Preparation and Characterization of Temperature-Responsive Polymeric Surfactants

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Canada has large reserves of heavy oil stored in the form of oil sands in the Athabasca region. This type of heavy oil does not flow at room temperature and its agglomeration with sand complicates its extraction. Consequently, extraction of the oil is costly and remains challenging. This project aims to use a temperature-responsive polymeric surfactant (TRPS) to improve the extraction of oil. The temperature-responsive polymeric surfactant (TRPS) poly(ethylene glycol)-b-poly[2-(2-methoxyethoxy) ethyl methacrylate] (PEG-b-PMEO$_2$MA) was successfully prepared by atom transfer radical polymerization (ATRP) and its efficacy at extracting oil from oil sands was investigated. First, several PEG-b-PMEO$_2$MA samples were synthesized having an absolute molecular weight ranging from 17,000 to 20,000 g/mol as determined by NMR and an apparent PDI ranging from 1.1 to 1.5 as determined by GPC analysis. Then, the lower critical solution temperature (LCST) was found to equal 34 ± 1°C for all samples by turbidity measurements. The PEG$_{113}$-b-PMEO$_2$MA$_{64}$ micelles in aqueous solution, whose hydrodynamic diameter (d_h) determined by dynamic light scattering (DLS) equaled 26.3 ± 0.3 nm, had an aggregation number (N_agg) of 100 ± 8. After characterization of this TRPS, PEG-b-PMEO$_2$MA was used for oil extraction and showed promising results. With the addition of 60 to 65 mg of toluene on top of 15 mL of a 1 mg/mL PEG-b-PMEO$_2$MA aqueous solution, complete oil recovery could be achieved by putting the TRPS solution with 1 g of oil sands in a shaker at 45 or 50 ℃ for 24 hrs. In addition, a time-dependent oil extraction experiment showed that by using a 1 mg/mL TRPS aqueous solution, 100% oil recovery was reached after only 6 hrs. Furthermore, the PEG-b-PMEO$_2$MA aqueous solution could be recycled for several oil extraction cycles while still maintaining a high oil recovery.

Acknowledgements

Dedication

To my loving parents,

Xiaojin Yang and Haixin Zhao,

And to my loving grandparents,

Ming Li, Guojun Yang, Qunying Lin and Ruchu Zhao.

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List of Abbreviations

ATRP	Atom transfer radical polymerization
c	Concentration
CHWE	Clark hot water extraction
COFCAW	Combination of forward combustion and water flood
DCM	Dichloromethane
d_h	Hydrodynamic diameter
dn/dc	Refractive index increment
DLS	Dynamic light scattering
DMSO	Dimethyl sulfoxide
DRI	Differential refractive index
DP_n	Number-average degree of polymerization
GPC	Gel permeation chromatography
η_{rel}	Relative viscosity
η_{sp}	Specific viscosity
$[\eta]$	Intrinsic viscosity
^{1}H NMR	Proton nuclear magnetic resonance
LALS	Low angle light scattering
LCST	Lower critical solution temperature
LS	Light scattering
MEO_2MA	2-(2-Methoxyethoxy)ethyl methacrylate
M_n	Number-average molecular weight of the copolymers
$M_{n,mic}$	Number-average molecular weight of the micelles
m_{tol}	Mass of toluene
MW	Molecular weight
MWD	Molecular weight distribution
N_A	Avogadro's number

N_{agg}	Aggregation number
NIPAM	N-Isopropylacrylamide
NFT	Naphthenic froth treatment
PDI	Polydispersity index
PEG	Poly(ethylene glycol)
PEG-b-PNIPAM	Poly(ethylene glycol)-$block$-poly(N-isopropylacrylamide)
PEG-b-PMEO2MA	Poly(ethylene glycol)-$block$-poly[2-(2-methoxyethoxy)ethyl methacrylate]
PFT	Paraffinic froth treatment
PMDETA	N, N, N, N'', N''-Pentamethyldiethylenetriamine
PNIPAM	Poly(N-isopropylacrylamide)
PS	Polystyrene
RALS	Right-angle light scattering
rpm	Revolutions per minute
r.t.	Room temperature
SAGD	Steam-assisted gravity-drainage
TEA	Triethylamine
THF	Tetrahydrofuran
TRPS	Temperature-responsive polymeric surfactant
UV-Vis	Ultraviolet-Visible
V_h	Hydrodynamic volume
$wt\%[oil]$	Weight fraction of oil extracted from the oil sand

Chapter 1
Introduction

1.1 Background Information

Oil sands, also known as tar or bitumen sands, are deposits of silica particles soaked in bitumen, a high molar mass viscous petroleum.[1,2] Oil sands are found throughout the world. Canada and Venezuela have the world's two largest reserves of bitumen, with combined oil sands reserves estimated to be equal to the world's total reserves of conventional crude oil.[1,3] The largest deposit, and the only one of present commercial importance is in the Athabasca region located in the northeastern part of Alberta, Canada. The extraction of bitumen from oil sands is of high economic interest but presents some difficult challenges. Since bitumen are heavy oils consisting of large hydrocarbon molecules that are usually in the solid state at room temperature,[4] their extraction is difficult. In addition, the Athabasca region possesses 250 billion barrels worth of bitumen located in beds of sand and clay where the oil and sand usually stick to each other,[2,4] further complicating the oil extraction process.

For more than one hundred years, numerous scientists, engineers, and individuals have investigated how the bitumen can be recovered from the oil sands economically and efficiently. Several bitumen extraction processes have been developed over the years and these processes can generally be divided into two main families. The first family is referred to as open pit mining technology,[1] where the oil sands are mined and transported to a processing plant where the bitumen is extracted. The second family aims to separate the bitumen from the sand directly in the geological formation without moving the sand and it is referred to as in-situ technology.[1]

The methods applied for in-situ technology always require a high temperature since this technology uses heat to melt the bitumen trapped in the oil sands and make it mobile in

order to collect the bitumen as a fluid. For example, the heat generated during fire flooding[5] by igniting the oil in the oil formation decreases the viscosity of the bitumen and makes it sufficiently mobile that it can be recovered from the production wells. In this example, the required temperature is above 340 °C. Similarly to fire flooding, a combination of forward combustion and water flood referred to as the COFCAW process[6] is another example of in situ technology, whereby the heat is generated by injecting hot air and water into the formation at temperatures ranging from 90 to 820 °C. The emulsion-steam drive process[7] is another method related to in-situ technology. In this case, a caustic aqueous solution of NaOH is used at a relatively low operating temperature of 180 °C to drive the bitumen out of its formation. Regardless of the procedure employed, all methods require vast amounts of energy to generate the heat necessary to lower the viscosity of the bitumen trapped in oil sands and are costly and environmentally unfriendly since they generate large quantities of CO_2, a greenhouse gas.

Like the in situ technology, open mining also requires energy for bitumen extraction. The first reported commercial process for the extraction of bitumen from Athabasca oil sands was developed by Karl Clark in the 1920s.[1,2] Interestingly, most companies involved in Alberta bitumen extraction today, such as Syncrude Canada Ltd., Suncor Energy Inc., or Albian Sands Energy Inc. still use variations of the Clark Hot Water Extraction (CHWE) process. The temperature used in the CHWE process ranges from 50 to 80 °C depending on the application.[8]   Direct coking of the oil sands[1] is the most straightforward bitumen extraction method, whereby the oil sand is heated up by contact with a bed of clean sand in a coker or still maintained at temperatures that range from 480 to 760 °C. The advantage of this method is that the hot sand recovered after the extraction process can be recycled as a

fluidized bed to melt the bitumen in the oil sands as a way to save energy. In the 1990s, a cold water process[9,10] was introduced by Sury to lower the temperature of bitumen extraction. This method used water with a conditioning agent that is mixed with the oil sands at temperatures ranging from 5 to 25 °C and with a mixing speed ranging from 1500 to 3200 rpm. This extraction process resulted in a bitumen recovery ranging from 50 to 70% depending on the temperature and the mixing speed applied.

Water-based extraction of bitumen from Athabasca oil sands causes environmental issues, regardless of whether it is based upon in situ or open pit mining technologies.[2,11] First, the heat necessary for bitumen extraction causes greenhouse gas emission, which is a known contributor to global warming.[2,11] Second, tailing ponds are oil-in-water emulsions that are generated by the bitumen extraction. They have had an adverse impact on the local environment.[2,11] Since water-based bitumen extraction consists of a sequence of mining (for open mine technique), extraction, froth treatment, and water management in the tailing ponds,[8] there is a demand for new techniques that could be applied towards the extraction process or froth treatment to try to eliminate these steps that cause environmental hazards. Considering the bitumen froth treatment, it must be pointed out that a typical bitumen froth is composed of 60 wt% bitumen, 30 wt% water, and 10 wt% mineral solids.[12,13] In the last twenty years, notable progress has been made in the handling of bitumen froth to enhance overall bitumen recovery and reduce the number of tailing ponds. Paraffinic (PFT) and naphthenic (NFT) froth treatments are two of the methods that are applied in industrial operations. Naphthenic and paraffinic solvents are employed to increase the organic content of the bitumen froth and lower its viscosity so that the inorganic impurities (water and mineral

particles) can be separated from the solution of bitumen and organic solvent. As compared to PFT, the NFT process consumes much more energy but recovers bitumen at a higher yield. Due to the higher recovery, NFT has been applied to most projects of the Athabasca oil sands industry. Although both methods enhance bitumen recovery and generate fewer tailing ponds, both PFT and NFT use large quantities of organic solvent, such as paraffin and naphtha which are environmentally unfriendly and more difficult to deal with as compared to water.[12,13]

Despite the advances that have been made to improve bitumen extraction from oil sands, the extraction process of the oil sands remains costly since it requires burning oil to reach a temperature high enough to melt the bitumen and is not environmentally friendly as it generates greenhouse gases and stable oil-in-water emulsions that end up in tailing ponds. This thesis proposes to use a temperature-responsive polymeric surfactant that would enable bitumen extraction at a lower temperature and minimize the formation of stable oil-in-water emulsions. The following discussion describes how this will be accomplished.

1.2 Temperature-Responsive Polymeric Surfactant (TRPS)

1.2.1 Temperature-Responsive Polymer and Lower Critical Solution Temperature (LCST)

A temperature-responsive polymer is a polymer that changes one of its physical properties with an external thermal stimulus. Here, temperature-responsive polymer describes hydrophilic polymers that become hydrophobic above a specific temperature, namely the lower critical solution temperature (LCST). Temperature-responsive polymers have been investigated as smart materials for various applications, especially in nano- and biotechnology.[14-20] Since temperature-responsive polymers self-assemble in aqueous solution

above their LCST, they have been used in phase separation immunoassays,[14] hyperthermia-induced drug delivery,[15] environmentally responsive Pickering emulsions,[16] the treatment of hospital surfaces and medical devices,[17,18] filtration devices,[19] and food manufacturing.[20]

Poly[2-(2-methoxyethoxy)ethyl methacrylate] (PMEO$_2$MA), poly(*N*-isopropylacrylamide) (PNIPAM), and poly(ethylene glycol) (PEG) are three temperature-responsive polymers commonly encountered in scientific studies[21-23] and some of their properties will be discussed in this thesis. PMEO$_2$MA has a LCST of 26 °C,[24] while the LCST of PNIPAM is 32 °C.[25,26] However, PEG has a much higher LCST of 98 °C,[26] which is close to the boiling point of water. Consequently, PEG is usually viewed as a hydrophilic polymer in aqueous solutions.

1.2.2 Surfactant

An amphiphilic molecule consisting of a hydrophobic and a hydrophilic part is called a surfactant. Within the temperature range where PMEO$_2$MA is dehydrated and PEG remains solvated in water, poly(ethylene glycol)-block-poly[2-(2-methoxyethoxy)ethyl methacrylate] (PEG-*b*-PMEO$_2$MA) qualifies as a polymeric surfactant as it consists of a hydrophobic PMEO$_2$MA block and a hydrophilic PEG block. Above its LCST, PEG-*b*-PMEO$_2$MA has been shown to form polymeric micelles consisting of a hydrophobic PMEO$_2$MA core and a hydrophilic PEG shell in aqueous solution, as described in Figure 1.1.[24-26]
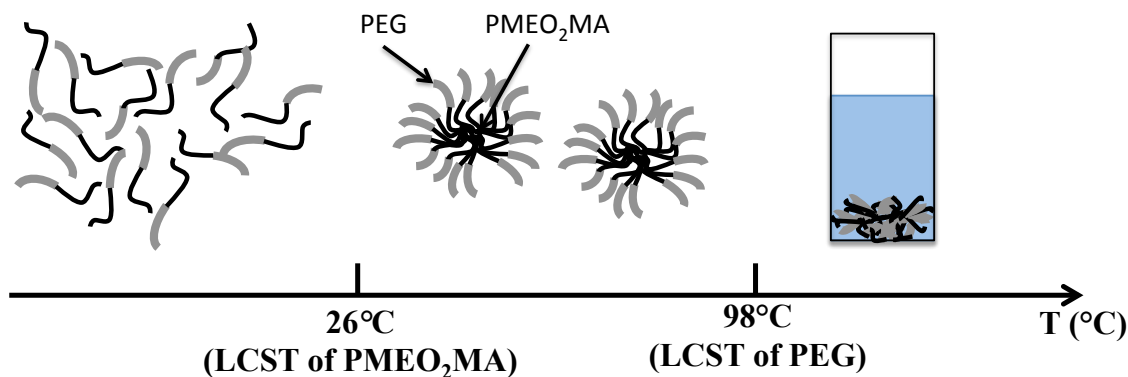
Figure 1.1: Expected temperature response of PEG-*b*-PMEO2MA in aqueous solution as a function of temperature.[21,22]

As shown in Figure 1.1, both PEG and PMEO$_2$MA blocks are water-soluble at T < 26 °C. Above T = 98 °C, both blocks are insoluble in water and the copolymer precipitates. A polymeric surfactant such as PEG-*b*-PMEO$_2$MA, whose hydrophobicity is sensitive to temperature, will be referred to as a temperature-responsive polymeric surfactant or TRPS. PEG-*b*-PMEO$_2$MA can be synthesized by atom transfer radical polymerization (ATRP), which is a polymerization technique that enables the synthesis of polymers with a narrow molecular weight distribution (MWD) and a low polydispersity index (PDI).

1.3 Extraction of Bitumen from Oil Sands by Using a Temperature-Responsive Polymeric Surfactant

In this thesis, a bitumen extraction protocol is proposed that uses a temperature-responsive polymeric surfactant to extract bitumen from oil sands. This protocol is described in Figure 1.2. The block copolymer PEG-*b*-PMEO$_2$MA will be used as an example to explain the procedure.
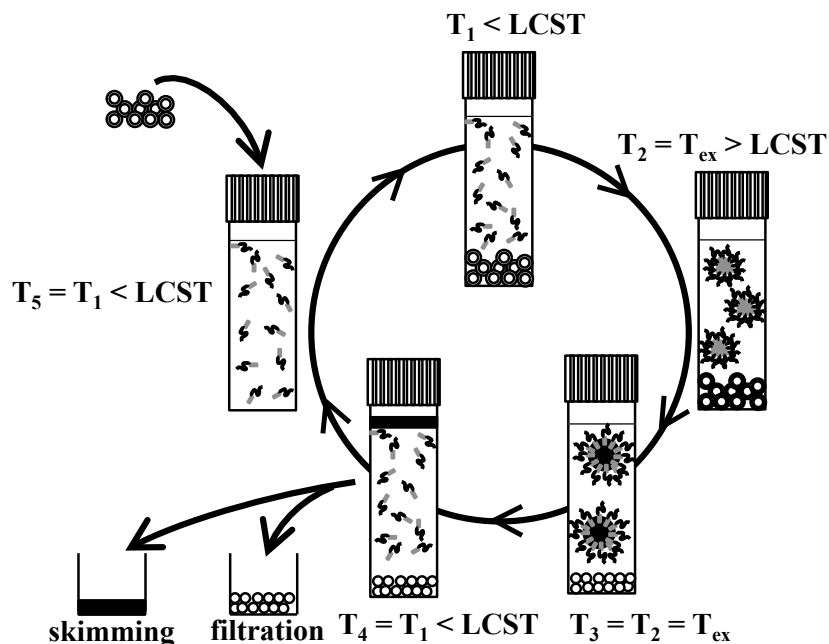
Figure 1.2: Proposed process for oil extraction from oil sands by using the temperature-responsive block copolymer PEG-*b*-PMEO$_2$MA.

On the left of Figure 1.2, oil sands are introduced into a vial filled with a TRPS aqueous solution at a temperature T_1 where they sink to the bottom of the vial. At $T_1 <$ LCST, the temperature-responsive block copolymer is water-soluble and no micelle forms. When the temperature increases to T_2 above the LCST of the temperature-responsive block of the copolymer, it becomes hydrophobic while PEG remains hydrophilic. Thus block copolymer micelles form with a hydrophobic PMEO$_2$MA core and a hydrophilic PEG shell. If T_2 is selected such that it is greater than the melting temperature of the oil, the hydrophobic oil trapped in the sand particles will flow and swell the hydrophobic core of the micelles to generate an emulsion. At T_4, when the temperature is lower than the LCST of PMEO$_2$MA, the PMEO$_2$MA block becomes water-soluble again and micelles no longer exist. The oil being less dense than water phase-separates at the surface of the aqueous phase and the oil-free sand

particles sink to the bottom of the vial. Finally, the oil and sand can be separated. After this is done, a new extraction cycle can be started using the recovered TRPS aqueous solution.

To accomplish the bitumen extraction cycle shown in Figure 1.2, the TRPS must fulfill a number of requirements. Firstly, the TRPS should be water-soluble at room temperature (T = 25 °C) because it is easier to deal with experimentally. In addition, the water-soluble block of the TRPS should be soluble in water over the temperature range where water is liquid, i.e. from 0 to 100 °C. These criteria ensure that micelle formation can be controlled by the temperature-responsive block only. Third, the temperature-responsive block should interact with the bitumen above its LCST. These features led us to select PEG-*b*-PMEO$_2$MA for this study. PEG is soluble from 0 to 98 °C and PMEO$_2$MA has an LCST at 26 °C.[24] Although the LCST of PMEO$_2$MA is close to 25 °C, it increases if a water-soluble component is present, such as the PEG block.[21,22] Finally, PMEO$_2$MA is soluble in toluene which, as it turns out, is also a good solvent for the bitumen trapped in the oil sands. As a result, PMEO$_2$MA should also be able to interact with bitumen.

1.4 Outline of the Thesis

The primary goal of this study was to demonstrate that TRPS can be employed to extract oil from oil sands. To achieve this goal, a well-defined temperature-responsive block copolymer was synthesized by ATRP. The composition of the selected TRPS was determined by a combination of gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. After determination of the chemical composition of this block copolymer, its ability to form block copolymer micelles in solution was investigated as a function of temperature. The lower critical solution temperature (LCST) of the copolymer was

measured by turbidimetry with a UV-Vis spectrophotometer. Dynamic light scattering (DLS) was applied to demonstrate the formation of block copolymer micelles above the LCST of the temperature-responsive block and to determine the diameter of the block copolymer micelles. Furthermore, viscosity measurements were carried out to determine the number of block copolymer molecules per micelle. This was achieved by using the intrinsic viscosity of the block copolymer solution measured above the LCST and the hydrodynamic diameter (d_h) of the block copolymer micelle determined by DLS. Ultimately, these properties were applied to establish conditions for using PEG-*b*-PMEO$_2$MA aqueous solutions for oil extraction. This information was then applied to design a series of oil extraction experiments aimed to maximize the extraction of oil from oil sands by using this TRPS.

This thesis is organized in the following manner. Chapter 1 is an introduction where the background material needed to understand the goal of this thesis has been presented. Chapter 2 describes the experimental procedures that were applied for the synthesis of the block copolymer PEG-*b*-PMEO$_2$MA by ATPR, the characterization of this TRPS, and the oil extraction protocol based on the use of PEG-*b*-PMEO$_2$MA. Chapter 3 presents and discusses the results obtained by following the experimental protocols outlined in Chapter 2. Finally, Chapter 4 summarizes the main results of Chapter 3, provides some concluding remarks, and suggests some future work.

Chapter 2

Experimental Section

2.1 Materials

2-Bromoisobutyryl bromide (Aldrich, 98%), *N,N,N,N'',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 2-(2-methoxyethoxy)ethyl methacrylate (MEO$_2$MA, Aldrich, 95%), magnesium sulfate (MgSO$_4$, Aldrich, $\geq$ 99.5%), 2,2'-bipyridine (Aldrich, 98%), toluene (Aldrich, 99.9%), tetrahydrofuran (TEA, Aldrich, $\geq$ 99.5%), *n*-hexane (Aldrich, $\geq$ 98.5%) and methanol (Aldrich, $\geq$ 99.9%) were used as received. PEG terminated at a single end with a hydroxyl group (M$_n$ = 5000, Aldrich) was purified by dissolving it in dichloromethane (DCM, Aldrich, $\geq$ 99.8%) followed by precipitation with cold diethyl ether (Aldrich, $\geq$ 99.0%). The precipitation was repeated twice. Tetrahydrofuran (THF, Aldrich, $\geq$ 99.0%) and ethanol (Aldrich, HPLC Grade) were distilled prior to use. CuBr (Aldrich, 99.999%) was washed with deionized water, acetic acid (Fisher, ACS reagent, glacial), ethanol, and ether in that sequence and then dried in vacuum and stored under nitrogen before use. Milli-Q Millipore filtered water (18 MΩ·cm) was used in all experiments. Praxair Ultra Pure 5.0 nitrogen was used in all syntheses. An oil sands sample was provided by Dr. Chakrabarty from Imperial Oil.

2.2 Synthesis of the Temperature-Responsive Polymeric Surfactant

2.2.1 Synthesis of 2-Bromopropionate PEG Macroinitiator[27]

A PEG macroinitiator was first prepared according to a published procedure (Scheme 2.1).[27] The hydroxyl end group of PEG was reacted with 2-bromoisobutyryl bromide to give the 2-bromoisopropionate PEG macroinitiator.
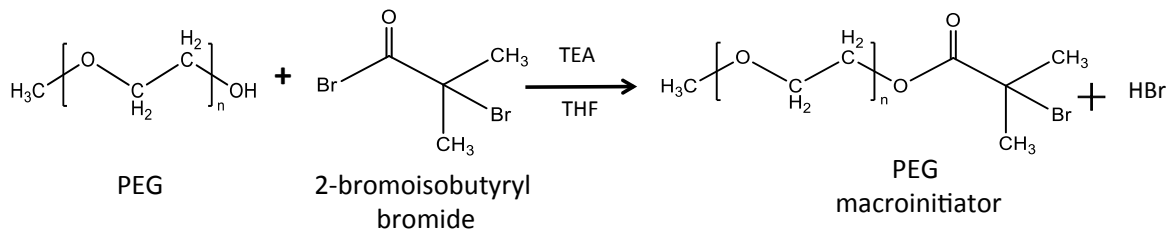
Scheme 2.1: Synthesis of PEG macroinitiator.[23]

PEG (5.5 g, 1.1 mmol) was dissolved in freshly distilled THF (50 mL) in a three-neck round bottom flask that had been dried beforehand by flaming under vacuum followed by purging with nitrogen. TEA (0.46 mL, 3.3 mmol) was then added under nitrogen. The flask was lowered in an ice-water bath at 0 °C and 2-bromoisobutyryl bromide (0.82 mL, 6.6 mmol) was injected by using a glass pipette into the reaction flask. All the processes were conducted under a positive nitrogen pressure to prevent the introduction of moisture from the air. After the addition of 2-bromoisobutyryl bromide, the reaction was stirred at room temperature (r.t.) for 24 hours. During the reaction, a precipitate of TEA hydrobromide formed. The precipitate was removed by centrifugation. Magnesium sulfate (~0.2 g) was added to remove any traces of water that might be absorbed by the mixture during the centrifugation process. A clear solution was collected. Finally, the macroinitiator was purified with 4 cycles of precipitation into *n*-hexane at −72 °C (by keeping the vessel on dry ice), filtration, and drying under vacuum.

2.2.2 Synthesis of PEG-*b*-PMEO₂MA by ATRP

With the PEG macroinitiator, a conventional ATRP procedure was applied to synthesize the PEG-*b*-PMEO₂MA copolymer according to Scheme 2.2.[24]
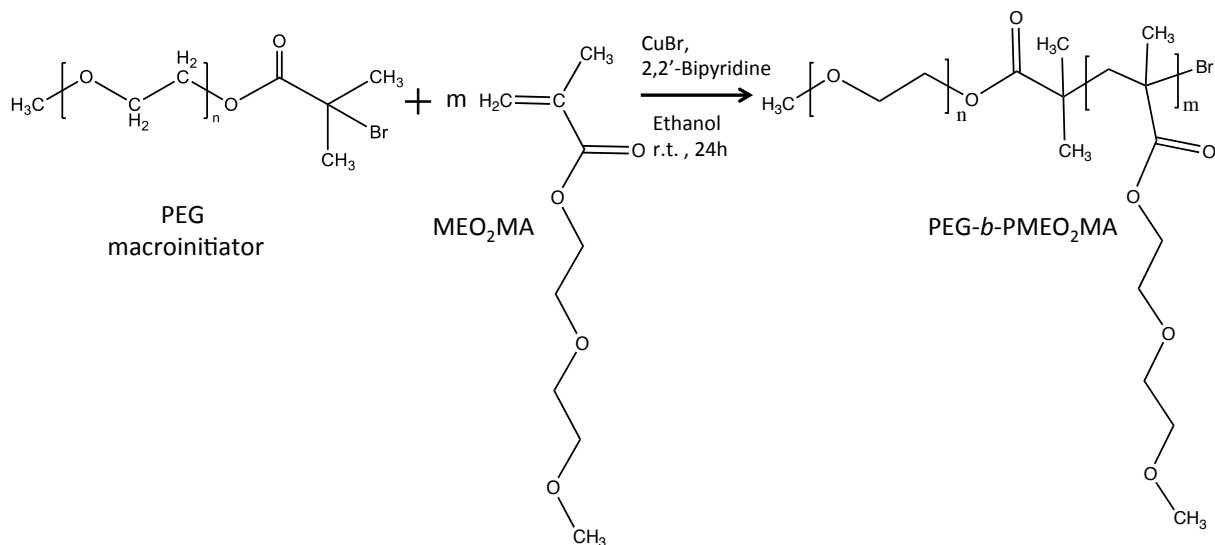
Scheme 2.2: Synthesis of PEG-*b*-PMEO₂MA by ATRP.[24]

The 2-bromopionate PEG macroinitiator (0.990 g, 0.192 mmol), MEO₂MA (2.7 mL, 15 mmol), and 2,2'-bipyridine (91.2 mg, 0.584 mmol) were dissolved in ethanol (3.3 mL) and the solution was placed in a schlenk tube. The mixture was degassed by three freezing-evacuation-thawing cycles. In the last cycle, the Schlenk tube was filled with N_2 and the mixture was kept frozen. The catalyst CuBr (60 µL, 0.28 mmol) was added as a fine powder through a Pasteur pipette to the surface of the frozen solid against a positive pressure of nitrogen. After addition of the catalyst, the mixture was degassed with one more freezing-evacuation-thawing cycle. Finally, the tube was filled with N_2, tightly sealed and stirred at r.t. for 24 hours.

After 24 hours, the reaction was terminated by purging the vessel with air. The ethanol was left to evaporate. The resulting oily mixture was dissolved in methanol.[24] Then the brownish mixture was passed through a short (3-5 cm) silica gel column (neutral, 40-60 µm) (eluent, methanol) to remove the copper complex.[27] Finally, the product was dialyzed in a

regenerated cellulose membrane tubing (molecular weight cut-off, 8,000; Spectrum, Rancho Dominguez, CA) against methanol for several days to remove small molecules. The methanol was removed with a rotary evaporator, and the polymer sample was dried under vacuum at room temperature.

2.3 Characterization of the Temperature-Responsive Copolymers

2.3.1 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analysis was used to obtain the molecular weight distribution (MWD) of the copolymers from their number-average degree of polymerization (DP_n) and polydispersity index (PDI). Tetrahydrofuran (THF) was chosen as the GPC solvent for PEG-*b*-PMEO$_2$MA.

The GPC instrument (Viscotek GPCmax VE2001, Malvern instruments Ltd., Malvern, UK) using THF as the eluent was equipped with right-angle light scattering (RALS), low-angle light scattering (LALS), ultraviolet absorbance (UV), and differential refractive index (DRI) detectors, and the GPC traces obtained with these four detectors could theoretically be used to determine the absolute molecular weight and PDI of a polymer. In practice, however, the small PEG-*b*-PMEO$_2$MA sample that was prepared did not scatter enough light to yield reliable light scattering data and GPC analysis based on the light scattering signal could not be used. Therefore, the apparent molecular weight of this sample was reported using a calibration curve based on polystyrene (PS) standards.

2.3.2 Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy

The absolute molecular weight of the copolymer could be determined from ^{1}H NMR spectroscopy. Since the protons associated with different functional groups of the copolymer

resonate at different frequencies in the ^{1}H NMR spectrum, the molar ratio of the protons associated with two different functional groups can be determined from the ratio of the areas under the two peaks. In turn, this information can be utilized to determine the absolute DP_n of a copolymer.

2.4 Determination of Micelle Formation

2.4.1 Turbidity Measurements

The transmittance of a 5 mg/mL polymer aqueous solution was monitored at 400 nm by using a UV-Vis spectrophotometer (Model CARY-100, Welltech Enterprises, INC., Maryland, US). The temperature was increased at a rate of 0.5 ºC/min. The temperature where the transmittance began to decrease was defined as the LCST.[28]

2.4.2 Dynamic Light Scattering (DLS) Measurements

After the polymer was dissolved in water at a concentration of 5 mg/mL, the solution was centrifuged at 13,300 rpm for 10 min to remove dust particles. Then, the hydrodynamic diameter (d_h) of the polymer species present in solution was measured as a function of temperature with a Brookhaven 90 Plus particle sizer (Brookhaven Instruments, Inc., Holtzville, NY), which measures the scattered light at a 90° angle, and a Zetasizer Nano-ZS (Malvern Instruments Ltd., Worcestershire, UK), which measures the scattered light at a 173° angle.

2.4.3 Viscosity Measurements

Solutions were prepared at polymer concentrations ranging between 5 and 25 mg/mL. The viscosity of the solutions was determined at 50 °C with an Ubbelohde viscometer (Model D504, Cannon Instrument Company, Stage College, PA).

2.5 Oil Extraction

2.5.1 Soxhlet Extraction

To quantify the total mass of oil recovered from one gram of oil sands, Soxhlet extraction was applied following a protocol established by Jacobs and Filby.[29] Approximately 5 g of oil sands wrapped in filter paper was placed inside the main chamber of the Soxhlet apparatus. Then the apparatus was used to extract the bitumen from the oil sand sample using refluxing toluene (110 °C) or THF (66 °C) as the solvent. The round bottom flask of the apparatus was immersed in an oil bath which was heated and stirred with a magnetic stirrer. For both the toluene and THF extractions, the set up was left to reflux for 24 h. After the extraction was complete, the clean sand was dried in a vacuum oven at room temperature for 24 h, and the bitumen from the oil sand sample that had dissolved in toluene or THF was dried under a stream of nitrogen before placing it in a vacuum oven at room temperature for 24 h to remove any residual solvent.

2.5.2 Extraction Protocols

Extraction Protocol #1. An oil sand sample (1 g) was placed in a 20 mL scintillation vial. Then 15 mL of a 1 mg/mL aqueous solution of different polymers was added to the vial as shown in Figure 2.1(a). The vial was placed in an incubator shaker (Innova 4000, New Brunswick Scientific Co., Inc., Nijmegen, Netherlands) where it was left to stir at 250 rpm at 45 °C or 50 °C. After 24 h the shaker was stopped, the vial was taken out, and a picture was taken.

Extraction Protocol #2. At the bottom of a 20 mL scintillation vial, 1 g of oil sand was deposited before adding 15 mL of different aqueous solutions. Toluene (27 mg – 140 mg) was

placed on top of the aqueous solution as shown in Figure 2.1(b). The vials were left in the shaker for 24 h at 250 rpm at T = 45 °C or 50 °C.
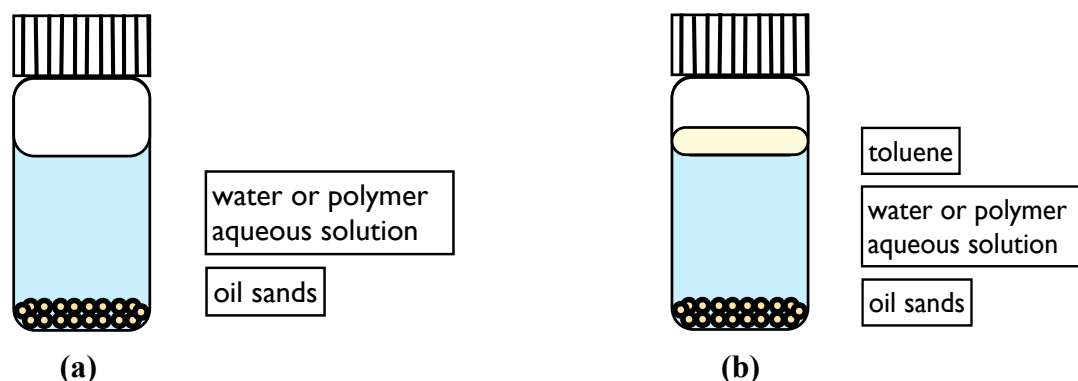
Figure 2.1 Extraction protocol #1 (a) and #2 (b).

Separation of Oil and Sand after Extraction. After the bitumen extraction was completed, the vials were taken out and the oil present at the top of the aqueous solution and on the vial wall was recovered by rinsing the wall with a few drops of toluene and collecting the oil-loaded toluene with a Pasteur pipette. The toluene was evaporated under a gentle flow of nitrogen. Then the aqueous solution was removed and the oil that remained stuck to the sand at the bottom of the vial was collected by rinsing the oily sand with THF. The oil recovered in the top layer, the oil recovered in the bottom layer, and the sand free from oil were placed in a vacuum oven at room temperature overnight to remove any traces of water, THF, or toluene. The mass of sand and oil recovered after extraction were added and the total mass was compared to that of the mass of oil sands that was weighed originally. If the two masses differed by more than ± 10%, the results from the extraction experiment were discarded.

2.5.3 Recovery of PEG-*b*-PMEO$_2$MA after Extraction

After an oil extraction cycle was completed according to *Extraction Protocol* #2, the aqueous layer was collected after removal of the toluene layer laced with oil. To remove small sand particles that might have been introduced in the aqueous solution during the oil extraction process, the mixture was centrifuged at room temperature at 10,000 rpm for 15 min. The supernatant was collected and freeze-dried for two days to remove the water. After the removal of water, a white cotton-like solid was recovered which was dissolved in THF. The amount of THF added was recorded for later calculations. The solution was injected into the GPC and the DRI signal of the PEG-*b*-PMEO$_2$MA solution in THF was measured with the DRI detector of the GPC instrument to determine the concentration of the PEG-*b*-PMEO$_2$MA copolymer in the THF solution.

To this end, a calibration curve was built to relate the DRI signal to the PEG-*b*-PMEO$_2$MA concentration in THF. Several solutions of PEG-*b*-PMEO$_2$MA in THF were prepared with different concentrations of the block copolymer. The solutions of known block copolymer concentration were injected into the GPC and the maximum DRI intensity in the GPC trace was plotted as a function of polymer concentration. This plot yielded a straight line which was used as a calibration curve to determine the unknown concentration of the PEG-*b*-PMEO$_2$MA solutions in THF that were injected into the GPC.

2.5.4 Extraction Efficiency as a Function of the Number of Oil Extraction Cycles

The aqueous solution of block copolymer PEG-*b*-PMEO$_2$MA was used for 5 oil extraction cycles conducted according to *Extraction Protocol* #2, to evaluate its reusability after an oil extraction cycle. As described in *Extraction Protocol* #2, the first extraction cycle used 15 mL

of a 1 mg/mL PEG-b-PMEO$_2$MA aqueous solution with a 65 mg toluene layer on top of the aqueous solution to extract the oil trapped in 1 g of oil sands. After the first cycle, the amount of oil recovered was determined, and the aqueous solution was isolated for the following oil extraction cycle. Due to the loss of aqueous solution during the oil extraction and separation process, the recovered PEG-b-PMEO$_2$MA solution was topped to 15 mL with the necessary amount of water to maintain the same volume of aqueous solution in each extraction cycle. This procedure was applied because the amount of aqueous solution used for an extraction was found to affect the yield of oil recovery. The adjusted PEG-b-PMEO$_2$MA aqueous solution was used for the second oil extraction cycle following *Extraction Protocol #2*. The same procedure was applied in the third, fourth, and fifth oil extractions. After determination of the yield for oil recovery after each cycle, a plot of the mass of oil recovered as a function of the number of oil extraction cycles was built to investigate how the extraction efficiency of the reused PEG-b-PMEO$_2$MA aqueous solution would change with repeated extraction cycles.

Chapter 3
Results and Discussion

3.1 Synthesis of a Temperature-Responsive Polymeric Surfactant

3.1.1 Synthesis of 2-Bromopropionate PEG Macroinitiator

As described in Chapter 2, the PEG macroinitiator was synthesized by reacting the hydroxyl end group of PEG with 2-bromoisobutyryl bromide.[27] The ^{1}H NMR spectrum and GPC traces confirmed the successful preparation of the PEG macroinitiator as described in Figures 3.1 and 3.2, respectively. Figure 3.1 shows the ^{1}H NMR spectrum of the purified PEG macroinitiator. Each proton of the macroinitiator could be assigned in the ^{1}H NMR spectrum. The absolute molecular weight of the PEG macroinitiator could be calculated based on the integrated intensities of peaks B and C. The number-average degree of polymerization, DP_n, of PEG was found to equal 113 resulting in an absolute molecular weight of 5,129 mol/g. The enlarged spectrum around 4.5 ppm in Figure 3.1 showed that the broad peak at 4.5 ppm representing the hydroxyl end group of PEG had disappeared, further confirming the successful synthesis of the 2-bromopropionate PEG macroinitiator. In addition, the GPC trace of the purified product presented in Figure 3.2a shows a single peak that appears at the same elution volume as the single peak of the unmodified PEG, indicating that the size of the purified product was the same as that of the unmodified PEG. Therefore, it could be concluded that the synthesis of the 2-bromopropionate PEG macroinitiator was successful, as confirmed by ^{1}H NMR and GPC analysis.
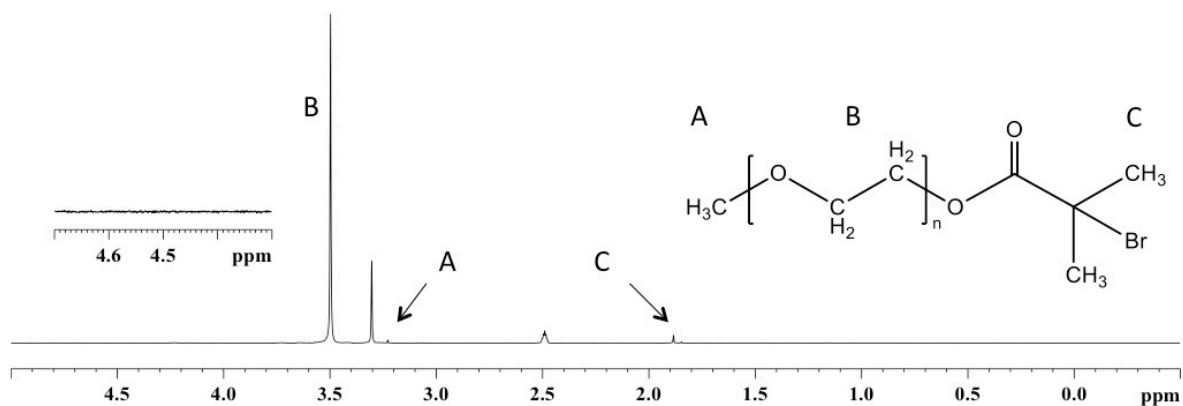
Figure 3.1 ^{1}H NMR spectrum of the purified 2-bromopropionate PEG macroinitiator together with peak assignment. The small peak at 2.5 ppm is for DMSO.

Elution Volume (mL)
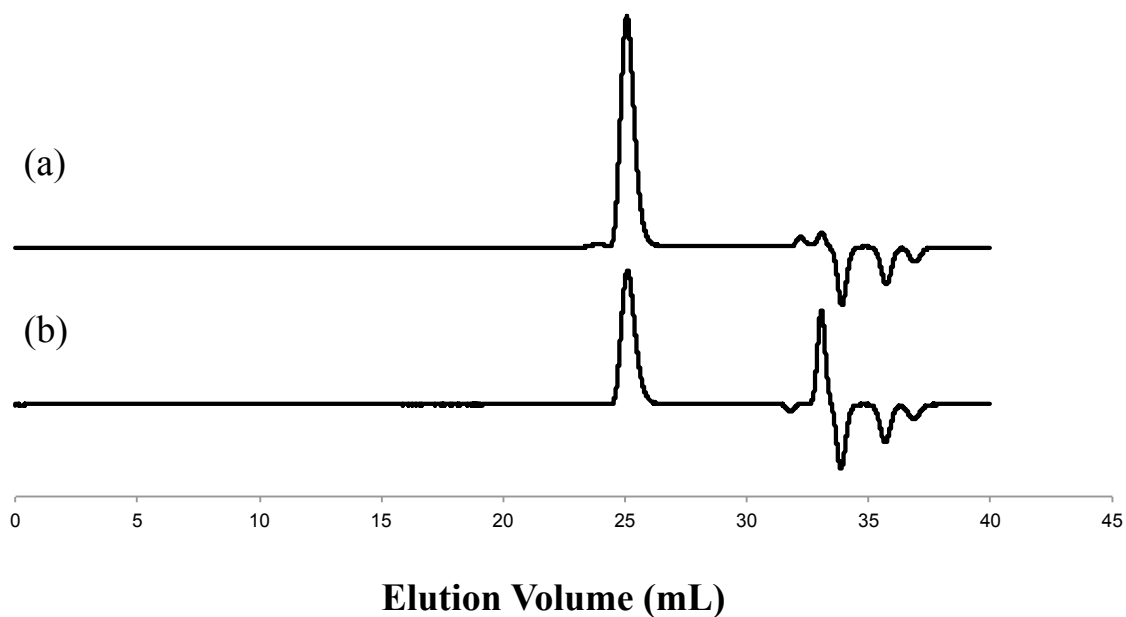
Figure 3.2 GPC traces of (a) the purified 2-bromopropionate PEG macroinitiator and (b) the unmodified PEG.

3.1.2 Synthesis of PEG-*b*-PMEO$_2$MA

The synthesis of PEG-*b*-PMEO$_2$MA was conducted by conventional ATRP using copper (I) bromide as catalyst and 2,2'-bipyridine as ligand. The polymerization was carried out in ethanol at room temperature for 24 h as described in Scheme 2.2. As for the 2-bromopropionate PEG macroinitiator, the synthesis of the block copolymer PEG-*b*-PMEO$_2$MA was confirmed by GPC measurements and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum for the purified product is shown in Figure 3.3.
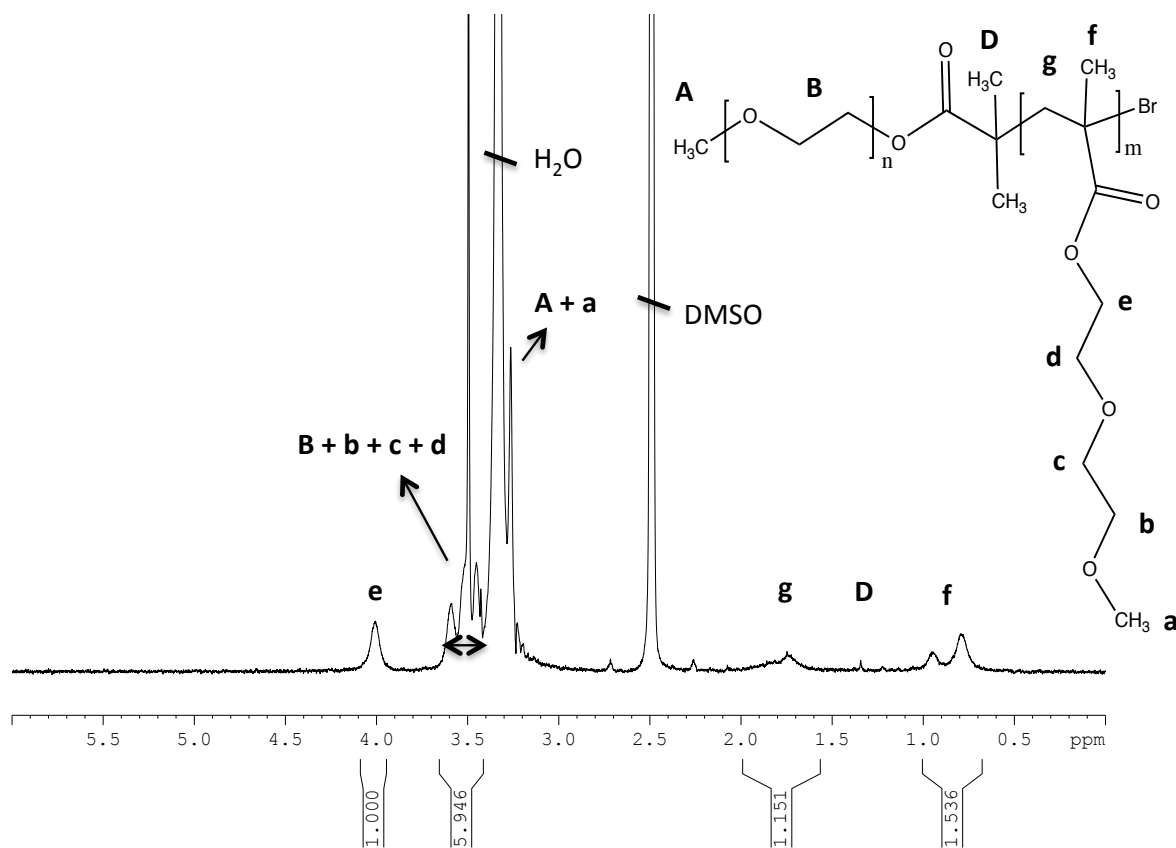
Figure 3.3 Chemical structure and ^{1}H NMR spectrum of PEG-*b*-PMEO$_2$MA.

Figure 3.3 indicates that the ratio of the peak areas related to protons e and $B+b+c+d$ can be expressed as a function of n and m which are the number-average degrees of polymerization of the PEG and PMEO$_2$MA blocks, respectively. The relationship between the NMR signal and the degree of polymerization is shown in Equation 3.1.

$$\frac{I_e}{I_B + I_b + I_c + I_d} = \frac{2m}{4n + 6m} = \frac{1.000}{5.946}$$

3.1

Isolating for the degree of polymerization n and m yielded the relationship shown in Equation 3.2.

$$m = 0.679n$$

3.2

Since n was found to equal 113 from the analysis of the ^{1}H NMR spectrum obtained for the macroinitiator (Figure 3.1), application of Equation 3.2 led to the conclusion that m equals 77 and that the absolute number-average molecular weight (M_n) of the copolymer equals 19,000 $\pm$ 200 g/mol resulting in a chemical composition for the copolymer of PEG$_{113}$-b-PMEO$_2$MA$_{77}$. The narrow peak eluting at 22 mL in the GPC trace shown in Figure 3.4 represents the PEG$_{113}$-b-PMEO$_2$MA$_{77}$ copolymer. The apparent molecular weight based on polystyrene standards was determined to be 20,000 $\pm$ 200 g/mol with a PDI of 1.54 $\pm$ 0.01. In Figure 3.5, the peak eluting at 23 mL representing the PEG macroinitiator was absent in the GPC trace of the purified product, which further confirmed the successful synthesis of the copolymer. Since the peak representing the PEG macroinitiator did not appear in the GPC trace for the unpurified product, it indicates a high conversion of the macroinitiator.
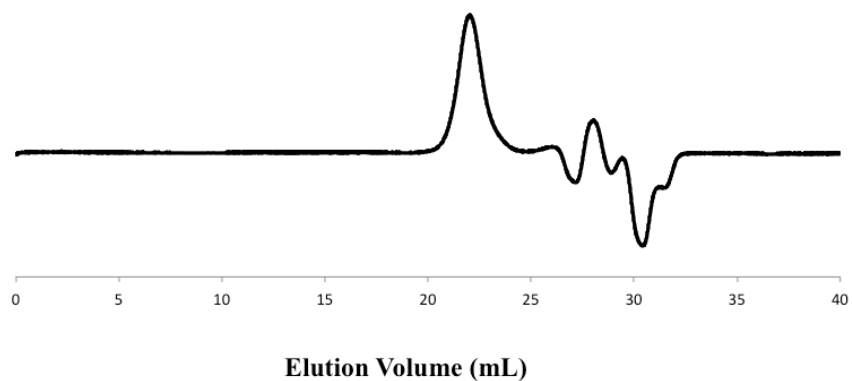
Figure 3.4 GPC trace for purified PEG-*b*-PMEO$_2$MA.
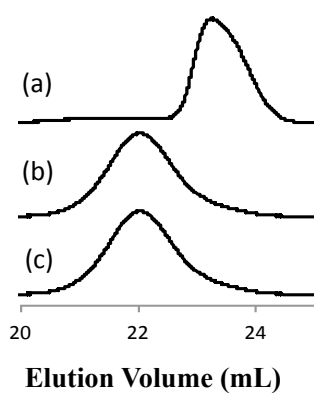
Figure 3.5 Zoomed-in GPC traces for (a) the macroinitiator, (b) the unpurified PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ sample, and (c) the purified PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ sample.

All the polymers synthesized by ATRP for this study are listed in Table 3.1. As the polymers were consumed during the course of the study, new polymers were synthesized as the need arose. Polymers 1, 4, 5, and 6 were used to study micelle formation by the TRPSs. Polymers 5 and 6 were employed for the oil extraction experiments.

Table 3.1 Summary of the polymers synthesized by ATRP

#	Polymer	$M_{n, NMR}$ (g/mol)	PDI	Chemical Composition
1	PMEO$_2$MA	26000	1.8	PMEO$_2$MA$_{138}$
2	PEG (Aldrich)	5000	1.1	PEG$_{113}$
3	PEG-*b*-PMEO$_2$MA	14000	1.5	PEG$_{113}$-*b*-PMEO$_2$MA$_{48}$
4	PEG-*b*-PMEO$_2$MA	19000	1.5	PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$
5	PEG-*b*-PMEO$_2$MA	17000	1.1	PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$
6	PEG-*b*-PMEO$_2$MA	20000	1.2	PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$

3.2 Characterization

3.2.1 Lower Critical Solution Temperature (LCST) Determined by Turbidimetry

The LCST of the TRPSs was determined with a UV-Vis spectrophotometer to measure the transmittance of the polymer aqueous solution as a function of temperature. Figure 3.6(a) and (b) show the same typical trend for the PMEO$_2$MA$_{138}$ homopolymer and the PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ block copolymer, respectively. At low temperature, the polymer solution is clear and the transmittance takes its maximum value of 100%. In the case of PMEO$_2$MA$_{138}$, the transmittance decreases precipitously at 26 ºC reflecting an increased turbidity of the solution. This drop in transmittance coincides with the reported LCST of 26 ºC for PMEO$_2$MA.[21] In Figure 3.6(b), the drop in transmittance at 35 ºC was attributed to the LCST of the copolymer PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$. Compared to the LCST of 26 ºC obtained for the PMEO$_2$MA$_{138}$ homopolymer, the LCST of 35 ºC found for the PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ copolymer is higher. This difference can be explained by the presence of the hydrophilic PEG block in the copolymer which increases the solubility of the block copolymer in water, and thus its LCST. An indication that the PEG-*b*-PMEO$_2$MA copolymers formed micelles came from the

comparison of the trends shown in Figure 3.6(a) and (b). It can be seen that, when the temperature passed through the LCST, the transmittance of the $PMEO_2MA_{138}$ homopolymer solution reached 0% while that of the PEG_{113}-b-$PMEO_2MA_{77}$ copolymer decreased to about 95% only. This difference in behavior is due to the more hydrophilic PEG block in the copolymer. At temperatures higher than the LCST, the $PMEO_2MA_{138}$ homopolymer became water-insoluble and precipitated out, resulting in a milky solution. The PEG_{113}-b-$PMEO_2MA_{77}$ copolymer on the other hand became a polymeric surfactant above 35 ºC that formed stable micelles resulting in a translucent solution. As a result, the transmittance of the PEG_{114}-b-$PMEO_2MA_{77}$ copolymer solution did not reach 0% but stabilized at about 95% above the LCST.
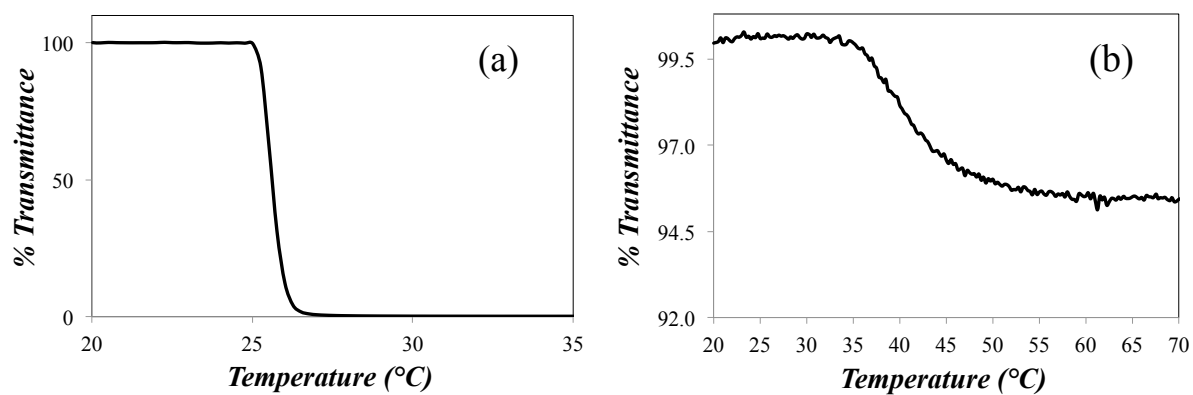
Figure 3.6 Plot of transmittance at 400 nm versus temperature for (a) the $PMEO_2MA_{138}$ homopolymer solution and (b) the PEG_{113}-b-$PMEO_2MA_{77}$ copolymer solution.

The LCSTs of the PEG-b-$PMEO_2MA$ samples determined by turbidimetry are summarized in Table 3.2. Whereas the $PMEO_2MA_{138}$ homopolymer exhibits an LCST of 26 ºC, all copolymers had an LCST of 34 ± 1 ºC. Although the copolymers had slightly

different chemical compositions with a PEG weight fraction ranging between 25.0 and 29.4%, the small difference observed between the LCSTs listed in Table 3.2 cannot be easily related back to the chemical composition of the copolymer. Furthermore, the LCST can also be affected by the PDI of the copolymers which are substantially different.

Table 3.2 Summary of LCSTs of a homopolymer PMEO$_2$MA and a series of copolymer PEG-*b*-PMEO$_2$MA

Polymer	$M_{n, NMR}$ (g/mol)	Weight % of PEG	PDI	LCST (°C)
PMEO$_2$MA$_{138}$	26000	0%	1.8	26.0
PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$	17000	25.0%	1.1	33.0
PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$	20000	29.4%	1.2	34.0
PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$	19000	26.3%	1.5	35.0

3.2.2 Hydrodynamic Diameter (d_h) and Dynamic Light Scattering (DLS) Measurements

Since the block copolymers underwent an LCST transition at 34 ± 1 °C in water, dynamic light scattering (DLS) measurements were carried out to determine the size of the polymer species present in solution as a function of temperature. As shown in Figure 3.7, the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ solutions showed a single polymer species at low temperature, whose hydrodynamic diameter d_h was small and remained constant with temperature. At 33 °C, the particle size started to increase with the block copolymers forming micelles, as expected from the LCST of 34.0 ± 1 °C determined by turbidimetry. The particle size increased rapidly above 33 °C reaching a maximum hydrodynamic diameter of 26.3 nm that remained constant at temperatures greater than 40 °C. As shown in Figure 3.8(a), the number distribution of the diameters of the species found in the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ aqueous solutions at 25, 30, 40

and 50 °C showed a single peak indicating that a single species was present in solution at temperatures below and above the LCST. The three block copolymers behaved in a similar manner. At low temperature a single macromolecular species with a small d_h of about 5 nm was observed which would correspond to PEG-b-PMEO$_2$MA unimers. Above the LCST, a single larger species was observed with a d_h value of 26.3 ± 0.3, 27.1 ± 0.4, and 36.6 ± 0.3 nm for the PEG$_{113}$-b-PMEO$_2$MA$_{64}$, PEG$_{113}$-b-PMEO$_2$MA$_{80}$, and PEG$_{113}$-b-PMEO$_2$MA$_{77}$ samples, respectively. These large d_h values would be expected for block copolymer micelles. Based on the trace shown in Figure 3.7, the LCST of PEG$_{113}$-b-PMEO$_2$MA$_{77}$ determined by DLS appears to occur at 30 ± 5 °C, which is smaller than the LCST of 35 °C previously determined by turbidimetry (see in Table 3.2). The difference can be explained by the 5 °C increment used for the DLS measurements conducted with this sample. As the PEG$_{113}$-b-PMEO$_2$MA$_{77}$ copolymer was the first sample to be investigated, the 5 °C temperature increment turned out to be too large and it was adjusted to a 1 °C increment for the other PEG-b-PMEO$_2$MA samples.

The hydrodynamic diameters of the micelles formed by the PEG-b-PMEO$_2$MA samples listed in Table 3.3 suggest that the PDI of the copolymers seem to have a strong effect on the micellar diameter, the copolymer having the largest PDI yielding the largest block copolymer micelles. The increase in the d_h value observed for the block copolymer micelles with large PDIs can be explained as follows. For larger PDI, the shorter polymer chains locate themselves at the core-corona interface. As a result, the longer chains are squeezed out of the interface region and need to extend deeper into the core for the hydrophobic blocks. The process induces an enlargement of the radius of the core which is accompanied by an increase

of the overall micellar dimension. This explanation is based on a study where the spacing between lamellae formed by block copolymers was found to increase as a function of the PDI of the block copolymer.[30] The shorter chains of the distribution were found to locate themselves at the interfacial region forcing the larger chains to stretch in a process resulting in larger interlamellar distances.
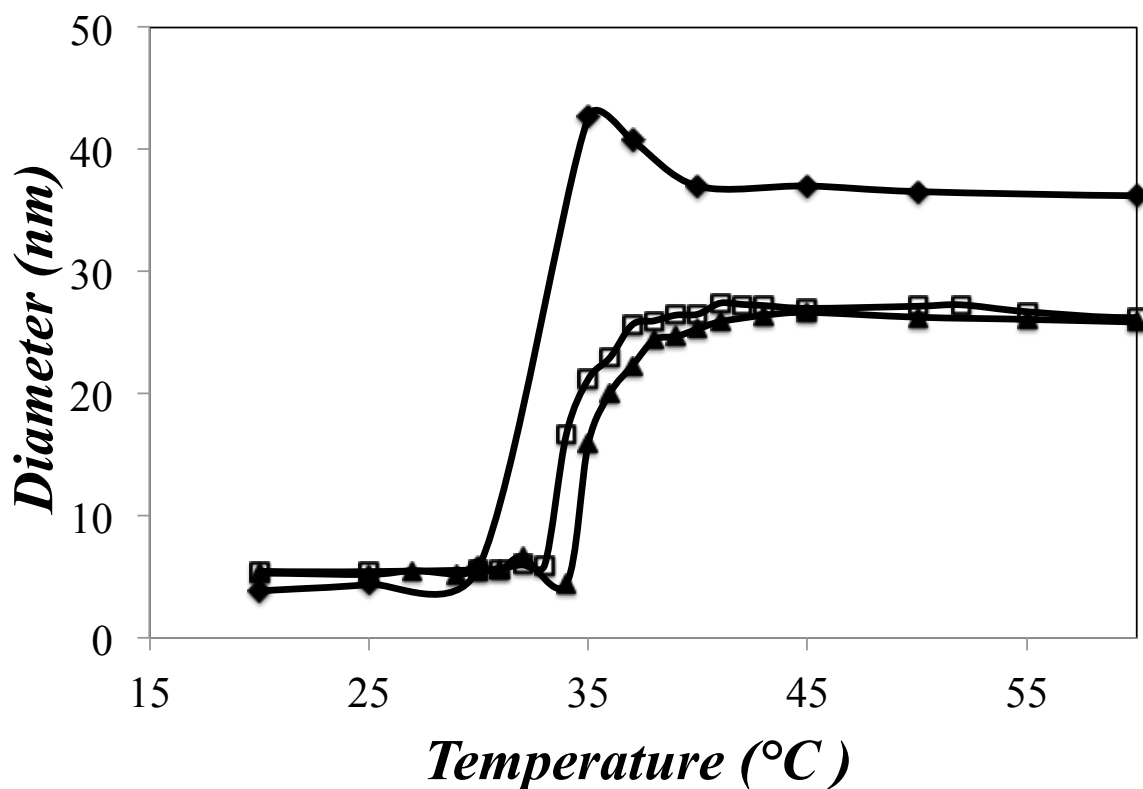
Figure 3.7 Plot of the hydrodynamic diameter (d_h) as a function of temperature for the block copolymers PEG_{113}-b-$PMEO_2MA_{64}$ ($\square$), PEG_{113}-b-$PMEO_2MA_{77}$ ($\blacklozenge$), and PEG_{113}-b-$PMEO_2MA_{80}$ ($\blacktriangle$) in water. Polymer concentrations equal 5 mg/mL.
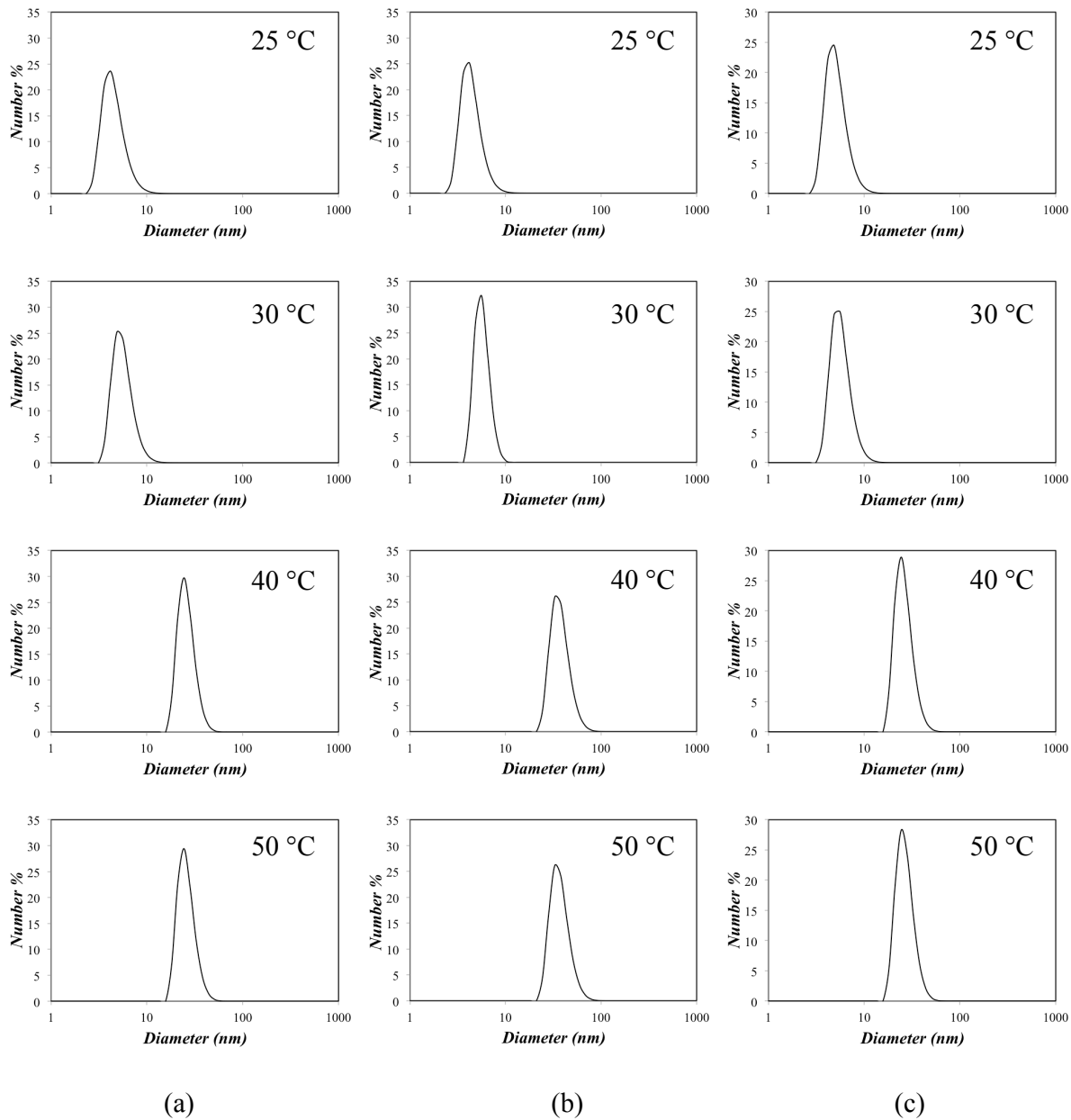
Figure 3.8 Histograms of the hydrodynamic diameters of block copolymers (a) PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$, (b) PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$, and (c) PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$ at different temperatures.

Table 3.3 Summary of the hydrodynamic diameters of the micelles formed by the PEG-*b*-PMEO$_2$MA block copolymers.

Polymer	M$_{n, NMR}$ (g/mol)	PDI	Diameter (nm)	LCST$_{DLS}$ (°C)
PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$	17,000	1.1	26.3 ± 0.3	33 ± 1
PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$	20,000	1.2	27.1 ± 0.4	34 ± 1
PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$	19,000	1.5	36.6 ± 0.3	30 ± 5

3.2.3 Viscosity Measurements

Viscosity measurements were carried out to determine the intrinsic viscosity [η] at 50 °C of the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ copolymer. Figure 3.8 shows plots of *ln(η_{rel}/c)* and η_{sp}/*c* versus the copolymer concentration (*c*) in g/mL. The parameters η_{rel} and η_{sp} represent the relative and specific viscosity, respectively. The data shown in Figure 3.9 could be fitted with two straight lines that intercepted the y-axis at the same position. Their y-intercept yielded the intrinsic viscosity of the copolymer as provided by Equations 3.3 and 3.4.

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \qquad\qquad 3.3$$

$$[\eta] = \lim_{c \to 0} \frac{\ln \eta_{rel}}{c} \qquad\qquad 3.4$$

From the common intercept of the straight lines, the intrinsic viscosity of PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ was found to equal 8.1 ± 0.2 mL/g.
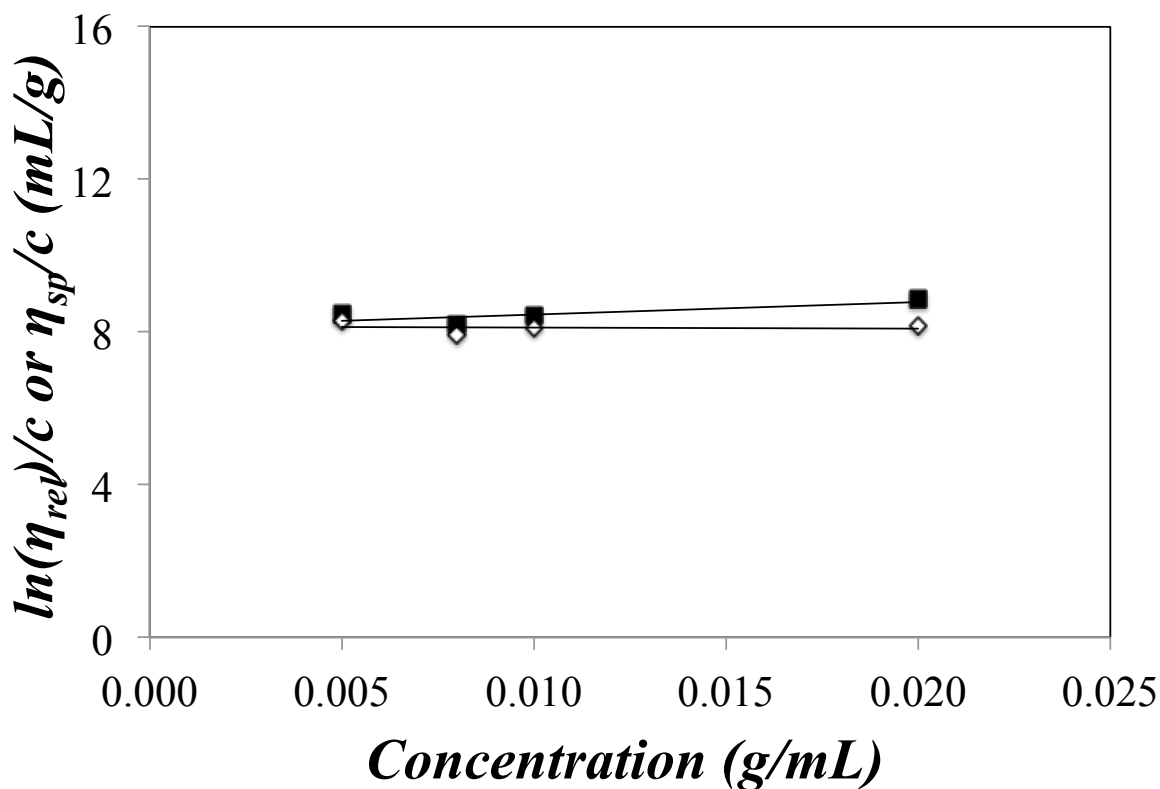
Figure 3.9 Plot of *ln(η_rel/c)* (◇) and *η_sp/c* (■) versus polymer concentrations for the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ block copolymer in aqueous solution at 50 ºC.

After having determined the intrinsic viscosity $[\eta]$ of the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ solution at 50 ºC, the aggregation number (N_{agg}) of the block copolymer micelles could be estimated by using Equation 3.5.

$$[\eta] = 2.5 \times N_A \frac{V_h}{M_{n,mic}} = 2.5 \times N_A \frac{V_h}{N_{agg} M_n} \qquad 3.5$$

In Equation 3.5, N_A is Avogadro's number, V_h, $M_{n,mic}$, and N_{agg} are, respectively, the hydrodynamic volume, the molecular weight, and the aggregation number of a block copolymer micelle, and M_n is the number-average molecular weight of the copolymer. Since

V_h can be calculated from the hydrodynamic diameter (d_h) of the copolymer found to equal 26.3 nm from DLS measurements and [η] was found to equal 8.1 mg/mL, N_{agg} in Equation 3.5 was determined to equal 100 ± 8 for PEG$_{113}$-b-PMEO$_2$MA$_{64}$.

3.3 Application: Oil Extraction

Although the use of water at high temperature enhances the bitumen recovery from oil sands in most bitumen extraction techniques such as the Clark Hot Water Extraction (CHWE), fire floods, and steam-assisted gravity-drainage (SAGD), these procedures require a large amount of energy and, at the same time, produce CO_2, a greenhouse gas. An organic solvent[1,12,13] and surfactants[1] have also been utilized to enhance the yield and lower the temperature of bitumen extraction. However, these procedures also led to serious environmental issues such as the formation of tailing ponds due to the use of surfactants, the large consumption of energy to melt the oil and induce its flow, and the use of vast quantities of organic solvents for the paraffinic (PFT) and naphthenic (NFT) froth treatment. In summary, all these procedures remain costly and environmentally unfriendly. Therefore, PEG-b-PMEO$_2$MA was synthesized and applied as a TRPS for oil extraction, with the goal of lowering the treatment temperature and enhancing the yield of oil extraction.

3.3.1 Determination of Optimal Conditions for Oil Extraction

Determination of Temperature. The LCST of the PEG-b-PMEO$_2$MA copolymers determined by turbidimetry equals 34 ± 1 ºC, which corresponds to the temperature at which micelles start to form, while the plot obtained by DLS for the block copolymers in Figure 3.6(a) indicates that micelle formation is complete at temperatures greater than 45 ºC. As more micelles

generate more hydrophobic domains in the solution, a temperature of 45 or 50 ºC was selected

for oil extraction to ensure the formation of a large number of block copolymer micelles.

Determination of the Optimal Composition of the Aqueous Solution. First, a set of extractions

were conducted according to *Extraction Protocol* #1 with aqueous solutions of different block

copolymers and their constituting homopolymers. The types of polymer used are listed in

Table 3.4. The results from these extractions are summarized in Figure 3.10.

Table 3.4 Information of polymers used for the determination of the optimal composition of

the aqueous solution.

Polymer	$M_{n, NMR}$ (g/mol)	PDI	Chemical Composition
PEG	5000	1.1	PEG_{113}
$PMEO_2MA$	26000	1.8	$PMEO_2MA_{138}$
PEG-*b*-$PMEO_2MA$	19000	1.5	PEG_{113}-*b*-$PMEO_2MA_{77}$
PNIPAM	20000-25000	unknown	
PEG-*b*-PNIPAM	76000	1.4	PEG_{113}-*b*-$PNIPAM_{600}$*

* This sample was prepared by Lu Li, a graduate student in Prof. Duhamel's laboratory.

The aqueous solutions that were used for extraction in Figure 3.10 are listed hereafter

starting from the left side of the figure: pure water, aqueous solutions of 1 mg/mL PEG

homopolymer, $PMEO_2MA$ homopolymer, PEG-b-$PMEO_2MA$ block copolymer, and PNIPAM

homopolymer. Visual inspection of the vials led to the obvious conclusion that none of these

aqueous solutions could extract the oil from the oil sands efficiently. This conclusion was

reached by noting the extremely thin oil layer at the top of the aqueous solution and the big oil

blobs remaining at the bottom of the vials. In other words, all the aqueous solutions

investigated in Figure 3.10 extracted very little oil from the oil sands by application of *Extraction Protocol* #1. To improve the efficiency of oil extraction, a small amount of toluene was added to the aqueous solution as described in *Extraction Protocol* #2. Surprisingly, the addition of 60 mg of toluene resulted in a significant improvement in oil extraction efficiency, as illustrated in Figure 3.11. The aromatic character of toluene appeared to enhance oil extraction from the oil sands, certainly due to the presence of a certain amount of aromatic chemicals in the oil sands.[8]

Pure Water	1 mg/mL PEG	1 mg/mL PMEO$_2$MA	1 mg/mL PEG-*b*-PMEO$_2$MA	1 mg/mL PNIPAM
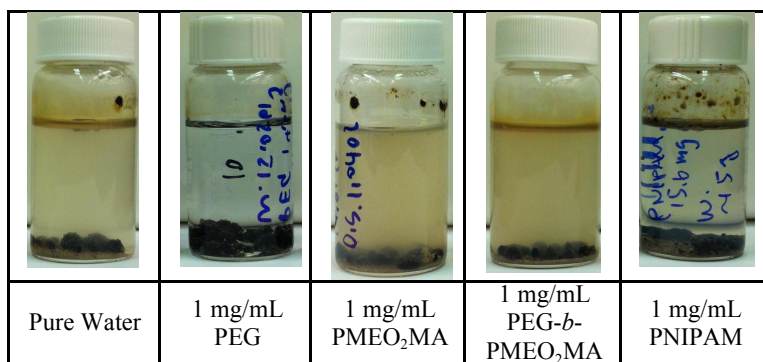
Figure 3.10 Pictures of the vials containing 1 g of oil sand and 15 mL of aqueous solution after shaking for 24 h at T = 45 °C. *Extraction Protocol* #1 was applied.

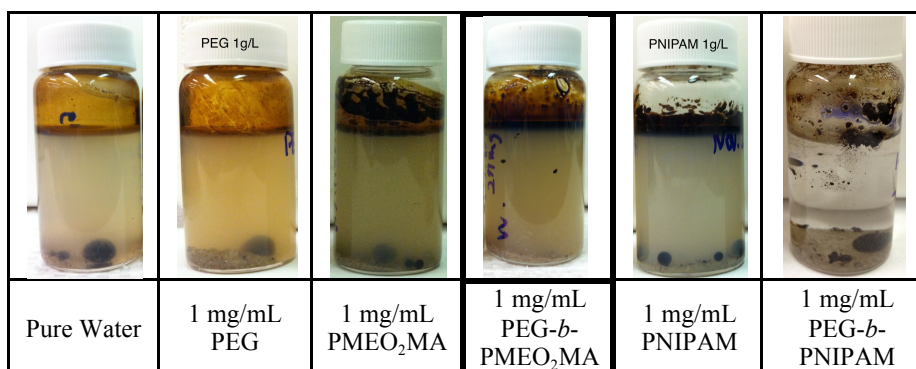| Pure Water	1 mg/mL PEG	1 mg/mL PMEO$_2$MA	1 mg/mL PEG-*b*-PMEO$_2$MA	1 mg/mL PNIPAM	1 mg/mL PEG-*b*-PNIPAM

Figure 3.11 Pictures of the vials containing 1 g of oil sand, 15 mL of aqueous solution, and 60 mg of toluene after shaking for 24 h at T = 45 °C. *Extraction Protocol* #2 was applied.

In comparison to the results obtained from *Extraction Protocol* #1 in Figure 3.10, the results obtained by applying *Extraction Protocol* #2 with 60 mg of toluene in Figure 3.11 reflect more efficient extraction: The oily layer at the top of the aqueous solution is thicker, and fewer black oil blobs are present at the bottom of the vials. Most importantly, it was noticeable that the aqueous solution of PEG-*b*-PMEO$_2$MA copolymer resulted in the most efficient extraction: A very thick layer of oil could be found at the top of the aqueous layer, while no black oil blobs remained at the bottom of the vial. As a matter of fact, a 100% extraction yield was obtained in this case. Comparison of the extraction results obtained in Figure 3.10 and 3.11 led to the conclusion that using 15 mL of a 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution with 60 mg of toluene yielded the most efficient extraction.

Optimization of the Amount of Toluene Used with Extraction Protocol #2: The oil content of the oil sand samples supplied by Dr. Chakrabarty from Imperial Oil was determined by Soxhlet extraction. Soxhlet extraction with toluene and tetrahydrofuran (THF) established that the oil sand samples were constituted of 11 ± 1 wt% of oil and 89 ± 1 wt% of sand. This oil sand composition was used as a reference point against which the amount of oil recovered from an oil extraction cycle would be compared.

As mentioned earlier, the results shown in Figure 3.11 demonstrated the superiority of the 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution at extracting oil using *Extraction Protocol* #2. This conclusion was further confirmed by comparing the weight percentage of oil extracted from the oil sand (*wt%*[*oil*]) as a function of the mass of toluene (m_{tol}) added at the top of   15 mL of either pure water or a 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution. As determined earlier by Soxhlet extraction, the maximum *wt%*[*oil*] equals 0.11 ± 0.01. A plot of

$wt\%[oil]$ versus m_{tol} is shown in Figure 3.12. For m_{tol} greater than or equal to 100 mg, $wt\%[oil]$ equaled 0.11 within experimental error indicating complete oil recovery. It must be pointed out that some of the extraction experiments yielded $wt\%[oil]$ greater than 0.11 ± 0.01. These results are certainly a consequence of having collected some sand particles with the oil that artificially increased the weight of the recovered oil. However, for all other m_{tol} smaller than 100 mg, $wt\%[oil]$ determined with the 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution was consistently larger than $wt\%[oil]$ obtained with water alone. The trend shown in Figure 3.12 demonstrates that PEG-*b*-PMEO$_2$MA enhances oil extraction substantially when *Extraction Protocol* #2 is being used. It also suggests that when using more than 60 mg of toluene with 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution, 100% oil recovery can be expected.
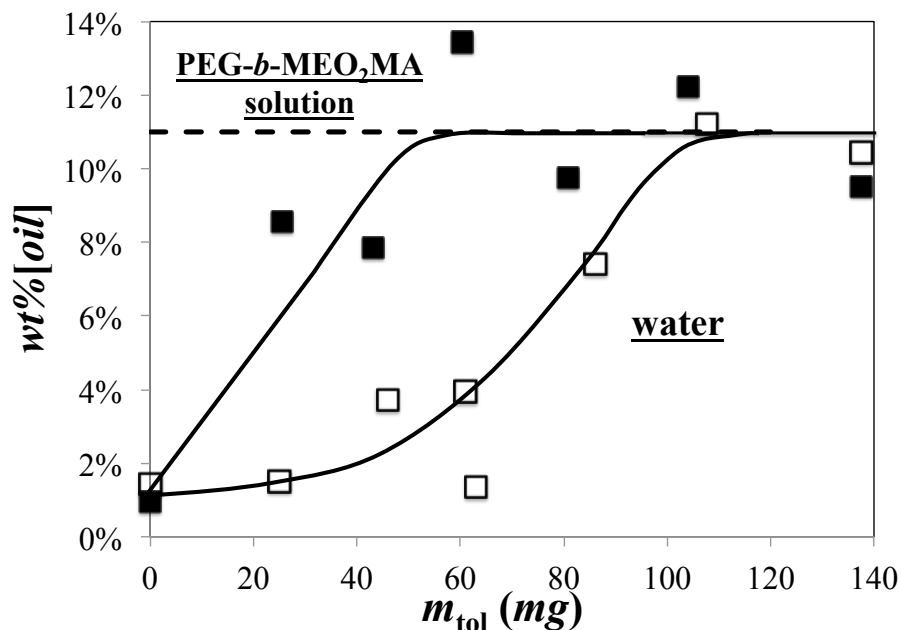
Figure 3.12 Plot of the weight percentage of oil recovered ($wt\%[oil]$) versus the mass of toluene added (m_{tol}). (■) 1 mg/mL PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ aqueous solution; (□) pure water.

3.3.2 Time-Dependent Experiment

After having determined the optimal solution composition for oil extraction, time-dependent experiments were carried out to determine the minimum time required for a complete oil extraction cycle. A plot of *wt%*[*oil*] versus time from 0 to 24 h is shown in Figure 3.13. As discussed in Figure 3.11, a *wt%*[*oil*] value of 0.11 indicated complete oil recovery. In Figure 3.13, the *wt%*[*oil*] value obtained with the 1 mg/mL PEG-*b*-PMEO₂MA aqueous solution increased continuously with time in the first 6 h, reaching complete oil recovery after 6 h and remaining constant afterwards. By comparison, the *wt%*[*oil*] percentage obtained for pure water was lower, and maximum recovery was achieved after 6 h.
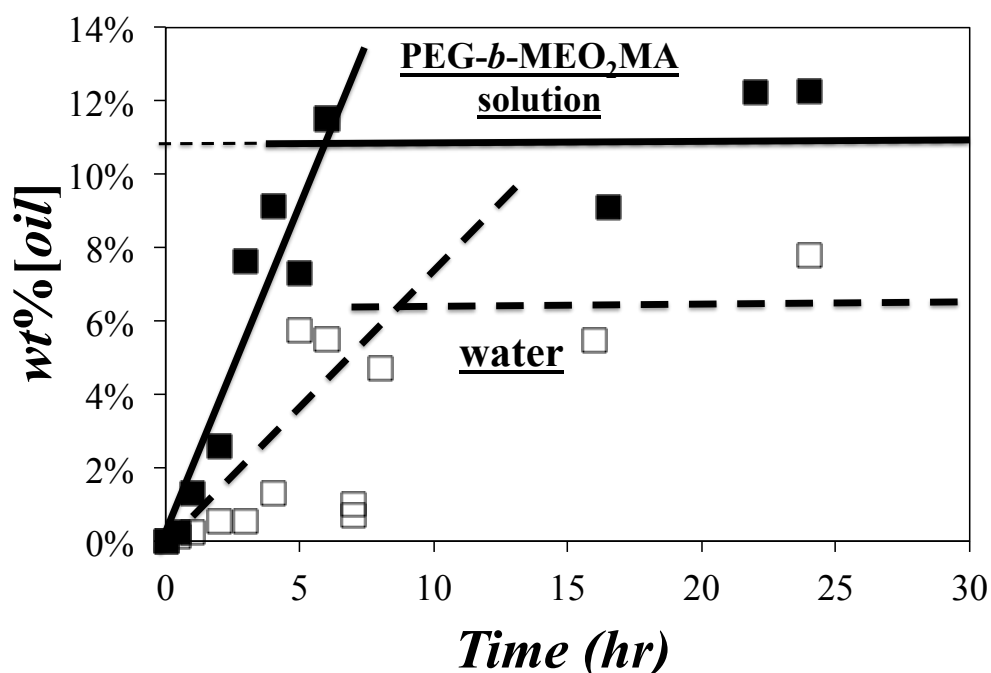

Figure 3.13 Plot of the weight percentage of oil recovered (*wt%*[*oil*]) versus the shaking time with addition of 60 mg of toluene. *Extraction Protocol* #2. (■) 1 mg/mL PEG₁₁₃-*b*-PMEO₂MA₇₇ aqueous solution; (□) pure water. Data were acquired by Tom Gibson.

In other words, the percentage $wt\%[oil]$ recovered with the 1 mg/mL PEG-b-PMEO$_2$MA aqueous solution was always consistently larger than that obtained with water alone, and the $wt\%[oil]$ percentage of the PEG-b-PMEO$_2$MA aqueous solution reached a maximum value of 11% relatively earlier than with pure water. In conclusion, the trend shown in Figure 3.13 indicates that the 1 mg/mL PEG$_{113}$-b-PMEO$_2$MA$_{77}$ aqueous solution resulted in a more efficient oil recovery as compared to pure water, and that maximum recovery was achieved after 6 h.

3.3.3 Oil Extraction as a Function of the Number of Extraction Cycles

To achieve a cheaper and more environmentally friendly way to extract the oil from oil sands, the PEG-b-PMEO$_2$MA aqueous solution should be recyclable and reusable time after time. In reality, a certain amount of PEG-b-PMEO$_2$MA copolymer might dissolve in toluene, leading to a decrease in polymer concentration which might have an effect on the efficiency of oil extraction. A plot of $wt\%[oil]$ versus the number of extraction cycles is shown in Figure 3.14. These experiments were conducted in triplicate to gauge the reproducibility of the extraction protocol. Out of 15 data points resulting form the 5 extraction cycles carried out in triplicate, 13 yielded $wt\%[oil]$ value of $11 \pm 1\%$, indicating close to 100% oil recovery. Two data points, one with a $wt\%[oil]$ of 7% after the first extraction cycle and another with a $wt\%[oil]$ of 4% after the fifth extraction cycle seem to be outliers. A slight decrease in $wt\%[oil]$ was observed for the fourth and fifth cycles. This might be due to the gradual loss of PEG$_{113}$-b-PMEO$_2$MA$_{64}$ copolymer that must occur with increasing number of oil extraction cycles. The loss of PEG-b-PMEO$_2$MA copolymer after an extraction cycle will be confirmed in the following

section. At this stage, it can be concluded that the PEG-*b*-PMEO$_2$MA aqueous solution enabled a high oil recovery even after 5 extraction cycles.
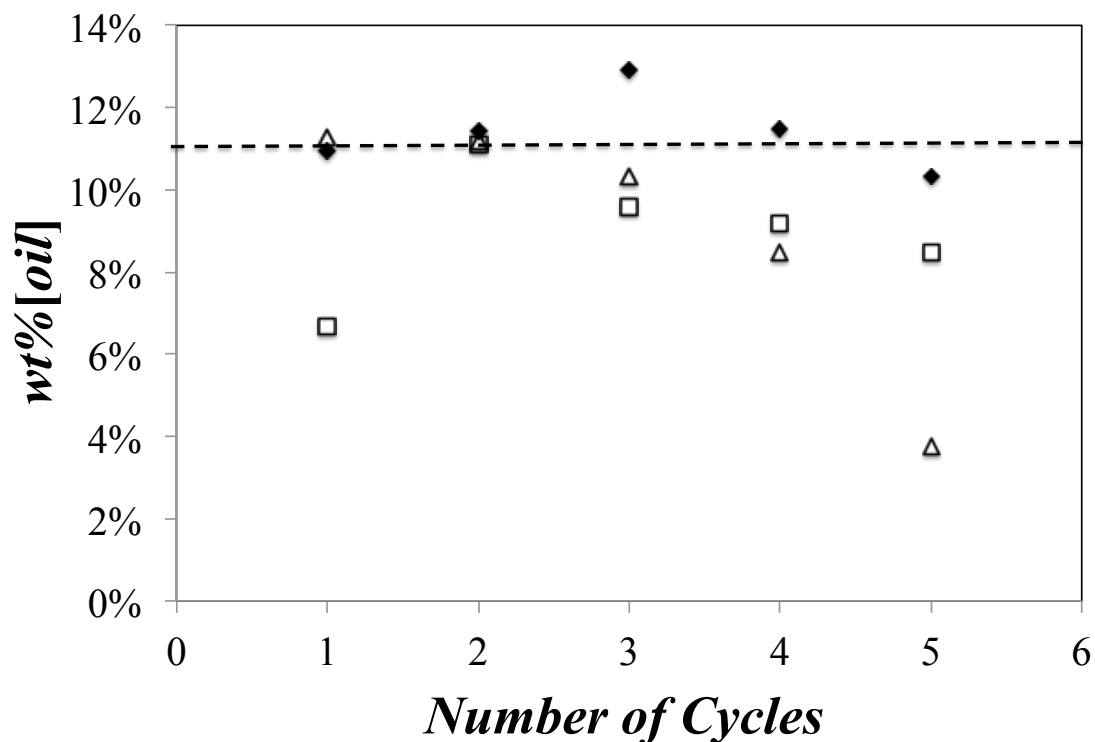
Figure 3.14 Plot of the weight percentage of oil recovered (*wt%[oil]*) versus number of cycles.

3.3.4 Determination of Polymer Recovery

3.3.4.1 Calibration curve

Considering how important the presence of 1 mg/mL PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$ copolymer was to ensure efficient oil recovery from oil sands, it became necessary to quantify the amount of PEG$_{113}$-*b*-PMEO2MA$_{80}$ that could be recovered in the aqueous solution after each extraction cycle. The polymer recovery was determined by conducting GPC experiments. Taking advantage of the fact that the DRI signal is directly proportional to the massic polymer

concentration in the solution, the DRI detector of the GPC instrument was used to build a calibration curve that would relate the DRI signal to the block copolymer concentration. To this end, a series of PEG_{113}-*b*-$PMEO_2MA_{80}$ solutions of known concentration were prepared and injected into the GPC instrument. A plot of the differential refractive index (DRI) response versus PEG_{113}-*b*-$PMEO_2MA_{80}$ copolymer concentrations in THF is shown in Figure 3.15. The straight line obtained in Figure 3.15 confirms that the DRI signal is strongly correlated to the block copolymer concentration. In turn, this straight line could be used to determine the concentration of a PEG_{113}-*b*-$PMEO_2MA_{80}$ aqueous solution after each oil extraction cycle.

Figure 3.15 Calibration curve obtained by plotting the DRI signal of the GPC instrument as a function of PEG_{113}-*b*-$PMEO_2MA_{80}$ concentration.

3.3.4.2 Determination of Polymer Recovery

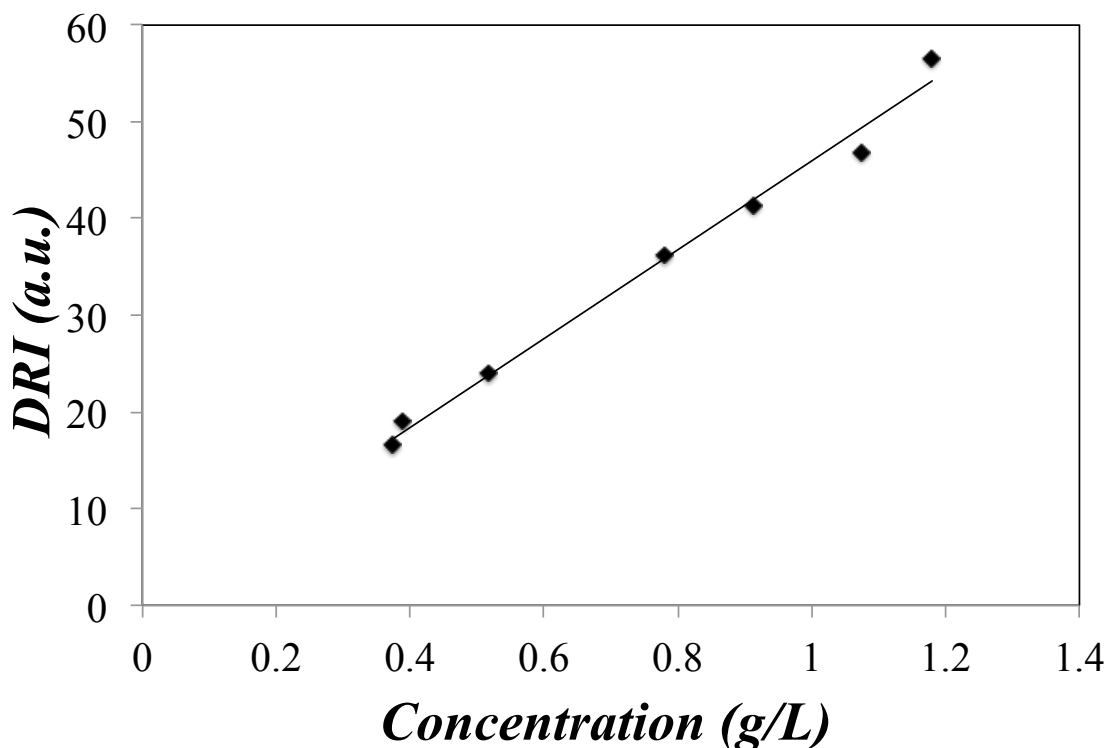Three vials containing 65 mg of toluene, 15 g of a 1 mg/mL PEG$_{113}$-b-PMEO$_2$MA$_{80}$ aqueous solution, and 1 g of oil sands were prepared and placed in the shaker for 24 h as described in *Extraction Protocol* #2. After oil extraction the aqueous layer of the three samples was collected and freeze-dried, and the lyophilized polymer was dissolved in THF. This solution was injected in the GPC instrument and its DRI intensity was determined. The DRI signals of the GPC traces obtained for the three samples are shown in Figure 3.16 and their MWD was compared to that of the block copolymer before extraction. PEG$_{113}$-b-PMEO$_2$MA$_{80}$ before and after bitumen extraction all eluted at 24 mL yielding similar MWDs with an M$_n$ value of 21,000 ± 1,000 g/mol and a PDI value of 1.2 ± 0.0. Together, the similar MWDs recovered for the block copolymer before and after bitumen extraction suggest that PEG$_{113}$-b-PMEO$_2$MA$_{80}$ was not degraded after one extraction cycle. The percentage of block copolymer recovered for these three samples, calculated from the calibration curve shown in Figure 3.15 equalled 0.83, 0.73, and 0.79. Therefore, the fraction of block copolymer recovered after one oil extraction cycle equals 0.78 ± 0.05, which indicates that each extraction cycle results in a 22% loss of PEG-b-PMEO$_2$MA. However, it also indicates that 78% of polymer remains in the aqueous solution for the next cycle.

Since it was shown in Figure 3.14 that oil extraction was still efficient after 5 cycles, it suggests that a polymer concentration smaller than 1 mg/mL can still successfully extract oil from the oil sands according to *Extraction Protocol* #1. In the future, the effect that the PEG-b-PMEO$_2$MA concentration has on the extraction recovery will be investigated.
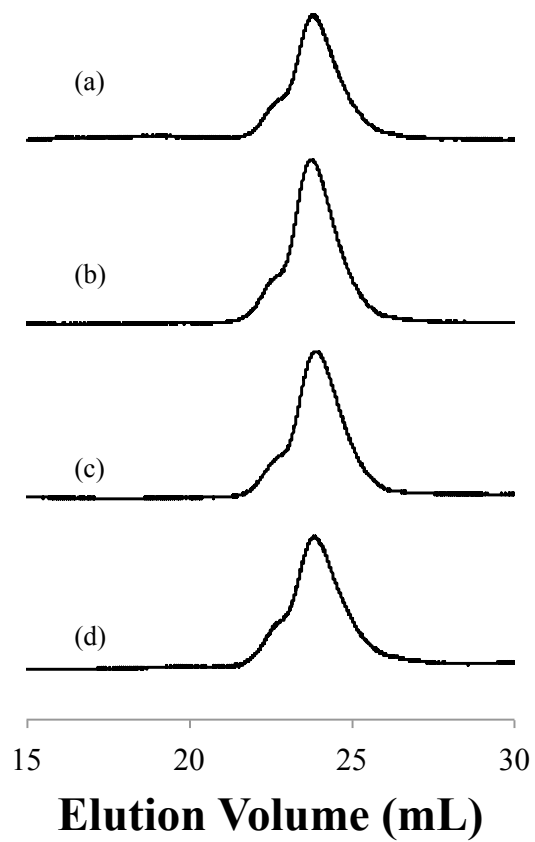
44

Figure 3.16 Zoomed-in DRI signals for block copolymer PEG$_{113}$-*b*-PMEO$_2$MA$_{80}$ (a) in THF before bitumen extraction, and after conducting (b) the first, (c) second, and (d) third extraction experiments. (a) M_n = 20,000 g/mol, PDI = 1.2; (b) M_n = 21,000 g/mol, PDI = 1.2; (c) and (d) M_n = 22,000 g/mol, PDI = 1.2.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

This project aimed to design a possibly cheaper and more environmentally friendly way to extract the oil from oil sands using temperature-responsive polymeric surfactants (TRPSs). This thesis described the synthesis, characterization, and applicability to oil extraction of a TRPS, namely PEG-*b*-PMEO$_2$MA. In particular, conditions were established to efficiently extract oil from oil sands by using this block copolymer.

A series of PEG-*b*-PMEO$_2$MA block copolymers were synthesized by atom transfer radical polymerization (ATRP). The use of ATRP was a priority because it is a living polymerization technique that generates polymers with narrow molecular weight distributions (MWD). It is also a free radical polymerization that is substantially less sensitive to the presence of minute amounts of impurities, in contrast to ionic living polymerization techniques. Consequently, the block copolymer synthesis described in this study should be more easily scalable in an industrial context. To prepare the block copolymer, a poly(ethylene glycol) (PEG) macroinitiator was synthesized first by reacting the hydroxyl end group of PEG with 2-bromoisobutyryl bromide. The composition of the PEG macroinitiator was determined by a combination of gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Then, the synthesized macroinitiator was used to polymerize MEO$_2$MA to prepare several PEG-*b*-PMEO$_2$MA samples having an absolute number-average molecular weight of 14,000, 17,000, 19,000, and 20,000 g/mol as determined by ^{1}H NMR and with corresponding apparent PDIs of 1.5, 1.1, 1.5, and 1.2 as determined by GPC analysis.

After confirmation of the successful synthesis of these TRPSs, the ability of PEG-*b*-PMEO$_2$MA to phase-separate and form micelles was characterized. The LCST of the PEG-*b*-PMEO$_2$MA samples was determined by turbidity measurements using a UV-Vis spectrophotometer. The LCST represents the temperature where the micelles start to from, namely the temperature above which the block copolymer behaves as a TRPS that could be used for oil extraction. The chemical composition and molecular weight distribution (MWD) of the copolymers had little effect on the LCST which was found to equal 34 ± 1 °C for all samples. The hydrodynamic diameter of the PEG-*b*-PMEO$_2$MA micelles was determined by DLS. The results showed that the block copolymer having a broader MWD with a PDI of 1.5 yielded substantially larger micelles, possibly due to the localization of the shorter chains at the interface of the core and the corona. Viscosity measurements were carried out to determine the intrinsic viscosity of the PEG$_{113}$-*b*-PMEO$_2$MA$_{64}$ solutions at 50 °C. From the value of the intrinsic viscosity and the hydrodynamic diameter of the micelles, the aggregation number (N_{agg}) of the block copolymer micelles was found to equal 100 ± 8.

Finally, the TRPS PEG-*b*-PMEO$_2$MA was applied to oil extraction. Series of experiments were carried out to determine the optimal solution composition for oil extraction using the block copolymer PEG-*b*-PMEO$_2$MA as a TRPS. The temperature used for oil extraction was set at 45 or 50 ºC, to ensure that PEG-*b*-PMEO$_2$MA micelle formation was complete. A 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution topped with 60 mg of toluene was determined to extract effectively the oil from oil sands, since it yielded complete oil recovery while pure water and other polymer aqueous solutions did not. The minimum amount of toluene necessary to achieve full oil extraction was determined to equal 60 mg by plotting the

weight percentage of oil recovered ($wt\%[oil]$) versus the mass of toluene (m_{tol}) added to the aqueous solution. This amount of toluene represents 0.4 wt% of the total aqueous solution. Finally, a time-dependent experiment was carried out to determine the minimum time required to achieve complete oil extraction. When using a 1 mg/mL PEG-*b*-PMEO2MA solution, this minimum time was found to equal 6 h.

The fraction of PEG-*b*-PMEO2MA copolymer recovered after one oil extraction cycle was found to equal 0.78 ± 0.05. This fraction was calculated from the DRI signal obtained from the GPC instrument. Thus some PEG-*b*-PMEO2MA was lost in an extraction cycle. Despite this copolymer loss during the extraction process, the PEG-*b*-PMEO2MA aqueous solution was capable of extraction of oil from the oil sands for several cycles. Together, these results indicate that a PEG-*b*-PMEO2MA aqueous solution should enhance oil extraction at concentrations lower than 1 mg/mL.

In summary, the TRPS selected in this study was a PEG-*b*-PMEO2MA block copolymer where the PEG was water-soluble and the PMEO2MA block was insoluble in water at temperatures greater than 34 °C. The TRPS was prepared by ATRP. The chemical composition and the molecular weight distribution (MWD) of the copolymer were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography, respectively. Most block copolymers had a narrow MWD (polydispersity index < 1.2) with a typical chemical composition of PEG$_{113}$-*b*-PMeEG2MA$_{80}$. Although the LCST of the PMEO2MA homopolymer equals 26 °C, it increased to 34 °C for the copolymer due to the good water-solubility of the PEG block to which the PMEO2MA block was attached. Above the LCST where the PMEO2MA block was insoluble, PEG$_{113}$-*b*-PMEO2MA$_{80}$ formed monodispersed

block copolymer micelles. Albertan oil sands provided by Dr. Chakrabarty from Imperial Oil were used to test the ability of PEG_{113}-b-$PMEO_2MA_{80}$ to extract oil. Soxhlet extraction of the bitumen trapped in the oil sands using toluene and THF demonstrated that 1 g of the supplied oil sands contained 0.11 g of oil. The extraction experiments were conducted by placing 1 g of oil sand in a vial to which 15 mL of a 1 mg/mL solution of TRPS was added. The optimal conditions for oil extraction from the oil sands using this TRPS were determined. It was found that with the addition of 60 to 65 mg of toluene to 15 mL of 1 mg/mL PEG-b-$PMEO_2MA$ aqueous solution, complete oil recovery could be achieved by putting the TRPS solution with 1 g of oil sands in a shaker at 45 or 50 ºC for 6 h. Furthermore, this TRPS was proven to be reusable for at least 5 bitumen extraction cycles when starting with a concentration of 1 mg/ mL. The recovery of the TRPS after one extraction cycle was also investigated and found to equal 78%. Under the optimal experimental conditions determined in this thesis, PEG-b-$PMEO_2MA$ shows promising results in bitumen extraction from oil sands. However, there are still improvements to be made to further enhance bitumen extraction in a more environmentally friendly way, such as avoiding the use of toluene (a toxic organic solvent) in the extraction process.

4.2 Future Work

In this thesis the effects of temperature, the type of polymer, mass of toluene, and extraction time on the efficiency of oil extraction have been studied, and an efficient protocol based on the use of PEG-b-$PMEO_2MA$ was established for oil extraction. However, the loss of PEG-b-$PMEO_2MA$ was shown to occur during the oil extraction process. Since the oil recovery was still very efficient after several extraction cycles, this observation suggests that PEG-b-

PMEO$_2$MA aqueous solutions can extract oil efficiently at concentrations lower than 1 mg/mL. Therefore, experiments need to be carried out to study the effect that the copolymer PEG-*b*-PMEO$_2$MA concentration has on oil extraction. PEG-*b*-PMEO$_2$MA aqueous solutions with concentrations ranging from 0.1 to 1 mg/mL should be applied to extract the oil from oil sands following *Extraction Protocol #2*. This experiment would determine the lowest concentration of copolymer that can be used in these extractions.

To further improve the oil extraction protocol, a new TRPS with a similar chemical composition as PEG-*b*-PMEO$_2$MA should be prepared that incorporates aromatic groups into the thermoresponsive block of the TRPS. This new TRPS would be designed to replace toluene in the oil extraction process. This modification is expected to have two main effects: It would simplify the oil extraction process, and make it more environmentally friendly. After the synthesis of the new TRPS, turbidity, DLS, and viscosity measurements should be carried out to study the micelle formation by this polymer. Finally, the new TRPS should be applied to oil extraction to test the efficiency of oil recovery by using this TRPS alone (without toluene). Depending on these results, the structure of the new TRPS could be further adjusted to incorporate more aromatic groups and obtain a better oil recovery.

References

1. Camp, F. W. *Tar Sands of Alberta, Canada, Third Edition*; Cameron Engineers Inc.; Denver, CO, **1976**.

2. Masliyah, J.; Zhou, Z.; Xu, Z.; Czarnecki, J.; Hamza, H. Understanding of water-based bitumen extraction from Athabasca oil sands. *Can. J. Chem. Eng.* **2004**, *82*, 628-654.

3. Saniere, A.; Hénaut, I.; Argillier, J. F. Pipeline transportation of heavy oils, a strategic, economic and technological challenge. *Oil Gas Sci. Tech.* **2004**, *59*, 455-466.

4. Larter, S.; Adams, J.; Gates, I. D.; Bennett, B.; Huang, H. The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoirs. *J. Can. Petrol. Tech.* **2008**, *47*, 52-61.

5. Perry, R. H.; Green, D. W.; Campbell, J. M. Reverse combustion - a new oil recovery technique. *J. Petrol. Tech.* **1960**, *12*, 14-15.

6. Parrish, D. R.; Craig, F. F. Laboratory study of a combination of forward combustion and waterflooding - the COFCAW process. *J. Petrol. Tech.* **1968**, *21*, 753-761.

7. Carrigy, M. A. Ed. *Athabasca oil sands: a collection of papers presented to K. A. Clark on the 75th anniversary of his birthday.* Research Council of Alberta, Edmonton, Alberta, Canada, **1963**, 123-141.

8. Rao, F; Liu, Q. Froth treatment in Athabasca oil sands bitumen recovery process: a review. *Energy Fuels* **2013**, *27*, 7199-7207.

9. Sury, K. N. Low temperature bitumen recovery process. *US Patent* 4 946 597, **1990**.

10. Sury, K. N. Low temperature bitumen recovery process. *Canadian Patent* 1 302 327, **1992**.

11. Yang, H.; Wang, Y.; Ding, M.; Hu, B.; Ren, S. Water-assisted solvent extraction of bitumen from oil sands. *Ind. Eng. Chem. Res.* **2012**, *51*, 3032-3038.

12. Kirpalani, D. M.; Matsuoka, A. CFD approach for simulation of bitumen froth settling process – Part I: Hindered settling of aggregates. *Fuel* **2008**, *87*, 380-387.

13. Long, Y.; Dabros, T.; Hamza, H. Stability and settling characteristics of solvent-diluted bitumen emulsions. *Fuel* **2002**, *81*, 1945-1952.

14. Mortisen, D.; Peroglio, M.; Alini, M.; Eglin, D. Tailoring thermoreversible hyaluronan hydrogels by "click" chemistry and RAFT polymerization for cell and drug therapy. *Biomacromolecules* **2010**, *11*, 1261–1272.

15. Kulkarni, S.; Schilli, C.; Mueller, A. H. E.; Hoffman, A. S.; Stayton, P. S. Reversible Meso-scale smart polymer−protein particles of controlled sizes. *Bioconjugate Chem.* **2004**, *15*, 747-753.

16. Han, H. D.; Choi, M. S.; Hwang, T.; Song, C. K.; Seong, H.; Kim, T. W.; Choi, H. S.; Shin, B. C. Hyperthermia-induced antitumor activity of thermosensitive polymer modified temperature-sensitive liposomes. *J. Pharm. Sci.* **2006**, *95*, 1909-1917.

17. Santos, A. M.; Elaissari, A.; Martinho, J. M. G.; Pichot, C. Synthesis of cationic poly(methyl methacrylate)-poly(N-isopropyl acrylamide) core-shell latexes via two-stage emulsion copolymerization. *Polymer* **2005**, *46*, 1181-1188.

18. Ikeda, I.; Tazuke, S.; Suzuki, Y. Synthesis and antimicrobial activity of poly(trialkylvinylbenzylammonium chloride)s. *Makromol. Chem.* **1984**, *185*, 869-876.

19. Ravikumar, T.; Murata, H.; Koepsel, R. R.; Russell, A. J. Surface-active antifungal polyquaternary amine. *Biomacromolecules* **2006**, *7*, 2762-2769.

20. Gilbert, P.; Moore, L. E. *J.* Cationic antiseptics: diversity of action under a common epithet. *Appl. Microbiol.* **2005**, *99*, 703-715.

21. Lutz, J.-F.; Hoth, A. Preparation of ideal PEG analogues with a tunable thermosensitivity by controlled radical copolymerization of 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene glycol) methacrylate. *Macromolecules* **2006**, *39*, 893–896.

22. Lutz, J.-F.; Akdemir, O.; Hoth, A. Point by point comparison of two thermosensitive polymers exhibiting a similar LCST: Is the age of poly(NIPAM) over? *J. Am. Chem. Soc.* **2006**, *128*, 13046-13047.

23. Topp, M. D. C.; Dijkstra, P. J.; Talsma, H.; Feijen. J. Thermosensitive micelle-forming block copolymers of poly(ethylene glycol) and poly(N-isopropylacrylamide). *Macromolecules* **1997**, *30*, 8518–8520.

24. Kitano, H.; Kondo, T.; Suzuki, H.; Ohno, K. J. Temperature-responsive polymer-brush constructed on a glass substrate by atom transfer radical polymerization. *Colloid Interface Sci.* **2010**, *345*, 325-331.

25. Holmberg, K. *Surfactants and Polymers in Aqueous Solution.* Chichester: John Wiley, **2003**.

26. Bandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook, Fourth Edition*; Wiley Sons: NY, **1999**.

27. Mei, A.; Guo, X.; Ding, Y; Zhang, X; Xu, J; Fan, Z; Du, B. PNIPAm-PEO-PPO-PEO-PNIPAm pentablock terpolymer: Synthesis and chain behavior in aqueous solution. *Macromolecules* **2010**, *43*, 7312-7320.

28. Kitano, H.; Hirabayashi, T.; Gemmei-Ide, M; Kyogoku, M. Effect of macrocycles on the temperature-responsiveness of poly[(methoxy diethylene glycol methacrylate)-*graft*-PEG]. *Macromol. Chem. Phys.* **2004**, *205*, 1651–1659.

29. Jacobs, F. S.; Filby, R. H. Solvent extraction of oil-sand components for determination of trace elements by neutron activation analysis. *Anal. Chem*. **1983**, *55*, 74-77.

30. Noro, A.; Cho, D.; Takano, A.; Matsushita, Y. Effect of molecular weight distribution on microphase-separated structures from block copolymers. *Macromolecules* **2005**, *38*, 4371-4376.

31. Mayes, A. M.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. Homopolymer distributions in ordered block copolymers. *Macromolecules* **1992**, *25*, 6523-6531.

32. Torikai, N.; Takabayashi, N.; Noda, I.; Koizumi, S.; Mori, Y.; Matsushita, Y. Lamellar domain spacings of diblock copolymer/homopolymer blends and conformations of block chains in their microdomains. *Macromolecules* **1997**, *30*, 5698-5703.