Polymers for Asphaltene Dispersion: Interaction Mechanisms and Molecular Design Considerations

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ABSTRACT

The prevention of asphaltene self-assembly is a technical challenge of broad scope since asphaltene aggregates can precipitate and cause fouling in production facilities, pipelines and refineries. Although polymeric dispersants are often used as flow improvers and offer great promise for affordable and effective prevention of deposition, the mechanism by which they affect aggregation is relatively understudied. In order to clarify the nature of interactions between polymers and asphaltenes in aliphatic solvents, systematic molecular dynamics simulations were employed to test several organic polymer structures that were reported to be effective in previous experimental studies. Bulk phase simulations with model asphaltenes with different functional groups revealed that several particular structural attributes are effective for maintaining asphaltene dispersity while preventing full aggregation. A specific polymer was determined to be most effective due to its unique capability to occupy the active stacking sites of asphaltene aggregates (i.e. aromatic cores), thereby preventing further π - π stacking of asphaltenes. In addition, the favored polymer was shown to possess superior solubility in aliphatic solvents and exhibit less chain collapse when compared to the other structures tested. Several suggestions are presented to provide insight to the design of more effective polymeric flow improvers.

1. INTRODUCTION

One of the most critical challenges facing the oil industry today is assuring fluid flow through ultra-deep sub-sea wells such as those found in the Gulf of Mexico. Potential impediments include the formation of asphaltene deposits in flow lines due to changes in fluid composition, leading to significantly high intervention costs. Variations in fluid composition usually occur due to mixing with lighter oils or release of light alkanes near the bubble point pressure. Since asphaltenes comprise the heaviest and most polarizable portion of crude oils, they tend to aggregate into nanoscale clusters that constitute the building blocks of flocculates in aliphatic media.¹ Flocculation is a kinetic process that occurs as soon as asphaltene aggregates are destabilized.² As a result, effective chemical inhibition strategies should target asphaltenes in their early stages of aggregation in the bulk phase. Several polymeric dispersants have been used in the past to prevent asphaltene precipitation due to their wide array of possible functional groups and relative ease of production. In general, the structure of these polymers consists of two main parts: (i) a polar organic backbone with functional groups that favorably interact with asphaltenes, and (ii) aliphatic chains that provide sufficient solubility in alkane solvents.³ Among these polymers, two classes were particularly investigated in the past, organometallic and organic.

1.1. Organometallic Polymers

Hernández-Altamirano et al. studied a class of organometallic polymers that were shown to be effective as bactericidal corrosion inhibitors and asphaltene dispersants.⁴ They synthesized a butyl substituted bis-di-organotin (IV) compound that showed the best efficiency at curbing asphaltene aggregation, resulting in nearly 30% reduction in asphaltene aggregation at 0.1 g/L dispersant concentration in liquid heptane. As in other studies, the *n*-butyl chains were presumed

to be responsible for enhancing the steric repulsion between the asphaltene aggregates.^{4,5} Li et al. also used an organometallic polymer to enhance upgrading effectiveness in heavy oils. The cupric-grafted polymer combinations enabled the enhanced cleavage of C-C and C-S bonds while reducing the viscosity of the mixture, which was noted as an indication of the enhancement in asphaltene dispersity.⁵ A positive correlation was observed between increasing alkyl polymer side chain length and the effectiveness of the polymer in dispersing and cleaving the asphaltenes.

1.2. Organic Polymers

Polymers containing both aromatic portions as well as strongly polar functional groups such as amide or carbonyl have been quite successful for preventing asphaltene precipitation.⁶⁻⁸ Ghaffer et al. tested a series of propoxylated dodecyl phenol formaldehyde polymers with three different molecular weights using heavy crude oils in heptol solutions.⁶ The oil mixtures in toluene were slowly titrated with heptane to induce precipitation while the light absorbance was measured. The results showed that the onset of asphaltene precipitation increased with increasing polymer molecular weight. The study postulated that the presence of the propoxy (C_3H_7O) side and end chains allowed greater interaction with the asphaltenes, resulting in overall higher absorbance and better performance compared to the non-substituted poly(dodecyl phenol formaldehyde). A similar study tested various dendronized polyamidoamine (PAMAM) polymers as possible asphaltene dispersants using the same light absorbance test as well as DLS and rheological tests.⁷ The results showed that the PAMAM polymer was most effective in its third generation dendrimer, most likely due to the high degree of branching resulting in steric hindrance between aggregates. Overall, the PAMAM polymers showed better dispersing effects than the propoxylated polymers. Castro et al. used a terpolymer of styrene, *n*-butylacrylate and vinyl acetate as a viscosity reduction agent for heavy oil. Results indicated that higher percentages of

styrene in the terpolymer resulted in better flowability due to the favorable aromatic interactions with the asphaltenes.⁸

Polymers based on succinimide have also shown promise as effective asphaltene dispersants.⁹⁻¹³ Nassar et al. found that polyisobutylene succinic anhydride (PIBSA), an industrial dispersant, was highly effective for preventing sedimentation and fouling in engine lube oils.⁹ Chávez-Miyauchi et al. synthesized several polyisobutylene succinimides and tested for their asphaltene dispersive effect in heptane.¹⁰ The succinimides with both hydroxyl groups *and* benzene structures were most effective, showing nearly 68% dispersion efficiency at 0.1 g/L additive concentration. In a different study, trials conducted with varying di-substituted polyisobutylene succinimide polymers indicated that phenol substituted-(polyisobutylenesuccinimidyl) oxazolidines were the most effective stabilizers for asphaltenes in crude oil. The isobutylene tail was cited as being responsible for the favorable steric repulsive effects.³ Barcenas & Orea showed that the dispersive effect of an oxizolidine-based polymer was comparable to that of nonylphenol.¹¹ Succinimide-based polymers have also been used in other studies for flow improvement and as a lubricant additive to prevent asphaltene fouling.^{12,13}

Maleic anhydride is a ring structured molecule containing three oxygens and is chemically comparable to succinimide. Due to its reactive properties, polymers or co-polymers of maleic anhydride can be readily synthesized for asphaltene dispersants and heavy oil viscosity reducers. A co-polymer of octadecyl acrylate and maleic anhydride with substituted benzene was shown to be effective at reducing the pour point of a heavy crude by 9 °C when added at a concentration of only 0.05 g/L.^{14,15} The benzene rings are presumed to interact with the asphaltenes via π - π interactions, allowing a change in the aggregate structure that prevents thickening. Xu et al. studied the cold flowability of waxy oils in the presence of comb-type poly(maleic alkylamide-co- α -octadecene) copolymers.¹⁶ These polymers are characterized by alternating amide and

carboxylic acid backbone groups with octadecene “combs” bonded to the amide nitrogen. Results indicated that flowability could be correlated to the polar/non-polar copolymer ratio. A ratio of 0.4 was found to promote the best flowability in the asphaltenic gels, probably due to favorable interaction between the polar groups and the asphaltenes combined with the steric hindrance provided by the octadecene side chains.¹⁶

Li et al. used a polymer built from maleic anhydride to delay the asphaltene onset point in heavy crude samples.¹⁷ Interestingly, Pillon et al. found that poly(maleic anhydride-1-octadecene) was too reactive to serve as a favorable dispersant.¹⁸ FTIR analysis showed that the asphaltenes reacted with the anhydride group and precipitated out of n-heptane solution. The conclusion was that the anhydride group must be altered, by reacting with an amide for instance, in order to be effective as a dispersant. Atta et al. demonstrated the ability of vinyl acetate-maleic acid copolymers to depress the pour point in waxy crude oils.¹⁹ Multiple other studies have used variant polymers of maleic anhydride to show large reductions in the pour point of heavy crude oils and reduced organic deposition.²⁰⁻²⁶

A broad class of polyolefin alkeneamines have been used as asphaltene dispersants as well as combined with succinimide and maleic anhydride to create a wide array of dispersant types. Hashmi and Faroozabadi released a series of papers demonstrating the effectiveness of a proprietary polyolefin alkeneamine dispersant for maintaining asphaltene dispersity.²⁷⁻²⁹ Although the exact formula was not given, a general structure for a similar type of dispersants was published in a patent filing.³⁰

Most asphaltene dispersants or inhibitors presented in the literature possess distinctly similar chemical features. Nearly all effective dispersants contain aromatic functionalities that allow π - π interactions between the dispersant and the aromatic core of asphaltenes.¹⁰ In addition, the presence of aliphatic chains is critical for providing steric hindrance between the aggregates.

Typically, the larger, more branched chains are more effective.^{3,19} Polar functional groups are necessary to facilitate increased interaction with asphaltenes. The highly polar succinimide and maleic acid structures have been shown to be effective in addition to amide, carboxylic acid and propoxy functional groups.

Although succinimide, maleic acid, and polyolefin alkeneamine polymers show promise as asphaltene dispersants in the laboratory, there is currently no fundamental research examining the exact molecular mechanisms of interaction for these dispersants. In addition, solid molecular structure design criteria have not been suggested for creating more effective asphaltene dispersants. In this study we propose a systematic molecular dynamics approach to determine the effect of several polymeric dispersants on asphaltene aggregation, and use these results to suggest design criteria for guiding the synthesis of better polymeric dispersants. We present details of polymer selection, simulation methods and analysis tools employed for assessing dispersant effectiveness. A discussion and presentation of the results follows, outlining the specific outcome of each polymer dispersant. Conclusions are presented and the impact of the simulation results is addressed.

2. METHODS

2.1 Polymer Selection

Three polymers were selected based on common structures found in the literature, as shown in **Figure 1**. Two succinimide-based structures (S1, S2) and one maleic anhydride derived copolymer (M1) were selected for testing in simulation. One of the succinimidyl structures contained an interior alkeneamine chain (S2), while the other was coupled to a phenol substituted oxazoladine group (S1).

The asphaltene structures were also chosen using a systematic approach in order to better understand the dispersing mechanism of each polymer. Three groups of asphaltenes were selected with each possessing unique functional groups. The base asphaltene was designed without any functional groups while the O-group and N-group asphaltenes possessed oxygen and nitrogen based functional groups. **Figure 2** shows the model asphaltene structures adopted in this work. The OPLS-AA force field was used to parameterize the polymers and the asphaltenes while an OPLS united atom (UA) model was used to represent the pentane solvent. Pentane was chosen since it is a poor solvent for asphaltenes, causing complete and rapid asphaltene aggregation. By using pentane, it was easier to note changes induced by the polymers. All simulations were conducted using GROMACS 5.1.1 molecular simulation package.

2.2 Bulk Phase Simulations

To initialize the simulations, 100 asphaltene molecules were placed in a simulation box. For the N-group and O-group asphaltenes, 50 of each type were added. The simulation box size was $17 \times 17 \times 17 \text{ nm}^3$ with approximately 20,000 *n*-pentane molecules added as solvent. Each type of polymer was introduced separately at 10 wt%, 5 wt% and 1 wt% by weight of *n*-pentane solvent. For all simulations, the asphaltenes were set at a fixed 5 wt% by weight of *n*-pentane solvent and a set of three base simulations were conducted with each asphaltene group in *n*-pentane without additives for comparison. Each simulation was initially subjected to energy minimization using the steepest descents algorithm in order to minimize unfavorable contacts. After energy minimization, a 5 ns equilibration simulation was conducted to allow the mixtures to reach 1 bar and 300 K. The Berendsen algorithm was used to control both temperature and pressure. Following equilibration, simulations were conducted for 200 ns at 300 K and 1 bar to observe the aggregation behavior of each asphaltene type in *n*-pentane and the effects of each polymer on

asphaltene interaction. The Parrinello-Rahman pressure coupling and Nose-Hoover thermostat were employed to maintain equilibrium with coupling times of 6 and 2 ps, respectively. Long-range electrostatics were calculated using the PME approximation with a cut-off length of 1.4 nm. The Lennard-Jones cut-off was also set to 1.4 nm. Hydrogen bonds were constrained using the LINCS algorithm enabling a simulation time-step of 2 fs.

2.3 Polymer Solubility Simulations

Each of the three polymers was simulated separately in *n*-pentane for 100 ns in order to assess and compare their solubilities. Polymers were inserted randomly into a cubic simulation and *n*-pentane solvent was added to reach a polymer concentration of 5 wt%. The simulations were carried out using the same parameters used in the bulk phase simulations. At the end of simulation, the average cluster size was calculated from each trajectory frame. The damped oscillations in the velocity autocorrelation function provided confirmation that the system had reached a pseudo-equilibrium state.

2.4 Analysis Methods

Following the 200 ns production simulations, the z-average aggregation number was calculated for the asphaltenes in order to determine the effect of the polymers on the aggregation state of the asphaltenes. The aggregation number was calculated by grouping the asphaltenes according to pair-wise distance and binning the clusters based on a set cut-off distance of 1.35 nm.^{31,32} In addition, the polymer-asphaltene and asphaltene-asphaltene interaction energies were extracted from the simulation trajectory.

To aid in determining the structure of the aggregates after each simulation with and without the polymer additives, the radial distribution function was calculated between the center of mass of each asphaltene and polymer molecule in the system as given by Eq. 1,

$$g(r) = \lim_{dr \rightarrow 0} \frac{V}{N(N-1)4\pi r^2 dr} \langle \sum_i^N \sum_{j \neq i}^N \delta(r - r_{ij}) \rangle \quad (1)$$

where V and N are the volume and number of non-solvent molecules in the system. δ is the Kronecker delta function and r_{ij} is the distance between the center of mass of two non-solvent molecules.³³ The radial distribution function allows the visualization of the degree of separation between the molecules within the system and consequently, a good estimate of the degree of aggregation.

The pair-density distribution function, $p(r)$, is a useful extension of scattering intensity and can be calculated experimentally via small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) intensity profiles or determined theoretically from MD simulation. In order to quantify the degree of aggregate structure within the systems, the pair-density distribution functions were calculated for each simulation. The theoretical calculation of the pair-density distribution function for MD is based on the SANS lengths of the different atomic species present within the system. $p(r)$ (Eq. 2) can be obtained from MD simulations by forming a weighted histogram of a modified form of the radial distribution function $G(r)$.³⁴

$$p(r) = \frac{\sum_i G_i(r)}{\sum_i \int_0^\infty G_i(r) dr} \quad (2)$$

Where i is the trajectory frame number. The pair-density distribution function is calculated based on tabulated atomic scattering lengths for the coefficients (b_i) and employing the expression for the $G(r)$ function given in Eq. 3.³⁵

$$G(r) = \sum_{i,j} b_i b_j \quad (3)$$

During the calculation of the pair-density distribution function, molecules were wrapped back into the unit cell such that they were physically grouped with the cluster to which they belonged in order to avoid splitting an aggregated cluster across a periodic boundary. It is worth noting that the pair-density distribution data (see **Figure 6**) is reported beyond 17 nm which the size of

the simulation box vector. This is due to the fact that the probability for pairs to exist is non-zero up to the largest length of the scattering object or aggregate within the system. The data for the $p(r)$ function goes to zero as the radius reaches $D_{\max}$, the maximum length of the aggregate within a given system.

By using the radial distribution function coupled with the pair-density distribution function, semi-quantitative arguments can be made concerning the structure and size of the aggregates. In addition, both analysis methods provide useful results for comparative analysis between individual simulations.

3. RESULTS AND DISCUSSION

3.1 Asphaltene Aggregation

After simulations were completed, the z-average aggregation number was calculated for the asphaltenes in each simulation. In order to calculate the aggregation number, the solvent and polymer were removed from the simulation box prior to discretizing the simulation box into a three dimensional matrix. The total distance between each asphaltene in time was calculated and aggregates were determined based on a cut-off distance of 1.35 nm. **Figure 3** shows the aggregation for each group of asphaltenes with and without each of the additives. The aggregation number for all simulation sets at 10 wt% and 1 wt% polymer concentration were also calculated however it was found that no additional benefit was gained from 5 wt% to 10 wt% and that little dispersion was noted at 1 wt%, therefore the results reported were based solely on the 5 wt% polymer additive simulations. As can be seen in **Figure 3**, each of the polymers effectively reduced the aggregation number of the asphaltenes. In terms of aggregation number, all the polymers showed rough equivalency for both the base and N-group asphaltenes.

For the O-group asphaltenes, the M1 polymer performed slightly less effectively than the S1 and S2 polymers.

Table 1 shows the calculated interaction energy and number of hydrogen bonds between the asphaltene molecules averaged over the last 25 ns of the trajectory. In order to obtain the correct intermolecular potential, the energy of one asphaltene in *n*-pentane was calculated and multiplied by the total number of asphaltenes in the bulk. This energy was then subtracted from the total potential obtained from the trajectory in order to screen out the intramolecular potential energy. As may be expected, the base asphaltenes showed the least intermolecular attraction in *n*-pentane without any additives. This is due to the absence of any heteroatoms that enhance the coulombic contribution of the intermolecular potential. The O-group asphaltenes showed the largest average intermolecular energy in *n*-pentane due to the strong affinity for hydrogen bonding between the carbonyl and hydroxyl groups. The heteroatoms apparently compliment the aromatic stacking, evidenced by the large Van der Waal's contribution. This is also confirmed by the highly aggregated state that the N and O-group asphaltenes achieved during the 200 ns simulation shown in **Figure 3**.

Although the M1 and S2 polymers reduced the asphaltene-asphaltene interaction energy the most and displayed the best dispersion effects, asphaltenes with these polymers did appear to undergo some amount of undesirable clustering. **Figure 4** shows snapshots from near the end of the bulk simulations with the base asphaltene for each polymer at a concentration of 5 wt%.

It is worth noting that the S1 polymer showed better reduction in hydrogen bonding between the O-group asphaltenes compared to the other polymer types. This is due to the fact that the succinimide oxygen atoms within the S1 structure are easily accessible to the hydroxyl groups of the asphaltenes. By coordinating with the hydroxyl groups, the S1 polymer prevented the asphaltenes from forming the same number of hydrogen bonds as without a dispersant additive.

3.2 Asphaltene Clustering

The snapshots presented in **Figure 4** demonstrate that although each of the polymers were effective at reducing the asphaltene aggregation number by increasing asphaltene core-core separation, there is a notable difference in the actual dispersity obtained with each polymer type. **Figure 4 (a)** shows the fully aggregated state of the base asphaltenes, which have stacked in order to create a large flocculate. Interestingly, the S1 polymer showed the best solubility and visually seemed to achieve the best asphaltene dispersity in contrast to the S2 polymer, which formed a separate polymer-asphaltene cluster. The results shown in **Figure 4** demonstrate that the z-average aggregation number is a useful for a first estimate but does not give an accurate picture of the microscopic phase behavior of the system.

In order to better quantify the degree of cluster formation that was prevented or induced by each polymer, the intermolecular radial distribution functions were extracted from the last 50 ns of the trajectory. The radial distribution functions were calculated between the centers of mass of the asphaltene and polymer molecules. Since the pentane solvent was a united atom model and did not represent the fully atomistic representation of pentane, it was completely removed prior to calculation in order to reduce computation load. The radial distribution functions for each case are shown in **Figure 5**. The peaks in the plot are directly indicative of the structure that is present in a system. In this case, the denser aggregates resulted in a higher peak of the radial distribution function. As can be seen in the figure, the S1 polymer consistently maintains lower peaks compared with the other two polymer types, indicating that there is less packing density within the system. This finding is supported by the snapshots from the end of the simulation trajectory.

The pair-density distribution function of the system, $p(r)$, was calculated at the beginning and end of the simulation trajectories to give better insight into the structure of the aggregates in the presence of the polymers (see **Figure 6**). While the radial distribution function gives the density

distribution of a system, the pair-density distribution function allows a better visualization of the structural distribution of the system. The S1 polymer showed more consistent peak shifts that did not display bimodal behavior or large increases in peak height. The strongly bimodal peaks that are present in the endpoint distributions for several of the M1 and S2 polymer simulations are characteristic of the progression in aggregation and the development of increasing inhomogeneity. Bimodality is indicative of increasing dissimilarity in size and shape of the scattering particles (i.e., a densely packed asphaltene-polymer aggregate contrasted with a single polymer).³⁶

By observing the plots in **Figure 6**, it is clear that the S1 polymer stands out as providing the best asphaltene dispersity. With the base asphaltene group (top row), both the M1 and S2 polymers display bimodal and multimodal tendencies indicating the presence of more than one underlying distribution. With the N-Group asphaltenes, the trend is less pronounced and all the polymers show a fairly significant shift in the primary peak except the M1 polymer, which shows a strongly bimodal tendency, consistent with **Figure 7**. The O-Group again shows that the S1 polymer is superior in terms of the amount of peak shift and height change in the $p(r)$. While the radial distribution function profile for the O-Group asphaltenes may suggest that the S1 and S2 polymers cause similar clustering effects, the plots in **Figure 6** suggest that the S2 polymer actually causes the formation of more densely packed, inhomogeneous aggregates, which is also confirmed by the snapshots in **Figure 8**. The M1 polymer causes a very tall, sharp peak in the $p(r)$ function indicating the presence of one densely packed aggregate.

3.3 Polymer Solubility in *n*-Pentane

Each of the polymers was also tested independently for solubility in *n*-pentane. Simulations were conducted for 100 ns with each polymer at 5 wt% in order to observe which dispersants were most soluble. At the end of the simulation, the average polymer cluster size was calculated over

the entire trajectory. A cut-off criteria of 0.35 nm, implemented by GROMACS, was used for determining whether a polymer atom was classified as independent or in a clustered group. In order to allow direct comparison of each polymer, the cluster sizes were normalized according to the total number of the respective polymers in each simulation. **Figure 9** showed the clustered fraction for each polymer type in time. The M1 polymer showed the worst solubility with the highest cluster fraction and the S1 polymer was the best, again consistent with the images in **Figures 4, 7 and 8**.

Table 2 presents the average polymer-polymer interaction energy over the last 25 ns in each simulation. As with asphaltenes, the energy of a single oligomer in pentane was calculated and subtracted from the energy obtained from the trajectory in order to screen out intramolecular interactions. The energies are not normalized due to the fact that each of the simulations was the same size and the polymers were at a set concentration of 5 wt%. The M1 polymer had the highest self-interaction due to the large coulomb interaction energy which was likely a driving factor for the poor solubility in *n*-pentane and cluster formation with asphaltenes. S1 consistently had the lowest total interaction energy due to large positive coulomb forces caused by repulsive forces within and between the polyisobutylene tail structures. The S1 polyisobutylene tail-tail repulsion contributed an average of about 20 kJ/mol of interpolymer repulsive energy per molecule.

Similarly, the S2 polymer possessed positive Coulomb forces but these were damped due to the massive amount of interpolymer hydrogen bonding. The S2 polymer created a semi-crosslinked structure due to the formation of intra and intermolecular hydrogen bonds. Due to the presence of secondary amine groups as well as the uncoordinated oxygen on the succinimide rings of S2, the formation of intramolecular hydrogen bonds also caused the polymer to collapse, as shown in **Figure 10**, likely limiting the dispersive effectiveness.

3.4 Polymer Dispersing Mechanisms

Combining all of the previous analyses allowed for a more complete picture of the dispersing mechanism and formulation of suggested design criteria. In order to aid in determining the dispersing mechanism, the interaction energies between the asphaltenes and each polymer type were extracted as an average over the last 25 ns of simulation. **Table 3** shows the energies and hydrogen bonding between the polymers and the asphaltenes. The M1 polymer showed the largest interaction with the asphaltenes compared to the other two polymers. The S2 polymer interacted primarily through large Van der Waals interaction energy, due to the long polyisobutylene chains. S2 also formed the highest number of hydrogen bonds due to the large number of receptor and donor sites within the polymer chains while the M1 polymer had a large interaction with the asphaltenes through aromatic interactions between the styrene rings and the asphaltene aromatic cores (See **Figure 11**). Both M1 and S2 showed strong incorporation into the interior aggregate structure of the asphaltenes resulting in a mixed cluster with polymers interspersed throughout the stacks of asphaltenes.

The S1 polymer showed generally the lowest interaction energy with asphaltenes except for the O-Group asphaltenes. In addition, the S1 polymer did not incorporate with the asphaltenes as the other polymers did. On the contrary, the polymer coordinated with the periphery of the asphaltene aggregates and interacted via the succinimide core group with the asphaltenes on the end of the aggregate stacks, as shown in **Figure 12**. The core group of the S1 polymer interacted strongly with the aromatic core of the end asphaltene, thereby allowing the polyisobutylene tail to extend into the solvent and provide enhanced steric hindrance that prevented further stacking. This unique effect was observed in all of the S1 simulation trajectories. In this way, the S1 polymer acted as a “capping” agent by effectively blocking the active sites of further asphaltene

aggregation. The other polymers were unable to interact as effectively with the active stacking sites due to the layout of their functional groups within the polymer chain.

In order to provide quantitative evidence of this effect, the S1 polymer was partitioned into the core group, comprised of the phenol substituted succinimidyl oxazolidine portion, and the tail group, comprised of the polyisobutylene chain. The energy was calculated between the asphaltenes and the core and tail groups separately. The energy was then normalized by the number of atoms present in each respective group. The results tabulated in **Table 4** show that the core-asphaltene interaction is about ten times stronger than the tail-asphaltene interaction, which agrees with the results observed in the visual trajectories. Similar calculations were performed with the S2 polymer, however the core group did not interact significantly more with the asphaltenes than the two polyisobutylene tail groups (See **Table 5**).

This unique stacking behavior observed in the simulation trajectories with the S1 polymer was not observed with the other two types of polymers. One possible explanation is that both the M1 and the S2 polymer exhibit some degree of stereoregularity, in that they both possess regularly alternating functional groups throughout their structure rather than a functional group that is directly accessible on one end of the polymer. This structural symmetry may have prevented the M1 and S2 polymers from strategically coordinating with the unoccupied stacking sites on the aggregates while still providing ample steric hindrance. In contrast, the S1 polymer does not possess the same degree of alternating group symmetry which allows the core group to stack on the end of an aggregate while still allowing the polyisobutylene tail to have a full range of motion to provide repulsion between aggregates. This finding is consistent with Mena-Cervantes who found that a polymer with two aliphatic end chains was less effective than a polymer with only one polyisobutylene group.³

4. CONCLUSIONS

Polymeric dispersants have shown promise as a new class of effective asphaltene dispersants for use in field applications. In order to gain molecular level insight into this class of dispersants, molecular dynamics simulations were conducted with three different polymeric dispersants combined with model asphaltenes in *n*-pentane solvent. All three polymeric dispersants were shown to be effective at reducing the z-average aggregation number of the asphaltenes in bulk solution when compared with base simulations in which no dispersant was added. The degree of clustering of the asphaltenes prevented by each of the polymers was investigated using the radial distribution function combined with the calculated pair-density distribution function. The S1 polymer was found to provide the maximal dispersing benefit while reducing apparent clustering. In addition, each of the polymers was tested alone in *n*-pentane to evaluate solubility. Clustering calculations showed that the M1 polymer exhibited poor solubility in *n*-pentane solvent when compared with the other two polymers. The S2 polymer interacted strongly with itself, causing large amounts of intramolecular hydrogen bonding that hindered its effectiveness. Overall, the S1 polymer was found to be the most effective for maintaining asphaltene dispersity while preventing excessive formation of polymer-asphaltene clusters. Several conclusions can be drawn from the results that may be broadly applicable for dispersant design.

(1) Large interaction energies between a dispersing agent and the asphaltenes is not always desirable as it can lead to increased cluster formation and decreased solubility, as was evident in the simulations with M1 and S2 polymers. The results also showed that the z-average aggregation number is not always a good indicator of actual dispersant effectiveness when the further formation of combined polymer-asphaltene clusters is not also considered.

(2) Although hydrogen bonding is important for linking the polymer to the asphaltenes, too many hydrogen bond acceptor-donor pairs within the interior polymer structure may hinder its

effectiveness by permitting large coulombic self-interaction and promoting polymer chain collapse.

(3) The S1 polymer was effective due to its non-stereoregular structure allowing non-symmetrical interactions with the asphaltene aggregates. This was largely due to the phenol substituted succinimidyl oxazolidine group which interacted strongly with the asphaltene cores and acted as a “capping” agent by occupying the active stacking sites on the ends of the aggregate while the polyisobutylene tail aided in steric repulsion. The other two polymers being somewhat more stereoregular, in as much as they were symmetrical in group alternation, were unable to interact with the end of asphaltene aggregates while maintaining maximal inter-aggregate steric hindrance. This asymmetric combination of steric chain with a polar functional group appears to be effective and may be a valid consideration in future polymer design.

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6. REFERENCES

- [1] Goual, L.; Sedghi, M.; Wang, X.; Zhu, Z. Asphaltene Aggregation and Impact of Alkylphenols. *Langmuir* **2014**, *30*, 5394–5403.
- [2] Hoepfner, M. P.; Limsakoune, V.; Chuenmeechao, V.; Maqbool, T.; Fogler, H. S. A Fundamental Study of Asphaltene Deposition. *Energy Fuels* **2013**, *27* (2), 725–735.
- [3] Mena-Cervantes, V. Y.; Hernández-Altamirano, R.; Buenrostro-González, E.; Beltrán, H. I.; Zamudio-Rivera, L. S. Development of Oxazolidines Derived from Polyisobutylene

Succinimides as Multifunctional Stabilizers of Asphaltenes in Oil Industry. *Fuel* **2013**, *110*, 293–301.

[4] Hernández-Altamirano, R.; Mena-Cervantes, V. Y.; Chávez-Miyauchi, T. E.; Nieto-Álvarez, D. A.; Domínguez-Aguilar, M. A.; Zamudio-Rivera, L. S.; Barba, V.; Fernández-Perrino, F. J.; Pérez-Miranda, S.; Beltrán, H. I. New Bis-Di-Organotin Compounds Derived from Aminoacid-Imine-Hexadentate Ligands. Multifunctional Evaluation as Corrosion Inhibitors, Antibacterials and Asphaltene Dispersants/inhibitors. *Polyhedron* **2013**, *52*, 301–307.

[5] Li, J.; Wang, X.; Tang, X.; Wang, F.; Qing, D. Effect of Transition Metal Polymers with Varying Side Alkyl Chain on Viscosity Reduction of Crude Oil and Aggregation Behavior of Asphaltene. *Energy Fuels* **2015**, *29* (12), 7771–7780.

[6] Ghaffar, A. M. A.; Kabel, K. I.; Farag, R. K.; Maysour, N. E.; Zahran, M. A. H. Synthesis of Poly(dodecyl Phenol Formaldehyde)-B-Poly(oxypropylene) Block Copolymer, and Evaluation as Asphaltene Inhibitor and Dispersant. *Res Chem Intermed* **2013**, *41* (1), 443–455.

[7] Kabel, K. I.; Abdelghaffar, A. M.; Farag, R. K.; Maysour, N. E.; Zahran, M. A. H. Synthesis and Evaluation of PAMAM Dendrimer and PDPF-B-POP Block Copolymer as Asphaltene Inhibitor/dispersant. *Res Chem Intermed* **2014**, *41* (1), 457–474.

[8] Castro, L. V.; Flores, E. A.; Vazquez, F. Terpolymers as Flow Improvers for Mexican Crude Oils†. *Energy & Fuels* **2011**, *25* (2), 539–544.

[9] Nassar, A. M.; Ahmed, N. S.; El-Aziz, K. I. A.; Azim, A.-A. A. A.; El-Kafrawy, A. F. Synthesis and Evaluation of Detergent/Dispersant Additives from Polyisobutylene Succinimides. *International Journal of Polymeric Materials and Polymeric Biomaterials* **2006**, *55* (9), 703–713.

- [10] Chávez-Miyauchi, T. E.; Zamudio-Rivera, L. S.; Barba-López, V. Aromatic Polyisobutylene Succinimides as Viscosity Reducers with Asphaltene Dispersion Capability for Heavy and Extra-Heavy Crude Oils. *Energy Fuels* **2013**, 27 (4), 1994–2001.
- [11] Barcenas, M.; Orea, P. Molar-Mass Distributions of Asphaltenes in the Presence of Inhibitors: Experimental and Computer Calculations. *Energy & Fuels* **2011**, 25 (5), 2100–2108.
- [12] Cao, K.; Zhu, Q.; Wei, X.; Yao, Z. Study on the Influence of the Imidization Degree of Poly(styrene-Co-Octadecyl Maleimide) as a Flow Improver in Waxy Crude Oils with Asphaltenes. *Energy Fuels* **2015**, 29 (2), 993–1000.
- [13] O'Brien, J. P.; Papay, A. G. Polyalkylene Succinimide Lubricant Additives. US4448974 A, May 15, 1984.
- [14] Wu, Y.; Ni, G.; Yang, F.; Li, C.; Dong, G. Modified Maleic Anhydride Co-Polymers as Pour-Point Depressants and Their Effects on Waxy Crude Oil Rheology. *Energy & Fuels* **2012**, 26 (2), 995–1001.
- [15] Jiang, H.; Xu, J.; Wei, X.; Wang, T.; Wang, W.; Li, L.; Guo, X. Flow Improvement of Liaohe Extraheavy Oil with Comb-Type Copolymers. *Journal of Applied Polymer Science* **2014**, 131 (8).
- [16] Xu, J.; Xing, S.; Qian, H.; Chen, S.; Wei, X.; Zhang, R.; Li, L.; Guo, X. Effect of Polar/nonpolar Groups in Comb-Type Copolymers on Cold Flowability and Paraffin Crystallization of Waxy Oils. *Fuel* **2013**, 103, 600–605.
- [17] Li, L.; Xu, J.; Tinsley, J.; Adamson, D. H.; Pethica, B. A.; Huang, J. S.; Prud'homme, R. K.; Guo, X. Improvement of oil flowability by assembly of comb-type copolymers with paraffin and asphaltene. *AIChE Journal* **2012**, 58 (7), 2254–61.

- 468 [18] Pillon, L. Z. Effect of Dispersants and Flocculants on the Colloidal Stability of
469 Asphaltenes. *Petroleum science and technology* **2001**, 19 (7–8), 863–873.
- 470 [19] Atta, A. M.; El-Ghazawy, R. A.; Morsy, F. A.; Ali, A. M. S.; Elmorsy, A. Adsorption of
471 Polymeric Additives Based on Vinyl Acetate Copolymers as Wax Dispersant and Its
472 Relevance to Polymer Crystallization Mechanisms. *Journal of Chemistry* **2015**, 2015.
- 473 [20] Al-Sabagh, A. M.; El-Din, M. R. N.; Morsi, R. E.; Elsabee, M. Z. Styrene-Maleic
474 Anhydride Copolymer Esters as Flow Improvers of Waxy Crude Oil. *Journal of*
475 *Dispersion Science and Technology* **2009**, 30 (3), 420–426.
- 476 [21] Tinsley, J. F.; Prud'homme, R. K. Deposition Apparatus to Study the Effects of Polymers
477 and Asphaltenes upon Wax Deposition. *Journal of Petroleum Science and Engineering*
478 **2010**, 72 (1–2), 166–174.
- 479 [22] El-Ghazawy, R. A.; Farag, R. K. Synthesis and Characterization of Novel Pour Point
480 Depressants Based on Maleic Anhydride-Alkyl Acrylates Terpolymers. *J. Appl. Polym.*
481 *Sci.* **2010**, 115 (1), 72–78.
- 482 [23] Deshmukh, S.; Bharambe, D. P. Synthesis of Polymeric Pour Point Depressants for Nada
483 Crude Oil (Gujarat, India) and Its Impact on Oil Rheology. *Fuel Processing Technology*
484 **2008**, 89 (3), 227–233.
- 485 [24] Al-Sabagh, A. M.; Atta, A. M.; others. Water-Based Non-Ionic Polymeric Surfactants as
486 Oil Spill Dispersants. *Journal of Chemical Technology and Biotechnology* **1999**, 74 (11),
487 1075–81.
- 488 [25] Comer, D. G.; Stephenson, W. K. *Dispersing Asphaltenes in Hydrocarbon Refinery*
489 *Streams with α -Olefin/maleic Anhydride Copolymer*; Google Patents, 1993.
- 490 [26] Rossi, A. *Pour Point Depressant Additive for Fuels and Lubricants*; Google Patents, 1980.

- [27] Hashmi, S. M.; Firoozabadi, A. Controlling Nonpolar Colloidal Asphaltene Aggregation by Electrostatic Repulsion. *Energy Fuels* **2012**, 26 (7), 4438–4444.
- [28] Hashmi, S. M.; Firoozabadi, A. Field- and Concentration-Dependence of Electrostatics in Non-Polar Colloidal Asphaltene Suspensions. *Soft Matter* **2012**, 8 (6), 1878–1883.
- [29] Hashmi, S. M.; Firoozabadi, A. Effect of Dispersant on Asphaltene Suspension Dynamics: Aggregation and Sedimentation. *J. Phys. Chem. B* **2010**, 114 (48), 15780–15788.
- [30] Adams, P. E.; Wolak, T. J. Lubricant Compositions Containing Ester-Substituted Hindered Phenol Antioxidants. US6787663 B2, September 7, 2004.
- [31] Sedghi, M.; Goual, L.; Welch, W.; Kubelka, J. Effect of Asphaltene Structure on Association and Aggregation Using Molecular Dynamics. *The Journal of Physical Chemistry B* **2013**, 117 (18), 5765–5776.
- [32] Nagarajan, R. On Interpreting Fluorescence Measurements: What Does Thermodynamics Have To Say about Change in Micellar Aggregation Number versus Change in Size Distribution Induced by Increasing Concentration of the Surfactant in Solution? *Langmuir* **1994**, 10 (6), 2028–2034.
- [33] Levine, B.G., Stone, J.E. and Kohlmeyer, A. Fast analysis of molecular dynamics trajectories with graphics processing units—Radial distribution function histogramming. *Journal of computational physics* **2011**, 230 (9), 3556-3569.
- [34] Shvetsov, A. V.; Schmidt, A. E.; Lebedev, D. V.; Isaev-Ivanov, V. V. Method for Calculating Small-Angle Neutron Scattering Spectra Using All-Atom Molecular Dynamics Trajectories. *J. Synch. Investig.* **2014**, 7 (6), 1124–1127.
- [35] Sears, V. F. Neutron Scattering Lengths and Cross Sections. *Neutron news* **1992**, 3 (3), 26–37.

[36] Brunner-Popela, J.; Glatter, O. Small-Angle Scattering of Interacting Particles. I. Basic Principles of a Global Evaluation Technique. *Journal of Applied Crystallography* **1997**, *30* (4), 431–442.

Table 1. Intermolecular interaction energy and number of hydrogen bonds from the last 25 ns of simulation data between the asphaltenes with and without additives in units of kJ/mol

Asphaltene Group	Additive	Van der Waals Energy	Coulomb Energy	Total	H-Bonds
Base	No Additive	-16,978	294	-16,684	-
	5 wt% M1	-14,077	231	-13,846	-
	5 wt% S1	-14,678	224	-14,454	-
	5 wt% S2	-14,931	212	-14,720	-
N-Group	No Additive	-17,640	-428	-18,067	7
	5 wt% M1	-12,818	-95	-12,913	3
	5 wt% S1	-14,299	-260	-14,559	6
	5 wt% S2	-13,927	-117	-14,044	4
O-Group	No Additive	-18,056	-1,388	-19,445	22
	5 wt% M1	-13,273	-843	-14,116	17
	5 wt% S1	-14,648	-574	-15,222	8
	5 wt% S2	-13,623	-639	-14,261	12

Table 2. Interaction energy between polymers over the last 25 ns of simulation in units of kJ/mol

Polymer	Asphaltene Group	Van der Waals Energy	Coulomb Energy	Total	H-bonds
M1	Base	-4,001	-1,895	-5,896	-
	N-Group	-3,289	-1,609	-4,898	-
	O-Group	-3,260	-1,613	-4,873	-
S1	Base	-3,788	527	-3,261	54
	N-Group	-3,441	931	-2,510	44
	O-Group	-3,269	834	-2,435	50
S2	Base	-4,593	-46	-4,638	123
	N-Group	-3,490	328	-3,162	113
	O-Group	-3,199	384	-2,815	115

Table 3. Interaction energy and number of hydrogen bonds from the last 25 ns of simulation data between the asphaltenes and the additives in units of kJ/mol

Asphaltene Group	Polymer	Van der Waals Energy	Coulomb Energy	Total Energy	H-Bonds
Base	5 wt% M1	-4554	-487	-5041	-
	5 wt% S1	-4530	-273	-4802	-
	5 wt% S2	-6020	-536	-6556	-
N-Group	5 wt% M1	-7240	-1173	-8414	5
	5 wt% S1	-6909	-1065	-7974	17
	5 wt% S2	-7570	-1500	-9070	19
O-Group	5 wt% M1	-6751	-1231	-7982	9
	5 wt% S1	-6469	-1593	-8062	30
	5 wt% S2	-7625	-1879	-9504	30

Table 4. Core and tail group interactions of S1 with the asphaltenes normalized by number of atoms per group in units of kJ/mol/atom

Asphaltene Group	Core Group Interaction Energy	Tail Group Interaction Energy
Base	-78	-8
N-Group	-124	-14
O-Group	-135	-12

Table 5. Core and tail group interactions of S2 with the asphaltenes normalized by number of atoms per group in units of kJ/mol/atom

Asphaltene Group	Core Group Interaction Energy	Tail Group Interaction Energy
Base	-47	-21
N-Group	-55	-32
O-Group	-58	-34

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Figure 1. Polymer structures studied in the MD simulations

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Figure 2. Asphaltene models used for simulation.

Figure 3. Z-average aggregation number as a function of time for each asphaltene group at 5 wt% polymer.

Figure 4. Simulation snapshots at the end of 200 ns equilibration of the base asphaltene and polymers in n-pentane. Simulation with no polymer (a), 5 wt% M1 polymer (b), 5 wt% S1 polymer (c) and 5 wt% S2 polymer (d) are shown with polymers in red.

Figure 5. Radial distribution function profiles for the three polymer types with each asphaltene group.

Figure 6. Pair-density distribution functions calculated at the beginning and end of simulation

Figure 7. Simulation snapshots at the end of 200 ns equilibration of the N-Group asphaltenes and polymers in n-pentane. Simulation with no polymer (a), 5 wt% MAC polymer (b), 5 wt% S1 polymer (c) and 5 wt% S2 polymer (d) are shown with polymers in green.

Figure 8. Simulation snapshots at the end of 200 ns equilibration of the O-Group asphaltenes and polymers in n-pentane. Simulation with no polymer (a), 5 wt% MAC polymer (b), 5 wt% S1 polymer (c) and 5 wt% S2 polymer (d) are shown with polymers in green.

Figure 9. Normalized average cluster size for each polymer type throughout the 100 ns solubility simulations in n-pentane.

Figure 10. S1 and S2 polymers before (top row) and after (bottom row) simulation. Hydrogen bonding is shown as red dashed lines

Figure 11. Interaction of the styrene rings (blue) of the MAC polymer with the asphaltene (green) aromatic cores

Figure 12. Stacking of S1 core group on the end of asphaltene aggregate. Asphaltenes are shown in graphite color for clarity

TOC Graphic

Polymers for Asphaltene Dispersion: Mechanisms and Molecular Design Considerations

Evan Lowry, Mohammad Sedghi, Lamia Goual