with polymers in EOR with reduction in the interfacial tension between water and oil and alteration of reservoir wettability to improve the oil recovery. Various surfactants and polymers are used in the conventional surfactant-polymer flooding, in which surfactants act as emulsifiers and polymers to increase the viscosity of the water. However, due to the different properties, such mixtures often separate into two phases in a flow stream and have unwanted interactions between chemicals. And also the loss of surfactant to reservoir rock surface by adsorption occurs. In the past two decades, enormous efforts have been concentrated on modification of polyacrylamides. Hydrophobically associating polyacrylamides are important derivatives. As a small fraction of hydrophobic comonomer is incorporated into the polymer backbone, the modified polyacrylamide has improved thickening capability compared to conventional hydrolyzed polyacrylamides; however, such an enhancement in viscosity is significantly dependent on the polymer concentrations, operational shear rate, and conditions of reservoir; this has inhibited the widespread applications of such polymers. When a surfactant-like monomer is incorporated into polyacrylamide backbone, this modified polyacrylamide has surface activity and is called polymeric surfactant. A lot of studies have shown that compared with hydrolyzed polyacrylamides, polymeric surfactants have a lower molecular weight, stronger temperature and salt resistance, and a certain interfacial activity. Polymeric surfactants are thus considered to be a promising chemical applied in field tests and production after polymer flooding.

To recover the heavy oil from the reservoir, it is necessary to reduce its viscosity and improve the mobility. Although conventional surfactants can emulsify the heavy oil to form stable oil-in-water emulsion together with a polymeric stabilizer, such system is not applicable under the reservoir conditions. It is highly desirable to develop a novel polymeric surfactant not only to emulsify heavy oil, but also to increase the viscosity of the fluid at the reservoir conditions. Polymeric surfactants are usually amphiphilic polymers. The use of poly(ethylene glycol) acrylate in the preparation of surface-active polymers has attracted a lot of attention in the past few years. In some cases, the polymers were water-soluble and salt-tolerant. On the other hand, polymeric surfactants based on hydrophobically modified polyacrylamides have been emerged as promising candidates for EOR applications. Herein in this paper, with the aim of exploring new candidates for reduction in viscosity of heavy oil in EOR, iso-tridecyloxypolyethylene glycols, a type of typical nonionic surfactants, were treated with acrylic acid to give corresponding acrylates. These acrylates were copolymerized with acrylic amide (AM) and 2-acylamido-2-methylpropane sulfonic acid (AMPS) to provide the copolymers PAAI with different numbers of ethylene oxide (EO) units. The rheological properties of PAAI aqueous solution and their emulsification ability for heavy oil were studied and discussed.

EXPERIMENTAL SECTION

2.1 Materials and instruments

iso-Tridecyloxypolyethylene glycols TO-7, TO-10, and TO-15; acrylic acid (AA); acrylic amide; and 2-acylamido-2-methylpropane sulfonic acid (AMPS) were purchased from an industrial source. Hydroquinone, p-toluenesulfonic acid (p-TsOH), sodium dodecyl sulfate (SDS), 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA), potassium persulfate (K2S2O8), sodium bisulfite (NaHSO3), sodium hydroxide, and toluene were purchased as analytical grade from the commercial sources and used without further purification. The heavy oil sample was from Liaohe oilfield. The components of formation water are listed in Table 1.
The $^1$H NMR spectra were measured on Bruker AV400 NMR spectrometer, and tetramethylsilane (TMS) was used as the internal standard. The FTIR spectra were recorded on Thermo Nicolet-IS10 FTIR spectrometer. The thermal gravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1 instrument under nitrogen atmosphere at the heating rate of 10°C/min from 30°C to 600°C. The intrinsic viscosity of PAAIx was measured by Ubbelohde capillary viscometer (ID 0.55 mm), and their viscosity-average molecular weights were calculated according to the method described in GB/T 12005.33 The apparent viscosity of polymer solution was measured using a MCR-301 rheometer (Anton-Paar Physica). The microscopic morphology of PAAIx molecules in aqueous solution was observed by environmental scanning electron microscope (ESEM) Quanta 250 (Quanta); the samples were prepared with 2.0 g/L PAAIx in deionized water by freeze-drying technique and observed with 20 kV of acceleration voltage. The morphology of the emulsion of PAAI15 and heavy oil was observed by Leica DM2500 optical microscopy (Leica).

2.2 | Synthesis of iso-tridecyloxypolyethylene glycol acrylates I13CxAA

As outlined in Scheme 1, iso-tridecyloxypolyethylene glycol TO-7, TO-10, and TO-15 were treated with AA in the presence of catalytic amount of $p$-TsOH and hydroquinone in reflux toluene.\(^{34}\) The corresponding acrylate monomers I13C7AA, I13C10AA, and I13C15AA were obtained, respectively. The $^1$H NMR data of the monomers were listed as follows.

- **I13C7AA**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 6.37 (dd, $J = 17.4, 1.4$ Hz, 1H), 6.08 (dd, $J = 17.4, 10.4$ Hz, 1H), 5.77 (dd, $J = 10.4, 4.8$ Hz, 1H), 4.27 (t, $J = 4.8$ Hz, 2H), 3.31-3.72 (m, 26H), 0.55-1.60 (m, 27H).

- **I13C10AA**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 6.37 (dd, $J = 17.4, 1.4$ Hz, 1H), 6.08 (dd, $J = 17.4, 10.4$ Hz, 1H), 5.77 (dd, $J = 10.4, 4.8$ Hz, 1H), 4.27 (t, $J = 4.8$ Hz, 2H), 3.31-3.72 (m, 38H), 0.55-1.60 (m, 27H).

- **I13C15AA**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 6.36 (dd, $J = 17.4, 1.4$ Hz, 1H), 6.09 (dd, $J = 17.4, 10.4$ Hz, 1H), 5.78 (dd, $J = 10.4, 4.9$ Hz, 1H), 4.25 (t, $J = 4.9$ Hz, 2H), 3.30-3.78 (m, 58H), 0.55-1.60 (m, 27H).

2.3 | Copolymerization of I13C$_x$AA, AM, and AMPS

The acrylate monomers I13C$_x$AA, AM, and AMPS were copolymerized by radical polymerization as outlined in Scheme 2. A mixture of I13C$_x$AA (0.4 g), AM (15.2 g), AMPS (4.4 g), and certain amount of SDS was dissolved in deionized water (60 mL), and the pH of the solution was adjusted to 9 with NaOH. The N$_2$ was bubbled into the solution for 15 minutes; then, certain amount of K$_2$S$_2$O$_8$, NaHSO$_3$, and AIBA was added. After N$_2$ was bubbled for another 10 minutes, the reaction vessel was sealed. The reaction mixture was kept at room temperature for 5 hours, and a gel was formed. The gel obtained was dried, crushed, and washed thoroughly with ethanol and vacuum-dried at 50°C to give copolymer PAAIx as off-white powders, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of I13C$_x$AA

The structures of I13C$_x$AA were characterized by $^1$H NMR spectra. As seen from the NMR data, in the range of 5.7-6.4 ppm, there were three H signals for CH$_2$=CH-, which is typical for acrylate structure, and in the range of 3.3-4.3 ppm, there were signals for various number of EO, and also the signal of iso-tridecyl group was presented in the range of 0.5-1.6 ppm. The $^1$H NMR spectrum of I13C$_{10}$AA is shown in Figure 1, and the structures of monomer I13C$_x$AA were then confirmed.

3.2 | Characterization of PAAIx

The structures of copolymer PAAIx were characterized by FTIR and $^1$H NMR spectra. As an example, the FTIR spectrum of PAAI15 is given in Figure 2. The absorption peaks at 3336 and 3197 cm$^{-1}$ were the stretching vibrations of -NH$_2$ and NH. The absorption peaks between 2950 and 2850 cm$^{-1}$ were assigned to the stretching vibrations of alkyl groups. The stretching vibration peak of C=O appeared at 1670 cm$^{-1}$. A characteristic absorption peak of -SO$_3$Na was presented at 1183 cm$^{-1}$. A peak at 1020 cm$^{-1}$ was assigned...
for C-O stretching vibration. Thus, it was confirmed that PAAI15 was the copolymer of AM, NaAMPS, and I13C15AA, respectively.

Meanwhile, the $^1$H NMR spectrum of PAAI15 in D$_2$O is shown in Figure 3. In the range of 0.6-1.35 ppm, the peaks were assigned to the H of alkyl group. The signals at 1.35-1.85 ppm were the -CH$_2$- of the skeleton of the polymer, and signals at 2.0-2.40 ppm were assigned to -CH- of the skeleton of the polymer. The signals appeared at 3.0-3.75 ppm were the H of -OCH$_2$- and -CH$_2$SO$_3$Na. It should be mentioned that there were no H signals for CH$_2$=CH- in the range of 5.5-7.0 ppm. This was indicated that PAAI15 was the copolymer of AM, NaAMPS, and I13C15AA, and there was no residue of acrylate monomers left in PAAI15. The structures of PAAI7 and PAAI10 were characterized in the same manner.

The viscosity-average molecular weights $\bar{M}_\eta$ of PAAIx were calculated from their intrinsic viscosity $[\eta]$ measured by the method described in GB/T 12 005.10-1992. The intrinsic viscosities for PAAI7, PAAI10, and PAAI15 were 1344.64, 1492.02, and 1978.49 mL/g, and the corresponding viscosity-average molecular weights were 6.53 x 10$^6$, 7.44 x 10$^6$, and 10.58 x 10$^6$ g/mol, respectively. The intrinsic viscosities as well as the viscosity-average molecular weights of PAAIx increased as the number of EO units in I13C$_x$AA increased. This might be due to the difference in solubilities in water for different I13C$_x$AA monomers. As the number of EO units
increased, I13C,AA became more soluble in water and this would result in a better polymerization for I13C,AA.

The thermal stability of PAAI15 was studied by TGA from 30°C to 600°C at a heating rate of 10°C/min under N2. The curves of TGA and derivative thermogravimetry (DTG) are given in Figure 4. There was a slight weight loss before 105°C. This was caused by loss of moisture and some low molecular weight compounds absorbed by the sample, as PAAI15 had plenty of amide group and EO units on its side chain, which were ready to cooperate with water and some solvents. When the temperature reached 230°C, nearly 20% of its weight loss occurred. This could be caused by dehydration and slight decomposition of the amide group. The most weight loss of PAAI15 appeared when the temperature reached 350°C; this could be assigned mostly by the decomposition of amide groups and some decomposition of polymer backbone skeleton. When the temperature reached 600°C, nearly 40% mass of PAAI15 was remained. PAAI7 and PAAI10 had similar thermal stability to PAAI15.

3.3 Effect of temperature on the viscosity of PAAIx

The effect of temperature on the viscosity of aqueous solutions of PAAIx was studied. PAAI7, PAAI10, and PAAI15 were dissolved in formation water in the concentration of 2.0 g/L, the apparent viscosities of the solutions were measured between 25 and 90°C under the shear rate of 6 s⁻¹, and the plots are given in Figure 5. As seen, the viscosities of all the solutions decreased at elevated temperature. Among the polymer samples, the solution of polymer with more EO units in the side chain had higher viscosity. This could be interpreted by the hydrogen bonds formed between EO groups and water to make the polymeric molecules more stretched in the solution, the aggregates of the polymer with more EO units would have larger hydrophilic domains, and also the aggregates formed were less compact due to the steric resistance of the longer EO chain.35 The polymer with more EO units would have larger hydrodynamic volume which led to higher viscosity. However, the hydrogen bond was sensitive to the temperature, and the disassociation occurred at higher temperature leading to the reduction in viscosity. From 25°C to 75°C, the viscosities of three samples were reduced gradually, but the reduction turned sharply after temperature reached 75°C, as high temperature would also enhance the curliness of polymer chains and lead to loss of viscosity.

3.4 Effect of shear rate on the viscosity of PAAIx

The shear viscosity plays an important role for many applications of water-soluble polymers, and especially for EOR. The polymer solution would experience different shear during the whole process, namely high shear near the injection point and
lower shear inside the reservoir. Thus, maintaining the viscosity of polymer solution is highly desirable for enhanced oil recovery by chemical flooding.\textsuperscript{36}

As an example, PAAI\textsubscript{15} was dissolved in formation water to provide 1.0 g/L, 2.0 g/L, 3.0 g/L, and 4.0 g/L solutions, respectively. The shear viscosities of these solutions were measured at 50°C under different shear rates. The curves of viscosity of PAAI\textsubscript{15} in different concentrations against shear rates are given in Figure 6. When the shear rate increased, the viscosities of all the solutions decreased rapidly. The shear-thinning behavior was more obvious for the solution with higher concentrations. Considering the structure of PAAI\textsubscript{15}, this was in line with the known literature about block polyelectrolytes.\textsuperscript{37,38} When the shear rate increased, the intermolecular twining and binding of the polymer were reduced, and thus, the viscosity of the solution decreased. After the shear rate reached 20 s\textsuperscript{-1}, the curves turned flat, and the viscosities of the solutions remained in certain extents. And also, it was shown that the viscosity of PAAI\textsubscript{15} solution increased along with increasing the polymer concentration.

3.5 | Effect of the salt on the viscosity of PAAI\textsubscript{x}

The water salinity plays an important role in determining the properties, both rheological and interfacial, of the polymer solutions, and the salinity is known to decrease the viscosity of solutions of polymers bearing charged groups along the chain.\textsuperscript{8} PAAI\textsubscript{7}, PAAI\textsubscript{10}, and PAAI\textsubscript{15} were dissolved in deionized water at a concentration of 2.0 g/L with addition of various amounts of NaCl or CaCl\textsubscript{2}. The apparent viscosities
of the solutions were measured at 50°C under the shear rate of 6 s⁻¹. As shown in Figure 7, the viscosities of PAAI₇ solutions decreased dramatically with the addition of NaCl. After the concentration of NaCl reached 5000 mg/L, the viscosities of the polymer solutions changed little and the curves turned flat. On the other hand, CaCl₂ had similar effect, as shown in Figure 8; once CaCl₂ was added, the viscosities of PAAI₇ solutions decreased rapidly. After the concentration of CaCl₂ reached 2000 mg/L, the curves turned flat. In the polymer solution, the intermolecular interaction between the functional polymeric chains resulted in the aggregation of the molecules and increased the viscosity. These polymers were polyelectrolyte, and the salt would have effect on their viscosities. When the concentration of NaCl or CaCl₂ increased, the electrostatic repulsion of the polymer chains reduced and resulted in a reduction of hydrodynamic volume, which led to lower viscosity. As PAAI₇, PAAI₁₀, and PAAI₁₅ had similar structures except the number of EO unit, NaCl and CaCl₂ had similar effect on their aqueous solutions.

### 3.6 The emulsification and viscosity reduction properties for heavy oil

PAAI₇, PAAI₁₀, and PAAI₁₅ were dissolved in formation water in concentration of 1.0 g/L. The emulsions were prepared by emulsifying heavy oil and polymer solution in various oil-water ratios. By taking 24.0 g, 18.0 g, 12.0 g, and 6.0 g of heavy oil with 6.0 g, 12.0 g, 18.0 g, and 24.0 g of PAAI₇ solutions, respectively, into test tubes, the mixtures were treated in an electric shaker with 70 round/min at 50°C until the emulsions were formed. The apparent viscosities of the emulsions (η) and the heavy oil sample (η₀) were measured at 50°C under the shear rate of 20 s⁻¹, and η₀ of the oil sample was 1076.0 mPa s. The results are given in Table 2. The viscosity reduction rates of polymer samples were calculated as reduction rate % = (η₀ - η)/η₀ × 100%. When the mass ratio of oil:water was in the range of 6:4-2:8, reductions in viscosities of the emulsions formed were observed, and the rates of reductions were 53.5%-97.5%, respectively. When the mass ratio of oil:water was 8:2, the viscosities of the samples were higher than that of the heavy oil. It was suggested the polymers could not emulsify the heavy oil properly under this circumstance, and a type of water-in-oil emulsion was formed. PAAI₁₅ gave better results in comparison with the other two. The emulsions with 4:6 mass ratio of oil:water had been kept in water bath at 50°C for 24 hours, and the photographs are shown in Figure 9. Various amount of water separated from the emulsions at the bottoms of three test tubes, and the emulsion formed with PAAI₁₅ had the least amount of water separated, which was indicated that this emulsion was comparatively stable to the other two. The emulsification properties of PAAI₇ were related to their amphiphilic structures which were in line with the findings in the literature.²²,³⁹

### Table 2

| Oil:water | η (mPa s) | Red.rate (%) | η (mPa s) | Red.rate (%) | η (mPa s) | Red. rate (%) |
|----------|----------|--------------|----------|--------------|----------|--------------|
| 10:0     | 1076.0   | /            | 1076.0   | /            | 1076.0   | /            |
| 8:2      | 1197.0   | /            | 1270.2   | /            | 1314.1   | /            |
| 6:4      | 138.3    | 87.1         | 369.8    | 65.6         | 500.2    | 53.5         |
| 4:6      | 127.9    | 88.1         | 180.3    | 83.2         | 239.9    | 77.7         |
| 2:8      | 26.9     | 97.5         | 50.1     | 95.3         | 76.2     | 92.9         |

### Figure 9

Photographs of PAAI₇ with heavy oil (A) before emulsification and (B) standing for 24 h at 50°C after emulsification. 1#-PAAI₁₅, 2#-PAAI₁₀, and 3#-PAAI₇
The effects of temperature and shear rate on the viscosity of the emulsions were studied. The emulsions in 4:6 mass ratio of oil:water with PAAI \textsubscript{x} were obtained in the same manner as described above at different emulsifying temperatures, and viscosities of the emulsions were measured at emulsifying temperature under shear rate of 20 s\textsuperscript{-1}; the results are given in Figure 10. As seen from the plots, viscosities of three emulsions decreased when emulsifying temperature increased. This could be explained by a decrease in the viscosity of oil which promoted the distribution in the aqueous phase when the emulsifying temperature increased.

The emulsions of PAAI\textsubscript{15} with heavy oil gave the lowest viscosities in comparison with those of PAAI\textsubscript{7} and PAAI\textsubscript{10}. In the meantime, viscosities of the emulsions prepared at 50°C in 4:6 mass ratio of oil:water were measured at the same temperature under various shear rates, and the plots are shown in Figure 11. As seen, in the low shear rate region, viscosities of the emulsions decreased when shear rate increased; after shear rate exceeded 20 s\textsuperscript{-1}, the curves turned flat, and viscosities of the emulsions changed in narrow ranges. The emulsion of PAAI\textsubscript{15} with heavy oil had the lowest viscosity, which was little effected by shear rate.

As the emulsion of PAAI\textsubscript{15} and heavy oil showed good stability and low viscosity (compared with original oil sample), the effects of temperature, shear rate, and ratios of oil:water on the viscosity of emulsion with PAAI\textsubscript{15} were further studied. The emulsions of 1.0 g/L PAAI\textsubscript{15} in formation water with heavy oil in various mass ratios were prepared in the same manner as described above at different temperatures. The viscosities of the formed emulsions were measured under the shear rate of 20 s\textsuperscript{-1} at the corresponding temperature, and the results are given in Figure 12.
As seen from the plots, when the mass ratio of oil:water was 8:2, the viscosity of such emulsion was even higher than that of original heavy oil, and a water-in-oil emulsion rather than an oil-in-water type was formed. When the mass ratio was in the range of 6:4 - 2:8, significant reductions in viscosities of the emulsions were observed, and the viscosities of these emulsions changed little when the temperature rose from 30°C to 80°C. It was indicated that stable oil-in-water emulsions were formed under these conditions. The curves of the shear rate on the viscosity of the emulsions in 4:6 mass ratio of oil:water at various temperature are plotted in Figure 13. The viscosities of the emulsions decreased gradually in narrow regions when shear rate increased while the emulsifying temperature was at 30-60°C. The shear rate had little effect on the viscosity of the emulsion at 70-80°C. This indicated that emulsions formed under these conditions were rather stable.

3.7 | The relations of structure and viscosity reduction property of the copolymer PAAI<sub>x</sub>

As discussed above, PAAI<sub>x</sub> solutions could emulsify the oil sample to form stable oil-in-water emulsions and reduce its viscosity. Such property and working mechanisms were related to their amphiphilic molecular structures. First of all, polymer PAAI had hydrophilic EO units which could form hydrogen bonds with water molecules, leading the side chains to stretch out in water. This would cause the formation of micro–cross-linked structures. The hydrophobic bulky iso-tridecyl groups at the terminal of side chains were aggregated on the interface between oil and water, the oil was then emulsified and dispersed into the polymer solutions, and the reduction in viscosity of heavy oil occurred, as it was illustrated in the sketch presented in Figure 14. The length of EO chain had effect on the aggregation behavior of the molecules. As PAAI<sub>15</sub> had more EO units within the structure, the side chains were more stretched in aqueous solution and this would cause the hydrophobic iso-tridecyl group to aggregate more compact on the interface. The microscopic image of freshly formed emulsion of heavy oil and 1.0 g/L PAAI<sub>15</sub> in formation water in a mass ratio of 4:6 is given in Figure 15. As seen from the image, oil was emulsified and dispersed in aqueous phase, and an oil-in-water emulsion was formed.

Secondly, the microstructure of PAAI<sub>x</sub> in aqueous solution also played an important role in viscosity reduction of oil, as aqueous solution of PAAI<sub>15</sub> with relatively high viscosity gave higher rate of reduction in viscosity of heavy oil than that of PAAI<sub>7</sub> and PAAI<sub>10</sub>. The microscopic morphology of 2.0 g/L PAAI<sub>x</sub> in deionized water was observed by ESEM, and the images are given in Figure 16. Some loose network was shown in the image of PAAI<sub>7</sub> solution, and more three-dimensional network was presented in the image of PAAI<sub>10</sub> solution. The meshes presented in the image of PAAI<sub>15</sub> solution were the most compact and well-formed among the three samples. This indicated that there were more micro–cross-linked structures and intermolecular hydrophobic association of PAAI<sub>15</sub> molecule, which led to good viscosity building ability, stabilizing the emulsion and enhancing the reduction in viscosity of heavy oil.

4 | CONCLUSIONS

In present work, copolymers PAAI<sub>x</sub> (x = 7, 10, 15) were prepared by copolymerization of AM, AMPS, and iso-tridecyloxypolyethylene glycol acrylates I13C<sub>x</sub>AA (x = 7, 10, 15) via ATRP.
which were prepared from corresponding iso-tridecyloxy(polyethylene glycol by esterification with acrylic acid. These polymers were characterized by FTIR, \textsuperscript{1}H NMR spectroscopy, and TGA. PAAI\textsubscript{x} showed good thermal stability as the decomposition temperature was above 350°C. The viscosity-average molecular weights of PAAI\textsubscript{x} were in the range of 6.53 \times 10^6 and 10.58 \times 10^6 g/mol. The effects of temperature, shear rate, and salinity on the viscosity of polymer solutions were studied, and PAAI\textsubscript{x} had reasonable rheological properties. The emulsification properties of PAAI\textsubscript{x} with heavy oil were studied. The results showed that solutions of PAAI\textsubscript{x} in formation water could emulsify heavy oil sample to form oil-in-water emulsion when mass ratio of oil:water was in the range of 6:4-2:8, respectively. The rates of reduction in viscosity of emulsions compared with that of original oil sample were 53.5%-97.5% at 50°C under shear rate of 20 s\textsuperscript{-1}. The effects of oil:water ratio, emulsifying temperature, and shear rate on the viscosities of emulsions were extensively studied, and the effect of the polymer structure on the emulsification and viscosity reduction of heavy oil was also discussed. Both emulsification property and viscosity of the polymer solution were important for the reduction in viscosity of heavy oil. Among three copolymers, PAAI\textsubscript{15} formed the most stable emulsion with heavy oil and the emulsion had the lowest viscosity. PAAI\textsubscript{15} had the potential as a viscosity reducer for heavy oil for further study.

ACKNOWLEDGMENTS
This work was financially supported by the National Science and Technology Major Project (2016ZX05010-004-002) and the PetroChina Science and Technology Major Project (No. 2019B-1410).

REFERENCES
1. Simon S, Nenningsland AL, Herschbach E, Sjoblom J. Extraction of basic components from petroleum crude oil. Energy Fuels. 2010;24(2):1043-1050.
2. Zhang SF, Sun LL, Xu JB, Wu H, Wen H. Aggregate structure in heavy crude oil: using a dissipative particle dynamics based mesoscale platform. Energy Fuels. 2010;24(08):4312-4326.
3. Alghanduri LM, Elgarni MM, Daridon JL, Coutinho JAP. Characterization of Libyan waxy crude oils. Energy Fuels. 2010;24(05):3101-3107.
4. Bava YB, Gerones M, Buceta D, Rodriguez DI, Lopez-Quintela MA, Erben MF. Elucidation of the average molecular structure of Argentinian asphaltenes. Energy Fuels. 2019;33(4):2950-2960.
5. Lv XB, Fan WY, Wang QT, Lao H. Synthesis, characterization, and mechanism of copolymer viscosity reducer for heavy oil. Energy Fuels. 2019;33(5):4053-4061.
6. Lake LW. Enhanced Oil Recovery. Old Tappan, NJ: Prentice Hall Inc.; 1989.
7. Sheng JJ. Modern Chemical Enhanced Oil Recovery: Theory and Practice. Burlington: Elsevier; 2010:648.
8. Wever DAZ, Picchioni F, Broekhuis AA. Polymers for enhanced oil recovery: a paradigm for structure-property relationship in aqueous solution. Prog Polym Sci. 2011;36:1558-1628.
9. Sheng JJ, Leonhardt B, Azri N. Status of polymer-flooding technology. J Can Pet Technol. 2015;54:116-126.
10. Kamal MS, Sultan AS, Al-Mubaiyedh UA, Hussein IA. Review on polymer flooding: rheology, adsorption, stability, and field applications of various polymer systems. Polym Rev. 2015;55(3):491-530.
11. Negin C, Ali S, Xie Q. Most common surfactants employed in chemical enhanced oil recovery. Petroleum. 2017;3(2):197-211.
12. Raffa P, Wever DAZ, Picchioni F, Broekhuis AA. Polymeric surfactants: synthesis, properties, and links to applications. Chem Rev. 2015;115(16):8504-8563.
13. Penott-Chang EK, Gouveia L, Fernandez I, Muller AJ, Diaz-Barrios A, Saez AE. Rheology of aqueous solutions of hydrophobically modified polyacrylamides and surfactants. Colloids Surf, A. 2007;295:99-106.
14. El-Hoshoudy AN, Desouky SEM, Elkady MY, Alsabagh AM, Betih MA, Mahmoud S. Hydrophobically associated polymers for wettability alteration and enhanced oil recovery-article review. Egypt J Petrol. 2017;26(3):757-762.
15. Afolabi RO, Oluwemi GF, Officer S, Ugwu JO. Hydrophobically associating polymers for enhanced oil recovery-Part A: a review on the effects of some key reservoir conditions. J Petrol Sci Eng. 2019;180:681-698.

16. Raffa P, Brockhuis AA, Picchioni F. Polymeric surfactants for enhanced oil recovery: a review. J Petrol Sci Eng. 2016;145:723-733.

17. Co L, Zhang Z, Ma Q, Watts G, Zhao L, Shuler PJ. Evaluation of functionalized polymeric surfactants for EOR applications in the Illinois Basin. J Petrol Sci Eng. 2015;134:167-175.

18. Chen X, Li Y, Gao W, Chen C. Experimental investigation on transport property and emulsification mechanism of polymeric surfactants in porous media. J Petrol Sci Eng. 2020;186:106687.

19. Dos Santos RG, Bannwart AC, Briceno MI, Loh W. Physico-chemical properties of heavy crude oil-in-water emulsions stabilized by mixtures of ionic and non-ionic ethoxylated nonylphenol surfactants and medium chain alcohols. Chem Eng Res Des. 2011;89:957-967.

20. Malkin AY, Zadymova NM, Skvortsova ZN, Traskine VYU, Kulichikhin VG. Formation of concentrated emulsions in heavy oil. Colloids Surf, A. 2016;504:343-349.

21. Malkin AY, Zaev KV, Arinina MP, Kulichikhin VG. Modifying the viscosity of heavy crude oil using surfactants and polymer additives. Energy Fuels. 2018;32:11991-11999.

22. Zhao YZ, Zhou JZ, Xu XH, et al. Synthesis and characterization of a series of modified polyacrylamide. Colloid Polym Sci. 2009;287:237-241.

23. Jiang GQ, Huang L, Li B, Lv CS, Li R, Liu FQ. Synthesis, characterization, rheological behavior, and shear response of hydrophobically modified polyacrylamide and network structure of its microhydrogel. J Appl Polym Sci. 2012;123:66-76.

24. Ye ZB, Zhang X, Chen H, et al. Synthesis and characterization of an associative polymer with an octylphenyl polyoxyethylene side chain as a potential enhanced-oil-recovery chemical. J Appl Polym Sci. 2014;131:41024.

25. Raffa P, Brockhuis AA, Picchioni F. Amphiphilic copolymers based on PEG-acrylate as surface active water viscosifiers: towards new potential systems for enhanced oil recovery. J Appl Polym Sci. 2016;133:44100.

26. Cheng ZP, Zhu XL, Kang ET, Neoh KG. Brush-type amphiphilic diblock copolymers from “living”/controlled radical polymerizations and their aggregation behavior. Langmuir. 2005;21:7180-7185.

27. Guo SH, Yin T, Ye ZB, et al. High-temperature resistance water-soluble copolymer derived from acrylamide, DMAAAC, and functionalized sulfonamide for potential application in enhanced oil recovery. J Appl Polym Sci. 2014;131:40727.

28. Al-Hashmi A, Al-Maamari R, Al-Shabibi I, Mansoor A, Al-Sharji H, Zaitoun A. Mechanical stability of high-molecular-weight polyacrylamides and an (acrylamido tert-butyl sulfonic acid)-acrylamide copolymer used in enhanced oil recovery. J Appl Polym Sci. 2014;131:40921.

29. Guo SH, Zhang Q, Ma YT, et al. Self-assembled acrylamide-based copolymer/surfactant with high-temperature resistance for enhanced oil recovery. J Appl Polym Sci. 2017;134:45202.

30. Mao JC, Liu JW, Peng YK, Zhang ZY, Zhao JZ. Quadrupolymers as viscosity reducers for heavy oil. Energy Fuels. 2018;32:119-124.

31. Hu X, Ke YC, Zhao Y, Lu SC, Yu CC, Peng FF. Synthesis and characterization of a β-cyclodextrin modified polyacrylamide and its rheological properties by hybriding with silica nanoparticles. Colloids Surf A. 2018;518:10-18.

32. Xie BQ, Liu XD, Wang HQ, Zheng LH. Synthesis and application of sodium 2-acrylamido-2-methylpropane sulphonate/N-vinylcaprolactam/divinyl benzene as a high-performance viscosifier in water-based drilling fluid. J Appl Polym Sci. 2016;133:44140.

33. GBT/T 12005. 10-1992, The Chinese Standardization Administration, China (in Chinese).

34. Ma J, Yang ZW, Liu XX, Zhen T. Synthesis and characterization of polymerizable nonionic surfactant containing Brij35. J South Chin Univ Technol (Nat Sci Ed). 2008;36(7):102-105 (in Chinese).

35. Hu CC, Li RQ, Yang H, Wang JB. Properties of binary surfactant systems of nonionic surfactants C12E10, C12E23, and C12E42 with a cationic gemini surfactant in aqueous solutions. J Colloid Interface Sci. 2011;356:605-613.

36. Zhang H, Dong M, Zhao S. Which one is more important in chemical flooding for enhanced Court heavy oil recovery, lowering interfacial tension or reducing water mobility? Energy Fuels. 2010;24:1829-1836.

37. Chassenieux C, Nicolai T, Benyahia L. Rheology of associative polymer solutions. Curr Opin Colloid Interface Sci. 2011;16:18-26.

38. Kimerling AS, Rochefort WE, Bhatia SR. Rheology of block polyelectrolyte solutions and gels: a review. Ind Eng Chem Res. 2006;45:6885-6889.

39. Sun JH, Xu XH, Wang JB, et al. Synthesis and emulsification properties of an amphiphilic polymer for enhanced oil recovery. J Dispersion Sci Technol. 2010;31:931-935.

How to cite this article: Zhang F, Lei Q, Liu G, Liao G, Xu X, Meng W. Synthesis and laboratory evaluation of iso-tridecylxylopolypeylene glycol acrylate copolymers as potential viscosity reducers for heavy oil. Energy Sci Eng. 2020;8:3303–3313. https://doi.org/10.1002/ese3.722