Preparation and Characterization of Temperature-responsive polymeric surfactants

B. Yang, J. Duhamel, IPR symposium

University of Waterloo, Department of Chemistry, ON N2L 3G1, Canada

Canada is the country with the second largest oil reservers with 1,700 Gbbl (=2.72×10^{11}m^3) of proven heavy oil reserves in the world.[1] However, Canada's heavy oil consist of large hydrocarbon molecules so that it is usually solid at room temperature,[2] making its extraction difficult. In the Athabasca region, 250 billion barrels worth of bitumen is located in beds of sand and clay, where the oil and sand usually stick together,[3] further complicating the oil extraction process. Several techniques having been introduced to enhance oil recovery form the oil sands. They include the use of hot water in steaming[2] or surfactants[4]. However, the extraction process of oil sands is costly since it requires high temperature, or loss certain amount of surfactants for these techniques. This proposal aims to improve the oil extraction process by using a temperature-responsive polymeric surfactant (TRPS) that extracts oil at a lower temperature.

The oil extraction protocol by using a TRPS of poly(ethylene glycol)-block-poly[2-(2-methoxyethoxy) ethyl methacrylate] (PEG-*b*-PMEO$_2$MA) as an example is shown in Figure 1.

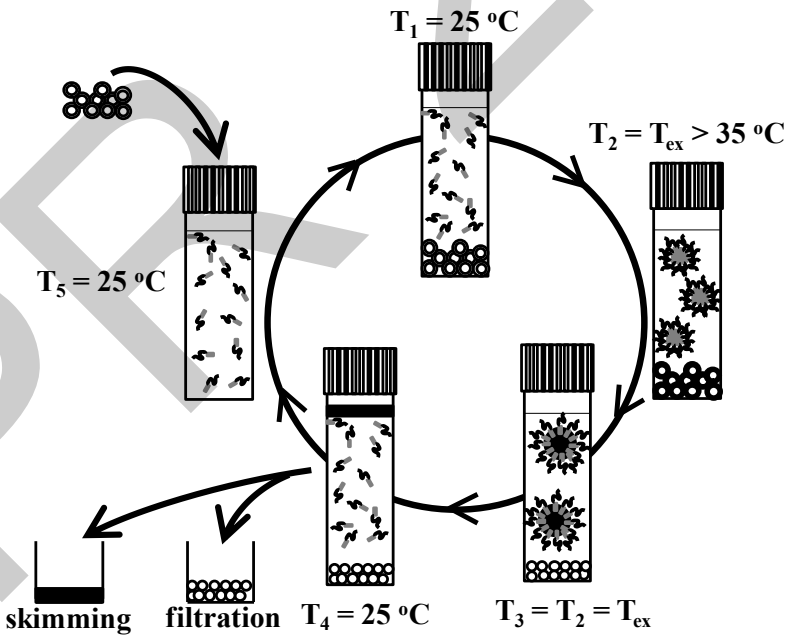


Figure 1: Proposed process for oil extraction from oil sands by using the temperature-responsive block copolymer poly(ethylene glycol)-block-poly(*N*-isopropylacrylamide) (PEG-*b*-PNIPAM).

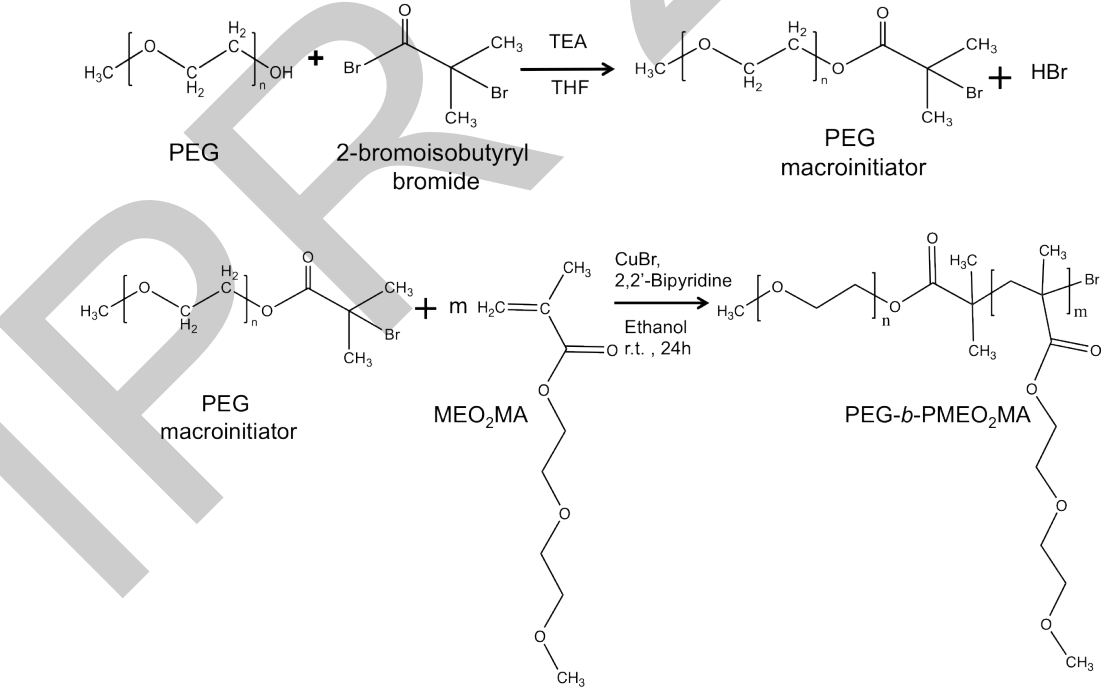
At T_1, oil sands are introduced into the vial where they sink at the bottom. The temperature-responsive block copolymer is water-soluble and no micelle forms. When the temperature increases to T_2, the PMEO$_2$MA block of the polymer becomes

hydrophobic while PEG is still hydrophilic. Thus block copolymer micelles form with a hydrophobic $PMEO_2MA$ core and a hydrophilic PEG shell. If T_2 is greater than the oil melting temperature, the hydrophobic oil surrounding the sands will flow and swell the hydrophobic core of the micelles generating an emulsion. At T_4, when the temperature is lower than the lower critical solution temperature (LCST) of $PMEO_2MA$, the $PMEO_2MA$ block becomes water-soluble again, and no micelle exists anymore. The oil being less dense than water phase-separates at the surface of the aqueous phase and the oil-free sand particles sink at the bottom of the vial. Finally, oil and sand can be separated. After the extraction of the oil and the removal of the sand, a new extraction cycle can be started using the recovered polymeric surfactant.

Experimental

A TRPS of poly(ethylene glycol)-block-poly[2-(2-methoxyethoxy) ethyl methacrylate] (PEG-*b*-$PMEO_2MA$) was successfully prepared by atom transfer radical polymerization (ATRP) and studied in extraction of the oil from oil sands.

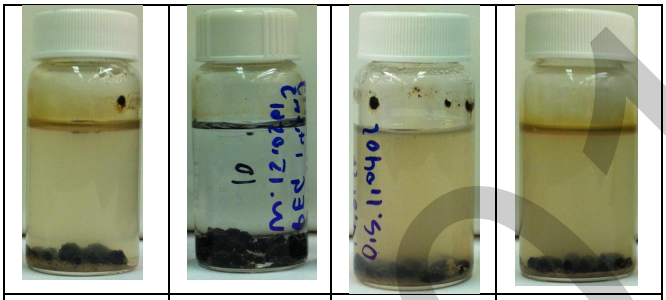
First, a poly(ethylene glycol) (PEG) macroinitiator was synthesized by reacting the hydroxyl end group of PEG with 2-bromoisobutyryl bromide. The composition of the PEG macroinitiator was determined by a combination of gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Then, the synthesized macroinitiator was used for the polymerization of PEG-*b*-$PMEO_2MA$. The absolute molecular weight equals 19,000±200 g/mol was determined by NMR, and PDI of 1.54±0.01 was determined by GPC analysis. The synthesis protocol is shown in Scheme 1.[5]



Scheme 1: The synthesis of PEG-*b*-$PMEO_2MA$ by atom transfer radical polymerization (ATRP).

Results

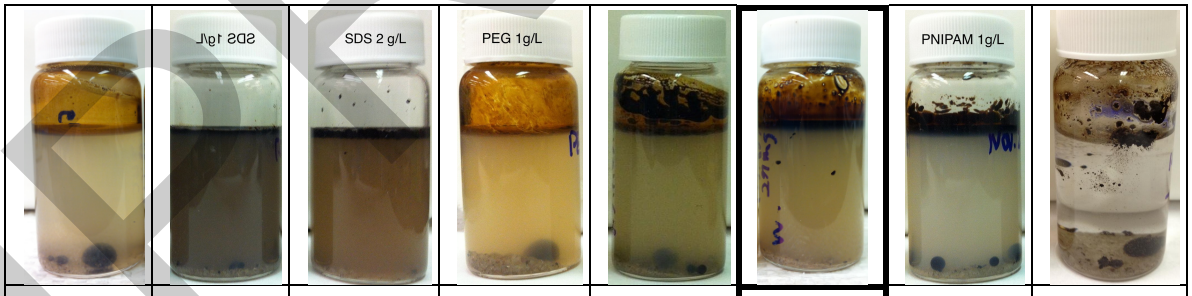
The purpose of this proposal is to develope a better oil extraction method by using TRPSs. A series of experiments were done by using water and the synthesized PEG-*b*-$PMEO_2MA$ for oil extraction with or without toluene. First, in Figure 2, by using different concentrations of PEG-*b*-$PMEO_2MA$ aqueous solutions alone (no toluene), at 45°C, the extraction of oil from oil sands was not efficient, whose results were closed to those of only using water, homoblockpolymer PEG and $PMEO_2MA$ aqueous solutions for oil extraction.



Pure Water	1 mg/mL PEG	1 mg/mL $PMEO_2MA$	1 mg/mL PEG-*b*-$PMEO_2MA$

Figure 2: Pictures of the vials containing 1 g of oil sand and 15 mL of aqueous solution after being shaken for 24 hrs at T = 45 °C.

However, the addition of toluene on top of PEG-*b*-$PMEO_2MA$ aqueous layer showed a significant improvement. Adding 65mg of toluene to 15g 1mg/mL PEG-*b*-$PMEO_2MA$ aqueous solution obtained a 100% extraction of oil from 1g of oil sands. Under the same conditions, Figure 3 demonstrates that the synthesized PEG-*b*-$PMEO_2MA$ gives the best extraction of oil by addition of 60mg of toluene.



Pure Water	1 mg/mL SDS	2 mg/mL SDS	1 mg/mL PEG	1 mg/mL $PMEO_2MA$	1 mg/mL PEG-*b*-$PMEO_2MA$	1 mg/mL PNIPAM	1 mg/mL PEG-*b*-PNIPAM

Figure 3: Pictures of the vials containing 1 g of oil sand, 15 mL of aqueous solution, and 60 mg of toluene after being shaken for 24 hrs at T = 45 °C.

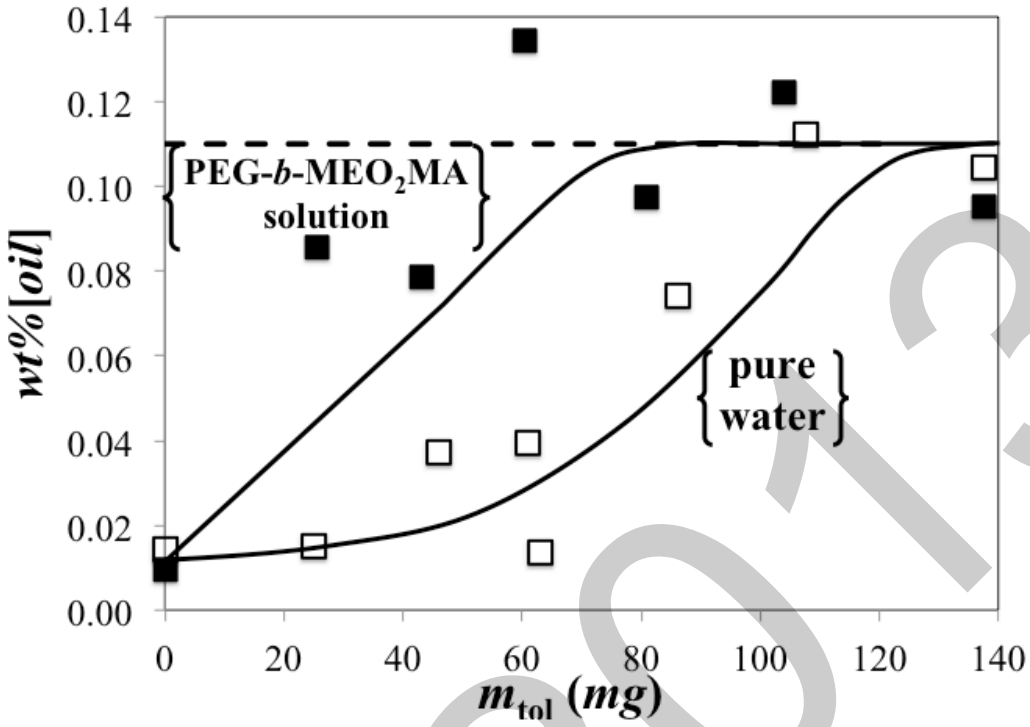


Figure 4: Plot of the weight fraction of oil recovered (wt%[oil]) versus the mass of toluene added (m_{tol}).

The results shown in Figure 3 demonstrate the superiority of the 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution at extracting oil using toluene. This conclusion was further confirmed by comparing the weight fraction of oil extracted from the oil sand (wt%[oil]) as a function of the mass of toluene (m_{tol}) added when 15 mL of pure water or a 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution was used. 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 4. For m_{tol} greater than or equal to 100 mg, wt%[oil] equaled 0.11 within experimental error indicating complete oil recovery. However, for all other m_{tol} smaller than 100 mg, wt%[oil] recovered with the 1 mg/mL PEG-*b*-PMEO$_2$MA aqueous solution was always consistently larger than wt%[oil] obtained with water alone. The trend shown in Figure 4 demonstrates that PEG-*b*-PMEO$_2$MA enhances oil extraction substantially when toluene is being used.

References

1. Saniere, A.; Hénaut, I.; Argillier, J. F. *Oil Gas Sci. Tech.* **2004**, *59*, 455-466.
2. Larter, S.; Adams, J.; Gates, I. D.; Bennett, B.; Huang, H. *J. Can. Pet. Tech.* **2007**, *47(1)*, 52-61.
3. Masliyah, J.; Zhou, Z.; Xu, Z.; Czarnecki, J.; Hamza. H. *Can. J. Chem. Eng*. **2004**, *82*, 628-654.
4. Holmberg, K. *Surfactants and Polymers in Aqueous Solution.* Chichester, West Sussex, England: John Wiley & Sons, 2003.
5. Bandrup, J. ; Immergut, E. H. ; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: NY, **1999**.

Preparation and Characterization of Temperature-Responsive Polymeric Surfactants

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Chemistry, University of Waterloo
IPR Symposium

May 8th, 2013

Introduction

Background Information:
Why did we come up with this project?

Background

oil sands

Problems of oil extraction:

(a)The heavy oil is usually solid at room temperature;

(b)The oil and sand stick together.

Attempt 1

Steaming with hot water

Require high temperature
Produce a large amount of CO_2

Attempt 2

Using surfactants

Stable emulsions

Tailing ponds (Loss of surfactants)

Oil extraction: costly & environmentally unfriendly

Better way?

Proposal:

To extract oil from oil sands using
a temperature-responsive polymeric surfactant

Temperature-responsive Polymers

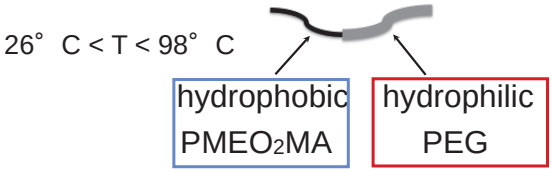
- A temperature-responsive polymer changes one of its physical properties with an external thermal stimulus.
- In this proposal
  - Temperature-responsive polymers describe soluble polymers that become insoluble above a lower critical solution temperature (LCST).

Temperature-responsive Polymer	LCST in Water
Poly[2-(2-methoxyethoxy)ethyl methacrylate] ($PMEO_2MA$)	26°C
Poly(N-isoporpylacrylamide) (PNIPAM)	32°C
Poly(ethylene glycol) (PEG)	98°C

Bandrup, J. ; Immergut, E. H. ; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: NY, 1999.

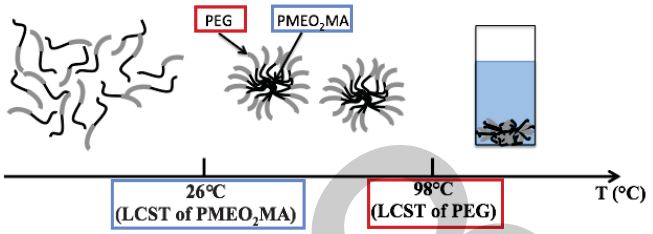
Surfactants

- An amphiphilic molecule consists of a hydrophobic group and a hydrophilic group.



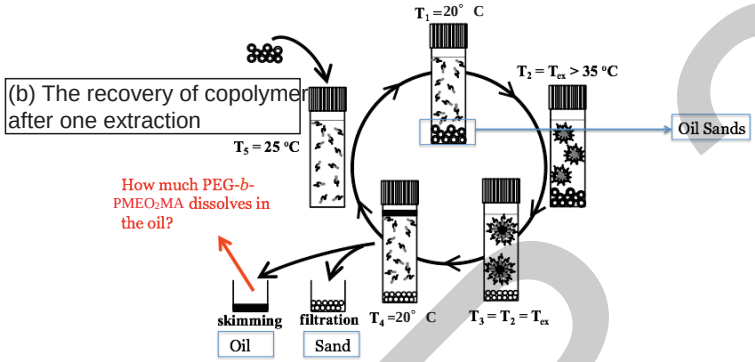
PEG-*b*-$PMEO_2MA$

Temperature-responsive Polymeric Surfactants (TRPSs)



Bandrup, J. ; Immergut, E. H. ; Grulke, E. A. *Polymer Handbook*, 4th ed.; John Wiley & Sons: NY, 1999.

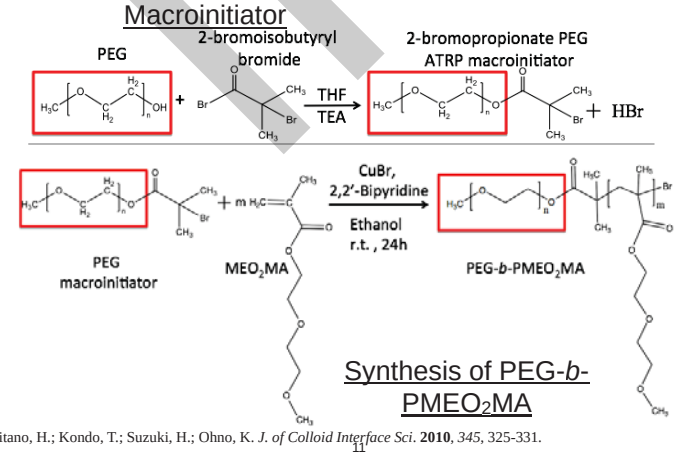
Proposed Protocol of the Extraction of Oil



Objectives

- Synthesis of a well-defined TRPS by atom transfer radical polymerization (ATRP), such as PEG-*b*-PNIPAM, PEG-*b*-$PMEO_2MA$.
- Determination of the chemical composition of the TRPS.
- Determination of the LCST of the copolymer.
- Determination of the efficiency of the copolymers at extracting oil from the oil sands by steady-state fluorescence or GPC.

Synthesis of PEG-*b*-$PMEO_2MA$ by ATRP



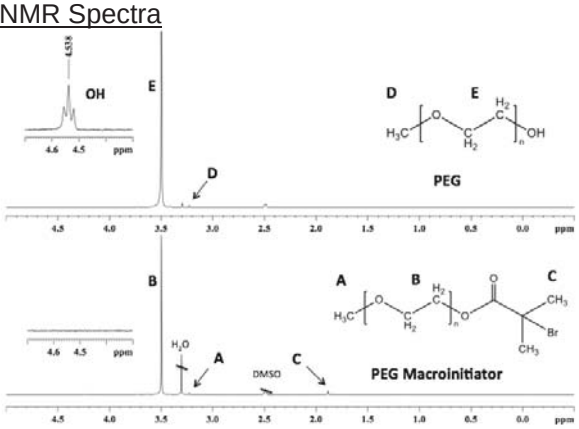
Kitano, H.; Kondo, T.; Suzuki, H.; Ohno, K. *J. of Colloid Interface Sci.* **2010**, *345*, 325-331.

Results

1. Synthesis of PEG Macroinitiator ✓
2. Synthesis of PEG-*b*-$PMEO_2MA$ by ATRP ✓
3. Study of Micelle formation - LCST
4. Oil Extraction Experiments

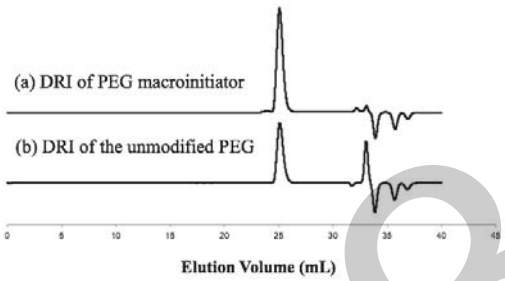
1. Synthesis of PEG Macroinitiator

^{1}H NMR Spectra



Gel Permeation Chromatography (GPC)

Traces



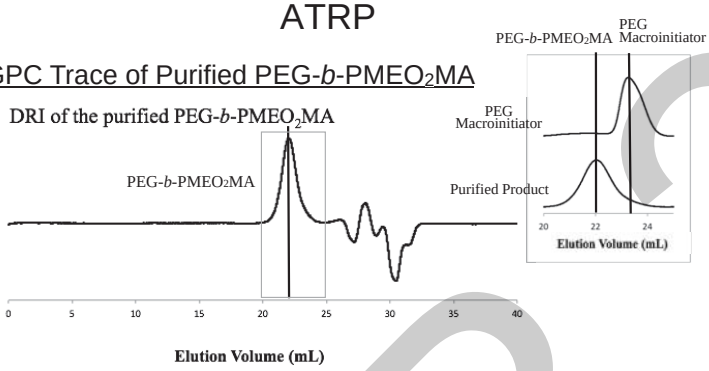
Conclusions

(a) The successful synthesis of PEG macroinitiator was confirmed by NMR spectra and GPC traces.

(b) The absolute number-average molecular weight (M_n) of this macroinitiator determined by NMR spectrum equals 5100±100 g/mol.

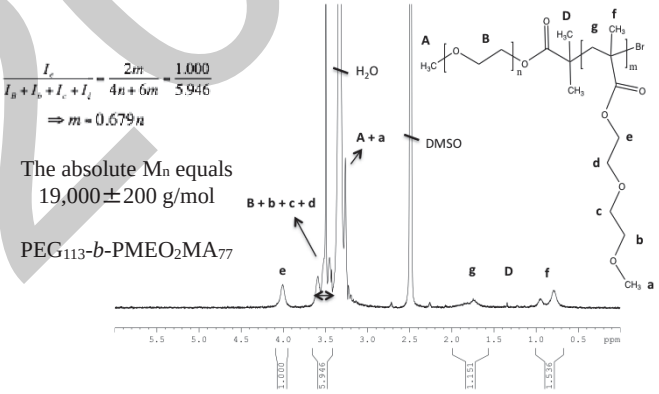
2. Synthesis of PEG-*b*-PMEO$_2$MA by ATRP

GPC Trace of Purified PEG-*b*-PMEO$_2$MA



➔ The apparent M_n calculated based on polystyrene standards equals 20,300±150 g/mol with a PDI of 1.54±0.01.

^{1}H NMR Spectrum of Purified PEG-*b*-PMEO$_2$MA



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

$$\Rightarrow m = 0.679n$$

The absolute M_n equals 19,000±200 g/mol

PEG_{113}-*b*-$PMEO_2MA_{77}$

Conversions of Macroinitiator and Monomer:

PEG_{113}-*b*-$PMEO_2MA_{77}$

$$\frac{n}{m} = \frac{113}{77} = 1.47(\pm 0.02)$$

PEG macroinitiator: 0.78 mmol

MEO_2MA: 14.6 mmol

fully reacted ⟶

$$\frac{n}{m} = \frac{0.78 \times 113}{14.6} = 1.5(\pm 0.1)$$

%Yield = 83%

➔ The macroinitiator and monomer in this reaction are in high conversions.

Table: Homopolymer $PMEO_2MA$ and copolymer PEG-*b*-$PMEO_2MA$ synthesized by ATRP

#	Polymer	Mn, NMR (g/mol)	PDI
1	PMEO2MA	26000	1.8
2	PEG	5000	1.1
3	PEG-b-PMEO2MA	14000	1.5
4	PEG-b-PMEO2MA	19000	1.5

Study of Micelle Formation:

(a) LCST by turbidity

(b) Molecular size by dynamic light scattering (DLS)

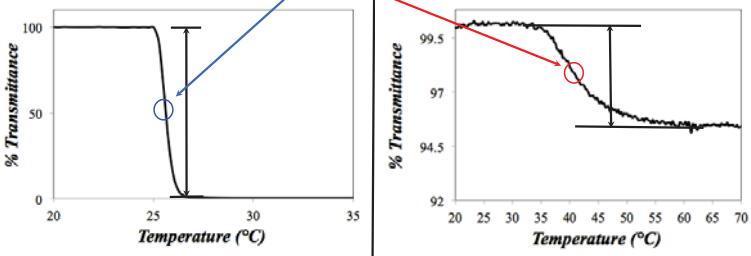
3. Study of Micelle Formation:

Determination of LCST by turbidity measurement

$PMEO_2MA$ (26K)

50% of transmittance

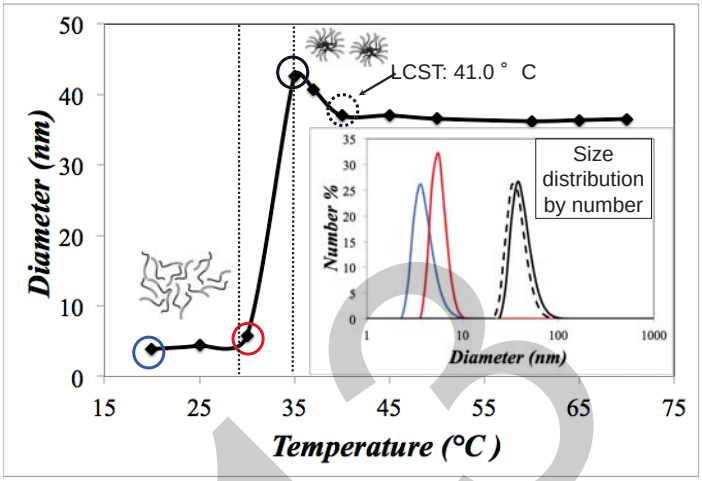
PEG-*b*-$PMEO_2MA$ (19K)



LCST of homopolymer $PMEO_2MA$ (#1) is 27.3 ° C (consistence with literature value). (C=4.9 mg/mL)

LCST of copolymer PEG-*b*-$PMEO_2MA$ (#4) is 41.0 ° C. (C=5.0 mg/mL)

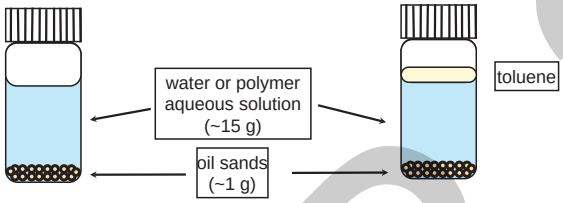
Determination of molecular sizes by DLS



4. Oil Extraction Experiments

Protocol #1

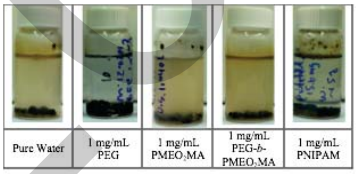
Protocol #2



Put samples in the shaker at 45 ° C and let them stays for 24 hrs

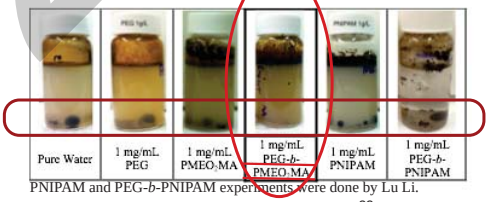
3. Oil Extraction Experiments

Protocol #1 - without toluene (24h)



➔ The oil extraction is not very efficient.

Protocol #2 - with 60 mg of toluene (24h)



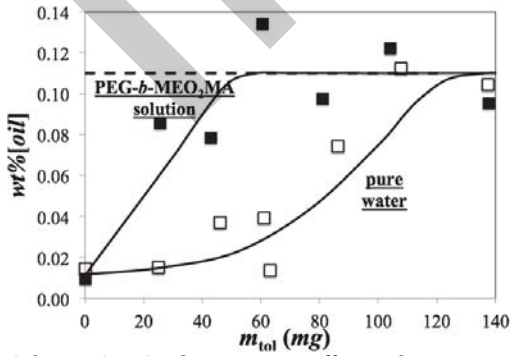
➔ 1) Adding toluene improves oil extraction.

2) 1 mg/mL of PEG-*b*-$PMEO_2MA$ is most efficient.

PNIPAM and PEG-*b*-PNIPAM experiments were done by Lu Li.

3. Oil Extraction Experiments

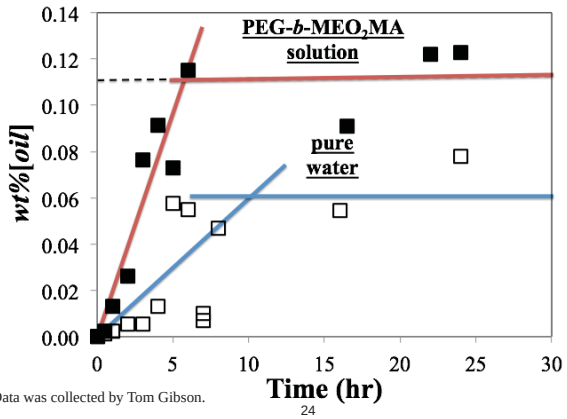
Protocol #2 - with 60 mg of toluene (24h)



➔ 1) PEG-*b*-$PMEO_2MA$ solution is more efficient than pure water.
2) The oil extraction is most efficient: 1mg/mL polymer solution with 60 mg toluene.

3. Oil Extraction Experiments

Protocol #2- Time-dependent Experiment

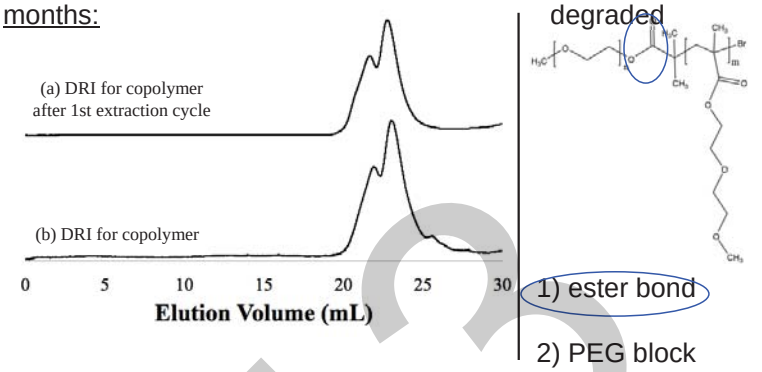


Data was collected by Tom Gibson.

Problem:

Polymer degrades over time

GPC Traces of PEG-*b*-PMEO$_2$MA after 2Polymer degraded months:



1) ester bond

2) PEG block

➔ Replace ester bond with amide bond

Summary and Future Work

- Two TRPS PEG-*b*-PMEO$_2$MA were successfully synthesized by ATRP, and PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ was applied to oil extraction experiments.
- With addition of 60 mg of toluene, 1 g/L PEG$_{113}$-*b*-PMEO$_2$MA$_{77}$ resulted in 100% recovery of oil from oil sands.
- Since PEG-*b*-PMEO$_2$MA degraded over time, a PEG-*b*-PMEO$_2$MA sample with a more stable amide bond will be synthesized.
- The LCST of these temperature-responsive polymers will be determined by turbidity or light-scattering measurements.
- The recovery of the copolymer after one oil extraction cycle and the micellization of the copolymer with temperature will be studied by GPC and DLS, respectively.
- Finally, the copolymers will be used to extract the oil from an oil sand sample provided by Imperial Oil.

Acknowledgements

- Funding from Imperial Oil and NSERC

Esso Imperial Oil NSERC CRSNG

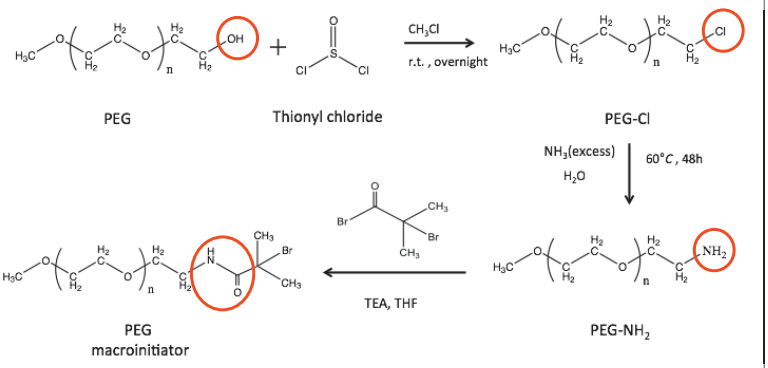
- Dr. Chakrabarty at Imperial Oil
- Lab members in the Duhamel and Gauthier Laboratories, and a special thank to Tom Gibson.

Thank you for attending!

Questions?

Synthesis of PEG-*b*-PMEO$_2$MA (amide)

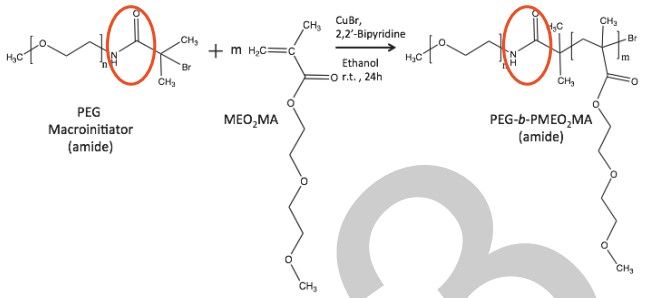
Synthesis of PEG Macroinitiator (amide)



Artizi, N.; Shazly, T.; Crespo, C.; Ramos, A. B.; Chenault, H. K.; Edelman, E.R. *Macromol. Biosci.* **2009**, *9*, 1-12.

Synthesis of PEG-*b*-PMEO$_2$MA (amide)

Synthesis of PEG-*b*-PMEO$_2$MA (amide)

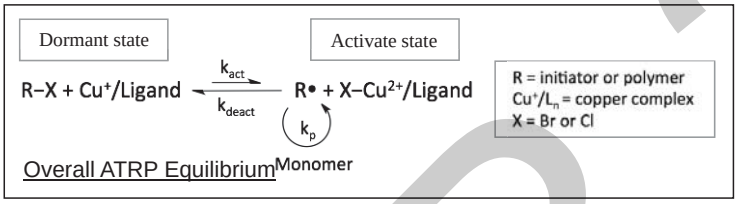


Synthesis of PEG-*b*-PMEO$_2$MA by ATRP

Atom transfer radical polymerization (ATRP)

The most effective and most widely used methods of controlled radical polymerization (CRP):

(a) Uses transition metal catalysts (usually copper (I) ion)



Overall ATRP Equilibrium

(b) Stop or restart by controlling the temperature or other factors

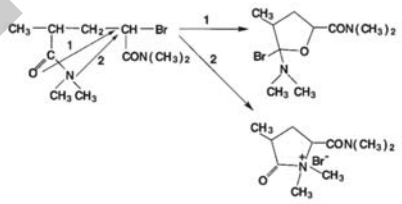
(c) Forms well-defined polymers (polydispersity index, PDI < 1.2)

Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348-7350.

Inherent Reasons for the Lack of Control of the Reaction:

(a) Deactivation of the copper catalyst through complexation with amide groups.

(b) Displacement of the terminal bromine atom by amide groups, as shown in the figure below.

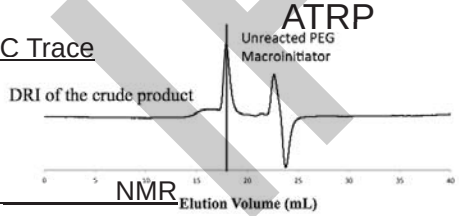


Cyclization of penultimate methacrylamide unit

Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826-4831.
Rademacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J. *Macromolecules.* **2000**, *33*, 284-288.

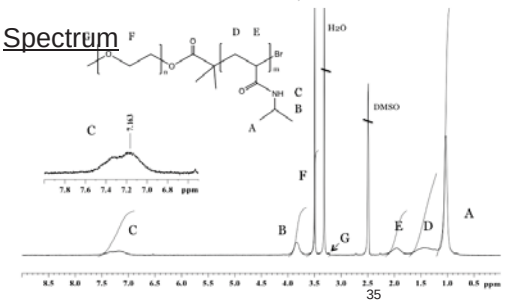
2. Synthesis of PEG-*b*-PNIPAM by ATRP

GPC Trace



➔ Consistent with:
(a) Low yield
(b) High PDI

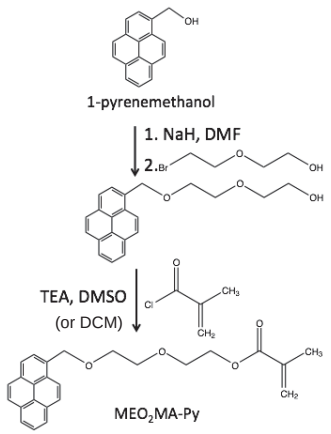
^{1}H NMR Spectrum



➔ Confirm the synthesis of PEG-*b*-PNIPAM

Synthesis of PEG-*b*-PMEO$_2$MA-Py by ATRP

Synthesis of Pyrene-labelled Monomer (MEO$_2$MA-Py)



Why Pyrene ?

(a) High extinction coefficient

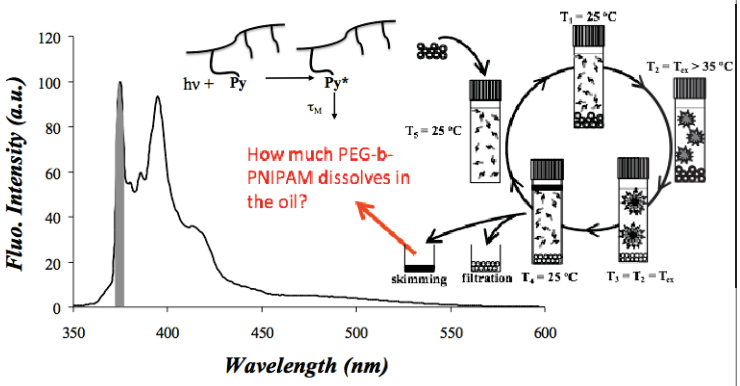
(b) High quantum yield

➔

Fluorescence is strong even at low pyrene concentrations.

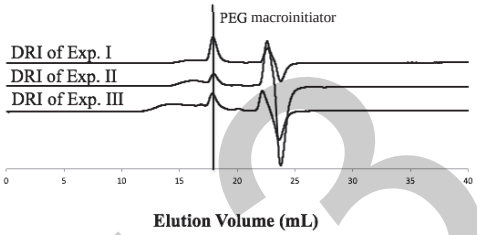
Determination of the Percentage Recovery of PEG-*b*-PMEO$_2$MA-Py

Pyrene Fluorescence



To improve yield and MW control of this reaction:

Exp.	[Macroinitiator] (mmol/L)	[NIPAM] (mmol/L)	[CuBr] (mmol/L)	[CuBr$_2$] (mmol/L)	[PMDETA] (mmol/L)
I	19.5	8.75×10^3	21.25	2.35	0.287
II	39.5 ×2	8.74×10^3	21.03	2.36	0.287
III	×1.5 29.3	13.2×10^3	31.89	3.60	0.457

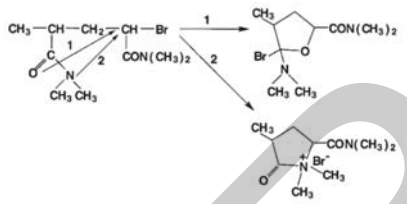


➔ No dramatic improvements by changing the concentrations of starting materials.

Inherent Reasons for the Lack of Control of the Reaction:

(a) Deactivation of the copper catalyst through complexation with amide groups.

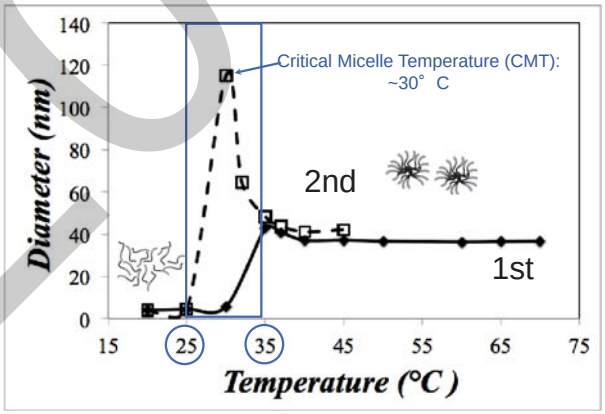
(b) Displacement of the terminal bromine atom by amide groups, as shown in the figure below.



Cyclization of penultimate methacrylamide unit

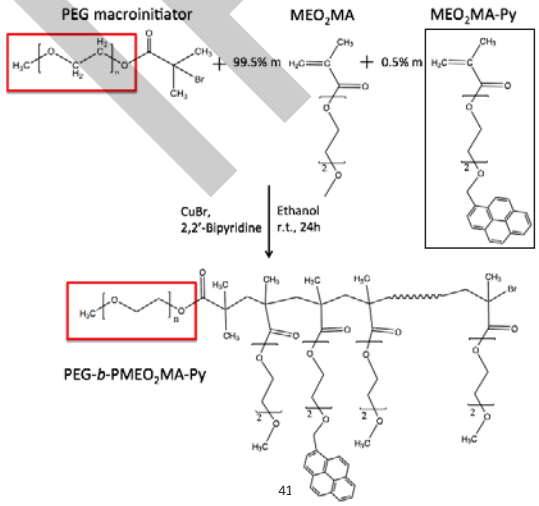
Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826-4831.
Rademacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J. *Macromolecules.* **2000**, *33*, 284-288.

Determination of molecular sizes by DLS (con't)

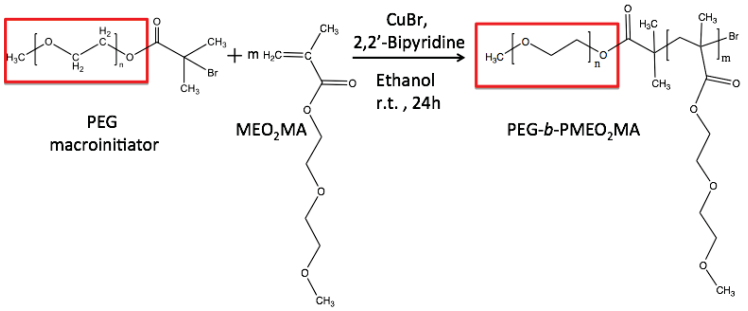


➔ Another measurement is required (temperature range: 25-35° C; interval: 1-2° C) to determine CMT.

Synthesis of PEG-*b*-PMEO$_2$MA-Py by ATRP



Synthesis of PEG-*b*-PMEO$_2$MA by ATRP



Kitano, H.; Kondo, T.; Suzuki, H.; Ohno, K. *J. of Colloid Interface Sci.* **2010**, *345*, 325-331.

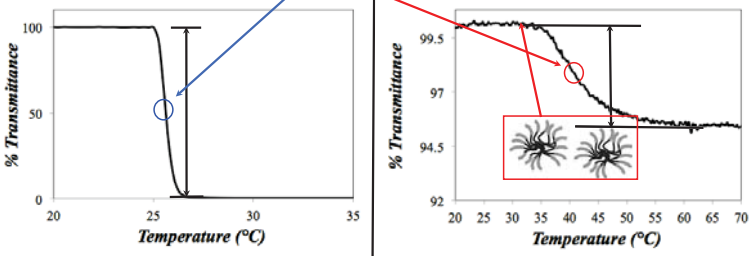
3. Study of Micelle Formation:

Determination of LCST by turbidimetry measurement

PMEO$_2$MA (26K)

50% of transmittance

PEG-*b*-PMEO$_2$MA (19K)



LCST of homopolymer PMEO$_2$MA (#1) is 27.3 ° C (consistence with literature value). (C=4.9 mg/mL)

LCST of copolymer PEG-*b*-PMEO$_2$MA (#4) is 41.0 ° C. (C=5.0 mg/mL)

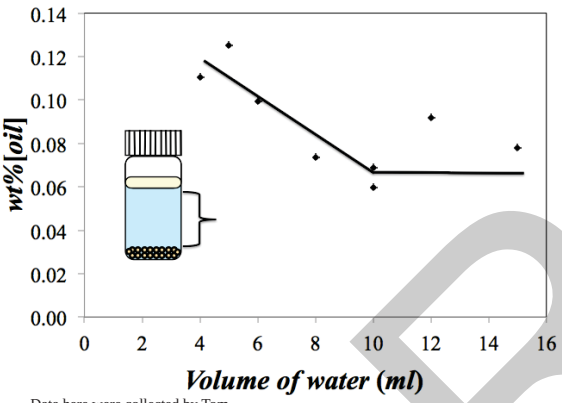
Table: Homopolymer PMEO$_2$MA and copolymer PEG-*b*-PMEO$_2$MA synthesized by ATRP

#	Polymer	Mn, NMR (g/mol)	PDI
1	PMEO2MA	26000	1.8
2	PEG	5000	1.1
3	PEG-*b*-PMEO2MA	14000	1.5
4	PEG-*b*-PMEO2MA	19000	1.5

Study of Micelle Formation

3. Oil Extraction Experiments

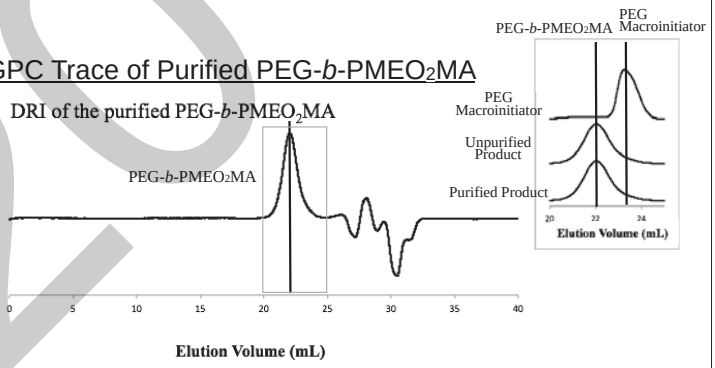
Effect of the volume of water (aqueous layer)



➔ less water, better extraction

Data here were collected by Tom.

GPC Trace of Purified PEG-*b*-PMEO$_2$MA



➔ The apparent M_n calculated based on polystyrene standards equals 20,300±150 g/mol with a PDI of 1.54±0.01. (Compared to the absolute M_n, 19,000±200 g/mol, calculated from NMR spectrum.)

Future Work

- A PEG-*b*-PMEO$_2$MA sample with amide bond will be synthesized.
- A PEG-*b*-PMEO$_2$MA sample with a shorter PEG will be prepared by using ATRP.
- The LCST of these temperature-responsive polymers will be determined by turbidity or light-scattering measurements.
- The recovery of the copolymer after one oil extraction cycle and the micellization of the copolymer with temperature will be studied by GPC.
- Finally, the copolymers will be used to extract the oil from an oil sand sample provided by Imperial Oil.