Effect of polar/nonpolar groups in comb-type copolymers on cold flowability and paraffin crystallization of waxy oils

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ABSTRACT

Comb-type poly(maleic alkylamide-co-α-octadecene) copolymers (MACs) with various ratios of polar carboxyl group/nonpolar octadecyl group were synthesized. Upon cooling, MACs change the size and shape of paraffin crystals, and reduce the pour point and yield stress of waxy oils, as observed by rheology, polarizing light microscopy, differential scanning calorimetry, and X-ray diffraction. They also reduce the paraffin crystallization temperature and enthalpies, inhibit the formation of layer structure of paraffin crystals. Their efficiency to improve the cold flowability was found to correlate to the ratio of polar/nonpolar group (r). MAC with r of 0.4, is more effective than the other two in improving the flowability of waxy oils. It seems that MAC2 can balance the competitive assembly behaviors of copolymers with paraffins and asphaltenes. The assembly between the carboxyl and amide groups of MACs with polar aromatic asphaltenes appears to stabilize crude oil by the steric effects of the long-chain alkyl branches of MAC polymers, thereby improving the flowability of paraffin/asphaltene gels formed upon cooling.

1. Introduction

Crude oil is a complex mixture mainly consisted of paraffins, aromatic hydrocarbons, resins and asphaltenes [1]. In high temperature reservoirs (70–150 °C), crude oil behaves as Newtonian fluids with low viscosity [2]. In pipelines without heating and petroleum production under low temperature, the solubility of long-chain paraffins and asphaltenes in hydrocarbons decrease remarkably. The resulting precipitation of long-chain paraffin solids and asphaltenes can lead to deposition at the walls of pipeline, reducing oil flow and potentially blocking the pipeline [3–8]. The remediation of plugged pipelines in deep seawater costs $1 million/mile, which is reported by U.S. Department of Energy [10]. In Petrochina Liaohe oil field, one crude oil is difficult to be exploited for its high paraffin content, which results in high pour point and viscosity and brings problems of prohibitive cost of oil recovery and transporta-

tion. To solve above problems, thermal, mechanical and chemical (wax inhibitors) methods are available. Among them, polymeric wax inhibitors plays an important role for their low cost and convenient feeding method [11].

Polymers with crystalline/amorphous diblock structures were reported to improve the cold flowability of waxy oil by modifying paraffin crystallization, such as ethylene-vinyl acetate copolymers (EVA) [12,13], polyethylene-poly (ethylene-propylene) [14], poly(ethylene-butene) (PEB) [15,16], and comb-type poly(maleic anhydride-co-α-olefin)s esterified by alkyl alcohols [17]. In our recent work, comb-type poly(maleic anhydride-co-α-olefin)s and poly(maleic anhydride-co-α-olefin-co-styrene)s amidated by alkyl amines were synthesized, and the crystallization of paraffins and rheological behaviors of model and crude oils after dosage of above copolymers were researched [18,19]. Typically, in these polymers, there are nonpolar branches and polar parts. Nonpolar branches can provide nucleation sites or co-crystallize with paraffins, and

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polar parts can limit the crystal size of paraffins [19,20], modify the shape and inhibit the formation of large crystals of paraffin [21]. In terms of paraffin inhibitor, it is reported that the more similar is the polymer structure to the paraffin component, the better is its performance [22].

In this work, poly(maleic acid alkylamide-co-α-octadecene) copolymers (MACs) with various ratios of polar/nonpolar groups were synthesized. These ratios were determined by $^1$H NMR and the molecular weight of MACs was measured by gel permeation chromatography (GPC). The effect of various ratios of polar/nonpolar groups on the long-chain paraffin crystallization and the flowability of waxy oils was examined by rheology, polarizing light microscope (PLM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

2. Experimental section

2.1. Materials

Decane (anhydrous, >99%), hexatriacontane (C36, >98%), maleic anhydride (99%), α-octadecene (95%), benzoyl peroxide (99%), o-xylene (98%), and octadecylamine (97%) were purchased from Alfa company and used as obtained.

Model oil were prepared by dissolving 8% of C36 in decane [23]. Solid crystal samples were prepared by heating at 20 °C/min to 70 °C and held for 5 min. Solid crystal samples was obtained by cooling the model oil from 70 °C to 0 °C at the rate of 1 °C/min, and separating the precipitated crystals by filtration with vacuum in an ice bath and dried under vacuum at room temperature for three days. Crystal samples were sealed and stored at −4 °C before using.

Crude oil studied in this work was obtained from Petrochina Liaohe oilfield. The content of paraffin and asphaltene are 38.5% and 15.6%, density is 0.8676 g/cm³, freezing point is 62 °C, and viscosity at 70 °C is 7.2 mPa.s.

2.2. Synthesis of MAC copolymers

MACs copolymers were synthesized by radical polymerization in two steps. In the first step, maleic anhydride and octadecylene were copolymerized in o-xylene at 120 °C for 1.5 h with benzoyl peroxide as initiator under nitrogen atmosphere protection, to give poly(maleic anhydride-co-α-octadecylene). In the second step, octadecylamine was fed in to react with the maleic anhydride groups in poly(maleic anhydride-co-α-octadecylene) copolymer at 105–110 °C for 12 h. Crude product of poly(maleic acid alkylamide-co-α-octadecene) copolymers (MACs) were isolated from the reaction mixture by precipitation with methanol, washed with hot water, and dried to constant weight by freeze dryer. MACs were obtained by varying the feeding ratios of maleic anhydride/amine (1:1, 1:1.6 and 1:2.5) and corresponding copolymers were named MAC1, MAC2 and MAC3, respectively.

2.3. $^1$H NMR spectrum and GPC

$^1$H NMR spectra were recorded on a BRUKER AVANCE 500 spectrometer operating at 500 MHz with deuterated chloroform as solvent. The molecular weight and molecular weight distribution of the MACs were measured by Waters 1525 GPC with THF as mobile phase using polystyrene samples as standards.

2.4. Pour point and yield stress tests

The pour point of oil samples was determined by the MCR501 rheometer from Anton-Paar Physica (Germany) equipped with the 25 mm parallel plate geometry. The testing procedure is as follows: after the initial holding time at 90 °C, the temperature was then decreased to 35 °C at 0.5 °C/min imposing a 0.05 Pa oscillatory stress at 2 rad/s. The onset of gelation was indicated by the increasing of the storage and loss modulus ($G'$ and $G''$) from low levels characteristic of a liquid to higher levels associated with a gel. Normally, the gelation temperature is taken as the temperature at which $G'$ cross above $G''$.

The yield stress ($\tau_y$) is defined as the stress below which no flow occurs. An operational definition of $\tau_y$ was adopted as the stress at the transition between the creep and liquid-like viscosity regimes [14]. As the stress increased, the gel crept for a brief period of time and then catastrophically failed. The stress at failure was recorded as the yield stress [18]. The tests were also performed on the Anton-Paar MCR501 rheometer equipped with the 25 mm parallel plate geometry. Oil samples were initially heated to 70 °C, kept for 15 min and then cooled to 0 °C at a rate of 10 °C/min.

2.5. Optical microscopy

Paraffin crystal morphologies were observed using a ChangFang-59X KA polarizing light microscope. Images were captured using a CCD camera connected to a PC via a WT-1000GM imaging board. A small quantity of oil sample was transferred from storage at −4 °C directly to a glass slide. All of the images were taken at 0 °C.

2.6. Differential scanning calorimetry (DSC)

DSC from Perink-Elmer Diamond Company was used to examine the crystallization of long-chain paraffin in solution [16,23]. Scanning rates was set at 10 °C/min. The enthalpies of crystallization and melting of paraffins were calculated from peak areas using the Pyris software.

2.7. X-ray diffraction

One-dimensional images were collected in the reflection mode from dried samples of long-chain paraffin crystals using Rigaku D/max-2550V X-ray diffraction equipped with an evacuated Statton camera. X-rays with a source wavelength of 0.154 nm were produced using a sealed tube generator with Cu target and a Huber graphite monochromater. The scattering patterns were recorded over the range of angles corresponding to 2θ from 5° to 60°.

3. Results and discussion

3.1. Ratios of polar/nonpolar groups and molecular weight of MACs

Fig. 1 shows the $^1$H NMR spectra of poly (maleic acid alkylamides-co-α-octadecene) copolymers (MACs). Chemical shift of protons in CH$_3$, CH$_2$ and CH in α-octadecene monomer unit appears at 0.99 ppm, 1.2–1.8 ppm and 2.0 ppm, respectively. Chemical shift of protons in maleic acid and alkylamide group is found at 3.3–3.6 ppm. The integration of protons in poly (maleic anhydride-co-α-octadecene) reveals that the copolymerization ratio of maleic anhydride/α-octadecene is 1:1.07.

The amidation ratio ($f$) gives the number of alkylamides (0 < $f$ < 2) formed from each maleic anhydride group of the polymer, estimated from the integrated area of $H_y$ and $H_a$ peaks in Fig. 1. Due to $\Delta f = \frac{2}{2 + 2} \times 100\%$, the amidation ratio ($f$) can be calculated by the equation of $f = \frac{\Delta H_{y0}}{\Delta H_{a0}} - 1.07$, or $f = \frac{2H_{a0}}{2H_{y0}} - 1.07$. In this equation, $H_{a0}$ and $H_{y0}$ are integrated area of proton $H_a$ and $H_y$, respectively. The ratio of polar group (−COOH)/nonpolar group (−C18) was calculated by the equation of $r$ (ratios of polar/nonpolar group) = $\frac{2f}{1 + f}$. The amidation ratio ($f$) of MAC1, MAC2 and MAC3
are 0.7, 1.1 and 1.6, and the ratios of polar/nonpolar group ($r$) are 0.7, 0.4 and 0.1, respectively.

The molecular weight of MAC1, MAC2 and MAC3, measured by GPC, are 6.34, 6.85 and 7.75 Kg/mol, and corresponding polydispersity of molecular weight of them are 1.71, 1.65 and 1.57, respectively.

3.2. Effect of MACs on model waxy oils

Fig. 2 shows the pour point and yield stress of model oil upon $r$ measured by rheological methods. All of the MAC copolymers exhibit a positive effect on the reduction of pour point of model waxy oil. The pour point of model oils has an identical reduction when $r$ are 0.1 and 0.4, but it increases as $r$ is increased to 0.7, which indicates that MACs with high $r$ is not benefit for the reduction of pour point. It is also found that the yield stress of model waxy oils is reduced by MACs. The yield stress exhibits a close reduction when the $r$ are 0.1 and 0.4, but is largely increased when $r$ is increased to 0.7, which coincides with the trend of pour point tests.

Observed by polarizing light microscopy, as shown in Fig. 3, it is found that the morphology of paraffin crystals are obviously changed by MACs. After the dosage of MACs, the shape of paraffin crystals varies from large plate-like to small needle-shaped. Moreover, MAC copolymers with lower $r$ lead to smaller size and better distribution of paraffin crystals, which benefits for the flowability of model waxy oil, well coincides with the results of yield stress tests (Fig. 2).

DSC curves during cooling are shown in Fig. 4. In this figure, all the samples exhibit two peaks, which also has been observed before [18]. The peak at higher temperature represents the formation of the rotator phase of crystallization, while the one at lower temperature is associated with the solid–solid phase transition between the monoclinic and rotator phase of crystallization [15]. The dosage of MACs declines the $T_{\text{onset}}$ of paraffin crystallization to slightly lower temperatures with a parallel trend to lower enthalpies of transitions. The monotonic decrease in $T_{\text{onset}}$ and crystallization enthalpy upon reduction of $r$, observed by DSC, reflects a better co-crystallization and assembly with paraffins for MACs with lower $r$. Moreover, MACs with lower $r$ lead to less paraffin crystals, smaller crystal size and delayed crystallization upon cooling. The trend of enthalpy of transitions correlates to the observation of optical microscopy.

Fig. 5 shows the X-ray scattering patterns of paraffin crystals from model waxy oil with and without MACs. The crystal morphologies of C36 from decane in the absence of polymers are large and plate-like (Fig. 3). The plate-like crystals tend to be in preferred orientation parallel to the support. As the support and detector are rotated in one plane with the stationary radiation source, these platelet samples should show the low-angle scattering well. Middle-angle scattering will show up increasingly with smaller and less plate-like crystals. These effects are observed, as shown in Fig. 5, MACs with lower $r$ reduce the low-angle scattering much from the layered structure of the paraffin crystals. The amorphous portion of copolymers would disturb the stacking of paraffin crystal platelets. Reduction of the $r$ in MACs eliminates the ordered low-angle scattering and intensifies two middle-angle scattering around 20° and 25° ($2\theta$), which are typical scattering of the monoclinic
We hypothesize that the more nonpolar alkyl chains in MACs molecules, the better MACs co-crystallize with decane and thus inhibit the formation and growth of large crystal platelets.

### 3.3. Effect of MACs on waxy crude oil

As shown in Fig. 6, it shows that the pour point and yield stress of the crude oil was reduced by the dosage of MACs. Two concentrations of MACs, which are 0.1% and 0.5%, were adopted to examine the effect of MACs on the pour point of crude oil. Concentration of 0.5% exhibits a better effect on the reduction of pour point than that of 0.3%. At the same concentration, MACs with lower reduce the pour point of crude oil much. The discrepancy with the trend of model oil is caused by the difference of components in crude oil and model oil. Beside nonpolar paraffins, asphaltene is the heaviest and most polar fraction in crude oil. They are generally composed of polyaromatics carrying aliphatic chains or rings with polar paraffin crystals [24].
groups. In crude oil, there are two competitive behaviors. One is the co-crystallization of nonpolar groups at the paraffin's surface, the other is the stabilization and dispersion of asphaltenes by polar groups. Only those MACs which have a medium $r$ can exhibit the highest reduction of pour point.

The effect of concentration on the yield stress of crude oil as a function of $r$ was also examined, as shown in Fig. 6. It shows that the yield stress of crude oil was reduced significantly by the dosage of MACs. The concentration of 0.5% exhibits the highest reduction of the pour point than the other two concentrations. At the same concentration, MACs with $r$ of 0.4 exhibit the highest reduction of yield stress, correlating to the trend of pour point test.

Observed by polarizing light microscopy, as shown in Fig. 7, the paraffin crystals, without the dosage of MACs, show a long cross-linked spindle shape. After the dosage of MACs, the size of paraffin crystals in crude oil was reduced and the distribution of paraffin crystals was improved. With the dosage of MAC1 ($r = 0.7$), the crosslinked paraffin crystal spindles disappear. It appears short spindle and tiny spot crystals, but few long crystals still remain.

The dosage of MAC2 ($r = 0.4$) results in the smaller and shorter spindle crystals. But for MAC3 ($r = 0.1$), paraffin crystals all changed into tiny spot crystals. Lower $r$ benefit for the co-crystallization of MACs with paraffin, and formation of smaller paraffin crystals and better distribution.

Finally, assembly model of MACs contribute to the improvement of cold flowability of crude oil, as showed in Fig. 8. In this model, the nonpolar alkyl branches of MACs can co-crystallize with long-chain paraffins to anchor into paraffin crystals, and the brush-like layer with polar groups can control the crystal size. In terms of asphaltene, the polar carboxyl groups and amide linkages can disperse them and prevent them from aggregation. Therefore, the cold flowability of crude oil is improved by the assembly behaviors of MACs. For those crude oil with high paraffin content, only those MACs who possess a medium $r$, can balance the competitive assembly behaviors of themselves with paraffins and asphaltenes, thus endow crude oils the best cold flowability.

4. Conclusions

Comb-type poly(maleic alkylamide-co-α-octadecene) copolymers (MACs) with various ratio of polar/nonpolar group ($r$) were synthesized by the amidation of poly(maleic anhydride-co-α-octadecene). The $r$ was calculated by integrating the protons in MACs. Model waxy oil was prepared to study the influence of polar/nonpolar group ratio on the crystallization of paraffins and cold flowability of model oil. The results show that these copolymers obviously reduce the pour point and yield stress of model oil, decrease the paraffin crystal size, suppress the formation of crystal platelets. MACs also reduce the paraffin crystallization temperature and enthalpies, inhibit the formation of layer structure of paraffins and intensify the growth of monoclinic paraffin crystals, revealed by DSC and XRD. Correlating to the results of model oil, they also reduce the pour point and yield stress of crude oil, change the paraffin crystals into smaller size and improve their distribution. MAC with the medium $r$, is more effective than the other two in improving the cold flow of crude oil, for which balances the competitive influence of copolymers on paraffins and asphaltenes.
Acknowledgments

Financial support by National Natural Science Foundation of China (51003028, 21004021 and 11076002/A06), the Fundamental Research Funds for the Central Universities the higher school specialized research fund for the doctoral program (20110 074110003), and the Key Basic Research Project of Shanghai Science and Technology Commission (10JC1403800) are gratefully acknowledged. The authors also thank Petrochina Liaohe Oilfield Company for affording oil samples and technological supports.

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