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Asphaltene Inhibition and Flow Improvement of Crude Oil with a High Content of Asphaltene and Wax by Polymers Bearing Ultra-Long Side Chain

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Abstract: A high content of asphaltene and wax in crude oil leads to difficulties in the recovery and transportation of crude oil due to the precipitation of asphaltenes and the deposition of waxes. Comb-like polymers were found to be capable of inhibiting the aggregation of asphaltenes and crystallization of waxes. In this work, comb-like bipolymers of α-olefins/ultra-long chain (C18, C22 and C28) alkyl acrylate were synthesized and characterized by FT-IR and 1H NMR spectra. The results show that, for a model oil containing asphaltene, the initial precipitation point (IPP) of asphaltene was prolonged by UV, and the asphaltene particle size was reduced after adding the biopolymers, as revealed by dynamic light scattering (DLS). The bipolar polymer containing the longer alkyl chain had a better asphaltene inhibition effect. However, DSC and rheological results show that the wax appearance temperature (WAT) of the typical high asphaltene and high wax content of crude oil was obviously reduced by adding biopolymers with shorter alkyl chains. The bipolar polymer (TDA2024-22) with a mediate alkyl chain (C22) reduced the viscosity and thixotropy of the crude oil by a much larger margin than others. Compared with the previously synthesized bipolar with phenyl pendant (PDV-A-18), TDA2024-22 exhibited a better performance. Therefore, biopolymers with appropriate alkyl side chains can act as not only the asphaltene inhibitors but also wax inhibitors for high asphaltene and wax content of crude oil, which has great potential applications in the oil fields.

Keywords: high asphaltene and high wax content of crude oil; asphaltene precipitation; wax crystallization; rheology

1. Introduction

With the decline of conventional oil reserves year by year, the global demand for unconventional crude oils, which often contain large amounts of asphaltene and wax, is increasing [1]. Asphaltenes is derived from condensed polyaromatic material, and the molecular structure of asphaltene can be divided into continental and archipelago models. Normally, asphaltene contains a large amount of strong polar groups such as carboxyl groups, amino groups and carbonyl groups. Therefore, asphaltene is the most polar portion of the crude oil, as it cannot dissolve in crude oil but disperses in the oil phase as aggregated colloidal particles. During crude oil pipeline transportation, the changes in temperature, pressure and crude oil composition will induce the precipitation and depo-
sition of asphaltene, which greatly impedes the safety and economic operation of the pipelines. In addition, the aggregation of asphaltene will obviously increase the viscosity of crude oil, which also leads to difficulty in crude oil pipeline transportation.

Wax usually refers to n-alkyls with a carbon number at the range of C_{15}–C_{30}. With the decrease of the crude oil temperature during pipelining, the wax becomes less soluble and crystallizes out of the crude oil. The precipitated wax crystals accompanying the aggregated asphaltene particles change the crude oils from simple Newtonian fluids to complex non-Newtonian fluids, and even induce gelation [2]. Therefore, crude oils containing high asphaltene and wax contents often have a high pour point and high viscosity, which is adverse for the safety and economic operation of crude oil transportation [3–5]. For example, there is type of African pipeline crude oil that is a typical unconventional oil with a high content of wax and asphaltene. In this case, the commonly used commercial pour point depressants (PPDs) are no longer as effective as they were before. Only by increasing the dosage of PPD above 2500 ppm (very high dosage), can the pour point of crude oil be reduced to less than 24 °C, which is the allowable operating temperature for the pipeline.

To inhibit the asphaltene precipitation and deposition, asphaltene dispersants are often used to change the dispersion state of asphaltene and then stabilize the asphaltene. At present, commonly used asphaltene dispersants can be divided into small-molecule asphaltene dispersants and polymeric asphaltene dispersants. Small-molecule asphaltene dispersants include acidic amphiphilic molecules, amides and imides and ionic liquids [6,7]. For example, dodecyl benzene sulfonic acid (DBSA) and dimethyl amide (DA) can form hydrogen bonds with asphaltene molecules, generating acid-base force to prevent the aggregation of asphaltenes and improve the fluidity of crude oil [8,9]. However, most small-molecule asphaltene dispersants have problems such as a high cost of preparation and poor compatibility with different crude oils. The polymeric asphaltene dispersants can provide more sites of adsorption and better interaction with asphaltene molecules [10,11]. At the same time, the non-polar alkyls of the polymeric asphaltene dispersants can provide steric hindrance, further reducing the size of asphaltene aggregates. [12] Commonly used polymeric asphaltene dispersants include poly-methacrylate, poly-styrene/maleate copolymer, alkylene/maleate copolymer, etc. [13–15]. Such polymers can change the types of their polar groups through chemical reactions, making them more compatible for crude oil.

To inhibit wax crystallization and improve crude oil flowability, polymeric PPDs are widely used in crude oil pipelining. According to the structural characteristics of polymeric PPDs, the PPDs can be classified as EVA-type PPDs and comb-like PPDs. The comb-like PPDs are widely studied due to the diversity of their molecular structure. The molecular structure of comb-like PPDs typically contains the non-polar groups that can co-crystallize with the paraffin waxes, and the polar groups (anhydride groups, ester groups, amide groups, etc.) that can interfere the crystallization process of waxes [16–18]. Researchers have prepared a series of comb-like PPDs derived from maleic anhydride, n-butyl acrylate, octadecyl acrylate, styrene and vinyl acetate, etc., to improve the low-temperature fluidity of waxy crude oil [19]. They found that the performance of comb-like PPDs varies significantly depending on the alkyl side chain length of the non-polar groups and the electronegativity of the polar groups. In another work, Zhang et al. [20] pointed out that the comb-like PPDs could not only affect the crystallization behavior of wax, but also synergistically improve the rheology of oil samples with asphaltenes. Yao et al. [21–23] also found that PPDs molecules can adsorb on asphaltenes, and then enhance the dispersion stability of asphaltene and improve the flowability of waxy oils. Based on the above work, a hypothesis was proposed that the comb-like PPDs could be adsorbed onto the surface of aggregated asphaltene particles to form composite PPDs, thus resulting in a significant improvement in the rheology of waxy oils.

Until now, the recovery and transportation of crude oil with a high asphaltene and wax content are recognized as a challenge, due to the precipitation of asphaltenes and deposition of waxes. In our previous study, the influences of PDV-A-18 on the asphaltene
precipitation behaviors were investigated [24]. The results show that PDV-A-18 could adequately suppress the precipitation of asphaltenes by reducing the size and improving the distribution of asphaltene precipitates. To provide an effective strategy to solve the flowability of high asphaltene and crude oil with a high wax content during recovery and transportation, the mechanism of polymer bearing alkyl side chains with different length inhibiting the asphaltene precipitation and wax crystallization and the effect of various pendants are required to be studied. In the present work, α-olefin/ultra-long chain alkyl acrylate bipolymers were first synthesized. Then, the effect of the bipolymers on the asphaltene precipitation in a model oil was investigated; after that, the effects of the bipolymers on the wax crystallization behavior and rheology of crude oil with a high asphaltene and wax content was studied. The results show that the comb-like bipolymers with a suitable length of alkyl side chains could not only disperse the asphaltene, thus inhibiting asphaltene precipitation, but also inhibit the growth of wax crystals, thus improving the flowing ability of the crude oil, which is better than PDV-A-18.

2. Experimental Section

2.1. Materials

Octadecanol (>99%), docosanol (≥98%), octacosanol (>99%) and α-olefins mixture (99%) containing n-eicosane (40.7%), n-docosane (32.0%) and n-tetracosane (19.3%) were obtained from Sasol Chemical Co., Ltd. N-heptane (AR), toluene (≥99.7%) and o-xylene (99.5%) were purchased from Shanghai Lingfeng Chemical Co., Ltd. Acrylic acid (>99%), benzoyl peroxide (99.5%), hydroquinone (99.5%) and p-toluenesulfonic acid (99.5%) were purchased from Shanghai Aladdin Biological Co., Ltd. Sodium hydroxide (99.9%) and sodium carbonate (99.5%) were purchased from Sinopharm Group. The deionized water was made in the laboratory. Poly (maleic acid phenyl and octadecyl amide-covinyl acetate) (PDV-A-18) was synthesized following the protocols of our previous work [11,24].

The crude oil used in this work is a typical pipeline oil with a high wax and high asphaltene content from Africa. The elemental physical properties of this crude oil are shown in Table 1.

Table 1. The elemental physical properties of African pipeline oil.

| Output Of Pipeline (BBL/D) | Wax Content (%) | Density (G/Cm³, 15 °C) | Water Content (%) |
|---------------------------|-----------------|------------------------|-------------------|
| 80,000–100,000            | 18.0            | 0.864                  | 0.4               |
| Viscosity (mPa·s, 25 °C, 10 s⁻¹) | WAT(°C) | pour point (°C) | asphaltene content (%) |
| 487                       | 35.9            | 27.0                   | 25.0              |

2.2. Preparation of α-Olefins/Ultra-Long Alkyl Acrylate Bipolymers

Synthesis of ultra-long alkyl acrylate. Octadecanol acrylate is taken as an example: 100 g (0.38 mol) of octadecanol, 50 mL of toluene and 0.50 g of hydroquinone as an inhibitor were added into a 250 mL three-neck flask equipped with a water separator. Above mixture was heated to 50 °C and stirred thoroughly. Then, 25 g (0.31 mol) of acrylic acid and 1 g of p-toluene sulfonic acid as catalyst were added in. The reaction temperature was set to 60–70 °C, and reaction time was 1 h. Afterwards, the temperature was raised to 110 °C, and the reaction continued for another 1 h. The water in the separator was collected and weighed (the theoretical amount of generated water is about 5.0 g). The crude product was purified by washing it with 5% Na2CO₃ solution, then washed with distilled water to neutral, vacuum distillated to remove toluene, and dried in an oven. The synthesis method of other ultra-long alkyl acrylates is similar to this procedure.

Synthesis of α-olefins/ultra-long alkyl acrylate bipolymers. Taking the bipolymer of α-olefins/octadecyl acrylate as an example: A total of 9.5 g of α-olefin mixture, 50 g of
octadecyl acrylate, 56.9 mL of o-xylene solvent and 0.54 g of benzoyl peroxide (BPO) as an initiator were added into a 250 mL flask. The above mixture was strongly stirred to allow the reactant and initiator to fully dissolve in the solvent. Under the protection of nitrogen, the temperature was raised to 120 °C, and the reaction lasted for 1.5 h. At the end of the reaction, most of the solvents were removed by vacuum evaporation, and then the crude product was obtained. Afterward, methanol was added in to precipitate the bipolymer. By filtration and drying, a pure product was acquired. The synthesis method of other bipolymers is similar to this procedure.

Bipolymers of α-olefins/octadecyl acrylate (TDA 2024-18), α-olefins/behenyl acrylate (TDA 2024-22) and α-olefins/octacosyl acrylate (TDA 2024-28) were synthesized here, and the chemical structures of these polymers are shown in Figure 1.

![Chemical structures of α-olefins/long alkyl acrylate bipolymers and PDV-A-18.](image)

**Figure 1.** Chemical structures of α-olefins/long alkyl acrylate bipolymers and PDV-A-18.

Chemical structure characterization of synthesized bipolymers. The chemical structure of synthesized bipolymers was characterized by Fourier transform infrared (FTIR) and 1H nuclear magnetic resonance (1H NMR) approaches. The FT-IR was performed by Nicolet 6700 FTIR spectrometer with KBr pellet applied for all samples [1]. H NMR spectra were collected by AVANCE 400Hz NMR spectrometer with CDCl3 as the solvent.

2.3. Methodology

An African crude oil with a high asphaltene and wax content was chosen to explore the effect of α-olefin/ultra-long chain alkyl acrylate bipolymers on asphaltene precipitation and wax crystallization behaviors. Since it is difficult to detect the asphaltene precipitation behaviors in crude oil, a model oil containing asphaltene was prepared and used to analyze asphaltene precipitation behaviors. In the presence and absence of bipolymers, UV–Vis spectroscopy was applied to measure the IPP of asphaltenes. Dynamic light-scattering (DLS) analyzer was utilized to study the size and size distribution of asphaltenes. The morphology of asphaltene precipitates was observed by optical microscope. Then, the crystallization behaviors of waxes in crude oil were researched via a differential scanning calorimetry (DSC) apparatus. The morphology of wax crystals was observed with a polarized light microscope. Finally, to verify the effect of bipolymers on the asphaltene and
wax, the rheological behaviors of crude oil were studied by the rheometer. The methodology of the study on the asphaltene precipitation and wax crystallization by biopolymers is shown in Table 2.

Table 2. Methodology of the study on the asphaltene precipitation and wax crystallization by biopolymers.

| Study Content | Asphaltene Precipitation Behaviors | Crystallization Behaviors of Waxes | Rheological Behaviors of Crude Oil |
|---------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Method        | UV–Vis spectroscopy               | differential scanning calorimetry | rheometer                         |
|               | dynamic light scattering          | polarized light microscope        |                                   |
|               | optical microscope                |                                   |                                   |

2.4. Asphaltene

The asphaltene used in this work was isolated from an African pipeline crude oil. The specific extraction method is as follows: An amount of 1 g crude oil was added to 40 mL of n-heptane in a flask. The solution was ultrasonic dispersed for 40 min and kept overnight. The next day, the mixture was subjected to ultrasonic dispersion for 15 min, then filtered. The resulting solid product was dried in a vacuum oven to obtain purified asphaltene powder.

The chemical structure of asphaltene was characterized by FTIR, elemental analysis, \(^1\)H and \(^13\)C NMR spectra and time-of-flight mass spectrometry (TOFMS). The instrument used for infrared spectroscopy was the same as that mentioned above. VARIO EL III element analyzer was used for elemental analysis. \(^1\)H and \(^13\)C NMR spectra were measured by AVANCE 400Hz and ASEND 600Hz NMR spectrometers, respectively. Samples were 2 wt% asphaltene solution in CDCl3. The molecular weight and molecular weight distribution of asphaltene were measured by TOFMS using an AB Sciex 4800 equipped with coupled an ionic source.

2.5. Precipitation Behaviors of Asphaltenes

Preparation of model oil. Standard model oil was prepared with toluene as a solvent, in which the asphaltene and biopolymer concentrations were 250 and 500 mg/L, respectively. A typical standard model oil sample consists of 0.02 g of asphaltene, 0.04 g of the biopolymer and 80 mL toluene. Ultrasonic mixing was utilized to help disperse asphaltenes in the standard model oil. Heptane, as the poor solvent for asphaltene, was added into the standard model oil, with the toluene volume ratio changing from 20% to 80%. Standard model oil was diluted by toluene first, then heptane was fed in. Finally, the above solution was centrifuged at 5000× g rpm for 10 min to isolate asphaltene precipitates, and then supernatant liquid was separated out as model oil.

Initial precipitation point. The IPP of asphaltene refers to the ratio of poor solvent at which asphaltene flocculent starts to precipitate from solution. It was measured by using UV–Vis spectroscopy (Shimadzu UV-2550, Kyoto, Japan). The quartz cell with a 10-millimeter optical path was employed. The characteristic absorption of asphaltenes is around 280 nm.

Size and size distribution. The hydrodynamic diameter of asphaltene was measured by DLS analyzer (Nicomp 380 ZLS, CA, USA). The mean particle size of asphaltene aggregates was determined by using the autocorrelation function of the scattered light with fast, 32-bit auto-correlator. Intensity-weight Gaussian distribution and the PDI (polydispersity index) of the aggregates were represented. Since the light transmission intensity of model oil was too weak to be detected at a high asphaltene concentration, the asphaltene concentration in testing model oils was diluted to 20 mg/L. Theses samples were also used for the optical microscopic observation.
Morphology. The morphology of asphaltenes was observed by Leica DM2500P optical microscope (OM). Images were recorded using a charge coupled device (CCD) camera connected to a PC via a WT-1000GM imaging board. A small drop of diluted solution was transferred onto a glass slide and observed after the solvent was evaporated at room temperature. The statistical analyses of size were operated by ImageJ 1.51j8 (National Institutes of Health, Bethesda, USA).

2.6. Measurement of the Crude Oil

Rheological behaviors. The rheological behaviors of the undoped and doped crude oil were measured by the MCR501 rheometer from Anton GmbH (Austria) with a parallel-plate geometry with a 20-millimeter diameter. Viscosity of the crude oil as a function of temperature was measured at the constant shear rate of 10 s⁻¹ from 80 °C to 10 °C. Thixotropy of the crude oil as a function of shear rate was measured at 50 °C.

Wax crystallization behaviors. Crystallization of waxes in the undoped and doped crude oil was measured via TA2000/MDSC2910 DSC apparatus from TA Instruments. Enthalpies and temperatures were calibrated with indium and cyclohexane standards. Samples were kept at 90 °C for 30 min to remove any thermal history. A 10 °C/min cooling rate was employed from 90 °C to 10 °C. The enthalpy and onset temperature of transitions were analyzed using the TA universal analysis software.

Morphology. A Leica DM2500P polarized light microscope equipped with cross-polarization optics was employed to observe the morphology of wax crystals. The temperature was controlled by a Linkam THMS 600 cold/hot stage. Pictures were recorded by a Leica MC120 CCD camera with high-definition (HD) resolution. A very small amount of oil sample was put on a glass slide to observe at 20 °C. The statistical analyses of shape and size were also operated by ImageJ 1.51j8.

3. Results and Discussion

3.1. Chemical Structure of Synthesized Bipolymers

FT-IR spectra of synthesized bipolymers are shown in Figure 2. The absorptions at 2917 cm⁻¹ and 2845 cm⁻¹ are attributed to the stretching vibration of the C-H bonds of the methyl and methylene groups, respectively. Characteristic adsorption of C=O stretching peaks for acrylate was found at 1738 cm⁻¹. The bending vibration adsorptions of C-H bonds appeared at 1476 cm⁻¹ and 1379 cm⁻¹. The characteristic absorption of -CH₃ in long-chain aliphatic chains was revealed at 720 cm⁻¹.
Figure 2. FT-IR spectra of the α-olefins/ultra-long alkyl acrylate bipolymers.

$^1$H NMR spectra of the three bipolymers are shown in Figure 3. The peak at 0.8 ppm is attributed to the protons in the methyl group. Peaks ranging from 0.9–1.5 ppm is from the protons in methylene group. Besides, the peak at 4.0 ppm was due to the proton adjacent to the oxygen atom (−OCH$_2$) in methylene group. The peak at 7.26 ppm was due to the CDCl$_3$ deuterated solvent.

Figure 3. $^1$H NMR spectra of the α-olefins/ultra-long alkyl acrylate bipolymers.
3.2. Characterization of Asphaltene

The FT-IR spectra of asphaltenes extracted from African crude oil are shown in Figure 4. The characteristic adsorptions of functional groups in the asphaltene were analyzed and summarized in Table 3.

![FT-IR spectra of asphaltene](image)

**Figure 4.** FT-IR spectra of the asphaltene isolated from African pipeline crude oil.

**Table 3.** Functional groups in the asphaltene analyzed from FT-IR spectra.

| Wavelength of Adsorption (cm⁻¹) | Function Group                                      |
|---------------------------------|-----------------------------------------------------|
| 3430                            | -OH                                                 |
| 2920, 1600                      | C = C stretching vibration on the benzene ring       |
| 2850                            | CH stretching vibration                              |
| 1460                            | CH (asymmetric, in-plane) stretching vibration       |
| 1380                            | CH (symmetric, in-plane)                             |
| 1120, 1030                      | CH (in-plane)                                        |

The element content of asphaltene was measured with an elemental analysis instrument, and the results are shown in Table 4. From this table, it can be observed that the molar ratio of H/C is close to 1, indicating that the aromaticity of asphaltene is high. The asphaltene also contains a high content of S, which is higher than that of O.

**Table 4.** Elemental content of asphaltene revealed by elemental analysis.

| Asphaltene | Elemental Composition (%) | \( \text{N}/\text{N}_c \) |
|------------|---------------------------|--------------------------|
|            | C | H | O | N | S |                |
| Asphaltene | 85.97 | 6.896 | 2.036 | 1.105 | 3.993 | 0.9626          |

By analyzing the \(^1\text{H}\) and \(^13\text{C}\) NMR spectra (Figure S1), the aromaticity \((f_A)\) and aromaticity condensation \((H_{\text{tot}}/C_{\text{A}})\) of asphaltene were calculated (Table S1). The molecular weight and molecular weight polydispersity of the asphaltenes were measured by TOFMS (Figure S2 and Table S2). Ultimately, the chemical structure of asphaltene molecule was deduced and is shown in Figure 5.
3.3. Effect of the Bipolymers on the Precipitation Behaviors of Asphaltenes

Effect of aliphatic chain length on the IPP of asphaltenes. The IPP of asphaltenes in the model oil without and with bipolymers at 500 ppm was measured by UV–vis spectroscopy, as shown in Figure 6. It was found that the IPP of asphaltenes increases with the aliphatic chain length of the TDA bipolymers. In other words, the IPP of asphaltenes in the presence of TDA 2024-28 was the highest. This result is consistent with our previous research. The longer is the length of aliphatic chain, the stronger the van der Waals force is between the bipolymer and asphaltenes. It is conducive to the adsorption of bipolymer on the asphaltene surface. This adsorption is also enhanced by the hydrogen bonding formed between the ester group in the bipolymer and the hydroxyl group in the asphaltene molecule. Aliphatic chains also afford extra steric effect on inhibiting the precipitation of asphaltenes, which can prevent asphaltene from aggregating into large-size aggregates. According to the slope of downward line in the precipitation curve, the asphaltene precipitation rate was calculated (Table 5). Differing from the results of IPP, the asphaltene precipitation rate increased first and then decreased with the increase of aliphatic chain length. TDA2024-22 was the most effective in reducing the asphaltene precipitation rate. In the presence of PDV-A-18, the IPP was close to that achieved by the presence of TDA2024-22. Apparently, phenyl pendant assists PDV-A-18 in inhibiting the precipitation of asphaltenes.

Figure 5. The deduced chemical structure of asphaltene molecule.
Figure 6. IPP of asphaltenes in model oils without and with bipolymers at 500 ppm.

Table 5. IPP and asphaltene precipitation rate of asphaltenes in model oils with different bipolymers at 500 ppm.

| Bipolymer        | IPP (%) | Initial Precipitation Rate |
|------------------|---------|----------------------------|
| None             | 34.90   | −0.0224                    |
| TDA 2024-18      | 41.62   | −0.0181                    |
| TDA 2024-22      | 43.21   | −0.0303                    |
| TDA 2024-28      | 44.17   | −0.0272                    |
| PDV-A-18         | 43.05   | −0.0268                    |

Effect of aliphatic chain length on the size of asphaltene aggregates

The Gaussian mean particle size of asphaltene aggregates in model oil in the absence and presence of bipolymers was measured using DLS, as shown in Figure 7. It was found that the diameter of asphaltene aggregates in the model oil without any bipolar polymer was 1928 nm. With the increase of aliphatic chain length, the diameter of the aggregates decreased to 988 nm (TDA 2024-18), 934 nm (TDA 2024-22) and 865 nm (TDA 2024-28). Interestingly, the diameter of the aggregates in the presence of PDV-A-18 (940 nm) was also close to that achieved in the presence of TDA 2024-22.
The morphology and distribution of asphaltene aggregates in the model oil were observed by optical microscope without and with bipolymers (Figure 8). The size and precipitation amount of asphaltene aggregates were analyzed by ImageJ software. Without any bipolymer, the average diameter of asphaltene aggregate was around 2.50 μm (Figure 8a). After the addition of 500 ppm bipolymer, the asphaltenes were significantly dispersed, and the precipitation amount was also largely reduced (Figure 8b–d). Moreover, with the increase of the length of aliphatic side chain, both the size and precipitation amount of asphaltene aggregates decreased. After the feeding of TDA2024-28, the size of asphaltene aggregates was reduced to 1.29 μm, which is almost half its original size (Figure 8d). The size of aggregates in the presence of TDA2022-28 (1.54 μm) was also close to that achieved in the presence of PDV-A-18 (1.58 μm). Although the size of asphaltenes observed with a microscope was not identical to that measured using DLS, the tendency of asphaltene aggregates size to be reduced by bipolymers was found to be consistent.
3.4. Effect on the Crystallization Behaviors of Waxes in Crude Oil

Wax appearance temperature (WAT) and enthalpy of waxes. A thermogram of the African pipeline crude oil without and with bipolymers at 500 ppm are presented in Figure 9. Apparently, as we observed, the WAT of crude oil was reduced by the addition of various bipolymers. Additionally, the WAT of crude oil increased with the increase of aliphatic chain length. The WAT of crude oil was reduced most (by 4 °C) in the presence of TDA2024-18. Although the crystallization enthalpy of waxes does not strictly follow the sequence revealed by the abovementioned results, the enthalpy of oil with TDA2024-28 was still the highest. Crude oil with TDA2024-22 showed the lowest enthalpy at 5.464 J/g, indicating that TDA2024-22 has the greatest ability to reduce wax precipitation in crude oil. Oil with PDV-A-18 exhibited a close WAT (33.1 °C) to that of TDA2024-22 (32.9 °C), but its enthalpy was higher.
Morphology of waxes. The morphology of wax crystals in crude oil was observed through a polarizing light microscope, and the average size and occupied area of wax crystals (corresponding to the wax precipitation amount) were analyzed with ImageJ software (Figure 10). Without the addition of any polymer, the wax crystals fully grew and showed long, thick rods (Figure 10a). After adding various polymers, the wax crystal size decreased significantly (Figure 10b–d). However, unlike the effect of a polymer on asphaltene aggregate size, the wax crystal size increased with the increase in the aliphatic chain length in the polymer. This is because the average carbon number of wax crystals is about 18 (Table S3), and the length of the aliphatic chain in TDA2024-18 was the closest to this number. So, TDA2024-18 showed the best wax inhibiting capability (Figure 10b). With the increase in aliphatic chain length, the carbon number was lower than that of the waxes. Therefore, the size of the wax crystals increased. The size of wax crystals in the presence of PDV-A-18 was also close to that in the presence of TDA2024-22, but not to TDA2024-18, which indicates that the phenyl pendants impair the effect of octadecyl group on the waxes.

Figure 9. DSC curves of crude oil without and with different polymers at 500 ppm.
Figure 10. Polarized light microscopic images of wax in crude oil without and with the addition of bipolymers at 500 ppm, and the calculated average diameter and occupied area of wax (corresponding to precipitation amount) using ImageJ software. (a) No bipolymer, (b) TDA2024-18, (c) TDA2024-22, (d) TDA2024-28 and (e) PDV-A-18.

3.5. Effect on the Rheology of Crude Oil

In order to confirm the effect of bipolymers on asphaltenes and waxes, the rheological behaviors of crude oil in the presence of various bipolymers were studied, as shown in Figure 11. First, the viscosity–temperature curves of crude oil were measured with the bipolymers at 250 ppm (Figure 11a) and 1000 ppm (Figure 11b). As shown in Figure 10a, at the same temperature, with the increase in aliphatic chain length, the viscosity of crude oil decreased first and then increased. TDA2024-22 reduced the viscosity of crude oil most. In addition, the condensation point of crude oil with bipolymers was obtained by tangent to the curve of the low temperature section. When fed with bipolymers at 250 ppm, the condensation points of crude oils were 23.0 °C (TDA2024-18), 22.5 °C (TDA2024-22), 23.0 °C (TDA2024-28) and 22.8 °C (PDV-A-18). It is found that the condensation point also exhibited a similar tendency to the change of viscosity, which also decreased first and then
increased with the increase in aliphatic chain length in TDA bipolymers. This is more apparent when the concentration of bipolymers was increased to 1000 ppm. The condensation points of crude oils are 16.5 °C (TDA2024-18), 16.5 °C (TDA2024-22), 18.0 °C (TDA2024-28) and 18.6 °C (PDV-A-18), which are much lower than the condensation point of crude oil itself (24.0 °C).
Figure 11. Effect of bipolymers on the viscose–temperature property of an African crude oil in the presence of different bipolymers at (a) 250 ppm and (b) 1000 ppm. (c) TDA2024-22 at varying concentrations.

Then, the effect of TDA2024-22 concentration on the viscosity–temperature property of crude oil was studied (Figure 11c). The condensation points of crude oils were also obtained. Obviously, with the increase in bipolymer concentration, the viscosity and the condensation point of crude oil decreased. The condensation point of crude oil was reduced to 16.5 °C with the bipolymer at 1000 ppm, with the largest reduction of 7.5 °C.

In addition, the effects of different bipolymers at 1000 ppm (Figure 12a) and TDA2024-22 at varying concentrations (Figure 12b) on thixotropy of crude oil were studied. Similar to the results of viscosity–temperature measurements, the area of thixotropic loop decreased first and then increased with the increase in aliphatic chain length. The thixotropic loop area of TDA2024-22 is quite similar to that of PDV-A-18. In addition, with the increase in TDA2024-22 concentration, the thixotropic loop area decreased monotonically. This indicates that TDA2024-22 and PDV-A-18 can effectively destroy the original internal stable structure of crude oil, including the stable network structure formed by asphaltene aggregates and wax crystals, thus making the crude oil more prone to deformation and flow.
Figure 12. Thixotropy of African crude oil in the presence of (a) different bipolymers at 1000 ppm, and (b) TDA2024-22 at varying concentrations.

Based on the above results, the mechanism of oil flow improvement by inhibiting asphaltene precipitation and wax crystallization in the presence of bipolymers with ultralong aliphatic chain lengths is proposed, as shown in Figure 13. As is already known, colloidal asphaltenes are natural crude oil pour point depressants, since they can adsorb
on the surface of wax crystals and hinder the precipitation of wax crystals. However, as the asphaltene content increases, this effect will be impaired, and it even accelerates the wax precipitation when the content exceeds a certain concentration. If the large aggregates of asphaltene are dispersed or their precipitation is inhibited, the growth of wax crystals in the crude oil can also be suppressed. In the presence of bipolymers with ultra-long side chains, with the increase in aliphatic chain length, they can inhibit the precipitation of asphaltenes more effectively through van der Waals force and steric repulsion. On the contrary, the inhibition of wax crystal growth and reduction in the size of precipitated wax crystals by bipolymers becomes worse with the increase in aliphatic chain length. Therefore, as a compromise, TDA2024-22, with a medium aliphatic chain length, shows a significant capability of both dispersing asphaltenes and inhibiting wax crystallization. It has been proven to be more efficient than PDV-A-18, which possesses phenyl pendant. Thus, this bipolymer apparently improves the rheological behaviors of crude oil with a high wax and asphaltene content.

![Figure 13. Improvement of oil flow by inhibiting asphaltene precipitation and wax crystallization in the presence of bipolymers with ultra-long aliphatic chain lengths.](image)

4. Conclusions

To solve the recovery and transportation difficulties of crude oil with a high asphaltene and wax content, the present study was carried out, and the following conclusions were formed:

1. Bipolymers of α-olefins and aliphatic acrylate with ultra-long aliphatic chain (18, 22 and 28) were synthesized, and their chemical structures were confirmed by FT-IR and 1H NMR.
2. The chemical structure of asphaltene characterized by FTIR, 1H NMR, elemental analysis and TOFMS shows that the asphaltene has a relative high aromaticity, indicating that this asphaltene is apt to aggregate and precipitate.
3. As revealed by UV–Vis spectra, with the increase in aliphatic chain length of polymers, the IPP of asphaltenes were increased. The sizes of asphaltene aggregates measured by DLS and observed using an optical microscope also showed similar results to IPP. Bipolymers with longer aliphatic chains can better suppress the precipitation of asphaltenes and disperse them.
4. As revealed by DSC and polarized optical microscope, biopolymer s shorter aliphatic chains can inhibit the growth of wax crystals more effectively, since the size and precipitation amount of wax crystals in crude oil are smaller.

5. From the rheological results, TDA2024-22 reduces the oil viscosity and thixotropic loop area most. So, a biopolymer with a medium aliphatic chain length (C22) can inhibit the asphaltenes and disperse the wax crystals simultaneously, thus significantly improving the flowability of crude oil; thus, it has better results than PDV-A-18 for containing phenyl pendants.

6. The biopolymers with suitable aliphatic chain lengths are promising to enhance the flow of oil with a high wax and asphaltene content in recover and, transportation, and therefore they present great potential applications in the oil fields.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/en14248243/s1, Figure S1: The 1H (a) and 13C (b) NMR spectra of asphaltene isolated from African crude oil, Figure S2: The molecular weight and molecular weight distribution of asphaltene measured by TOFMS, Figure S3: Composition of n-alkanes and iso-alkanes in waxes extracted from crude oil measured by GC-MS; Table S1: The aromaticity ($f_a$) and aromaticity condensation ($H_{aro}/C_{aro}$) of asphaltene, Table S2: The average molecular weight of asphaltene measured by TOFMS.

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