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Influence of Wax Inhibitor Molecular Weight on Solution Crystallization and Rheology of Monodisperse Waxes

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ABSTRACT: Molecular weight fractionation via stepwise precipitation or chain scission is performed on four pour point depressant polymers to study the pour point reduction mechanism. An homologous series of model oils is prepared by dissolving 5 wt % of a single-component paraffin wax (n-C₂₄, n-C₂₈, n-C₃₂, or n-C₃₆) in n-C₁₂. The polymers are dosed at 500 ppm in the model oils and moderately reduce crystallization temperatures by elevating the nucleation barrier. Polymers containing carboxylate or acrylate moieties also modestly enhance equilibrium wax solubility. Reduction in crystallization temperature is largely independent of polymer molecular weight, except for carboxylate polymers where low molecular weight fractions are largely ineffective. In general, model fluids containing shorter wax chains show a larger reduction in crystallization



temperature than model fluids containing longer wax chains. However, yield stress reduction often shows a distinct dependence on polymer molar mass. Low molecular weight fractions of carboxylate and acrylate polymers provide smaller reductions in yield stress than the overall parent fraction. Cross-polarized microscopy reveals that polymers reduce the crystal size, alter the crystal morphology from platelet to needle-like, and induce branching. Crystal branching and formation of dendrite-like structures result from strong polymer binding at the wax crystal interfaces. Hence, single-component wax crystal branching occurs phenomenologically along with yield stress reduction.

1. INTRODUCTION

Flow assurance strategies for prevention, mitigation, and remediation of production problems caused by paraffin wax typically involve implementation of thermal, mechanical, or chemical management measures.¹ Treatment of produced petroleum fluid with pour point depressants (PPD) or wax inhibitors is a common chemical management strategy that may be implemented on an exclusive basis or in conjunction with supplementary management measures. Continuous injection of formulated PPD solutions into the production fluid stream effectively reduces the pour point temperature, wax appearance temperature (WAT), and low-temperature gel strength.^{2–5} The influence of PPD polymers on wax crystallization has been well documented. However, the effective activity mechanisms of PPDs are incompletely understood.

Commonly proposed activity mechanisms of PPDs include nucleation, cocrystallization, and adsorption,⁶ inducing morphological modulation and/or imparting steric/entropic repulsion between wax crystals. Nucleation is the initial generation of stable paraffin wax crystal nuclei of critical size in the petroleum fluid. The initial nucleation event is followed by crystal growth. At temperatures above the WAT, poly-(ethylene–propylene) (PEP) polymers may self-assemble into micelle-like aggregates characterized by a crystalline core surrounded by single alkyl chain brushes.^{7,8} The micelle-like structures facilitate heterogeneous wax nucleation, generating abundant paraffin nuclei of subcritical size (polynucleation) and ultimately resulting in smaller and more numerous wax crystals.^{6,9,10} The crystal size reduction effectively weakens the rheological strength of the wax–oil gel network structure. In addition, smaller wax crystals may retain extended stability in the produced oil phase.

PPD polymers typically incorporate linear aliphatic moieties that exhibit high affinity toward paraffin molecules and may cocrystallize and interfere with the development of a wax crystal network structure. Holder and Winkler report that the growth of *n*-paraffin wax crystals can be poisoned by polymeric additives.¹¹ Molecular dynamics simulations show that polyethylene backbone moieties or pendant alkyl chains may adsorb onto the wax crystal lattice and disrupt further deposition of paraffin layers on top of the adsorbed

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Table 1. Characteristics of PPD

parent PPD	chemistry based on	PPD alias	treatment	fractionation yield (wt %)	number-average MW ²⁵ (kDa)	hydrodynamic radius ²⁵ (Å)	precipitation temperature ^{<i>a</i>} (°C)
PPD α	polycarboxylate (proprietary)	PPD α			17.70	20.4	5.4
		PPD α low	fractionation >15 °C	45.2	2.76	9.0	-3.9
		PPD α mid	fractionation 8–15 °C	38.3	20.29	23.2	2.0
		PPD α high	fractionation <8 °C	16.5	23.33	23.9	6.0
PPD β	PA, EVA (proprietary)	PPD β			43.46	42.6	9.2
		PPD β low	fractionation >15 °C	71.4	6.53	17.0	1.6
		PPD β high	fractionation <15 °C	28.6	65.37	54.3	10.0
PPD τ	PS- <i>block</i> -poly(ethylene- <i>ran</i> - butylene)- <i>block</i> -PS	PPD $ au$			142.72	88.0	NA
		PPD $ au$ short US	ultrasonification 15 min		103.64	75.6	NA
		PPD $ au$ long US	ultrasonification 60 min		69.47	58.4	NA
PPD Ω	EVA, 25% vinyl acetate	PPD Ω			72.02	61.9	12.7
		PPD Ω long US	ultrasonification 60 min		7.29	62.0	13.1

^aPrecipitation peak temperature of 1000 ppm PPD in dodecane at cooling rate of 5 °C/min.

PPD.^{12–14} The poisoned crystal surface results in deformation of the final paraffin crystal morphology to a more irregular shape characterized by a lower crystal aspect ratio and a lower overall specific surface area. Adopting irregular morphologies, poisoned paraffin wax crystals are less prone to aggregate and interlock in comparison to neat paraffin wax crystals. Ultimately, formation of gel network structures is hindered by the presence of PPD polymers.

PPD polymers are categorizable into the classes of comb polymers, polymeric surfactants, and copolymerized ethylene.⁶ The comb-architecture PPDs often incorporate (meth)acrylic acid, maleic anhydride, or their combination.^{15,16} The inhibition performance of comb polymers is attributed to interaction between incorporated pendant alkyl chains and paraffin wax crystals.^{6,16,17} Ethylene copolymers are synthesized from a polyethylene backbone in conjunction with amorphous moieties such as polybutylene base units or polypropylene base units. The ethylene–vinyl acetate (EVA) copolymer is the most prevalent commercial wax inhibition agent.¹⁶

From an operational perspective, the demonstrated performance of paraffin inhibitors/PPDs is dependent on the crude oil composition and the additive activity.¹⁸ Efforts to select optimal PPDs for specific petroleum fluid compositions and specific wax types have been reported.^{2–5,19,20}

Studies have been performed to ascertain PPD selectivities to specific paraffin wax components using model systems comprising monodisperse paraffin dissolved in a solvent. Wang reported that among three polymethacrylate wax inhibitor polymers tested, the polymer with the longest alkyl side-chain (C18) exhibited the strongest effect in suppressing the WAT and elevating the WDT of a model fluid consisting of $n-C_{24}$ dissolved in $n-C_{10}$.²¹ Jung et al. demonstrated that varying the vinyl acetate content of EVA influences the nucleation, structure, and morphology of treated $n-C_{32}$ wax crystals.²² Application of poly(ethylene-butylene) random copolymers of various ethyl side branching frequencies to model monodisperse *n*-paraffin solutions reveals that lower ethyl side branching frequencies (i.e., higher crystallinity) are more effective toward longer *n*-paraffin components, while conversely, higher ethyl side branching frequencies (i.e., lower crystallinity) are more effective toward shorter *n*-paraffin molecules.²³ Optimal pour point depression efficacy for systems containing 20 wt % wax has been shown to occur when the PPD polymer solubility threshold temperature is ~15 $^{\circ}$ C lower than the WAT.²⁴

The current report investigates the influence of PPD molecular weight on the treatment efficacy of various PPD chemistries for monodisperse *n*-paraffin solutions. Selected PPDs, derived PPD fractions, and PPD scission products²⁵ are doped into an homologous series of monodisperse model fluids containing n-C₂₄, n-C₂₈, n-C₃₂, or n-C₃₆ in dodecane. The utilized series of paraffin carbon chain lengths facilitates elucidation of component-specific efficacies and interactions.

2. EXPERIMENTAL SECTION

2.1. Materials. Dodecane $(C_{12}H_{26}$ >99% purity from SigmaAldrich) was used as the solvent for the paraffinic model oils. Four nalkanes with even carbon numbers were used as wax components, including tetracosane ($C_{24}H_{50}$, hereafter abbreviated as C24, 99% purity from Alfa Aesar), octacosane (C₂₈H₅₈, hereafter abbreviated as C28, 98% purity from Aldrich), dotriacontane $(C_{32}H_{66})$, hereafter abbreviated as C32, 97% purity from Aldrich), and hexatriacontane (C36H74, hereafter abbreviated as C36, 98% purity from Aldrich). Four PPD polymers and eight associated derived fractions or scission products, comprising a total of 12 PPD additives, were assessed in this work. PPD α , with a chemistry based on polycarboxylate, and PPD β , with a chemistry based on polyacrylate (PA) and ethylene-vinyl acetate (EVA), were obtained from BASF. PPD α and PPD β were purified, as the PPDs were originally supplied in solution form. Purification of PPD α and PPD β was performed by repeated addition of toluene in a rotary evaporator followed by oven drying at 60 °C. PPD τ, poly(styrene-block-(ethylene-ran-butylene)-block-styrene), and PPD Ω (EVA, 25% vinyl acetate) are purchased from Sigma-Aldrich and used as received.

2.2. Sample Preparation. Waxy model oil samples were formulated as solutions of 5 wt % single-component paraffin wax dissolved in dodecane. Doped waxy model oil samples were formulated as 5 wt % single-component paraffin doped with 500 ppm PPD additive dissolved in dodecane. The model oils containing



Figure 1. DSC thermogram of PPD solutions in dodecane. Thermograms are shifted on the y-axis for better overview.

C24, C28, C32, and C36 in dodecane are hereafter abbreviated as Oil-24, Oil-28, Oil-32, and Oil-36, respectively. Prior to each experiment, the samples of model oil are thermally preconditioned by heating to 60 °C (65 °C for Oil-36) in an oven for at least 1 h to ensure that wax components are in a soluble state and that any thermal history has been removed.

2.3. Precipitation Fractionation, Scission, and Characterization. PPD α and PPD β were both subjected to fractionation by stepwise precipitation using solutions containing 1 wt % PPD in dodecane at temperatures of 15 and 8 °C. Controlled-temperature centrifugation was utilized to separate the solid precipitate and supernatant liquid, followed by solvent evaporation to recover the PPD from both phases. PPD τ and PPD Ω were subjected to chain scission via ultrasonic disintegration. Ultrasonication was performed at a power of 400 W for a 15 min interval (for short treatment) or 4 × 15 min intervals (for long treatment) by using a Digital Sonifier 450 CE from BRANSON Ultrasonics Corporation. Detailed protocols for the precipitation fractionation and ultrasonic disintegration are presented elsewhere.²⁵

Molecular weight distributions and molecular weight averages for the original PPDs, derived precipitation fractions, and derived scission products were characterized by HPLC-SEC (high performance liquid chromatography–size exclusion chromatography). NMR-DOSY (nuclear magnetic resonance–diffusion ordered spectroscopy) was used to determine the hydrodynamic radius of the PPD polymers in solution. Detailed protocols of the HPLC-SEC and NMR-DOSY techniques are presented elsewhere,²⁵ and obtained number-average molecular weights and hydrodynamic radii are summarized in Table 1. Precipitation temperatures of the PPD solutions were estimated by using differential scanning calorimetry.

2.4. Differential Scanning Calorimetry (DSC). DSC was used to monitor precipitation occurring in wax solutions and PPD solutions. DSC experiments were conducted by using an indium

calibrated Q2000 DSC from TA Instruments. The solutions were contained in Tzero aluminum hermetic pans to prevent solvent evaporation. A Mettler Toledo XPR56C microanalytical balance with an accuracy of 0.01 mg was used to weigh the samples within the range of 10–25 mg. The DSC protocol applied to the wax solutions consists of initial thermal equilibration of the samples at 80 °C for 5 min to remove the thermal history before ramping the temperature to -20 °C at a constant rate of 1 °C/min. For monitoring precipitation occurring in the PPD solutions, a cooling rate of 5 °C was applied to establish an adequate signal-to-noise ratio. After the DSC analysis, the sample was weighed to confirm that no solvent loss had occurred. All data analysis including thermogram rotation, heat flow shifting, precipitation peak determination, and crystallization onset point for WAT estimation were performed by using the TRIOS software from TA Instruments. Representative thermograms are shown in Figure 1.

2.5. Rheometry and Yield Stress Determination. Rheological measurements were conducted by using an Anton Paar Physica MCR 301 rheometer equipped with a 4 cm diameter, 2° angle cone and plate measuring geometry with a truncation gap of 170 μ m. Sandblasted surfaces were utilized on the cone and plate to minimize slippage effects. The sample temperature was controlled by a Peltier plate thermal element. A thermally preconditioned and previously homogenized sample of model oil was loaded between the cone and plate and allowed to thermally equilibrate for 5 min at 60 °C (65 °C for Oil-36) prior to measurement. A rapid cooling rate of 20 $^\circ C \ min^{-1}$ was applied to reduce the temperature to \sim 20 °C above the respective WAT, and subsequently a cooling rate of 1 °C min⁻¹ was applied until a temperature of 4 °C was attained. The temperature was maintained at 4 °C for 10 min for equilibration prior to application of a constant shear rate of 0.1 s^{-1} , while the shear stress signal was recorded. The rheological yield stress measurements were repeated in duplicate to confirm experimental reproducibility.



Figure 2. Plot of PPD properties: hydrodynamic radius and precipitation temperature versus number-average MW.

2.6. Cross-Polarized Microscopy (CPM). A Nikon Eclipse ME600 microscope equipped with crossed polarizers was used for observing the wax crystal morphology. The combination of a 10X/22 ocular lens and an ELWD 10X/0.4 objective lens provides an overall visual magnification of 100 times. Fluid samples were filled into rectangular glass capillary tubes with an inner cavity cross section of $100 \times 50 \ \mu m^2$ (width × height) which were sealed at the ends by using 3M Scotch cyanoacrylate glue and fixed in place on the microscope slide. A Linkam LTS120 Peltier element control stage was used to regulate the temperature. The initial temperature was set to 60 °C (65 °C for Oil-36) and maintained for 5 min to ensure that the wax was completely dissolved. Subsequently, a rapid cooling rate of 20 °C min⁻¹ was applied to reduce the sample temperature to ~20 °C above the WAT. The sample was then further cooled to a temperature of 4 °C below the WAT at a cooling rate of 1 °C min⁻¹. The temperature of the sample was maintained at 4 °C for 30 min prior to acquiring the images of the wax crystals. A CoolSnap-Pro monochrome digital camera from Media Cybernetics was utilized for acquisition of the images. At 100× magnification, a single frame captures an image with an areal dimension of $640 \times 480 \ \mu m^2$. Hence, to capture a broader area, four adjacent images were taken and subsequently collated into a single image.

3. RESULTS AND DISCUSSION

3.1. PPD Characteristics. Table 1 presents characteristics of the initial PPD polymers as well as the respective constituent fractions and scission products. PPD α and PPD β are both proprietary additives tailored by the manufacturer to be used as commercial pour point depressants. HPLC chromatograms of PPD α and PPD β exhibit the characteristics of polydisperse polymers with broad molecular weight distributions. Conversely, PPD τ and PPD Ω are manufactured for general purposes, and HPLC chromatograms indicate that both PPDs have narrow molecular weight distributions.²⁵

Fractionation procedures are implemented to obtain PPD samples with common chemistries but with segregated molecular weight distributions. The prescribed stepwise precipitation procedure successfully separates the broadly polydisperse PPD α and PPD β into samples containing high and low molecular weight polymer fractions. Fractions precipitated at a higher temperature (PPD α HIGH and PPD β HIGH) have a higher number-average molecular weight as compared to the parent PPDs. The lowest fractions (PPD α LOW and PPD β LOW) exhibit a substantially lower number-average MW in comparison to the parent PPDs, as they comprise a lightest fraction of the total parent PPDs. PPD α MID exhibits a number-average MW value in between the corresponding values for the PPD α HIGH fraction and the parent PPD α .

Chain scission by ultrasonic disintegration in both cases reduces the number-average MW. For the case of PPD τ , the reduction in number-average MW is progressive, but the reduction occurs more rapidly in the case of PPD Ω . In the case of PPD Ω , long duration ultrasonic treatment cleaves the polymer into a vast number of light components, such as monomer and oligomer, and therefore the number-average MW is reduced from 72.02 kDa to 7.27 kDa. It is noted that the calculated MW averages are to a certain extent merely estimates, as a portion of the integration signal resides outside the instrument calibration region.²⁵

The PPD precipitation temperature is an essential property for interpretation of the interaction mechanism between PPD and wax at a given temperature. In the current work, PPDs are applied to model waxy oil samples at a polymer concentration of 500 ppm for subsequent rheological assessment after a cooling rate of 1 C min⁻¹. However, measuring the precipitation temperature of 500 ppm PPD polymer in dodecane at a scanning rate of 1 °C/min by DSC is not practically feasible as PPD precipitation at such a low polymer concentration provides an inadequate deviation in the total heat flow signal. Hence, to estimate the PPD polymer precipitation temperature, DSC experiments were performed on elevated concentrations of PPD in dodecane, 1 wt % and 1000 ppm, at a higher cooling rate of 5 $^{\circ}$ C min⁻¹. The DSC thermogram of a 1 wt % PPD solution provided an identification of adequately strong exothermic peaks associated with PPD precipitation. The PPD precipitation peak identified from 1 wt % PPD solution is utilized to track the analogous peak on the DSC thermogram of 1000 ppm PPD solution. The precipitation peak of 1000 ppm PPD solution, which appears at temperature of around 3–5 °C below the precipitation peak of 1 wt % PPD solution, is taken as an adequate estimation of the precipitation temperature of 500 ppm PPD in dodecane.



Figure 3. DSC thermograms of neat model oils at a cooling rate of 1 °C/min.

The precipitation peak temperatures of PPDs and PPD fractions are listed in Table 1.

Figure 2 presents the properties of PPDs, PPD fractions, and PPD scission products, featuring hydrodynamic radius and precipitation peak temperature versus number-average MW. The relationship between the polymer physical properties and molecular weight is nonlinear, reflecting solid—liquid thermodynamic equilibria and the scaling behavior of swollen random polymer coils. An overall monotonically increasing trend is clearly observed in the precipitation temperature and hydrodynamic radius of the PPDs as the number-average MW increases.

According to theoretical conformational scaling as represented by polymer end-to-end distance in (1) a collapsed globule state, (2) a theta solvent, and (3) a good solvent, the root-mean-squared end-to-end distance $\langle R^2 \rangle^{0.5}$ of the polymer, a proxy for the polymer size, scales with molecular weight according to the specific conformational state. In (1) the collapsed globule state, the root-mean-squared end-to-end distance of the polymer scales with the $\sim 1/3$ power of molecular weight owing to geometric constraints. In (2) a theta solvent (i.e., at the theta temperature), the polymer chain conformation follows random walk statistics, and the rootmean-squared end-to-end polymer distance scales with the 1/2power of the molecular weight. In a good solvent, the polymer conformation will follow self-avoiding walk statistics because of excluded volume interactions, and the root-mean-squared endto-end distance of the polymer chain scales with the 0.589 power of the molecular weight.

The experimentally obtained scaling exponent value of 0.5887 (shown in Figure 2) obtained from NMR-DOSY, with respect to the molecular weight, provides rigorous corroboration that dodecane constitutes a good solvent (imparting excluded volume interactions as observed by the coil size dependence on molecular weight) for the polymer chains. The experimentally obtained scaling exponent of 0.5887, in full agreement with scaling theory including excluded volume effects, thereby provides supporting and corroborative evidence of the measurement accuracy of the NMR-DOSY method with respect to hydrodynamic radius.

3.2. Wax Crystallization Onset Point. Figure 3 shows DSC thermograms of undoped model oils at a cooling rate of 1 °C min⁻¹, exhibiting strong exothermic peaks associated with wax crystallization. Upon cooling at a rate of 1 $^{\circ}$ C min ⁻¹, the wax crystallization onset appears as a sharp spike in the heat flow signal. The wax crystallization event is delayed with respect to the wax equilibrium solubility limit temperature because a finite supersaturation is necessary to initiate wax nucleation. Nucleation is followed by rapid crystallization (commensurate with the high supersaturation condition), manifested as a sharp crystallization peak on the thermogram. As the temperature is further reduced, the heat flow signal diminishes gradually, indicating that the crystallization rate is limited by the reduction in wax solubility. The observed crystallization pattern is typical for a single-component wax solution as also described by previous authors.²⁶

Wax crystallization onset points of undoped model oils measured by DSC at a cooling rate of 1 C min^{-1} are presented in Table 2. Heavier wax components are shown to exhibit

Table 2. Wax Crystallization Onset Point of UndopedModel Oil Obtained by DSC

model oil	WAT (°C)
Oil-24	9.4 ± 0.3
Oil-28	21.2 ± 0.4
Oil-32	31.6 ± 0.4
Oil-36	41.6 ± 0.2

higher wax crystallization onset temperatures. For each additional increment of four carbons in the *n*-alkane chain, the crystallization onset temperature increases by 10-12 °C.

Preliminary testing with addition of various PPD concentrations into model oil indicated that a dosage of 500 ppm PPD induces a substantial and reproducible reduction in the crystallization onset point as well as the gel strength. The dosage of 500 ppm, establishing a PPD to wax weight ratio of 1:100, was therefore used for the evaluation of PPD efficacy to provide consistency and comparability in the measured data.

Figure 4 exhibits the DSC thermogram of undoped and doped Oil-24, illustrating a shifted pattern of crystallization

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Figure 4. Thermogram profiles of doped and undoped Oil-24 at a cooling rate of 1 $^\circ\text{C}/\text{min}.$







Figure 5. Wax crystallization onset temperature depression of model oils doped with PPDs and PPD fractions.

event. Upon addition of 500 ppm PPDs, the crystallization onset points is delayed to a lower temperature. In addition, crystallization peaks of the doped model oils appear to be steeper and higher in signal intensity but narrower in the temperature range. The shift in onset temperature imparted by polymer is substantially larger than the compression in the overall peak width. The narrowing (compression) of the crystallization peak, caused by the presence of polymer, confirms a higher supersaturation condition at the nucleation point. The polymer increases the free energy of the critical nuclei, enabling an increased supersaturation ratio to be sustained at the nucleation onset. The higher supersaturation ratio temporarily increases the crystallization rate, resulting in a narrower



Figure 6. Gel breakage profiles of neat model oils.

crystallization peak. The polymer types containing polycarboxylate and polyacrylate (PA) appear to also elevate the inherent solubility of the wax in dodecane, as evidenced by an increase in the heat signal well into the equilibrium crystallization regime.²⁶ As such, for the polymers containing carboxylate and PA, a portion of the nucleation point suppression may be ascribed to a thermodynamic effect, and a portion of the nucleation point suppression may be ascribed to a kinetic effect (i.e., alteration of the critical nuclei free energy). In contrast, the polymers containing only EVA and styrene/butylene do not appear to enhance the inherent wax solubility, as evidenced by rapid convergence of the heat signal to the heat signal from the reference (undoped) sample. Reduced nucleation point suppression provided by the polymers containing only EVA and styrene/butylene (in comparison to the nucleation point suppression shown by the polymers containing PA and carboxylate) is fully consistent with the absence of a thermodynamic solubilization mechanism and the activity mechanism comprising only kinetic stabilization of the critical nuclei. We note that the observed nucleation hindrance mechanism of the polymers in this study stands in direct contrast to the nucleation enhancement mechanism of polyethylene-propylene (PEP) type wax inhibition polymers, often known as nucleating agents. PEP type inhibition polymers have longer contiguous ethylene segments on the backbone that provide crystallizable nucleation templates. The polymers used in this study lack such extended contiguous ethylene segments. In general, nucleation enhancement can be expected from copolymers that have longer contiguous ethylene segments allowing crystallization, while shorter contiguous ethylene segments located on the polymer backbone may provide solubility enhancement via tethered aliphatic (London-van der Waals or dispersion) interactions in the liquid phase.

To express the magnitude of PPD effects in delaying wax crystallization, a quantity of wax crystallization onset temperature depression is introduced. Wax crystallization onset temperature depression is defined as the wax crystallization onset difference between doped and undoped model oil, which is calculated as shown in eq 1. wax crystallization onset temperature depression

- = wax crystallization onset temperature of doped model oil
- wax crystallization onset temperature of undoped model oil

(1)

Larger crystallization temperature depression values correspond to improved performance in delaying the crystallization onset. Typically, larger crystallization temperature depression values correspond to a higher supersaturation ratio at the precipitation onset. Figure 5 shows experimental crystallization temperature depression values for the various model fluids. All of the studied polymers yield a statistically significant reduction in the crystallization onset temperature of several model fluids. PPD α and PPD β exhibit improved performance in depressing the onset temperature, in comparison to PPD τ and PPD Ω . The highest attained temperature depression value is 3.5 °C. In general, the efficacy in reducing the crystallization onset temperature decreases as the length of the carbon chain of the wax increases. In other words, the increased nucleation energy barrier attributed to the polymer is effectively counteracted by the higher crystallization enthalpy of longer paraffin chains.

For unfractionated PPD α , the crystallization onset temperature depression is as high as 3.5 °C for Oil-24 and as low as 1.2 °C for Oil-36. The PPD α MID fraction and PPD α HIGH fraction are found to provide a similar crystallization onset temperature depression values as the parent PPD. On the other hand, the PPD α LOW fraction provides a lower reduction in crystallization onset temperature than the remaining fractions. PPD α LOW is ineffectual in suppressing the wax crystallization onset temperature of Oil-32 and Oil-36. For Oil-24 and Oil-28, the various PPD β fractions provide similar performance in reducing the crystallization onset temperature. For Oil-32 and Oil-36, the low MW fraction of PPD β shows a weaker performance in reducing the wax crystallization onset temperature than the high MW fraction of PPD β . For PPD α and PPD β , the disparity in the performance of the high MW versus low MW fractions is generally observed for the model oils containing longer paraffin chains (e.g. Oil-32 and Oil-36). In fact, for Oil-24, the high MW as well as low MW fractions of both PPD α and PPD β show a high performance in suppressing the wax crystallization onset temperature.

Collectively, the trends point to a combined temperature and polymer molecular weight dependence. When incipient crystallization occurs at higher temperatures (i.e., for longer wax chains), the shorter polymers become progressively less effective in suppressing the crystallization onset temperature. In the context of polymer adsorption onto subcritical paraffin wax nuclei, the thermogram results for PPD α and PPD β are fully consistent with a smaller overall magnitude of the Gibbs free energy change of adsorption at higher temperatures. The thermogram results for PPD α and PPD β are also fully consistent with a larger overall magnitude of the Gibbs free energy change of adsorption at higher polymer molecular weights.

For PPD τ , PPD Ω , and their fractions, the overall magnitude of the wax crystallization onset temperature depression is lower than that of PPD α and β . Ultrasound treated PPD τ and PPD Ω appear to randomly increase and or decrease the wax crystallization onset temperature depression effects, in comparison to the parent PPDs. For PPD τ and PPD Ω , it can be concluded that ultrasound treatment does not sufficiently alter the polymer MW to an extent that influences the PPD efficacy in depressing the wax crystallization onset temperature.

3.3. Wax Gel Strength. The rheological performance of each PPD on waxy model oil is evaluated by measuring the yield stress of the waxy gel. Figure 6 shows the breakage profile of undoped model oil gels formed under quiescence condition at temperature of 4 °C. At low strain values in the gel breakage process, waxy oil gels exhibit an elastic-like response. As the strain increases, the measured stress diminishes, indicating a fragmentation process of the gel. The yield stress is defined as the highest stress at which the gel starts to yield.

The yield stress values of undoped model oil gels measured at temperature of 4 $^{\circ}$ C are listed in Table 3. The gel strength

Table 3. Yield Stress of Undoped Model Oil Gels

model oil	yield stress (Pa)
Oil-24	528 ± 18
Oil-28	844 ± 43
Oil-32	1178 ± 42
Oil-36	1101 ± 14

increases as the length of carbon chain of the wax component increases from 24 to 32. Zhao et al. demonstrated that waxy gel strength is dependent on the amount of precipitated solid wax.²⁷ The measured difference in gel yield stress among model oils, which is the range of 528–1178 Pa, therefore appears to be primarily caused by the difference in amount of precipitated solid wax at 4 $^{\circ}$ C.

Rheological profiles of Oil-32 and Oil-36 exhibit an uneven pattern shortly after the gel breaking event, indicating that an adhesive breakage mechanism, the slippage between gel and cone—plate surfaces, has taken place. The pure cohesive breakage itself may be higher than the apparent value. The apparent yield stress of Oil-32 is found to be 77 Pa higher than that of Oil-36. Considering that there are uncertainties arising from this adhesive breakage, it can be said that the difference is not significant.

Another issue in assessing the rheological properties of waxy oil by using cone-and plate geometry is the fact that the wax crystal particle may exceed the gap distance. In this work we employed a gap size of 170 μ m, while the wax crystal size can be more than 500 μ m. Japper-Jaafar suggested that rheology measurement would require a minimum gap greater than the particle size.²⁸ However, our result shows a good repeatability with the largest deviation of about 5% found on Oil-28.

In this work, application of PPD into waxy model oil can decrease the yield stress from a magnitude of 10^3 Pa to 10^1 Pa. A term of normalized yield stress is introduced and is calculated as in eq 2:

normalized yield stress = $\frac{\text{yield stress of doped model oil}}{\text{yield stress of undoped model oil}}$ (2)

By introduction of this normalized quantity, the general trend of change in yield stress as result of PPD addition can be better visualized. In addition, the normalized yield stress can be used to establish a relative comparison between model oils containing different wax components, which originally have a significant difference in magnitude. Normalized yield stress values of model oils doped by PPDs are plotted in Figure 7. A lower value of normalized yield stress represents an improved PPD performance in reducing the waxy gel yield stress. A value of 1 for the normalized yield stress indicates that PPD addition does not alter the waxy gel yield stress.

A unifying principle emerges upon inspection of the normalized yield stress values. In general, lower MW fractions of both PPD α and PPD β show poorer efficacy in reducing the yield stress in comparison to the respective mother PPD, consistent with a reduced adsorption free energy of the shorter polymer chains, as previously discussed considering crystallization onset point depression. For PPD τ , the yield stress reduction efficacy of the various fractions appears to depend on the wax carbon number, portending a temperature dependence of PPD τ with respect to solubility state. It is surmised that chain scission enhances the polymer solubility at low temperatures (i.e., for Oil-24 and Oil-28), facilitating additional adsorption onto paraffin wax crystal interfaces. For PPD Ω , the overall influence of MW fraction on the yield stress reduction efficacy is minimal.

Among the PPDs, PPD τ exhibits the smallest effect on yield stress. Upon reducing the MW of PPD τ by chain scission, reductions in normalized yield stress are observed for only Oil-24 and Oil-28, which crystallize at lower temperatures than Oil-32 and Oil-36. Chain scission appears to modestly improve the solubility of PPD τ at the low crystallization temperatures of Oil-24 and Oil-28, facilitating binding of PPD τ to waxes of chain lengths 24 and 28. At the higher temperatures relevant for Oil-32 and Oil-36, PPD τ is not solubility limited, and the lower molecular weight fractions of PPD τ exhibit reduced adsorption, fully consistent with a reduced adsorption free energy upon reducing the MW of PPD τ by chain scission.

As a general trend, it is observed that normalized yield stress decreases as the PPDs are added into model oil containing larger carbon chain of wax component, meaning that the relative gel weakening effect of the PPDs is greater on wax with a longer carbon chain. The exception to this general trend is the behavior of PPD τ .

Addition of unfractionated PPD α decreases the yield stress of Oil-32 from 1178 to 175 Pa, representing a normalized yield stress value of 0.15. For the model oils denoted Oil-24, Oil-28, and Oil-36, addition of PPD α decreases the normalized yield stress to values of 0.66, 0.59, and 0.29, respectively. PPD α HIGH and PPD α MID impart normalized yield stress values close to the normalized yield stress values of their parent PPD, suggesting minimal differences in their respective efficacies.



Figure 7. Normalized yield stress of model oil doped with PPD and PPD fractions. The normalized yield stress is calculated as yield stress of doped model oil divided by yield stress of neat model oil.

PPD α LOW exhibits a substantially higher value of normalized yield stress, indicating that this low MW fraction has the lowest efficacy compared to the heavier fractions. Yield stress reduction trends for PPD α are attributable to a MW dependence on the binding of the polymer to the wax crystals. The binding free energy of the polymer to the wax crystal is apparently reduced at lower MW values, giving rise to a reduced yield stress reduction efficacy. A similar trend in normalized yield stress value is observed among PPD β and its fractions. Unfractionated PPD β addition is capable of substantially reducing the yield stress of Oil-36 from 1100 Pa to as low as about 43 Pa, representing a normalized yield stress value of 0.05. The normalized yield stress values are higher for other model oils containing shorter carbon chain in the model wax component. The yield stress reducing effect of PPD β MID is similar to that of the parent PPD. Similar to PPD α LOW, PPD β LOW also exhibits a significantly higher normalized yield stress as compared to the parent PPD, suggesting that this fraction contains components with a lower efficacy in reducing gel strength. With the exception of Oil-28, the yield stress reduction trends for PPD β are consistent with a reduced binding free energy at lower MW values.

The trend of an increasing gel weakening effect on model oils containing longer carbon chain wax components is also observed for unfractionated PPD Ω . However, in general, the fraction PPD Ω long US does not exhibit any substantially dissimilar effect on yield stress reduction.

3.4. Wax Crystal Morphology under Cross-Polarized Microscopy. Figure 8 shows polarized microscopy images of four undoped model oils at about 5 °C below their respective WATs. The *n*-alkane crystals appear as bright objects on a dark background. The crystal shape is a thin platelet with a size that can exceed 500 μ m wide or long. For the purpose of comparison, in Figures 9A and 9B are presented SEM images of an extracted C24 crystal taken by Binks²⁹ and nonpolarized optical microscope images of 4 wt % C_{32} crystal in C_{10} reported by Jung,²² respectively. The SEM image as well as nonpolarized optical microscope image both show the similar structure of thin and wide platelets of *n*-alkane crystals. The wax crystals in Figure 8 are limited to grow in a space as thin as 50 μ m. Therefore, the crystals are oriented in the planar direction, and the image appears in low intensity due to the thinness. In Figure 9C is a polarized image of Oil-32 at 26 °C in a 400 μ m deep capillary, exhibiting wax crystals in a much higher intensity than that in Figure 8 because the wax crystals may grow on top of each other in a deeper space. In this experiment, we use a 50 μ m deep capillary to force the crystal to grow in a two-dimensional direction and eventually can be captured clearly by a polarized microscope.

Gelation occurs when the wax crystal plates form a threedimensional "house of cards" structure, which traps oil in its interstitial spaces by surface tension effects. PPD or wax inhibitor is doped into waxy oil systems with an intention to modify the crystal shape, which eventually prevents the gelation or weakens the gel strength. Figure 10 exhibits how



Figure 8. Cross-polarized micrograph of neat model oil at temperature about 5 °C below WAT: (A) Oil-24, (B), Oil-28, (C) Oil-32, and (D) Oil-36.

the wax crystal shape is altered when the PPD polymer exists in the system, in this case PPD α . Wax crystal shapes in all model oils are greatly altered by 500 ppm PPD addition. There are three postulated mechanism of interactions between wax and PPD: nucleation, adsorption, and cocrystallization. This series of images may provide possible visual evidence of those wax– PPD interaction mechanisms.

According to DSC data as presented in Table 1, the solid precipitation peak of PPD α solution is ~5.4 °C. In Figure 10D is the image of C₃₆ crystals that start forming at ~40 °C, at which PPD α is in a solution state, and therefore any nucleation enhancement mechanism by preformed PPD crystalline domains (such as in the case of PEP) facilitating wax–PPD interactions is extremely unlikely to occur. Instead, wax crystals may form before any wax–PPD cocrystallization is possible, and PPD will likely adsorb on wax crystal surfaces and even integrate the aliphatic moieties into the wax crystal. As a result, thin platelet wax crystals similar to undoped *n*-alkane crystals are found dominantly. The size of the doped wax crystals tend to be smaller than undoped ones because the growth is disturbed by polymer adsorption onto the interfaces.

The effect of PPD and wax molecular weight on wax crystal morphology was exemplarily investigated by PPD α and its fractions. Figure 10A presents the image of C₂₄ crystal formed in solution containing PPD α at around 5 °C. At this temperature, solid polymer particles of PPD α are more likely to form and may act as a heterogeneous nucleation site for subsequent wax crystallization. A heterogeneous nucleus or simply an adsorbed polymer molecule may alter the direction of the crystal growth. As a result, the crystal morphology is no longer a wide platelet but appears branched long needle-like. Most likely, polymer molecules or particles play a role in causing a crystal defect, which then alters the direction of wax crystal growth.

When the PPD α is highly soluble (e.g., for the case of Oil-36), with favorable interactions with the solvent, only moderate branching is evident (Figure 10D), but instead the crystal size is reduced in accordance with steric hindrance imparted by the adsorbed polymer at the growing crystal interface. When PPD progressively is reduced in solubility at the precipitation onset point (i.e., Oil-36 \rightarrow Oil-32 \rightarrow Oil-28 \rightarrow Oil-24), the branching becomes more pronounced. However, this is overlaid by a tendency toward larger crystal sizes for the smallest wax component (i.e., Oil-24). It may be speculated that higher diffusion and faster interfacial selfassembly of the smallest wax component (i.e., Oil-24) contribute to the larger crystal size, overlapped with polymer-induced branching.

Wax crystal shapes of C_{28} in Figure Figure 10B and C_{32} in Figure 10C are found to be in-between those two contrast appearances of C_{24} and C_{36} . The modified wax crystal shapes induce the formation of weaker waxy gels. Among those PPD α doped model oil samples, Oil-28 exhibits the highest absolute yield stress value, suggesting the strongest gel structure. Substantial gel weakening activities are exhibited by Oil-32 and Oil-36, which are represented by lower values of normalized yield stress. Among PPD α doped model oil samples, Oil-36 has the lowest depression value of DSC wax crystallization onset temperature, suggesting that the platelet dominant crystal shape is less influenced by any heteronucleation





Figure 9. SEM images of extracted wax crystals. (A) C24 crystals extracted from a 20 wt % solution in toluene. Reproduced with permission from ref 29. Copyright 2015 Royal Society of Chemistry. (B) Nonpolarized optical microscope images of the model waxy gels from 4 wt % C32 in C₁₀. Reproduced with permission from ref 22. Copyright 2016 Springer Nature. (C) Polarized image of C32 5 wt % in dodecane at 26 °C in a 400 μ m deep capillary.

mechanism, even if such a heteronucleation mechanism is facilitated by the chemical environment of the wax solvent interface.

If interfacial polymer adsorption, in molecular form, is responsible for branching, reduced polymer binding at the higher crystallization temperature (in accordance with a smaller overall magnitude of the Gibbs free energy change of adsorption) for Oil-36 may be responsible for the reduced degree of branching. Current experimental techniques are unable to distinguish between (1) a heteronucleation mechanism or (2) a molecular adsorption mechanism to account for the phenomenon of branching. However, in either case 1 or 2, strong binding of the polymer, in either molecular or particulate form, to the wax interface corresponds to the branching.

Figure 11 illustrates how different fractions of PPD α may alter the wax crystal morphology in a model oil, in this case Oil-24. The wax crystal shapes of C24 formed under the influence of PPD α , PPD α MID, and PPD α HIGH appear to be similar, representing a branched needles structure. The PPD α MID fraction produces small branches, which may result from a somewhat lower molecular weight that does not first precipitate out or adsorb as for the case of the longer polymer chains. In contrast, PPD α LOW does not substantially alter the crystal shape compared to the crystal shape of undoped Oil-24 (see Figure 8A), suggesting that PPD α LOW contains polymers with weak crystal modification activity, consistent with a smaller overall magnitude of the Gibbs free energy of adsorption for shorter polymer chains.

Figure 12 provides a description on how the wax crystal structure formed in Oil-36 is affected by PPDs from different origins. Under the influence of PPD α as seen in Figure 12A, a wide platelet C36 crystal shape is still dominantly found. Figures 12B and 12D of C36 under the influence of PPD β and PPD Ω , respectively, exhibit similar dendrite-like wax crystal shapes. To some extent, PPD β and Ω share component similarity of containing EVA as the active substance, which is well-known as a popular commercial PPD. EVA might be the substance that actively directs the crystal shape to become irregular dendrite-like. The wax crystal shape of C36 doped with PPD τ in Figure 12C is dominated by long needle structures. The chemistry of PPD τ is very close to polystyrene, a polymer which is rich in aromatic rings. It appears that PPD auhas less affinity for wax molecules; as a consequence, therefore wax-PPD cocrystallization is less likely to occur. In threedimensional space, the long needle crystal may form a strong matrix network structure, which eventually drives the whole system to be a firm gel. The gel yield stress of Oil-36 doped with PPD τ is found to be 1200 Pa, which is even higher than the gel yield stress of undoped Oil-36. PPD τ also showed a poor performance when doped into more complex waxy models and crude oil. Unlike PPD τ , additions of PPD α , PPD β_i and PPD Ω all decrease the yield stress value of Oil-36 gel. Among the three PPDs, the best gel weakening efficacies are



Figure 10. Cross-polarized micrograph of model oil doped with 500 ppm of PPD α at temperature about 5 °C below WAT: (A) Oil-24 at 4 °C, (B), Oil-28 at 16 °C, (C) Oil-32 at 26 °C, and (D) Oil-36 at 36 °C.



Figure 11. Cross-polarized micrograph of Oil-24 doped with 500 ppm of PPD α and the fractions (A) PPD α , (B), PPD α low, (C) PPD α mid, and (D) PPD α high at temperature about 5 °C below WAT.



Figure 12. Cross-polarized micrograph of Oil-36 doped with 500 ppm of different PPDs: (A) PPD α , (B), PPD β , (C) PPD τ , and (D) PPD Ω high at temperature about 5 °C below WAT.

exhibited by PPD Ω and PPD β , with PPD α at the last place. The small dendrite-like crystal shape induced by the EVA polymer seems to be responsible for formation of the weakest wax gel structure. However, the gel structure is most likely weak despite the presence of the branch points, and the branching seems to simply occur phenomenologically together with strong polymer binding.

Drawing a generalized relationship between crystal shape and waxy gel strength may be speculative. However, it is found that straight and long needle crystal induced by addition of polystyrene based PPD τ does not result in a weaker gel compared to the "house of cards" crystal structure of undoped model oil. A larger wax gel weakening efficacy is caused by branched needle crystal shape. The largest effect is depicted by small dendrite-like crystal structures, which can avoid interlocking between wax crystals.

4. CONCLUSION

Four polymeric PPD additives are fractionated by either stepwise precipitation or ultrasonic disintegration to produce PPD fractions with altered molecular weight. The PPDs and PPD fractions are doped into an homologous series of waxy model oils containing single-component waxes of varying carbon chain length. Wax crystallization temperature depression and gel weakening activity are evaluated to study the effect of altered PPD molecular weight.

Overall, unfractionated proprietary PPD α and PPD β exhibit better efficacy in depressing the wax crystallization onset temperature and reducing the waxy gel yield stress than PPD τ and PPD Ω . Low MW fractions of PPD α and PPD β obtained by stepwise precipitation show a substantially reduced effect in depressing the wax crystallization temperature as well as reducing the gel strength compared to their parent PPDs and high MW fractions. This reduced efficiency is also observed in CPM imaging, where PPDs lost the ability to induce wax crystal distortion. On the other hand, the ultrasonic disintegration altered MW fractions of PPD τ and PPD Ω do not exhibit a significant efficacy difference compared to the parent PPDs.

A more obvious trend is found by how a PPD influences the nature of model oils containing different carbon chain lengths of the wax component. A greater wax crystallization temperature depression effect by PPD is found in waxy oil with a shorter carbon chain component. On the contrary, the larger PPD effect of gel weakening is found in waxy oil with a longer carbon chain component. This contrast suggests that the two actions of wax crystallization temperature depression and gel weakening may be the result of different mechanisms related to the solubility temperature of PPD. Wax—PPD cocrystallization is favorable if wax crystallization occurs when PPD is in solubilized state. On the other hand, heterogeneous nucleation by PPD is more likely to occur at lower temperatures at which the PPD has precipitated out.

The underlying chemistry of a particular PPD also appears to be influential with regards to the efficacy of wax inhibition. Although demonstrating activity in delaying the WAT as well as changing the crystal morphology, PPD τ does not induce formation of weaker gels. Polystyrene-based PPD may not have sufficient affinity for the wax molecule to alter all three processes of nucleation, cocrystallization, and adsorption.

Cross-polarized microscope images reveal that monodisperse waxes precipitate out as thin platelet crystals which form a three-dimensional "house of cards", trapping the solvent in its interstitial spaces and turning the whole system into a gel. It is shown that addition of PPD greatly alters the wax crystal morphology to become needle or branched needle as well as dendrite-like. The dendrite-like crystal structure depicts the largest effect of gel weakening and is consistent with strong polymer binding at the interface.

Overall, the results are in full accordance with stronger binding of higher MW polymers to the wax crystal interface, such that lower MW fractions exhibit weaker binding to the wax crystal interface. In addition, a complex temperature dependency governs the PPD polymer performance. At increasing temperature conditions, the PPD polymer coils show more favorable interactions with the solvent than with the precipitating wax, and weaker binding is therefore observed to the wax crystals. Conversely, at sufficiently low temperatures, PPD polymers undergo a coil-to-globule transition, completely lose solubility, and therefore lose most modes of PPD activity. Successful PPD tailoring involves balancing the MW to optimize interactions with crystallizing paraffin wax while avoiding loss of PPD to a precipitated phase. Knowledge of these competing phenomena should guide future PPD tailoring practices, enabling optimal polymer molecular weight distributions for each specific petroleum fluid.

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Notes

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ACRONYMS

CPM, cross-polarized microscopy; DOSY, diffusion-ordered spectroscopy; DSC, differential scanning calorimetry; EVA, ethylene-vinyl acetate copolymer; HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance; PA, polyacrylate; PB, polybutene; PE, polyethylene; PEB, poly(ethylene-butene); PEP, poly(ethylene-propylene); PPD, pour point depressant; PS, polystyrene; SEC, size exclusion chromatography; SEM, scanning electron microscope; THF, tetrahydrofuran; WAT, wax appearance temperature.

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