RICE UNIVERSITY

Interfacial Properties of Polymeric Nanomaterials

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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HOUSTON, TEXAS
November 2017
ABSTRACT

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Polymeric nanomaterials such as nanoparticles and branched polymers are interfacially active and can be used to stabilize or increase the viscosity of an emulsion, which is potentially useful for enhanced oil recovery (EOR) process. However, nanoparticles can be limited in terms of compatibility with different environments, such as elevated salinities and temperature and present challenges for demulsification. The research presented in this dissertation mainly focuses on my work on the development of polymer-coated nanoparticles (PNPs) which are amphiphilic, surface active, and stimuli-responsive. Polymer-coated nanoparticles are prepared by covalently grafting polymers to the surface of the nanoparticles. The interaction of the PNPs with the environment can be tailored through variation of the polymer attached to the nanoparticle surface. In Chapter 2 is the work on the development of carbon black which can segregate to oil-water-surfactant bicontinuous microemulsions. These PNPs are prepared by attaching hydrophobic and hydrophilic chains to the surface of carbon black nanoparticles. By tuning the surface charge through variation of the degree of sulfation, the hydrophobic/hydrophilic properties and stability can be tuned. We find that highly-sulfated PNPs are stable to elevated salinities and spontaneously segregate to oil-
water-surfactant microemulsions. Chapter 3 is the development of pH-responsive PNPs. These are prepared by grafting a pH-responsive polymer to silica nanoparticles. These nanoparticles can emulsify crude oil, and be quickly demulsified through a change in pH. We demonstrate that the use of 0.1 wt % of pH-responsive PNPs enhance the recovery of crude oil in a sandpack. This work demonstrates the versatility and potential of PNPs for a variety of applications, including oil recovery, controlled emulsification and demulsification, and reduction of interfacial tension.

Chapter 4 is the study of aqueous self-assembly of bottlebrush block copolymers, which have similarity to polymer-coated nanoparticles in many aspects. It is able to self-assemble rapidly to form structures with large periodic domains and form stable micelles with very low critical-micelle concentrations (CMC). In this work, we have studied a library of amphiphilic bottlebrush polymers with different ratio of hydrophilic and hydrophobic chains, and demonstrated a lower CMC of bottlebrush polymer over linear copolymers. Some primary work to quantify the self-assembly of a model library of amphipilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurement is discussed.
Acknowledgments

First and foremost I want to thank my advisors Dr. Verduzco and Dr. Hirasaki for their guidance in the Ph.D. pursuit. I appreciate all their contribution of time, thoughts and funding to make my Ph.D. study enjoyable and productive. And I feel much honored to witness some important moments in their careers as well: Dr. Verduzco promoted to associate professor position and Dr. Hirasaki being awarded the Anthony F. Lucas Gold Medal by the Society of Petroleum Engineers (SPE). I feel very proud as their student.

I would like to sincerely thank Dr. Biswal and Dr. Tomson for serving in my thesis committee. I also acknowledge Rice Consortium for Process in Porous Media and Advanced Energy Consortium (AEC) for their financial support of my Ph.D. research.

The members of both Verduzco group and Hirasaki group have contributed tremendously to my personal and professional success at Rice University. I want to thank Dr. Li and Dr. Pesek for the help in my synthesis, Dr. Lin in SAXS analysis, Dr. Shamsilazeyi in phase behavior studies, Dr. Wang in data analysis and modeling, as well as Dr. Zeng and his help in my job interview. I would also like to thank collaborators at Virginia Tech, Dr. Matson and Mr. Mohammed Alaboalirat as well as collaborators at Oak Ridge National Laboratory (ORNL), Dr. Qian and Dr. Keum. Without them, none of my work would be possible. I’m also thankful with the underground students who had worked with me.
In the meantime I want to thank KRÜSS and its wonderful collaboration with my laboratory. And the internship experience at KRÜSS is wonderful. I want to thank KRÜSS friends Mr. Ferraco, Mr. McCarthy, Dr. Sanedrin etc. I had a really pleasant summer in Charlotte, NC.

Last but not least, I would like to thank my parents and my wife for the sacrifice they have made for me and their unconditional love. I owe a lot to them.
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Chapter 1

Introduction

This chapter covers the background information on oil recovery process, nanoparticles (NPs) and polymer-coated nanoparticles (PNPs), as well as some EOR mechanism of NPs/PNPs.
With the strong economic growth in the worlds, there is a growing demand for energy. EIA's released International Energy Outlook in 2013 (IEO2013) has predicted that world energy consumption will grow by 56% between 2010 and 2040, from 524 quadrillion British thermal units (Btu) to 820 quadrillion Btu.\textsuperscript{1}

Renewable energy and nuclear power are the world's fastest-growing energy sources, each increasing 2.5 % per year. However, fossil fuels continue to supply nearly 80 % of world energy use through 2040.\textsuperscript{2}

![Figure 1.1 World energy consumption by energy source](image)

Petroleum is currently having the largest consumption and demand among all the fossil fuels. Accordingly, the production of petroleum oil is going to increase with the demand. As the production rate of existing fields are declining and the frequency of new explorations become slow, exploration of newer oil production technology is always a desire.

**1.1. Oil Recovery Process**
Oil recovery is the process to extract crude oil from reservoir. It is well known that there exist three steps of recovery in the oil production process in reservoir, namely primary oil recovery, secondary oil recovery and tertiary oil recovery (Enhanced Oil Recovery).  

![Figure 1.2 Schematic of oil recovery process](image)

**1.1.1. Primary Oil Recovery**

Primary oil recovery is the first stage of oil and gas production. In this process natural reservoir drives are used to recover hydrocarbons. The natural pressure inside the oil reservoir originates from solution-gas drive, natural-water drive, gas-cap drive, gravity drainage and fluid expansion. Due to the difference in pressure within the reservoir and at the bottom of the well, hydrocarbons are driven towards the well and to the surface. Comparing with other steps of recovery, oil and gas companies will expend less money retrieving the resources from the ground during this stage. The pressure of the reservoir will deplete as the production is performed. And thus during primary recovery, typically only 5-15 % of initial hydrocarbons are produced for oil reservoirs.
1.1.2. Secondary Oil Recovery

During the second stage of oil production, an external fluid such as water or gas is injected into the reservoir through injection wells. The purpose of secondary recovery is to maintain reservoir pressure and to displace hydrocarbons toward the wellbore. The most common secondary recovery techniques are gas injection and water flooding.\(^5\)

Gas or water is normally injected into the production zone to sweep oil from the reservoir. The secondary recovery stage reaches its limit when the injected water or gas is produced in considerable amounts from the production wells and the production is no longer economical. The successive use of primary recovery and secondary recovery in an oil reservoir produces about 15% to 40% of the original oil in place.\(^6\)

1.1.3. Enhanced Oil Recovery

Tertiary oil recovery, which is also called enhanced oil recovery (EOR), comprises recovery methods that follow water flooding and pressure maintenance. And the techniques used in EOR usually include thermal methods, gas methods and chemical methods.\(^7\)–\(^11\)

Thermal methods mainly introduce heat into heavy oil reservoirs through various methods, such as CCS, steam flooding and SAGD, to better the flow ability of the heavy oil or bitumen in reservoirs by changing its viscosity and density.

Gas methods utilize hydrocarbon gases (CH\(_4\), C\(_3\)H\(_8\) or natural gas) or non-hydrocarbon gases (N\(_2\), or CO\(_2\)) that dissolve in the oil. In this way, the injected gas can improve oil recovery by decreasing oil viscosity and expanding oil volume.
Chemical methods mainly use surfactants, polymers, alkaline chemicals or micro-emulsions to increase the effectiveness and decrease interfacial tension (IFT) that often prevents oil from flowing in oil reservoirs

<table>
<thead>
<tr>
<th>EOR technique</th>
<th>Working Principle</th>
<th>Outcome / Results</th>
<th>When to use</th>
<th>Recovery rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Injection</td>
<td>Injecting gas or nitrogen (immiscible)</td>
<td>Push out crude or thinner, reduce rock-oil surface tension</td>
<td>Follow-up to water injection development (WAG – Water Alternating Gas Injection)</td>
<td>35% (variable)</td>
</tr>
<tr>
<td>Thermal Injection</td>
<td>Heat is injected into the reservoir to reduce the viscosity of the oil</td>
<td>Oil becomes lighter and flows more easily</td>
<td>Heavy crude fields</td>
<td>Up to 70%</td>
</tr>
</tbody>
</table>
| Chemical Injection | Different types of chemicals (Polymer, Surfactants and others) | • Reduce interfacial tension  
  • Increase flooded water viscosity | Follows waterflood to capture residual oil, Sandstone reservoir and less Limestone | up to 15% incremental |
| CO2 injection   | Injecting Carbon Dioxide (CO2)                        | CO2 swells oil and reduces viscosity         | Follows waterflood to capture residual oil (generally used in Limestone reservoir) | up to 15% incremental |

Figure 1.3 Comparison of different EOR techniques

1.1.3.1. Chemical EOR

In the process of chemical EOR, different combination of alkaline, surfactant and polymers may be used depending on the characteristics of the reservoir such as permeability, temperature, surface chemistry of the rock etc. Some common formulations include Surfactant-Polymer (SP) flooding, Alkaline-Surfactant Polymer (ASP) flooding, Alkaline-Polymer (AP) flooding.

Current challenges in chemical EOR process include high cost of chemicals, possible formation damages, and chemical loss. Therefore, the design of less expensive, more efficient and environment friendly material and method is always a desire.
1.2. Nanoparticles (NPs) and Polymer-coated Nanoparticles (PNPs)

NPs are defined as particles with size range from 1nm to 100nm, and some special characteristics make it potentially a good solution for the challenges in EOR.\textsuperscript{12}

Ultra-small size: The size of commonly used NPs is always smaller compared to pore size in porous media and thus they can easily flow through porous media without severe plugging or being trapped.

High surface to volume ratio: NPs have a high surface to volume ration due to the small particle size. The large surface area leads to a relatively higher surface energy and that provides a huge driving force to change the wettability and fluid properties.

Low cost: The NPs materials could be obtained from a variety of resources and the price is usually cheaper than chemicals.

Recently, there has been increasing interest in nanoparticles and polymer coated nanoparticles (PNPs), which are nano-size particles with polymer chains grafted to surface, as additive that could be used in oil recovery process.\textsuperscript{13–15} They are interfacially active and have been shown to stabilize macroscopic emulsions of oil and water. And the surface properties such as interfacial tension and salinity resistance are very tunable with the control of surface polymer coating.
1.3. EOR Mechanism of NPs/PNPs

The EOR mechanism has been studied for a long time; however, the EOR mechanism of NPs has not been totally understood yet. The commonly accepted approaches of NPs in EOR process include pore channel plugging, mobility ratio control, IFT reduction, wettability alternation and nanoemulsions.

1.3.1. Pore Channel Plugging

Log-jamming is one of the main reasons for core channel plugging. It happens when a nanofluid flows from pores to throats. The narrowing of flow area will lead to a difference between the velocity of water molecules and NPs, accumulating the slower NPs at the pore throats. With the blockage of pore throat, pressure builds up in the adjacent pores, and that helps the trapped oil to be pushed out. This phenomenon is correlated with the concentration and size of NPs, flow rates and pore size.$^{16,17}$

1.3.2. Mobility Ratio Control

The mobility ratio is defined by the following expression,$^{18}$

$$M = \frac{\lambda_i}{\lambda_o} = \frac{k_{ri}/\mu_i}{k_{ro}/\mu_o} = \frac{k_{ri}\mu_o}{k_{ro}\mu_i}$$

Equation 1.1 Mobility Ratio

In this equation, $\lambda_i$ and $\lambda_o$ are the mobility of injected fluid and oil, respectively; $k_{ri}$ and $k_{ro}$ are relative permeabilities of injected fluids and oil, respectively; $\mu_i$ and $\mu_o$ are viscosities of injected fluids and oil, respectively. The viscosity of injected fluid is
usually lower than that of crude oil, thus the mobility ratio is high without addition of NPs. For oil recovery process, a lower mobility ratio is desired in order to obtain a good sweeping efficiency.\textsuperscript{19,20}

The viscosity of a nanofluid depends on several factors including shear rate, temperature etc, and It has been shown that by adding NPs into traditional fluids, the viscosity of injected fluids can be essentially increased as well.\textsuperscript{21}

1.3.3. IFT Reduction

IFT is a main factor in determining the partitioning of crude oil into injected fluids as well as the movement of fluids in porous media. And reducing IFT between oil and water is one of the main mechanisms in EOR process. NPs and PNPs are surface active and can be potentially used for IFT reduction.\textsuperscript{22,23}

The IFT between crude oil and nanofluids is usually measured by pendant drop method. During the measurement, an oil droplet is generated from the end of a capillary needle in a nanofluid at experimental conditions (pressure and temperature). The IFT result is calculated by analyzing the shape of the oil droplet by an accurate video system and analysis software.

1.3.4. Wettability Alternation

The definition of rock wettability is the tendency of a fluid to adhere to the rock surface competing with another immiscible fluid. It is a key factor to govern oil recovery by affecting capillary pressure, fluids saturation, and relative permeability. Nanoparticles are surface active and can be absorbed onto the rock surface during the injection of
nanofluids, thus they have been widely explored as potential agents to alter wettability. Contact angle method is the mostly commonly used method for wettability measurement.24

1.3.5. Nanoemulsions

Nanoemulsion is defined as the emulsion stabilized by NPs. Compared with conventional emulsion stabilized by surfactant, nanoemulsions have some special characteristics.25

1) Nanoemulsions have better stability under harsh conditions. This is because the adsorption on NPs on interface is irreversible and it would require extra energy to removed NPs from interface.

2) Nanoemulsions tend to have higher viscosity and would have more significant effect on mobility control.

3) Nanoemulsions are small enough to penetrate through pore media without much retention.

All these characteristics of nanoemulsion make it a good approach for EOR process and already attract large numbers of researches on this.
Chapter 2

Segregation of Amphiphilic Polymer-Coated Nanoparticles to Bicontinuous Oil/Water Micro-emulsion Phases

Chapter 2 was published in Energy Fuels, 2017, 31(2), 1339-1346

In this chapter we show that properly designed amphiphilic polymer-coated nanoparticles spontaneously and preferentially segregate to the bicontinuous micro-emulsion phases of oil, water, and surfactant. Mixtures of hydrophilic and hydrophobic chains are covalently grafted onto the surface of oxidized carbon black nanoparticles and the polymer-coated nanoparticles are stable in the aqueous phase at salinities up to 15 wt% NaCl. These amphiphilic nanoparticles segregate to the bicontinuous micro-emulsion phases. We analyzed the equilibrium phase behavior of the nanoparticles, measured the interfacial tension, and quantified the domain spacing in the presence of nanoparticles. This work shows a novel route to the design of polymer-coated nanoparticles which are
stable at high salinities and preferentially segregate to bicontinuous micro-emulsion phases.

2.1. Chapter Introduction

Nanoparticles are of interest as additives for EOR processes since they can be used to tailor interfaces and can propagate through porous media. A number of studies have focused on micron-and nano-sized surface active nanoparticle additives for stabilizing oil-water emulsions, mobility control of the injected flood, and wettability alteration of the surface to increase the efficiency of EOR processes. For example, Binks et al. studied water-in-oil macro-emulsions stabilized by Latex particles and found that, in the case of micron-size colloidal particles, the interaction with the interface was dominated by irreversible adsorption. The group also demonstrated that silica nanoparticles could be used to stabilize oil-in water macro-emulsions when blended with anionic or cationic surfactant, respectively. Johnston and coworkers studied a series of iron-oxide nanoparticles coated with amphiphilic or charged polymers and found a decrease in the value of oil-water interfacial tension and, in the case of charged polymer coatings, both good stability in high-salinity environments and low adsorption onto silica surfaces. This group and Krishnamoorti et al. also studied iron-oxide clusters and silica nanoparticles coated with poly[oligo(ethylene oxide) monomethyl ether methacrylate] and demonstrated a significant reduction in interfacial tension at very low nanoparticle concentrations (1 – 10 ppm). Harwell and coworkers demonstrated that surfactants could be used to disperse multi-walled carbon nanotubes in aqueous solution and transport them through porous media with little or no adsorption. Cui et al. found that
nanoparticle/surfactant mixtures could be used to deform emulsion droplets into non-
spherical shapes due to jamming of the nanoparticles at the oil-water interface.\textsuperscript{38} Lead and coworkers reported polymer-coated nanoparticles that could be used to separate oil-
water mixtures.\textsuperscript{39,40} Other studies with polymer-coated nanoparticles at the oil-water
interface are discussed in recent review articles.\textsuperscript{41,42}

Bicontinuous micro-emulsions are thermodynamically stable phases formed by a
mixture of oil, water and surfactant.\textsuperscript{43–45} In addition to bicontinuous, nanoscopic domains
of oil and water, these phases are characterized by an ultralow interfacial tension between
oil and water. As such, these phases are of interest for surfactant-enhanced oil recovery,
in which oil can be solubilized and mobilized in the bicontinuous micro-emulsion
phase.\textsuperscript{46} While prior work has clearly demonstrated the potential of polymer-coated
nanoparticles for stabilizing emulsions, previous studies have not investigated the
interaction of such nanoparticles with oil-water micro-emulsions.

Here, we propose that properly designed, polymer-coated nanoparticles can
segregate to surfactant-stabilized oil-water micro-emulsions, as shown schematically in
Figure 1. We prepare a series of oxidized carbon black (OCB) nanoparticles with a
mixture of hydrophilic and hydrophobic chains covalently grafted to the surface. We find
that nanoparticles coated with a mixture of negatively charged polymer chains and
hydrophobic chains are stable in water at elevated salinities (up to 15 wt % NaCl). When
mixed with surfactants that stabilize the formation of bicontinuous oil-water phases, the
polymer-coated nanoparticles migrate preferentially to the bicontinuous micro-emulsion
phase. We detail the preparation of the polymer-coated nanoparticles, their phase
behavior in oil-water-surfactant mixtures, and their impact on oil-water interfacial
properties. This work points to a novel property of polymer-coated nanoparticles and their specific interaction with bicontinuous phases. Combined with other favorable properties of nanoparticle additives, we envision this work will lead to future developments of nanoparticle additives which can segregate to bicontinuous phases, propagate through porous media, modify interfacial properties, and enhanced the efficiency of enhanced oil recovery processes.

2.2. Experimental Methods

2.2.1. Chemicals

Carbon black nanoparticles were purchased from Cabot Corporation (Monarch 1300, Lot # 944884), with a diameter of 15 nm. Solvents and reagents were obtained from commercial suppliers and used as received. C<sub>12</sub>-orthoxylene sulfonate (OXS) surfactant was provided by Exxon, S13B 23-71SM surfactant was provided by TIORCO, and ALFOTERRA series surfactants (AF K2-4 1S and AF K3-4 1S) were obtained from Sasol. The surfactants used in this study are shown in Figure 2.1

![Chemical structure](image)

Figure 2.1 Chemical structure for (a) OXS (b) S13B 23-71SM (c) ALFOTERRA K2-4 1S (d) ALFOTERRA K3-4 1S
2.2.2. Preparation of Amphiphilic Oxidized Carbon Black Nanoparticles

The starting material is the commercially available carbon black nanoparticle. It is firstly modified by oxidation, followed by attaching hydrophobic/hydrophilic chains at different ratio. The amphiphilicity can also be controlled by different degree of sulfation of poly(vinyl alcohol) (PVA) chains. (Figure 2.2)

Figure 2.2 Reaction scheme for the surface modification of oxidized carbon black nanoparticles (OCB). sPVA: lightly sulfated PVA, ssPVA: highly sulfated PVA

Oxidation of OCB. Oxidized carbon black nanoparticles (OCB) were prepared as follows. 9:1 v/v mixture of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 mL) was added to a mixture of carbon black nanoparticles (3.0 g) and KMnO$_4$ (18.0 g). The reaction was heated to 50 °C and stirred for 12 h. The reaction was then cooled to room temperature and poured over ice (~ 400 mL) with 30 % H$_2$O$_2$ (3 mL). The dispersion was then centrifuged (6000 rpm, 4 h) and the supernatant discarded. The remaining solid material was then washed with 200 mL of 30 % HCl two times, each time followed by centrifugation and decanting of the supernatant. Finally, the OCB nanoparticles were dialyzed in water for one week using dialysis membrane (MWCO of 1 kD). The resulting
nanoparticles were then collected by filtration after adding hexanes to aggregate the nanoparticles and dried under vacuum.

**PVA-OCB.** Hydrophilic poly(vinyl alcohol) (PVA)-coated OCB nanoparticles were prepared by covalently attaching PVA to the OCB surface. First, OCB (25 mg) and PVA (2000 g/mol, 75-80 % hydrolyzed, 2.1 g) were dispersed in DMF (25 mL). Next, N,N'-dicyclohexylcarbodiimide (DCC, 206 mg) and 4-(dimethylamino)pyridine (DMAP, ~100 mg) were added to the reaction. The reaction mixture was bath ultrasonicated for 10 min prior to heating to 70 °C for one day. The resulting polymer-coated nanoparticles were dialyzed in water for one week using dialysis membrane (MWCO of 50 kD). The nanoparticles were collected by filtration after adding hexanes to aggregate the nanoparticles and dried under vacuum.

**C\textsubscript{16}-PVA-OCB.** Amphiphilic OCB nanoparticles were prepared by covalently attaching PVA and hydrophobic C\textsubscript{16}H\textsubscript{33}OH (C16) chains to the surface. First, OCB (25 mg), DCC (206 mg), DMAP (100 mg), and C16 (250 mg) were dispersed in DMF (25 mL). The reaction was carried out at 90 °C for 3 days. Next, PVA was attached to the surface of these nanoparticles. PVA (2.1 g) was added to the reaction along with additional DCC (150 mg), the reaction mixture was bath ultrasonicated for 10 min prior to stirring at 70 °C for one day. The resulting polymer-coated nanoparticles were dialyzed in DMF for 3 days at 50 °C and then in water for one week using dialysis membrane (MWCO of 50 kD). The nanoparticles were collected by filtration after adding hexanes to aggregate the nanoparticles and dried under vacuum.
sPVA-OCB, C_{16}-sPVA-OCB and C_{16}-ssPVA-OCB. Polymer-coated nanoparticles with sulfated PVA (sPVA) chains attached were prepared by sulfating PVA-OCB or C_{16}-PVA-OCB nanoparticles. For conducting full sulfation, sulfur trioxide pyridine complex (26 mg) was added to the nanoparticle (32 mg) dispersion in DMF (1.5 mL) at 60 °C under nitrogen purge, and the reaction was allowed to proceed for 1 day. For conducting partial sulfation, 6.4 mg of the pyridine complex is added to the same amount of nanoparticle (32 mg). sPVA-OCB was dialyzed in water for one week using dialysis membrane (MWCO of 50 kD). C_{16}-sPVA-OCB and C_{16}-ssPVA-OCB were dialyzed in DMF for 3 days at 50 °C and then in water for one week using dialysis membrane (MWCO of 50 kD). The nanoparticles were collected by filtration after adding hexanes to aggregate the nanoparticles and dried under vacuum.

**2.2.3. Instrumentation and Characterization**

**Dynamic Light Scattering (DLS) Measurement.** Dynamic light scattering was carried out using a Malvern Instruments Zen 3600 Zetasizer. Polymer-coated nanoparticles were dispersed in water at a concentration of 5-10 ppm for analysis.

**Phase Behavior Studies.** Phase behavior studies of oil, water, surfactant, and polymer-coated nanoparticle were carried out using 3 mL made from cutting 5 mL borosilicate, serological pipettes. First, the pipettes were filled with the desired amount of brine (aq. NaCl), oil (n-octane), surfactant, and polymer-coated nanoparticle. Except where noted, the surfactant was 2 vol % of the aqueous phase and the polymer-coated nanoparticle concentration was 0.2 wt % of the aqueous phase. 2.5 wt % sec-butyl alcohol was added to avoid the formation of thick macro-emulsion phases. To equilibrate the mixture in each
pipette, pipettes were sealed with a torch prior to mixing and mixed overnight on a shaker. The final mixtures were allowed to rest at room temperature and photographed when the phase was stabilized.

**Thermo-Gravimetric Analysis (TGA).** TGA measurements were carried out on a Q-600 TGA from TA instruments. The samples were heated from 25 °C to 900 °C at a rate of 10 °C/min under nitrogen atmosphere.

**Interfacial Tension (IFT) Measurement.** A spinning drop interfacial tensiometer (Krüss SITE100) was used to measure oil-water IFT.

**Small-angle X-ray Scattering.** Small angle X-ray scattering (SAXS) measurements were carried out on Sector 8-ID-E at the Advanced Photon Source Argonne National Laboratory. Beamline 8-ID-E operates at energy of 7.35 keV, and images were collected from a Pilatus 1MF camera (Dectris), with two exposures for different vertical position of the detector. After flat-field correction for detector nonuniformity, the images were combined to fill in the gaps for rows at the borders between modules, leaving dark only the columns of inactive pixels at the center. Using the GIXSGUI package for MATLAB (MathWorks), data were corrected for X-ray polarization, detector sensitivity, and geometrical solid angle.

SAXS samples were prepared from equilibrated phase behavior samples. Extracts were carefully taken from the micro-emulsion layer of phase-separated samples and transferred to quartz capillaries (Hampton Research, OD=1.5 mm). Immediately after that the top of capillary was sealed with wax. A series of ten samples were aligned onto a specially-made holder and then transferred into a vacuum chamber. Sample
measurements were carried out under vacuum which is in the range of $2 \sim 3 \times 10^{-6}$ bar, with the sample stage interfaced with a Lakeshore 340 unit. The beam size is 200 μm (h) x 20 μm (v). Sample detector distance was 208 mm.

A series of polymer-coated nanoparticles were prepared by either attaching hydrophilic poly(vinyl alcohol) (PVA) chains or a mixture of hydrophilic PVA and hydrophobic C16 alkyl chains to the surface of oxidized carbon black. Surface functionalities on carbon black nanoparticles were introduced through oxidation, and hydrophobic or hydrophilic chains were covalently grafted to the nanoparticle surface through a Steglich esterification reaction between carboxylate groups on the nanoparticle surface and hydroxyl groups on the polymer. In order to improve nanoparticle stability in high-salinity aqueous media, selected polymer-coated nanoparticles were partially sulfated, resulting in nanoparticles coated with charged sulfated PVA (sPVA) chains. (Figure 2.3) The phase behavior of these nanoparticles in aqueous media is detailed below.

![Library of NPs with amphiphilic polymer chains on the surface](image)

Figure 2.3 Library of NPs with amphiphilic polymer chains on the surface
The polymer content and size of the nanoparticles was measured through thermogravimetric analysis (TGA) and dynamic light scattering (DLS), respectively, and the results are shown in Table 2.1 and Figure 2.4. The polymer content is greater than 70 wt % for all samples prepared, and an increase in the size of the polymer-coated nanoparticles is observed after sulfation, which we attribute to electrostatic interactions between the charged sPVA chains on the nanoparticle surface. The lower polymer content for C\textsubscript{16}-ssPVA-OCB may be due to partial hydrolysis and removal of the chains attached to the nanoparticle surface during the extended sulfation reaction. This is also reflected in a drop in size of the C\textsubscript{16}-ssPVA-OCB nanoparticles after extended sulfation relative to C\textsubscript{16}-sPVA-OCB.

Table 2.1 Polymer fraction by TGA and size measurement by DLS

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Polymer content\textsuperscript{a} (wt %)</th>
<th>Size\textsuperscript{b} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCB</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>PVA-OCB</td>
<td>91</td>
<td>54</td>
</tr>
<tr>
<td>sPVA-OCB</td>
<td>81</td>
<td>170</td>
</tr>
<tr>
<td>C\textsubscript{16}-PVA-OCB</td>
<td>91</td>
<td>72</td>
</tr>
<tr>
<td>C\textsubscript{16}-sPVA-OCB</td>
<td>97</td>
<td>151</td>
</tr>
<tr>
<td>C\textsubscript{16}-ssPVA-OCB</td>
<td>72</td>
<td>123</td>
</tr>
</tbody>
</table>

\textsuperscript{a}measured by thermogravimetric analysis.
\textsuperscript{b}measured by dynamic light scattering in DI water.
2.3. PNP Interfacial Properties and its Segregation into Micro-emulsion

2.3.1. PNP Phase Behavior Without Addition of Surfactant

We investigated the equilibrium phase behavior of polymer-coated nanoparticles in the presence of oil and water of varying salinity. The nanoparticle concentration was kept at 0.2 wt %, and the solubility and dispersion of the NPs was monitored as a function of changing water salinities. Mixtures were equilibrated by shaking overnight at ambient temperature and then allowing 2 days for oil and aqueous phases to separate. We used a paraffinic, transparent oil (n-octane), and the distribution of nanoparticles can be identified visually, as shown in Figure 2.5. The polymeric coating had a significant
impact on nanoparticle solubility and stability. Unmodified OCB and PVA-OCB were only dispersed in the aqueous phase at low salinities but were aggregated at higher salinities (Figure 2.5a and 2.5b). These nanoparticles do not stabilize oil-water emulsions and precipitate out at elevated salinities, (0-4 wt % NaCl for OCB and 4-8 wt % NaCl for PVA-OCB).

By contrast, polymer coated nanoparticles with a charged polymer coating (sPVA-OCB and C$_{16}$-sPVA-OCB) remained dispersed in the aqueous phase over a range of salinities. As shown in Figures 2.5c and 2.5d, these polymer-coated nanoparticles do not aggregate even at salinities as high as 16 wt % NaCl. The particles were surface active and stabilized the formation of Pickering macro-emulsion phases, which did not break even after weeks at room temperature. The amphiphilic nanoparticles C$_{16}$-sPVA-OCB were found to stabilize Pickering macro-emulsions over a much broader range of salinities, from 0 to 16 wt % NaCl, while the more hydrophilic sPVA-OCB nanoparticles stabilized macro-emulsions over a narrower salinity range of 5.3-11.4 wt % NaCl (Figure 2.5c). None of the polymer-coated nanoparticle additives produced a bicontinuous micro-emulsion phase.
Figure 2.5 Equilibrium phase behavior for nanoparticles (0.2 wt %) in oil and water: (a) uncoated OCB; (b) PVA-OCB nanoparticles; (c) sPVA-OCB nanoparticles; (d) C\textsubscript{16}-sPVA-OCB nanoparticles. The upper phase is the oil phase and the bottom phase the aqueous phase for all samples shown.

### 2.3.2. PNPs Surface Tension and CMC Behavior

Nevertheless, we do note that the polymer-coated nanoparticles do exhibit some surface activity. As shown in Figure 2.6, a dispersion of C\textsubscript{16}-ssPVA-OCB nanoparticles exhibit a 25 mN/m decrease in surface tension (from 70 to 45 mN/m) at a concentration of just 500 ppm (0.05 wt %). Furthermore, a measurement of the interfacial tension at the oil-water interface shows a decrease from approximately 50 mM/m to 17.1 mN/m (sPVA-OCB) and 11.6 mN/m (C\textsubscript{16}-ssPVA-OCB) at just 0.1 wt % PNP concentration as shown in the Table 2.2. These reductions in oil-water interfacial tension are comparable to other nanoparticles in the literature, for example silica nanoparticles coated with poly(oligo(ethylene oxide) monomethyl ether methacrylate) which exhibit a reduction
down to 10 mN/m for < 10 ppm nanoparticles. These interfacial tension values are still too high, however, to stabilize a bicontinuous oil-water micro-emulsion phase.

Figure 2.6 Surface tension of C₁₆-ssPVA-OCB in aqueous dispersion. With the addition of PNP, a decrease of over 30 mN/m in surface tension is observed at PNP concentration of 500 ppm (0.05 wt %). Similar to critical micelle concentration, the PNP shows a characteristic of critical nanoparticle concentration (CPC) at concentration near to 300 ppm (0.03 wt %). Surface tension measured by Wilhelmy plate method with Force Tensionmeter K100 from Krüss.

Table 2.2 Interfacial tension measurement between n-octane without PNP and with 0.1 wt % sPVA-OCB, 0.1 wt % C₁₆-ssPVA-OCB. PNP concentration is higher than critical nanoparticle concentration for both cases. Interfacial tension measured by spinning drop method with Spinning Drop Tensiometer SITE100 from Krüss.

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Interfacial Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No PNP</td>
<td>50.8</td>
</tr>
<tr>
<td>sPVA-OCB</td>
<td>9.4</td>
</tr>
<tr>
<td>C₁₆-ssPVA-OCB</td>
<td>5.7</td>
</tr>
</tbody>
</table>
2.3.3. PNP Phase Behavior With Addition of Surfactant

The results above show that the polymer-coated nanoparticles are surface active, and that nanoparticles coated with a hydrophilic and negatively charged polymer (sPVA) are stable at high salinities, as high as 15.6 wt % NaCl. Further, polymer-coated nanoparticles with mixed hydrophobic and hydrophilic chains (C\textsubscript{16}-sPVA-OCB) stabilize oil-water macro-emulsions over a broad salinity range. However, these additives do not lead to the formation of bicontinuous oil-water phase which are of interest for enhanced oil recovery due to their characteristic ultralow oil-water interfacial tension. To investigate the interaction of polymer-coated nanoparticles with such bicontinuous phases, surfactants were added to the oil-water-nanoparticle mixture. Prior studies have been looked at mixtures of nanoparticles and surfactants in solution,\textsuperscript{48-51} but not for the formation of bicontinuous oil-water phases.

Four different surfactants were studied, as shown previously in Figure 2.1, each of which stabilizes a bicontinuous oil-water phase over a characteristic salinity range. Over this salinity range, the oil-water interfacial tension is ultralow (< 10\textsuperscript{-2} mN/m), and the optimal salinity is denoted as the minimum in oil-water interfacial tension.\textsuperscript{52} Figure 2.7 shows an example phase behavior study of OXS surfactant without nanoparticle (Figure 2.7a) and with either C\textsubscript{16}-sPVA-OCB polymer coated nanoparticle (Fig. 2.7b) or C\textsubscript{16}-ssPVA-OCB polymer-coated nanoparticle (Fig. 2.7c). The bicontinuous micro-emulsion phase can be visually distinguished as a hazy ‘middle phase’ between the upper oil phase and lower aqueous phase. OXS surfactant stabilized the formation of a bicontinuous micro-emulsion phase over the salinity range of approximately 1.6-1.9 wt % NaCl. At salinities below 1.6 wt % NaCl an oil-in-water macro-emulsion (lower phase) is observed.
and at salinities above 1.9 wt % NaCl a water-in-oil macro-emulsion (upper phase) is observed.

Figure 2.7 Phase behavior of C_{12}-orthoxylene sulfonate (OXS) and polymer-coated nanoparticles in octane-water mixtures: (a) OXS (2 wt %) (b) OXS (2 wt %) and 0.1 wt % C_{16}-sPVA-OCB and (c) OXS (2 wt %) and 0.1 wt % C_{16}-ssPVA-OCB. 2.5 wt % sec-butyl alcohol was added to all samples shown.

With the addition of C_{16}-sPVA-OCB and C_{16}-ssPVA-OCB polymer-coated nanoparticles, the middle phase persists and, notably, nanoparticles segregated exclusively to bicontinuous micro-emulsion phases. As shown in Figures 2.7b and 2.7c, the nanoparticles were clearly observed inhabiting only the middle phase over the range of salinities where a middle phase micro-emulsion phase forms. No nanoparticles were present in the upper oil or lower aqueous phases when a middle phase is present. At lower and higher extremes in salinity, the nanoparticles segregated to oil-in-water macro-emulsion or water-in-oil macro emulsion phases, respectively. In the presence of the polymer-coated nanoparticles, bicontinuous micro-emulsion phases were formed over a similar range of salinities, with a slight shift to higher salinities on the addition of polymer-coated nanoparticles.
2.3.4. Effect of Charge Repulsion - Degree of Sulfation

While both charged amphiphilic polymer-coated nanoparticles (C\textsubscript{16}-sPVA-OCB and C\textsubscript{16}-ssPVA-OCB) segregated exclusively to bicontinuous micro-emulsion phases of surfactants with relatively low optimal salinities, the degree of sulfation affected the stability of dispersed nanoparticles in the aqueous media. For example, in the cases of S13B surfactant which exhibits an optimal salinity near 4.3 wt %, we observed aggregation of C\textsubscript{16}-sPVA-OCB nanoparticles. By comparison, the more highly sulfated C\textsubscript{16}-ssPVA-OCB nanoparticles were stable at these higher salinities and segregated to the bicontinuous middle phases, as shown in Figure 2.8.

![Figure 2.8](image)

Figure 2.8 Phase behavior of S13B surfactant and polymer-coated nanoparticles in octane-water mixtures: (a) S13B (2 wt %) (b) S13B (2 wt %) and 0.1 wt % C\textsubscript{16}-ssPVA-OCB (c) S13B (2 wt %) and 0.1 wt % C\textsubscript{16}-sPVA-OCB. 2.5 wt % sec-butyl alcohol was added to each sample.

Next, we tested the phase behavior of the highly sulfated C\textsubscript{16}-ssPVA-OCB nanoparticles in the presence of surfactants with ultra-high optimal salinities, i.e. K3-4 1S and K2-4 1S. These surfactants exhibit optimal salinities at approximately 12 wt % NaCl and 15 wt % NaCl, as shown in Figures 2.9 a and 2.9 c. Even at these extreme salinities,
$C_{16}$-ssPVA-OCB remained dispersed and segregated exclusively to the oil-water middle phase. Aggregation of the nanoparticles was observed at 16 wt % NaCl, as shown in Figure 2.9d.

These results are surprising since most nanoparticles are not stable at such high salinities and the amphiphilic nanoparticles were found to segregate strongly and exclusively to bicontinuous micro-emulsion phases. Such segregation of nanoparticles to micro-emulsion middle phases has not been previously reported. These phase behavior studies clearly demonstrate that the use of an amphiphilic nanoparticle coating along with a charged, highly sulfated polymer results in polymer-coated nanoparticles that are stable at high salinities and migrate to micro-emulsion middle phases.

Figure 2.9 Phase behavior of K 3-4 1S, K 2-4 1S, and polymer-coated nanoparticle additives: (a) 2 wt % K3-4 1S (b) 2 wt % K3-4 1S and 0.1 wt % $C_{16}$-ssPVA-OCB (c) 2 wt % K2-4 1S (d) 2 wt % K2-4 1S and 0.1 wt % $C_{16}$-ssPVA-OCB. 2.5 wt % sec-butyl alcohol is added in all cases.
2.4. Influence of PNPs Additive on IFT of Oil-Water-Surfactant

Micro-emulsion

The formation of bicontinuous micro-emulsion phases reflect an ultralow oil-water interfacial tension (IFT), and we were interested in understanding the impact of the polymer-coated nanoparticles on the interfacial tension and domain size. Two methods were used to measure the oil-water IFT. First, the interfacial tension was directly measured through spinning drop tensiometry. A second approach was the application of an empirical relationship for the IFT for micro-emulsion phases that can be extracted from the phase behavior studies, as reported by Huh. This approach involves measuring the volume of oil \( V_o \) and water \( V_w \) incorporated into the middle phase along with the total volume of surfactant \( V_s \). These can be determined through the equilibrium phase behavior studies described above by determination of the relative volumes of the upper, lower, and middle phase. The IFT can then be given by:

\[
\sigma_{mo} = \frac{C}{(V_o/V_s)^2}, \quad \sigma_{mw} = \frac{C}{(V_w/V_s)^2},
\]

Equation 2.1 IFT calculated by solubilization ratio

where \( \sigma_{mo} \) is IFT between the micro-emulsion phase and the oil phase, \( \sigma_{mw} \) the IFT between the micro-emulsion phase and the water phase, and \( C \) is a constant equal to 0.3 mN/m. The ratios \( V_o/V_s \) and \( V_w/V_s \) are known as the solubilization parameters for oil and water, respectively, and they reflect the amount of oil or water present in the micro-emulsion phases normalized by the volume of surfactant \( V_s \). For these studies, we only focused on the OXS surfactant series, since this particular series provided very clear
boundaries between oil, water, and bicontinuous phases, enabling measurement and analysis through the empirical correlation.

Direct measurement of the oil-water interfacial tension through spinning drop IFT indicated that the nanoparticle additive had only a small impact on the IFT. We measured values of $1.8 \times 10^{-3}$ and $1.5 \times 10^{-3}$ mN/m with and without nanoparticle added, respectively (with 2 wt % OXS surfactant and 2.5 wt % sec-butyl alcohol). In Figure 2.10, we show the solubilization parameters for water and oil in micro-emulsion phases stabilized by OXS surfactant and both with and without $C_{16}$-ssPVA-OCB polymer-coated nanoparticle. At low salinities, an oil-in-water macro-emulsion (lower phase) is observed, as reflected by a much larger solubilization parameter for water. At higher salinities, a water-in-oil macro-emulsion (upper phase) is present, and solubilization parameter for oil is higher than that for water. Over the salinity range of 1.6 – 2.0 wt % NaCl, the solubilization parameters for oil and water are comparable, and this corresponds to the formation of a middle phase. The minimum in interfacial tension (optimal salinity) occurs at the point where the solubilization parameters cross. These phase behavior studies clearly show that the solubilization parameters are comparable both with and without nanoparticle present and that the optimal salinity occurs at approximately 1.8 wt % NaCl. Using the empirical Huh correlation, the IFT is $2.6$ and $2.7 \times 10^{-3}$ mN/m with and without polymer-coated nanoparticle added, respectively. Thus, but methods indicate that nanoparticle additives have only a small impact on the IFT.
2.5. Influence on PNPs Additive on Domain Size of Oil-Water-Surfactant Micro-emulsion

Next, we investigated the effect that polymer-coated nanoparticles had on the domain size of bicontinuous middle phases through small-angle X-ray scattering measurements. In order to carry out these measurements, a sample of the bicontinuous middle phase was extracted from equilibrated oil/water/surfactant/nanoparticle samples and transferred to a capillary for analysis. Micro-emulsion phases for OXS, K2-4, and K3-4 surfactant series were studied, but only the K2-4 and K3-4 samples provided a measureable correlation peak over the \( q \)-range of the X-ray measurements, as shown in Figure 2.11. A clear low-angle peak characteristic of a bicontinuous oil-water micro-emulsion phase was observed in these samples. In both cases, a small shift to lower-\( q \) values was seen on the addition of the C\(_{16}\)-ssPVA-OCB polymer-coated nanoparticles.
This indicated an increase in domain spacing with the addition of polymer-coated nanoparticles.

The model by Strey et al. was used to extract the domain size \( d \) and correlation length \( \xi \) from the data.\(^{55,56} \) As shown in Figure 2.11, this model was able to capture the features of the low-angle scattering curve accurately and provide quantitative estimates for \( d \) and \( \xi \). For both surfactants, an approximately 15 nm increase in the domain size was measured in the presence of polymer coated nanoparticles, as shown in Table 2.3. The polymer-coated nanoparticles are much larger than 15 nm, and therefore this suggests that the polymer-coated nanoparticles occupy the oil-water interface with chains extended into both phases, as shown schematically in Figure 1. The interaction of the amphiphilic chains with the aqueous phase and the hydrophobic chains with the oil phase helps stabilize the nanoparticles at the interface, and a small but measureable increase in the domain size was observed.
Table 2.3 Domain size $d$ and correlation length $\xi$ for micro-emulsion phases formed by K2-4 1S and K3-4 1S surfactants both with and without $C_{16}$-ssPVA-OCB nanoparticles present based on small-angle X-ray analysis of bicontinuous phases.

<table>
<thead>
<tr>
<th>Micro-emulsion stabilizer</th>
<th>$d$/nm</th>
<th>$\xi$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2-4 1S only</td>
<td>49.1</td>
<td>121.8</td>
</tr>
<tr>
<td>K3-4 1S only</td>
<td>63.0</td>
<td>333.3</td>
</tr>
<tr>
<td>K2-4 1S with PNP</td>
<td>58.6</td>
<td>119.1</td>
</tr>
<tr>
<td>K3-4 1S with PNP</td>
<td>74.3</td>
<td>162.1</td>
</tr>
</tbody>
</table>

2.6. Chapter Conclusion

We synthesized a series of oxidized carbon black nanoparticles with covalently attached hydrophilic and hydrophobic chains and investigated the equilibrium phase behavior of these nanoparticles in the presence of oil and water. A mixture of hydrophilic PVA and hydrophobic chains $C_{16}$ was observed to produce stable emulsions over a broad salinity range, and sulfation of the PVA chains significantly improved dispersion stability in aqueous media at elevated salinities. When mixed with surfactants that stabilized the formation of bicontinuous micro-emulsion phases, polymer-coated nanoparticles segregated strongly and preferentially to the middle phases. This reflects the interfacial activity of amphiphilic nanoparticle additives, and highly sulfated polymer-coated nanoparticles $C_{16}$-ssPVA-OCB were stable and surface active at elevated salinities, up to 15 wt % NaCl. A combination of IFT measurements and phase behavior studies showed that the nanoparticle additives had only a small impact on the IFT. Furthermore, SAXS measurements revealed a modest but measurable increase in the domain size on addition of the polymer-coated nanoparticles. These phase behavior studies clearly demonstrate that the use of an amphiphilic nanoparticle coating along with a charged, highly sulfated
polymer results in polymer-coated nanoparticles that are stable at high salinities and migrate to micro-emulsion middle phases. Combined with other favorable properties of nanoparticle additives, we envision this work will lead to future developments of nanoparticle additives which can segregate to bicontinuous phases, propagate through porous media, modify interfacial properties, and enhanced the efficiency of enhanced oil recovery processes.

In future studies, we expect systematic studies of a polymer coated nanoparticle that does lower the interfacial tension on order of tens of mN/m and its influence on micro-emulsion in the presence of a surfactant. The coating of nanoparticle with more surface active chains, as well as the tailoring of size of PNPs to be larger or smaller, are to be studied for the preparation of PNPs that bring lower interfacial tensions.
Chapter 3

**pH-responsive Polymer-coated Nanoparticle for Reversible Emulsification and Recovery of Heavy Oil**

Chapter 3 is to be submitted to *Langmuir*

Heavy crude oil has lower solubility and higher density than that of light crude oil, and it primarily comes in the form of natural bitumen from oil sand. Therefore, there are significant challenges in both the production and transportation of heavy oil. Emulsifiers can be used to produce low viscosity oil-in-water emulsions to recover the oil, but subsequent demulsification can be challenging. Here, we investigate pH-responsive polymer-coated nanoparticles (PNPs) that are interfacially active and can be used to reversibly stabilize and break oil/water emulsions through variations of the pH. This work demonstrates the applicability of polymer-coated nanoparticles as surface active materials for EOR processes and for heavy oil transportation.
3.1. Chapter Introduction

Large reserves of oil sands are found in locations across the globe including Venezuela, Canada and Russia. Oil sand usually comes in the form of a mixture of sand, water, clay, and bitumen, a thick heavy oil higher viscosity, higher density and lower solubility compared with other oil. These properties present challenges to the cost-effective recovery and transportation of heavy oils. Current methods of heavy oil recovery include surface mining, chemical flooding and some novel methods like steam assisted gravity drainage (SAGD) and Cyclic Steam Stimulation (CSS) etc, all with differing level of success. Single or combined methods can be applied depending on the actual underground circumstances. Chemical flooding is a relatively mature method in EOR with broader applicability for both light oil and heavy oil recovery and lower capital expenditure relative to SAGD and CSS. Prior work with nanoparticle additives and oil-water emulsions have demonstrated the potential and effectiveness of PNPs for oil recovery. A number of studies have focused on micron- and nano-sized surface active nanoparticle additives for stabilizing oil-water emulsions, mobility control of the injected flood, and wettability alteration of the surface to increase the efficiency of EOR processes. For example, Binks et al. studied water-in-oil macro-emulsions stabilized by Latex particles and found that, in the case of micron-size colloidal particles, the interaction with the interface was dominated by irreversible adsorption. The group also demonstrated that silica nanoparticles could be used to stabilize oil-in water macro-emulsions when blended with anionic or cationic surfactant, respectively. Johnston and coworkers studied a series of iron-oxide nanoparticles coated with amphiphilic or charged polymers and found a decrease in the value of oil-water interfacial tension and,
in the case of charged polymer coatings, both good stability in high-salinity environments and low adsorption onto silica surfaces. We developed a series of polymer-coated nanoparticles (PNPs) with charged polymers that could segregate to bicontinuous oil-water microemulsion phases and were stable at high salinities, as high as 14 wt %. Cui et al. found that nanoparticle/surfactant mixtures could be used to deform emulsion droplets into non-spherical shapes due to jamming of the nanoparticles at the oil-water interface. Lead and coworkers reported PNPs that could be used to separate oil-water mixtures. Tilton et al. reported the xylene-in-water emulsion and cyclohexane-in-water emulsion stabilized by DMAEMA-PNPs and the thermal responsiveness of DMAEMA-PNPs for breaking emulsions. Other studies with PNPs at the oil-water interface are discussed in recent review articles.

These studies demonstrate that very stable Pickering emulsions can be produced through the irreversible adsorption of nanoparticles to the oil-water interface. Attaching surface-active polymers to the nanoparticle surface increases the stability of the emulsion, even at very low nanoparticle concentrations. However, PNPs have not been developed or tested for the recovery of heavy oil, where stimuli-responsive nanoparticles capable of emulsifying and demulsifying heavy oil are desirable.

Here, we develop and demonstrate stimuli-responsive PNPs that can be used to stabilize and break oil/water emulsions by the variation of pH. Silica particles with poly(dimethyl ethyl acrylamide) (DMAEMA) chains covalently grafted to the surface are prepared through a reversible addition fragmentation chain transfer (RAFT) grafting-through technique. We show that DMAEMA PNPs can be used to stabilized Pickering emulsions of high viscosity Canadian bitumen from oil sand at additive concentration as
low as 0.1 wt % and at a neutral pH. The performance of the DMAEMA PNPs exceeds that of pure DMAEMA homopolymer additive or of just water with no additive. By reducing the pH of the aqueous solution, the interfacial activity of the DMAEMA decreases and the emulsion is destabilized, allowing the heavy oil to coagulate and settle. We demonstrate sandpack flooding experiments using 0.1 wt % DMAEMA PNPs as additives and find that the nanoparticles are able to recover approximately 10 wt % of the heavy crude oil in place. This work demonstrates the applicability of PNPs as surface active materials for EOR process and for heavy oil transportation.

Figure 3.1 Schematic for the use of PNPs additives to recover heavy oil trapped in porous media (top) and the phase behavior of PNPs with changes in pH (bottom).
3.2. Experimental Methods

3.2.1. Chemicals

Crude oil sample was bitumen oil from Athabasca in Alberta, Canada; silica nanoparticles were purchased from Nissan Chemical (MEK-ST, 30 wt % in MEK), with a diameter of 10-15 nm. Solvents and reagents were obtained from commercial suppliers and used without further purification unless otherwise specified. 3-aminopropyl(diethoxy)methylsilane (APDMES), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (chain transfer agent, CTA), 2-(dimethylamino)ethyl methacrylate, N,N’-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) and 2,2’-azobis(2-methylpropionitrile) (AIBN) were purchased and used as received.

3.2.2. Preparation of DMAEMA Coated Nanoparticles

The preparation of PNPs starts from attaching a chain transfer agent (CTA) molecule to silica nanoparticle through a saline linkage. And in order to grow polymer on surface of NPs, a controlled Reversible Addition-Fragmentation Polymerization (RAFT) was performed. (Figure 3.2)

APDMES-CTA. The coupling of APDMES and CTA was performed as follows: CTA (0.1 g, 0.27 mmol), DCC (0.1 g, 0.48 mmol), DMAP (10 mg, 0.08 mmol) and oleic acid (0.6 g, 2.12 mmol) were added to a 50 mL round bottom flask. Next, 20 mL DCM (anhydrous) was added, and the flask was purged with nitrogen for 20 minutes. APDMES was added to the mixture under the protection of nitrogen. The solution was stirred on ice
bath for 1 hour, and the reaction was conducted under room temperature for overnight with rigorous stirring. The solution was filtered prior to use in the next step.

**SiO$_2$-CTA.** 3 mL silica nanoparticle solution (30 wt %) and 20 mL THF were added into a 100 mL round bottom flask. The filtered APDMES-CTA solution was added drop by drop to the flask while stirring. The mixture was purged with nitrogen for 20 minutes and the reaction was conducted under room temperature for 72 hours with rigorous stirring. SiO$_2$-CTA was precipitated in methanol and was centrifuged at 3000 rpm for 15 min. Residual solvent was removed, and SiO$_2$-CTA was re-dissolved in THF. The precipitation and centrifugation was repeated for 3 times, and SiO$_2$-CTA was dried under vacuum.

**DMAEMA PNPs.** 2-(dimethylamino)ethyl methacrylate was passed through a basic alumina column to remove inhibitor before polymerization. For the preparation of DMAEMA PNPs, SiO$_2$-CTA (70 mg) was sonicated in 1,4-dioxane (4 mL) to produce a homogeneous solution prior to adding AIBN (0.63 mg, 0.004 mmol) and 2-(dimethylamino)ethyl methacrylate (150 mg, 0.95 mmol). The mixture was purged with nitrogen for 15 minutes and reacted at 70 °C overnight. The resulting product was purified by dialysis in water for 1 week using dialysis membrane (MWCO of 3000 Da) to produce a 5 wt % stock solution of DMAEMA PNPs in water.

**DMAEMA homopolymer.** For the preparation of linear DMAEMA, 2-(dimethylamino)ethyl methacrylate (2.98 g, 18.95 mmol), AIBN (12.4 mg, 0.075 mmol) and CTA (137.7 mg, 0.38 mmol) were dissolved together in 20 mL 1,4-dioxane. The mixture was purged with nitrogen for 15 minutes and reacted at 70 °C for 5 hours. The
resulting linear DMAEMA was precipitated in cold hexane for 3 times and dried under vacuum.

![Reaction scheme for the surface modification of silica nanoparticles.](image)

Figure 3.2 Reaction scheme for the surface modification of silica nanoparticles.

3.2.3. Instrumentation and Characterization

**Dynamic Light Scattering (DLS) Measurement.** Dynamic light scattering was carried out using a Malvern Instruments Zen 3600 Zetasizer. Polymer-coated nanoparticles were dissolved in water at a concentration of 0.1 wt % for analysis.

**Phase Behavior Studies.** Phase behavior studies of oil, water, surfactant, and PNPs were carried out in 30 mL vials. A desired amount of crude oil, PNP stock solution, and DI water was added to each vial sequentially. Except where noted, the amount of crude oil in each vial was 15 mg and a 15 mL solution of 0.1 wt % PNP. To homogenize
the mixture, the mixture was placed in an ice bath and sonicated for 5 minutes using a Q500 probe sonicator (power level 3). Samples were capped and sealed immediately after sonication to prevent evaporation and for long-term analysis.

**Thermo-Gravimetric Analysis (TGA).** TGA measurements were carried out on a Q-600 TGA from TA instruments. The samples were heated from 25 °C to 900 °C at a rate of 10 °C/min under nitrogen atmosphere.

**Contact Angle and Interfacial Tension (IFT) Measurement.** Contact angle and IFT measurement were performed with a tensiometer (Krüss DSA100). For IFT, sessile drop method was taken; size and angle parameters from drop image were fitted into the nonlinear functions by Dawe et al. to calculate the interfacial tension between crude oil and water with and without PNPs.

**Nuclear Magnetic Resonance Spectroscopy (NMR).** Proton NMR (\(^1\)H NMR) spectra were recorded using tetramethylsilane as an internal standard in CDCl\(_3\) on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm O.D. tubes with a concentration of 10 mg/mL.

**Microscopy.** Dispersion of oil drops in Pickering emulsion was observed under a polarizing optical microscope (Zeiss Axioplan 2). 40 μL of phase behavior solution was drop cast on a glass slide and covered carefully by glass coverslip.

**Total Carbon Analysis.** Emulsion carbon concentration analysis was performed with SHIMADZU TOC-V analyzer. Phase behavior solutions were settled on autosampler and programmed was set for analysis.
**UV-absorption.** UV absorption measurement was performed with a UV-Vis Spectrophotometer (Shimadzu UV-2550). The absorption was taken at wavelength 425 nm with a series of CTA and SiO$_2$-CTA samples of different concentrations in THF.

**Sandpack flooding.** Sandpack flooding was performed through a glass column (0.66 cm in D and 17 cm in L) loaded with oil sand (30 wt % oil and 70 wt % sand). A wire heater was wrapped around the column to maintain a temperature of 80 °C. A syringe pump was used to inject the mobile phase (water or water with 0.1 wt % DMAEMA PNPs) at a flow rate of 1 mL/min.

Both DMAEMA PNP and linear DMAEMA were prepared by reversible addition-fragmentation chain-transfer (RAFT) Polymerization. For the DMAEMA PNPs, CTA was first attached onto the surface of nanoparticle through the a 3-aminopropyl (diethoxy)methylsilane linker. The PNP was prepared through a “graft from” RAFT polymerization of 2-(dimethylamino)ethyl methacrylate in 1,4-dioxane at 70 °C for overnight. The existence of CTA guarantees the chain length of each attached polymer chain to be uniform. The polymer content and size of the nanoparticles was measured through thermo-gravimetric analysis (TGA) transmission electron microscopy (TEM), UV-absorption, and dynamic light scattering (DLS), and the results are shown in Table 3.1 and Figure 3.3. The polymer content of the DMAEMA PNPs is greater than 50 wt %. Using UV absorption to quantify the number of CTA functional groups attached to the nanoparticles, we are able to calculate the coating density and average number of repeat unit for each chain. The coating density is determined to be 1.8 chains/nm$^2$, consistent some previously reported polymer-coated nanoparticles. The $M_w$ of linear
DMAEMA is determined by NMR and calculated from the number ratio DMAEMA repeat unit and CTA.

Table 3.1 Polymer fraction by TGA and size measurement by DLS

<table>
<thead>
<tr>
<th>Item</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DMAEMA PNPs</strong></td>
<td></td>
</tr>
<tr>
<td>Polymer fraction(^a)</td>
<td>57 wt %</td>
</tr>
<tr>
<td>Number Avg. Diameter(^b)</td>
<td>110.3 nm</td>
</tr>
<tr>
<td>Coating density(^c)</td>
<td>1.8 chains/nm(^2)</td>
</tr>
<tr>
<td>Avg. DP of each chain(^d)</td>
<td>14</td>
</tr>
<tr>
<td>Avg. (M_n) of each chain(^e)</td>
<td>2600 g/mol</td>
</tr>
<tr>
<td><strong>Linear DMAEMA</strong></td>
<td></td>
</tr>
<tr>
<td>Avg. (M_n)(^f)</td>
<td>7600 g/mol</td>
</tr>
</tbody>
</table>

\(^a\)measured by thermogravimetric analysis (TGA). \(^b\)measured by dynamic light scattering (DLS) in DI water. \(^c,d,e\)calculated by the combination of DLS, TGA and Uv-absorption. \(^f\)measured by NMR.

Figure 3.3 (a) TGA analysis for DMAEMA PNP (b) TEM analysis of DMAEMA PNP (c) DLS analysis of DMAEMA PNP
3.3. Interfacial Properties of PNPs

3.3.1. Proposed Mechanism in DMEAME PNPs for EOR and Reversible Emulsion

Before the study of this newly designed PNPs on EOR, it is important to understand the mechanisms of some nano-assisted EOR process. Nanoparticle has its characteristics of ultra-small size and high surface to volume ratio. The smaller size makes it easy to go through porous media without severe plugging or being trapped; the high surface to volume ratio increases the efficiency of its interaction with oil, water or rock surface. Recent studies have explored the interactions of nanofluids, crude oil and rocks and have revealed some EOR mechanisms.\textsuperscript{86–88} However, the understanding of mechanism for nano-assisted EOR process is still not enough. Some commonly accepted approaches in nano-assisted EOR include: pore channel plugging,\textsuperscript{89} injected fluid mobility control,\textsuperscript{90} IFT reduction,\textsuperscript{91} wettability alternation\textsuperscript{92} and nanoemulsion\textsuperscript{93} etc.

Here for the case of DMAEMA PNPs, we assume and will demonstrate in the following sessions that the mechanism is the combined effect of IFT reduction and nanoemulsion. IFT will affect the miscibility of crude oil with water and a lower IFT will make difference in mobilizing the oil in place. Nanoemulsion is the emulsion that is stabilized by nanoparticles; comparing with conventional emulsions stabilized by surfactants or other colloidal solids, it can withstand harsh reservoir conditions and will remain stable because of the large absorption energy of nanoparticles at the oil/water interface.\textsuperscript{94} Figure 3.4 is the illustration of EOR process by our designed DMAEMA PNPs. The PNPs will be injected along with the injecting fluid into reservoir and migrate...
to the interface between oil/water, therefore lowering IFT and mobilizing oil in place. Oil will be recovered from the reservoir in the form of oil in water emulsion in the effluent fluid.

![Figure 3.4 Mechanism of PNP for EOR](image)

To separate the oil and water emulsions after oil recovery, people usually have to add certain amount of demulsifies to break the emulsions or use some other physical separation methods. And this will obviously take extra operations and increase the overall cost of oil recovery process. Some novel, integrated and environmental friendly oil-water separation method is always a desire.

With a highly dense coating of pH responsive DMAEMA polymer, the PNP as a whole can be protonated and hydrophilicity is tremendously increased. At a certain point where the pH is low enough, hydrophilicity will dominate. The hydrophilic PNP will have the tendency to leave oil-water interface and migrate to aqueous phase. And consequently, as no more PNP stabilizing emulsion at interface, the oil-in-water Pickering emulsions become very unstable that oil water separate from each other and becomes two individual bulk phase in a relatively short time. Contact angle measurements (Figure 3.5) were performed by casting drops of PNP solution at both
neutral and acidic (pH=2) condition on bitumen coated wafers. And a difference of 20 degree in contact angle was observed between PNP at natural and pH=2 conditions. We believe that DMAEMA PNPs become fully protonated and fully hydrophilic at pH=2 or below conditions.

Figure 3.5 contact angle measurement on crude oil coated surface with drop of (a) DI water (b) 0.1 wt % DMAEMA PNP at pH=7 (c) 0.1 wt % DMAEMA PNP at pH=2.
3.3.2. Phase Behavior Studies of Reversible Oil-in-Water Emulsion Stabilized by DMAEMA PNPs

We have demonstrated the potential of PNP for stabilizing reversible heavy oil in water emulsions by phase behavior studies (Figure 3.6). The emulsion was prepared by probe sonication at room temperature and left still for overnight; a drop of emulsion was pasted on glass and observed under microscopy.

As is shown, the bitumen oil was barely dispersed in DI water; and with the addition of 0.1 wt % linear DMAEMA polymer, oil drops still barely can be seen under microscope images. With the addition of 0.1 wt % DMAEMA PNP, dispersity of oil got greatly improved and an even distribution of micron-size oil drop was observed. This emulsion sample was stable and evenly distributed when observed after a month. And we assume this is because the PNPs that stabilized the emulsion and impede the droplet flocculation. The phase behavior studies showed well separated oil-water phases (Figure 3.6d) after the pH of emulsion being lowered to pH=2. Under this condition, oil drops were only left with limited number of aggregated oil droplet.
Figure 3.6 Phase behavior study of oil/water emulsion prepared with probe sonicator and microscopy observations. (a) crude oil in DI water with no addition. (b) crude oil in DI water with 0.1 wt % DMAEMA linear polymer at pH=7. (c) crude oil in DI water with 0.1 wt % DMAEMA PNP at pH=7. (d) crude oil in DI water with 0.1 wt % DMAEMA PNP at pH=2. All samples were added with 15 mg crude oil and total volume of 15 mL solution, observed after stabilized for overnight.

3.3.3. Carbon Number Analysis for Determination of Oil in Emulsion

For a quantity study of the reversible emulsions, all samples in Figure 3.6 were characterized by carbon number analysis. And based on the bitumen chemical formula approximation of $C_nH_{2n}$, the total amount of recovered oil was able to be calculated, as shown in Table 3.2. Similar to its phase behavior studies, bitumen with DI 0.1 wt % DMAEMA linear polymer only brings less than 10 wt % oil solubilization. With the addition of 0.1 wt % DMAEMA PNP, almost 80 wt % of crude oil became solubilized in oil-in-water emulsion. It is assumed that the low oil solubility with linear polymer addition is because of the instability of emulsions; the emulsion starts to break with a fast
rate once after it is formed. As pH is lowered to pH=2, emulsion stabilized by DMAEMA PNP breaks and the amount of solubilized oil decreases to below 10 wt %.

Table 3.2 Total carbon concentration analysis and comparison between 0.1 wt % PNP and 0.1 wt % linear polymer, oil was added at 15 mg for a 15 mL of total solution.

<table>
<thead>
<tr>
<th>Item</th>
<th>Total carbon concentration (mg/L)</th>
<th>Solubilized crude oil (mg)</th>
<th>Solubilized crude oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 wt % PNPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNP with no oil at pH=7(stock)</td>
<td>355</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PNP with oil at pH=7</td>
<td>1136</td>
<td>11.7</td>
<td>78.0</td>
</tr>
<tr>
<td>PNP with oil at pH=2</td>
<td>425</td>
<td>1.1</td>
<td>7.3</td>
</tr>
<tr>
<td>0.1 wt % Linear polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer with no oil at pH=7(stock)</td>
<td>665</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Polymer with oil at pH=7</td>
<td>743</td>
<td>1.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Polymer with oil at pH=2</td>
<td>686</td>
<td>0.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

3.3.4. IFT Approximation by Sessile Drop Method

As a parallel study, we investigated the equilibrium IFT between crude oil and water with/without adding PNPs through a sessile drop analysis method. For the measurement of two phases IFT that is higher than 10 mN/m, pendant drop method is a much more commonly used method. However, the ultra-high viscosity of this bitumen at room temperature makes it very challenging and almost impossible for the pendant drop to be prepared through syringe injection and measurement to be taken. As an alternative method, sessile drop method has been reported and demonstrated to be able to calculate the interfacial tension by the measurement of the drop height, maximum radius and contact angle. And the method gives negligible errors when comparing with other methods. About 15 mg of bitumen oil was deposited onto the glass cell followed by a
filling of DI water or 0.1 wt \% PNP solution at 80 ℃. The oil drop will deform as it is surrounded by aqueous solution and sessile drop image was taken by Krüss DSA100 tensiometer. Size and angle parameters from drop image were fitted into the nonlinear functions by Dawe et al.(Figure 3.7).

Figure 3.7 The sessile drop file of parameters

$C_1$-$C_8$ are coefficients that vary with contact angle and their values were found in the Dawe paper; $Z_\theta$ is the drop height and $X_k$ is the dimensionless drop radius that were read from the drop image. $\Delta \rho$ is the different in density between oil and water; $g$ is the gravity constant. Interfacial tension $\gamma$ was calculated in Equation 4.1 after $Z_k$ was calculated from Equation 3.1,

$$Z_k = f(X_k) = 2 \sum_{i=1}^{5} C_i X_k^i - \frac{1 - \cos \theta + C_8}{X_k + C_8} e^{0.1 C_6 X_k^{C_7}} + \frac{1 - \cos \theta + C_8}{X_k + C_8}$$

Equation 3.1 Calculation for dimensionless height

$$\gamma = \Delta \rho g Z_\theta^2 / Z_k^2$$

Equation 3.2 Calculation for Interfacial Tension
With the addition of 0.1 wt % PNP at interface, there is a difference in deformation of oil drop. Accordingly, the IFT decreases from 27 mN/m to approximately 14 mN/m. (Figure 3.8) And a lower IFT means easier mobility of oil with water flooding and enhanced solubility in water, although in this case the decrease in IFT is not significant. Compared with a more direct pendant drop method for measurement of IFT, this is a relatively rough measurement.

Figure 3.8 Interfacial tension between crude oil and water measurement by sessile drop: (a) IFT between oil and DI water is 27 mN/m (b) IFT between oil and 0.1 wt % PNP solution is 14 mN/m.

3.4. Bitumen Oil Recovery Experiment with DMAEMAE PNPs

The evaluation of EOR with PNP was conducted through a sandpack flooding study with a commonly used procedure\textsuperscript{97,98} and the setup of sandpack was reflected in Figure 3.9. Sand particle with size 106 to 250 μm was packed into a glass column. After
the column was prepared, the volume of liquid contained in the fully saturated column (pore volume) was calculated. A syringe pump was used to keep constant flow rate through the column and effluent was collected at each pore volume (0.5 mL). A wire heating system was wrapped densely around the column to maintain the temperature of flow to be approximately at 80 °C, as representation of reservoir condition. Water was injected through the column first and followed by bitumen oil flooding at 80 °C. After oil flooding, the column should be oil rich and that represents the actual oil reservoir conditions. And the approximate composition of 30 wt % crude oil and 70 wt % sand was close to the composition of actual oil sand reported in Alberta, Canada. Two independent groups of flooding, one with DI water flooding and the other with 0.1 wt % PNP solution flooding were performed individually with two columns of the same oil composition. Collection series of effluent were shown in Figure 3.10. For DI water flooding, barely no bitumen seems to be recovered even after 40 pore volumes of flooding, while PNP flooding obviously shows recovered oil in a wide range of pore volumes.

Figure 3.9 Setup of sandpack studies
Figure 3.10 Effluent of sandpack flooding studies: (a) effluent of water flooding without DMAEMA PNPs (b) effluent of 0.1 wt % DMAEMA PNP flooding. Both flooding studies were conducted under external wire heating at 80°C.

The effluents in each series of effluents were combined and total amount of carbon was determined through total carbon analysis. Based on the bitumen chemical formula approximation of $C_nH_{2n}$, the total amount of recovered oil was able to be calculated and listed in Table 3.3. Not surprisingly, the flooding of DI water barely recovered any bitumen, considering the ultra-high viscosity and ultra-low solubility. As comparison, 0.1 wt % PNP helps to mobilized and recover up to 10 wt % of crude oil in place. This demonstrates the applicability of PNP in the recovery of bitumen oil, considering the huge reserve of oil sand in the world and the low demand of PNP concentration.
Table 3.3 Crude oil recovered by DI water flooding and 0.1 wt % PNP solution flooding

<table>
<thead>
<tr>
<th>Item</th>
<th>Total oil in column (mg)</th>
<th>Oil recovery after 20 pore volume (mg)</th>
<th>Fraction of oil recovered (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flooding</td>
<td>806</td>
<td>2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>0.1 wt % PNP flooding</td>
<td>822</td>
<td>81</td>
<td>9.9</td>
</tr>
</tbody>
</table>

3.5. Discussion on Emulsification Between PNPs and Linear Polymer

PNPs and branchy polymers (bottlebrush polymers, star polymers etc.) have lots of similarities such as larger size and denser local polymer side chains, when comparing with linear polymers. And these properties thermodynamically favor the stability of Pickering emulsions when they are used as emulsion stabilizer. The adsorption energy of colloid particles at oil-water interface scales with the square of the particle radius. Thus, a larger size means a stronger confine to the interface and it will require more energy input to go against the energy barrier. Aside from that, the attachment of multiple chains onto the nano surface brings a cooperative effect on the energy barrier of droplet coalescence. Polymer chains confined to the surface of two droplets and impede the process of film drainage. The mechanism and comparison of PNP and linear polymer stabilizing emulsion was illustrated in Figure 3.11.
Figure 3.11 Comparison between linear DMAEMA and DAMEAM PNPs in oil/water emulsion phase behavior at different pH. (top: linear DMAEMA; bottom: DMAEMA PNPs).

3.6. Chapter Conclusion

In this chapter, a well-designed DMAEMA PNP was prepared and used for the study of stabilizing oil in water Pickering emulsion. These highly dense polymer coatings will form a shell structure outside nanoparticle and lowers the interfacial tension between high viscosity crude oil and water at low concentration of 0.1 wt %.

Sandpack oil recovery studies were performed under the actual reservoir temperature condition and actual oil/sand composition of Canada oil sand. It is demonstrated that the flooding of this low concentration (0.1 wt %) DMAEMA PNP solution was able to recover approximately 10 wt % of crude oil in place after injection.
Due to the pH responsiveness of this polymer coating, the simple adjust of pH will change the hydrophilicity of PNP as a whole, and that will in return decrease the stability of Pickering emulsion, which eventually to achieve the oil-water separation after oil recovery.

Comparison of emulsion stabilization effect was performed between PNP and linear polymers, and PNP has been demonstrated a better emulsion stabilizer than linear polymer at low concentration of addition (0.1 wt %). This is because of the relative larger size of PNP and the cooperative effect of the high concentration polymer coating on the surface, which effectively impedes the approaching droplet from coalescence.
Interfacial Properties of Amphiphilic Bottlebrush Polymers

In this chapter, we investigate the interfacial properties of a branched bottlebrush polymer family and its self-assembly in aqueous solutions. We characterized the self-assembly of bottlebrush copolymers at very low dilution and its ultra-low critical micelle concentration (CMC).
4.1. Chapter Introduction

In the previous two chapters, I have introduced two kinds of polymer coated nanoparticles and some interesting interfacial properties based on these PNPs, as well as their potential for EOR. In PNPs, the attached polymer chains determine the surface activity. Similar to PNPs, branched polymers could also have dense polymer side chains branched off from the main chains, and we assume there being much similarity between the surface activity of branched polymers and PNPs.

In this chapter, we have intensively investigated the surface activity and self-assembly of a category of branched polymer, bottlebrush polymers. We will demonstrate in the following discussions that the bottlebrush polymers have a substantially lower CMC when comparing with its linear analogs. And we were also able to quantify the self-assembly and phase behavior of a model library of amphiphilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurements.

4.1.1. Branched Polymers

Branched polymers are polymers with groups of units branch off from the long polymer chain. These branches which can be very long groups of repeating structures are often referred to as side chains. \(^{101,102}\) Depending on how sided chains are branched off from the main chains, branching polymers can be further categorized. For example, polymers with multiple branches are known as dendrimers, and these dendrimers can form webbings when cooled down and this behavior helps to make the polymer strong in the ideal temperature range. When heated at high enough temperatures and temperature
vibration overcomes the attractive forces between the molecules, both linear and branched polymers get softened.\textsuperscript{103,104}

4.1.2. Bottlebrush Polymers

Bottlebrush polymers have a single molecular conformation like a bottlebrush – polymeric side-chains densely grafted to a linear backbone extend radially outwards\textsuperscript{105} (Figure 4.1). The unusual architectures of bottlebrushes provide a number of unique and potentially useful properties, distinct from linear polymers: they are surface active, and segregate to film surfaces and interfaces; they have a high entanglement molecular weight, enabling rapid self-assembly of bottlebrush block copolymers into large domain structures, the self-assembly of bottlebrush block copolymer micelles in a selective solvent even at very low dilutions, and the functionalization of bottlebrush side-chains for recognition, imaging, or drug delivery in aqueous environments.\textsuperscript{106–108} A number of bottlebrush polymer review and perspective articles have appeared over the last decade. A viewpoint article by Rzayev highlights the potential of bottlebrushes as building blocks for complex and functional materials.\textsuperscript{109} Sheiko, Matyjaszewski, and coworkers have provided a number of very informative reviews, both on bottlebrush synthesis and physical properties.\textsuperscript{110} A tutorial review by Hu, Huang, and coworkers discusses advances in the synthesis of graft and bottlebrush polymers.\textsuperscript{111} A review article by Chen discusses work related to materials with densely tethered polymers, including bottlebrush polymers, polymer-coated nanoparticles, and other brushy materials.\textsuperscript{112} Our group recently reviewed the novel properties exhibited by bottlebrush polymers.\textsuperscript{113–115}
Bottlebrush polymers were first synthesized in the early 1980s, and early work was primarily focused on the development of polymer synthesis strategies. The application of controlled polymerization techniques - especially controlled radical polymerizations and ring-opening polymerizations - has enabled the preparation of bottlebrush polymers with a desired backbone and side-chain length and complex structures, including block copolymer and core-shell bottlebrushes. The field has also advanced significantly in the understanding of physical properties of bottlebrushes, and work is increasingly focused on bottlebrush assemblies in unique environments.

Bottlebrush copolymers contain two (or more) different types of polymeric side-chains. Recent work has explored the diverse properties and functions of bottlebrush copolymers in solutions, films, and melts, and applications explored include photonic materials, bottlebrush films for lithographic patterning, drug delivery, and tumor detection and imaging.

The solution self-assembly of bottlebrush copolymers has been of recent interest for their potential use in nanoparticle drug delivery and tumor imaging. While these studies have demonstrated the potential for bottlebrush block polymers to form large
(several hundred nanometer) micelles through aqueous self-assembly and their stability and low critical-micelle-concentrations (CMCs) a systematic study correlating molecular composition, self-assembly behavior, and CMC has not been reported. The objective of this project is to quantify the self-assembly and phase behavior of a model library of amphiphilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurements. Surface tension measurements will be carried out in parallel. This work has answered or will answer the following scientific questions: 1) How does the size of the hydrophobic polymer block – which governs micelle aggregation number - influence micelle stability and size? 2) Does increasing the side-chain length have a significant impact on micelle size and shape? 3) How does the size of the hydrophilic block influence micelle stability? 4) Do amphiphilic bottlebrush block polymers enable control over both CMC and micelle size through tailoring molecular composition? Small-angle neutron scattering experiments are particularly effective for analysis of polymer solution conformation and can provide information on micelle structure over a range of length scales.

4.1.2.1. Different Synthesis Approaches of Bottlebrush Polymer

In general, the synthesis of bottlebrush polymers is achieved with grafting-through, grafting-from, and grafting-to approaches\(^\text{120}\) (Figure 4.2).

Grafting-from synthesis was firstly reported by Beers et al. and it includes a controlled radical polymerization technique. In this approach, the bottlebrush backbone is synthesized first, and the side-chains are subsequently “grafted-from” the bottlebrush backbone. An advantage of the grafting-from approach is that bottlebrushes with very
long backbones can be prepared. The grafting density can also be controlled by co-polymerizing two monomers during backbone synthesis. Also, block copolymer side-chains can be incorporated in a straightforward way through sequential polymerization reactions, resulting in core-shell type bottlebrushes. A drawback of the synthesis is that protection and deprotection of functional groups is often required, increasing synthetic complexity. The preparation of mixed or bottlebrush block copolymers is possible using grafting-from, but three or more orthogonal polymerization chemistries (or protection-deprotection steps) may be required.

The grafting-through synthesis approach starts with the preparation of reactive polymeric side-chains also known as macromonomers. The macromonomers are then polymerized to form a bottlebrush polymer, and different backbone lengths can be obtained by varying the relative concentration of macromonomer to catalyst or initiator during polymerization. Solution viscosities can be very high at moderate macromonomer concentrations due to the high molecular weight of the macromonomers, and therefore highly active catalysts are needed to achieve significant conversion and control over molecular weight. Early studies implemented free radical polymerization, but macromonomer conversion was low (30–80%). A series of bottlebrush polymers were produced using this technique and studied in solution. Ring opening metathesis polymerization (ROMP) of norbornenyl macromonomers has been shown to be an effective grafting-through synthesis strategy. Jha et al. first demonstrated the grafting through synthesis of bottlebrush polymers by ROMP. Subsequently, in 2008, Xia et al. reported the use of a highly-active ruthenium catalyst for achieving improved control over bottlebrush molecular weight and molecular weight dispersity.
Finally, the grafting-to synthesis approach involves the preparation of the bottlebrush backbone and side-chains separately, followed by a ‘‘grafting-to’’ coupling reaction that attaches the side chains to the backbone. This approach faces some of the same challenges of the grafting-through approach, such as low reactivity of polymeric reagents, with the additional complication that the coupling reaction must overcome steric interactions between side-chains to achieve high grafting densities. As a result, grafting-to generally produces bottlebrush polymers with grafting densities of 60% or lower, although some examples of grafting efficiencies greater than 95% have been reported.38 Khan and coworkers reported an efficient grafting to procedure relying on thiol–epoxy coupling and giving grafting efficiencies in excess of 88%.123

Figure 4.2 Examples of grafting-from, grafting-through, and grafting-to bottlebrush polymer synthesis approaches. (A) Schematic of a grafting-from synthesis (B) Schematic of a grafting-through synthesis (C) Example of a grafting-to synthesis approach

4.2. Experimental Methods

In this project in particular, a library of amphiphilic bottlebrush polymers with poly(styrene) (PS) and poly(4-acryloylmorpholine) (PACMO) has been synthesized by
reversible-fragmentation addition chain-transfer (RAFT) followed by ring-opening metathesis polymerization. In all cases, the chain-transfer agent (CTA) was removed from the final bottlebrush to improve water solubility. The structure of the bottlebrushes is shown in Figure 4.3 and their characteristics in Table 4.1. Across the 16 samples, both the backbone length of each block (PS and PACMO) and side-chain length are varied. The molecular weight dispersity is low (below 1.1) for all samples.

Figure 4.3 Schematic for self-assembly of an amphiphilic bottlebrush block polymer with hydrophobic PS (red) and hydrophilic PACMO (blue) side-chains.
Table 4.1 Characteristics of amphiphilic bottlebrushes with PS and PACMO side-chains prepared for SANS analysis.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$M_{n,PS}$ (kg/mol)</th>
<th>$M_{n,PA}$ (kg/mol)</th>
<th>$M_n$ BB Total (kg/mol)</th>
<th>Final PDI</th>
<th>$f_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>565</td>
<td>1.06</td>
<td>54</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>623</td>
<td>1.04</td>
<td>35</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>617</td>
<td>1.02</td>
<td>20</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>676</td>
<td>1.03</td>
<td>9</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>463</td>
<td>1.04</td>
<td>43</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>496</td>
<td>1.05</td>
<td>26</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>522</td>
<td>1.03</td>
<td>14</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>4.1</td>
<td>557</td>
<td>1.03</td>
<td>6</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>2.2</td>
<td>412</td>
<td>1.07</td>
<td>71</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>2.2</td>
<td>400</td>
<td>1.04</td>
<td>50</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>2.2</td>
<td>355</td>
<td>1.03</td>
<td>32</td>
</tr>
<tr>
<td>$SE^{40}_{4k}$</td>
<td>4.2</td>
<td>2.2</td>
<td>312</td>
<td>1.03</td>
<td>17</td>
</tr>
</tbody>
</table>

**Gel-Permeation Chromatography (GPC).** Polymer molecular weights and molecular weight polydispersities (PDIs) were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10 000 Å pore sizes), an Agilent variable-wavelength UV/vis detector, a Wyatt technology HELEOS II multangle laser light scattering (MALLS) detector ($\lambda = 658$ nm), and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI), UV/vis (SEC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer dn/dc values were calculated by assuming 100% mass recovery and correcting the injected mass to account for unreacted macromonomer.

**Small-angle Neutron Scattering.** Small-angle Neutron Scattering (SANS) measurements was carried out on Sector CG-3 of Biological Small-Angle Neutron
Scattering Instrument (Bio-SANS), High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The CG-3 provides access to the necessary q-range along with a multi-sample holder and temperature control. The overall q-range is between 0.0009 and 1 Å⁻¹. Model fitting was performed using IGOR PRO software and the Guinier-Porod model. Schematic of SANS is shown in Figure 4.4

![Schematic of SANS](image)

**Figure 4.4 Schematic for SANS**

**Critical Micelle Concentration (CMC) Measurement.** In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles form and all additional surfactants add to the system go to micelles. Generally speaking, upon introduction of surfactants into the system, they will initially partition into the interface, reducing the system free energy by lowering the energy of the interface as well as removing the hydrophobic parts of the surfactant from contact with water. As the surface coverage by the surfactant increases, the surface tension decreases and the surfactants start aggregating into micelles. (Figure 4.5) The system’s free energy is decreased by decreasing the contact area of hydrophobic parts of
the surfactant with water. Upon reaching CMC, any further addition of surfactants will just increase the number of micelles.

![Figure 4.5 Surface tension of a surfactant solution with increasing concentration and determination of CMC](image)

The common procedure to determine the CMC from experimental data is to look for the intersection of two straight lines traced through plots of the measured property versus the surfactant concentration.

**CMC comparison between bottlebrush polymers and linear polymer**

Bottlebrush polymer micelles were prepared by solvent exchange dialysis method with dialysis bags (MWCO=3500). 50 mg bottlebrush polymer was firstly dissolve in 2 mL of THF and then transferred into dialysis bags. Solvent exchange was performed with running DI water for 7 days and after-dialysis solution was stored as stock solution. Surface tension was characterized from low concentration to high concentration with the addition of stock solution. A force tensiometer (Krüss K100) was used to measure the surface tension of bottlebrush micelle. The CMC results from the intersection between
the regression straight line of linearly independent region and the straight line passing through the plateau. Figure 4.6 shows some of the CMC plots in our bottlebrush polymer series and their comparison with linear polymers.

![Figure 4.6](image)

Figure 4.6 (a)-(e) CMC of a series of PS-PACMO bottlebrush polymer (f) CMC of PS-PACMO diblock copolymer

And from Figure 4.6, it is easy to tell that the CMC of PS-PACMO bottlebrush polymer is in the range of 10-40 mg/L. As comparison, CMC of linear PS-PACMO polymer is over 100 mg/L. The lower CMC of bottlebrush polymer can be explained by
the high entanglement molecular weight that favors the formation of micelles; also, compared with linear polymers, the branched structure would have larger volume space at unit molecule weight and that allows the surface area fully taken up at lower polymer concentrations and bottlebrush polymers aggregate in bulk solution.

**Morphology of bottlebrush polymers in good solvent by SANS analysis**

SANS measurements were carried out on solutions of bottlebrush polymer at 1 wt % in deuterated toluene (d8-tol), a good solvent for both PS and PACMO side chains as well as the polynorbornene backbone. SANS analysis was performed over a q range of 0.001 Å\(^{-1}\) up to approximately 0.4 Å\(^{-1}\). This broad q range provides information on the structure of bottlebrush polymers on multiple length scales. Roughly, the low-q region (q = 0.001-0.02 Å\(^{-1}\)) gives information on the overall size of the bottlebrush polymer, the mid-q region (q = 0.02 - 0.1 Å\(^{-1}\)) provides information about the cross-sectional size and stiffness, and the high-q region (q > 0.1 Å\(^{-1}\)) is indicative of thermal fluctuations on the molecular level. (Figure 4.7)\(^{126}\)

![Figure 4.7 low-q, mid-q and high-q regions in SANS plot](Image)
The slope at low q provides information on polymer conformation. Plateaus indicate globular or spherical particles. Alternatively, an increasing slope at low q indicates an elongated shape. In some cases, a sharp upturn at very low q (q < 0.07 Å⁻¹) reflects the presence of polymer aggregates. To obtain a quantitative measure of the bottlebrush solution size and conformation, SANS data were first fit to a Guinier-Porod model (Figure 4.8). This is an empirical model applicable to objects of arbitrary shape and provides an estimate of the radius of gyration, Rg, and dimension parameter, s.

As shown in Table 4.2, results from the Guinier–Porod model give Rg values in the range of 100−350 Å for PS-PACMO bottlebrush polymers studied. This is close to the expect range for the overall size of bottlebrush polymers with large backbone DPs. As concluded from Table 4.2, among each fours samples with same side chain length (for example M416, M417, M418 and M419), the Rg estimate from the Guinier–Porod model trends with the PS: PACMO ratios and generally increases as the portion of PACMO increases. And we can conclude that Guinier-Porod model provides a good estimate of the overall size of the molecule. This is further supported by comparison with model fitting using dimension parameters, as discussed below.

Dimension parameter s reflects the shape of the molecule: s = 0 corresponds to a spherical molecule, and s = 1 indicates that the molecule is elongated or rod-like. As shown in Figure 4.8 and Table 4.2, the dimension parameter is relatively lower for bottlebrush polymers with higher PS ratio, and increases significantly with the decrease of PS ratio (the increase of PACMO ratio). Dimension parameter s can be increased from very low value 0.01 to approximately 1 as the backbone DP ratio of PS: PMMA increases from 75:75 to 15:135. Thus, the Guinier-Porod model indicates an increasing bottlebrush
polymer radius with increasing PACMO ratio and increasing polymer elongation with increasing PACMO.

Figure 4.8 SANS scattering intensity for PS-PACMO bottlebrush polymer series

Table 4.2 Overall size and dimension parameters for PS-PACMO bottlebrush polymer series by Guinier-Porod model

<table>
<thead>
<tr>
<th>sample</th>
<th>Theoretical DP</th>
<th>Rg (Å)</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>M422</td>
<td>$S_{2k}^2 A_{75}$</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>M423</td>
<td>$S_{2k}^2 A_{180}$</td>
<td>230.91</td>
<td>0.164</td>
</tr>
<tr>
<td>M424</td>
<td>$S_{2k}^2 A_{120}$</td>
<td>256.88</td>
<td>0.511</td>
</tr>
<tr>
<td>M425</td>
<td>$S_{2k}^2 A_{135}$</td>
<td>185.64</td>
<td>1</td>
</tr>
<tr>
<td>M416</td>
<td>$S_{4k}^4 A_{75}$</td>
<td>241.41</td>
<td>0.405</td>
</tr>
<tr>
<td>M417</td>
<td>$S_{4k}^4 A_{100}$</td>
<td>268.13</td>
<td>0.511</td>
</tr>
<tr>
<td>M418</td>
<td>$S_{4k}^4 A_{120}$</td>
<td>271.63</td>
<td>0.854</td>
</tr>
<tr>
<td>M419</td>
<td>$S_{4k}^4 A_{135}$</td>
<td>341.31</td>
<td>0.992</td>
</tr>
<tr>
<td>M412</td>
<td>$S_{2k}^2 A_{75}$</td>
<td>273.86</td>
<td>0.098</td>
</tr>
<tr>
<td>M413</td>
<td>$S_{2k}^2 A_{100}$</td>
<td>284.55</td>
<td>0.347</td>
</tr>
<tr>
<td>M414</td>
<td>$S_{2k}^2 A_{120}$</td>
<td>254.79</td>
<td>1</td>
</tr>
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<td>M415</td>
<td>$S_{2k}^2 A_{135}$</td>
<td>N.A.</td>
<td>1</td>
</tr>
<tr>
<td>M426</td>
<td>$S_{4k}^4 A_{75}$</td>
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<td>0.006</td>
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<td>M427</td>
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<td>225.29</td>
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<tr>
<td>M428</td>
<td>$S_{4k}^4 A_{120}$</td>
<td>241.27</td>
<td>0.057</td>
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<tr>
<td>M429</td>
<td>$S_{4k}^4 A_{135}$</td>
<td>284.34</td>
<td>0.245</td>
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</tbody>
</table>
4.3. Chapter Conclusion

The work in this chapter can be seen as a continuity of the nanoparticle interfacial properties work in Chapter 2 and Chapter 3. In this chapter, we investigate the interfacial properties of a category of polymer in branched polymer family: bottlebrush polymer and its and self-assembly in aqueous solutions.

A series of amphiphilic diblock PS-PACMO bottlebrush copolymers have been prepared by reversible-fragmentation addition chain-transfer (RAFT) followed by ring-opening metathesis polymerization. The backbone has four kinds of PS:PACMO ratios combined with four side chain molecular weight ratios of 2k:2k, 4k:4k, 2k:4k, 4k:2k.

The polymers are able to form stable micelles in water at low concentrations through solvent dialysis methods. We characterized the self-assembly of bottlebrush copolymers at very low dilution and demonstrated its ultra-low critical micelle concentration (CMC).

With the aid of advanced neutron source at ORNL, we were also able to quantify the self-assembly and phase behavior of a model library of amphiphilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurements. And the ratio of PS:PACMO block has been shown to affect the overall size and dimension parameters in a good solvent.
Chapter 5

General Conclusions and Suggestion for Future Work
This thesis investigated a number of laboratory-made novel polymeric materials and their surface properties, including their stabilizing reversible oil-in water macroemulsions, their segregation into microemulsion and stabilizing microemulsion. What is also covered is the self-assembly of amphiphilic bottlebrush polymers in aqueous solution and ultra-low CMC. All these studies based on these polymeric materials have potential application in EOR process. In some cases like the reversible emulsification with DMAEMA PNPs, the study is completely developed and an enhanced oil recovery of bitumen heavy oil has been reported. In some other cases, at least a fundamental study is accomplished, and that will help future studies on understanding the interfacial properties of polymeric materials and EOR.

The originality and contributions in this thesis can be summarized in the following aspects:

1. Demonstrated that properly designed amphiphilic polymer-coated nanoparticles spontaneously and preferentially segregate to the bicontinuous micro-emulsion phases of oil-water-surfactant system and able to stabilize microemulsions. What was also demonstrated is the feasibility of application for X-ray scattering techniques in the study of microemulsion structures.

Mixtures of hydrophilic and hydrophobic chains are covalently grafted onto the surface of oxidized carbon black nanoparticles and the polymer-coated nanoparticles are stable in the aqueous phase at salinities up to 15 wt % NaCl. These amphiphilic nanoparticles segregate to the bicontinuous micro-emulsion phases. We analyzed the
equilibrium phase behavior of the nanoparticles, measured the interfacial tension, and quantified the domain spacing in the presence of nanoparticles. This work shows a novel route to the design of polymer-coated nanoparticles which are stable at high salinities and preferentially segregate to bicontinuous micro-emulsion phases.

For future studies, we expect systematic studies of a polymer coated nanoparticle that does lower the interfacial tension on order of tens of mN/m and its influence on micro-emulsion in the presence of a surfactant. The coating of nanoparticle with more surface active chains, as well as the tailoring of size of PNPs to be larger or smaller, are to be studied for the preparation of PNPs that bring lower interfacial tensions.

2. Developed and demonstrate stimuli-responsive PNPs that can be used to stabilize and break oil/water emulsions by the variation of pH. And I accomplished a set of studies that eventually enhanced the bitumen crude oil recovery by 10 wt %.

Silica particles with poly(dimethyl ethyl acrylamide) (DMAEMA) chains covalently grafted to the surface are prepared through a reversible addition fragmentation chain transfer (RAFT) grafting-through technique. We demonstrated that DMAEMA PNPs can be used to stabilized Pickering emulsions of high viscosity Canadian bitumen from oil sand at additive concentration as low as 0.1 wt % and at a neutral pH. The performance of the DMAEMA PNPs exceeds that of pure DMAEMA homopolymer additive or of just water with no additive. By reducing the pH of the aqueous solution, the interfacial activity of the DMAEMA decreases and the emulsion is destabilized, allowing the heavy oil to coagulate and settle. We demonstrate sandpack flooding experiments using 0.1 wt % DMAEMA PNPs as additives and find that the nanoparticles are able to
recover approximately 10 wt % of the heavy crude oil in place. This work demonstrates the applicability of PNPs as surface active materials for EOR process and for heavy oil transportation.

For future studies, I suggest a thorough microfluidic flowing study to fully investigate the detailed process of bitumen recovery in porous media. Although we have successfully demonstrated a enhanced oil recovery with addition of PNPs, the process and role of PNPs in porous media haven’t been fully revealed. It could be emulsion stabilized combined with IFT reduction or wettability alternation, but has to be visualized and demonstrated.

3. Extensively investigated the self-assembly and phase behavior of a model library of amphiphilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurements. And this study also revealed the relationship between polymer structure and its assembly behavior in solution. And the ultra-low CMC of bottlebrush polymer compared with linear analogy was first time reported by us.

A series of amphiphilic diblock PS-PACMO bottlebrush copolymers have been prepared by reversible-fragmentation addition chain-transfer (RAFT) followed by ring-opening metathesis polymerization. The polymers are able to form stable micelles in water at low concentrations through solvent dialysis methods. We characterized the self-assembly of bottlebrush copolymers at very low dilution and demonstrated its ultra-low critical micelle concentration (CMC). We were also able to quantify the self-assembly and phase behavior of a model library of amphiphilic bottlebrush block polymers through small-angle neutron scattering (SANS) measurements. And the ratio of PS:PACMO
block has been shown to affect the overall size and dimension parameters in a good solvent.

For future works, I would first suggest a thorough microscopy, i.e. cryo-electron microscopy study of polymer micelles to couple with the SANS studies we have accomplished so far. The advantage of cryo-TEM is that it makes the visualization of micelle possible, and it would perfectly reproduce the state of micelle in solution. With the combination of cryo-TEM studies and SANS study, we would have a clearer picture of bottlebrush polymer micelle behaviors. Secondly, since this works so far is some fundamental study of polymer assembly, I would suggest some active search of actual application with this study, for example crude oil emulsification or drug delivery.
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