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RU RYERSON Department of CHEMICAL ENGINEERING

# Effect of Ligands on Controlled Polymerization of Methyl Methacrylate by AGET Method in Emulsion System

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# Outline

1- Introduction

2- Materials and Methods

3- Experimental Procedure

4- Results and Discussion

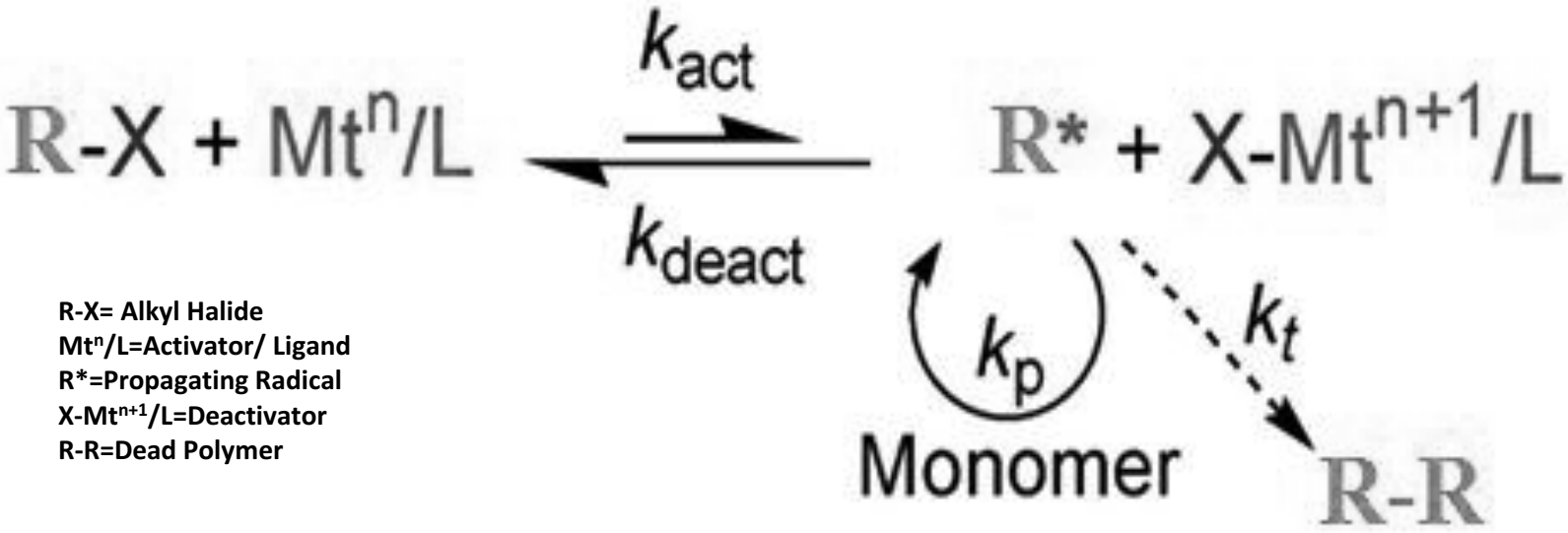
5- Conclusion

6- Future Work

7- Acknowledgment.

# 1- INTRODUCTION

- **ATRP has been investigated independently in 1995.**
- **All ATRP systems are composed of monomer, initiator and catalyst.**



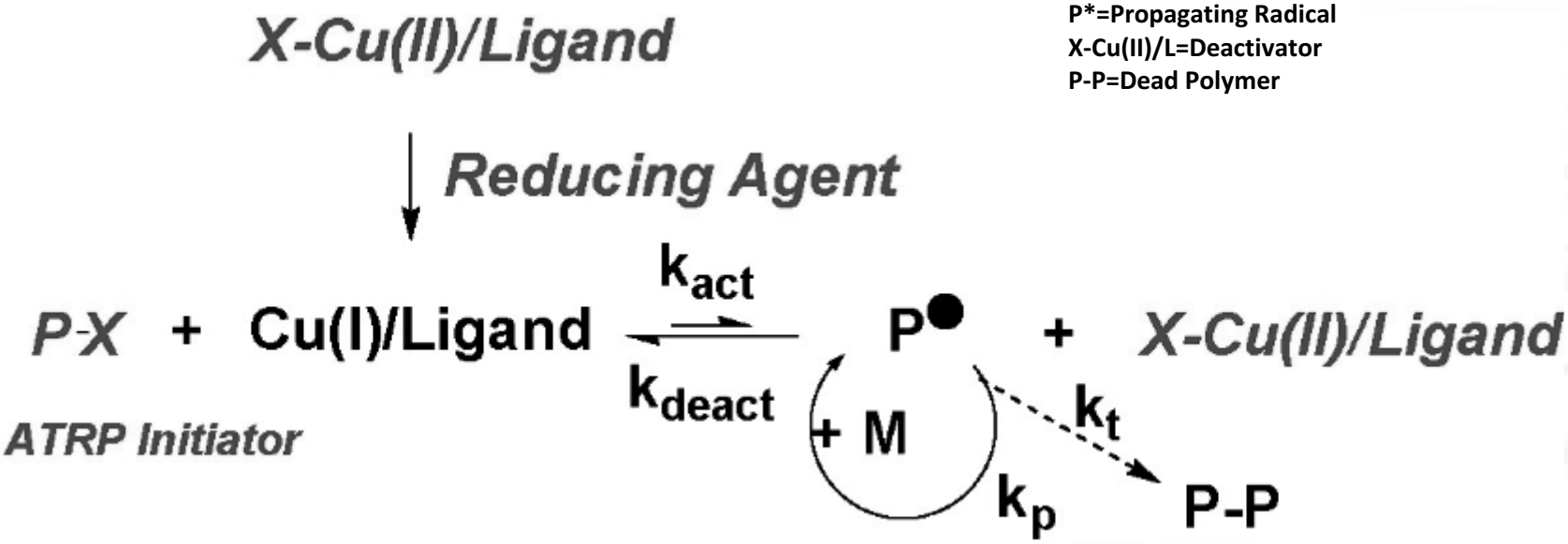

**R-X= Alkyl Halide**
**$Mt^n$/L=Activator/ Ligand**
**R*=Propagating Radical**
**X-$Mt^{n+1}$/L=Deactivator**
**R-R=Dead Polymer**

**Jia, Di. "Atom transfer radical polymerization in microemulsion." (2008).**

# AGET ATRP Mechanism

- **Developed recently where reducing agent is employed to generate the activator.**

**P-X= Alkyl Halide Initiator**
**Cu(I)/L=Activator/ Ligand**
**P*=Propagating Radical**
**X-Cu(II)/L=Deactivator**
**P-P=Dead Polymer**




Min, K.; Matyjaszewski, K. Macromolecules (2005).

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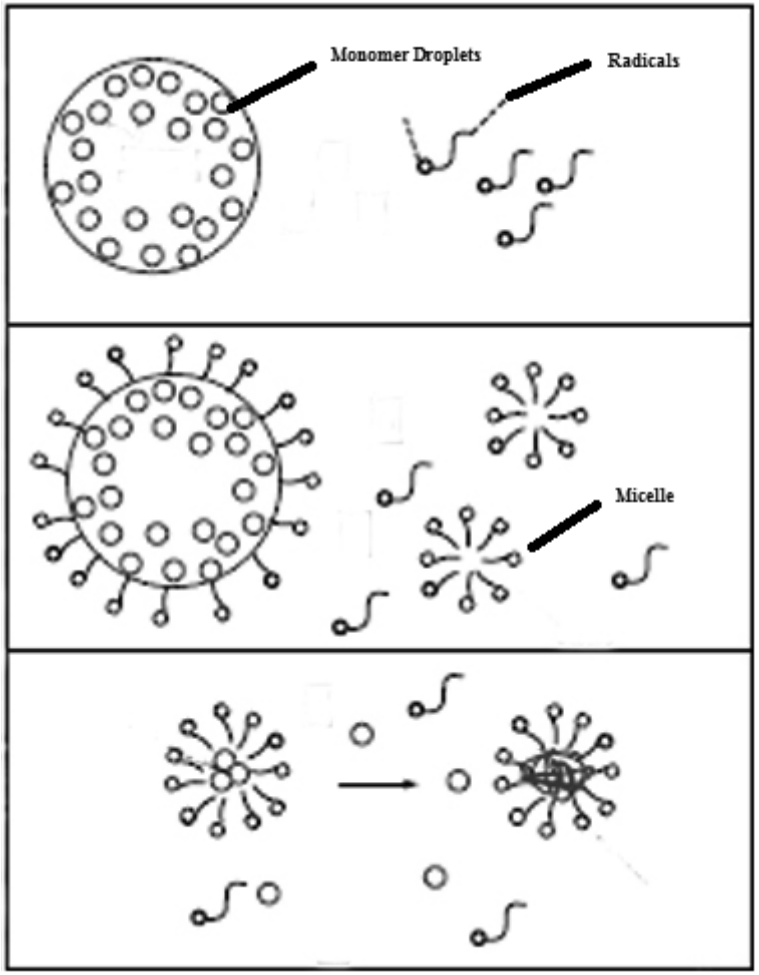
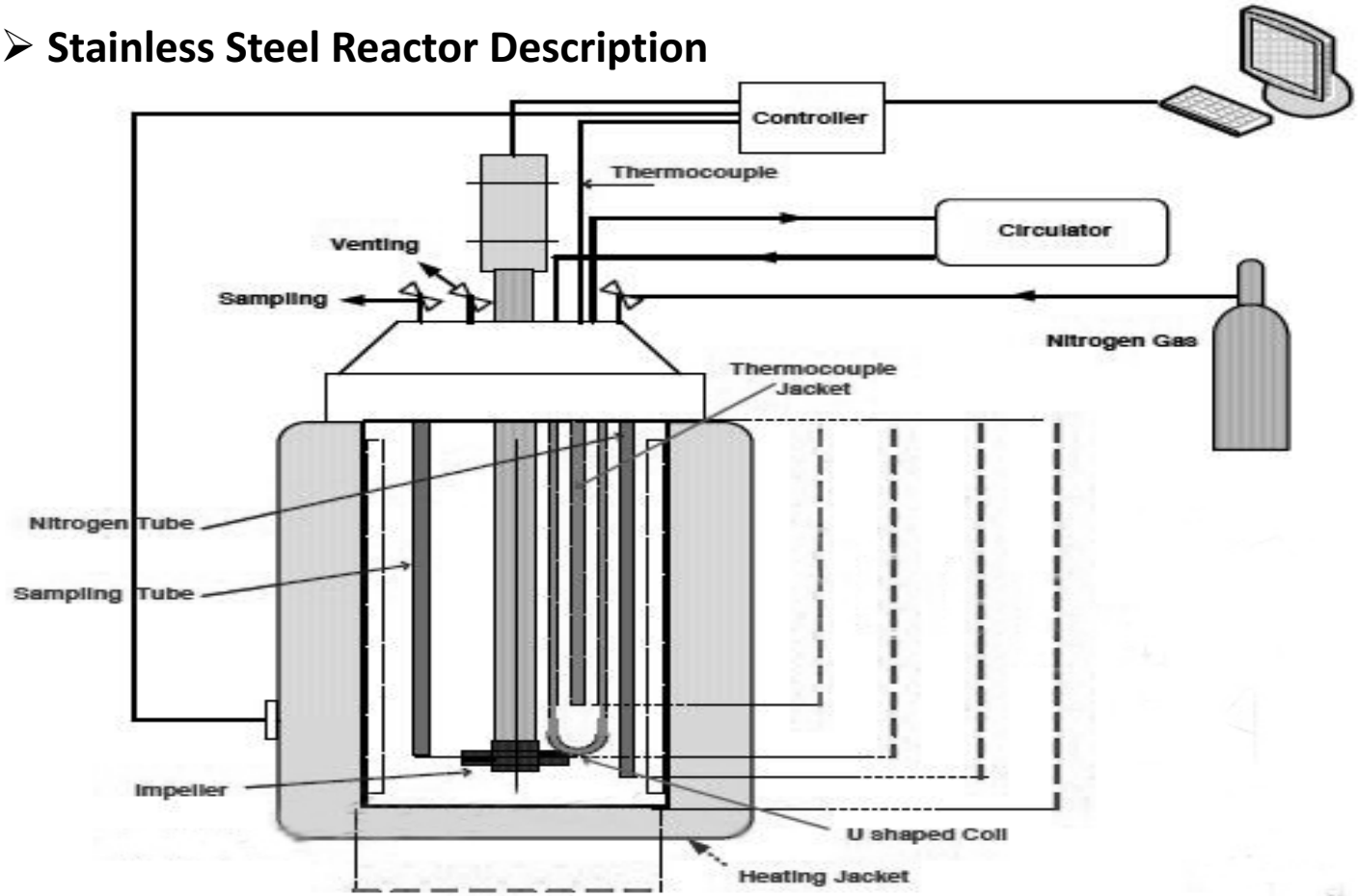
# Emulsion Polymerization

- **Radicals enter micelles and form polymer particles.**
- **Particles grow as they absorb monomer from monomer droplets.**
- **Polymerization continues within the particles until the monomer is consumed.**



# 2- MATERIALS AND METHODS

- **Stainless Steel Reactor Description**




**ROUDSARI, SHIDEH FATHI.** ***Experimental and CFD Investigation of the Mixing of MMA Emulsion Polymerization in a Stirred Tank Reactor*****. Diss. Ryerson University, 2015.**

# 2- MATERIALS AND METHODS

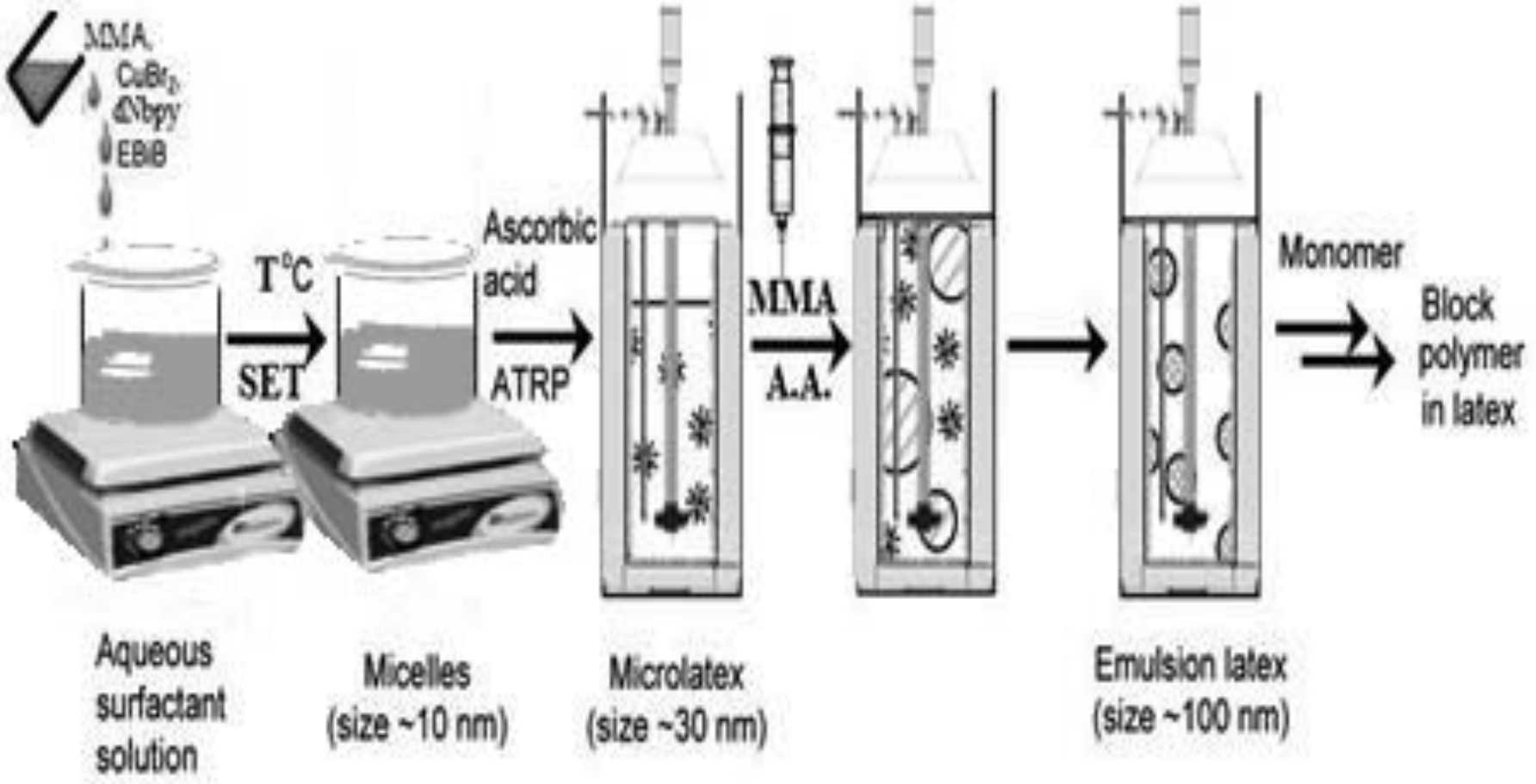
- **Gravimetry: to Measure Monomer Conversion (Penlidis, 1986)**

$$W.f.solids = \frac{(weight\ of\ cup + dry\ residue) - (weight\ of\ cup)}{(weight\ of\ cup + wet\ sample) - (weight\ of\ cup)}$$

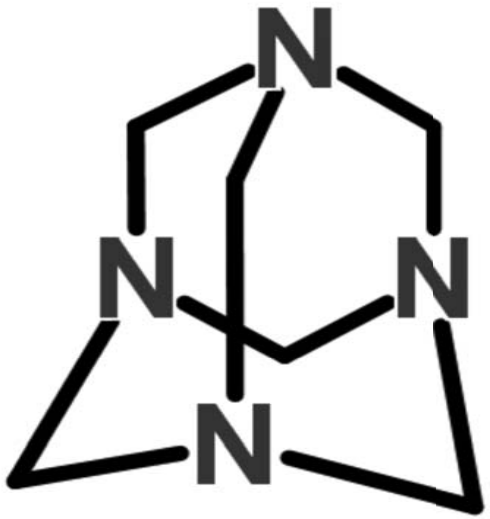
$$x(t) = \frac{w.f.solids - (w.f.initiator + w.f.catalyst\ complex + w.f.surfactant + w.f.reducing\ agent)}{w.f.monomer}$$

- **Gel permeation chromatography (GPC) was used to measure the molecular weight and polydispersity of the polymer samples.**
- **The GPC that will be used is (Viscotek TDA, Model 302) equipped with a triple detector array.**

# 3- EXPERIMENTAL PROCEDURE



# HMTA Ligand

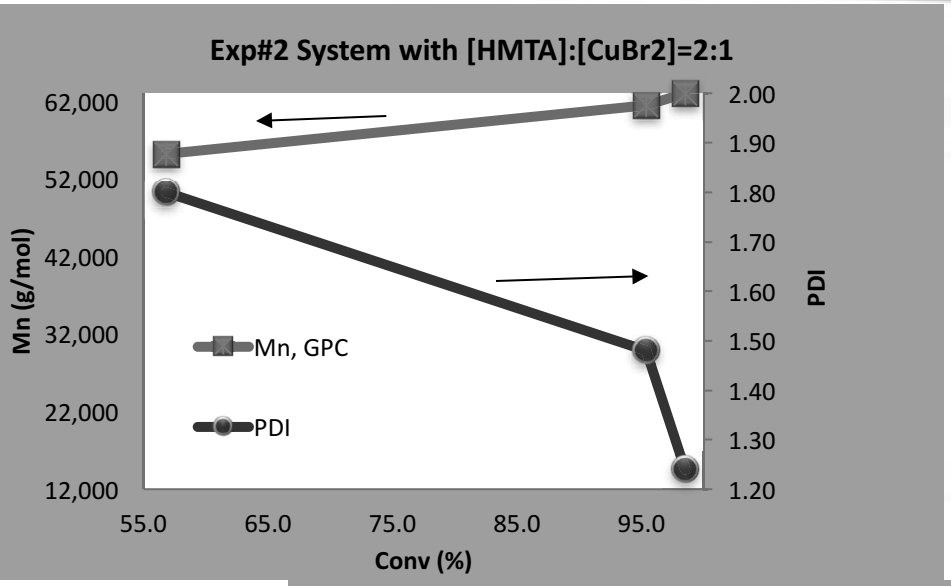


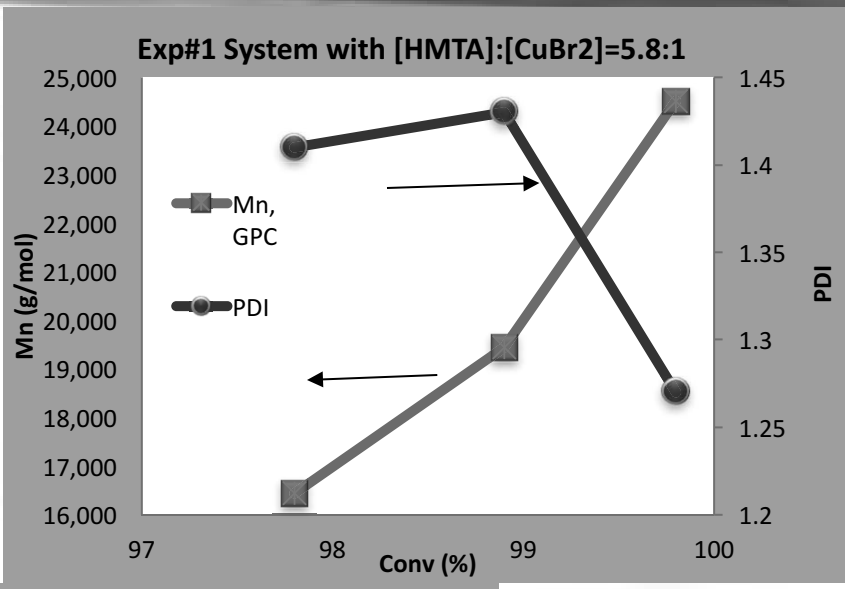

http://www.chemspider.com/Chemical-Structure.3959.html

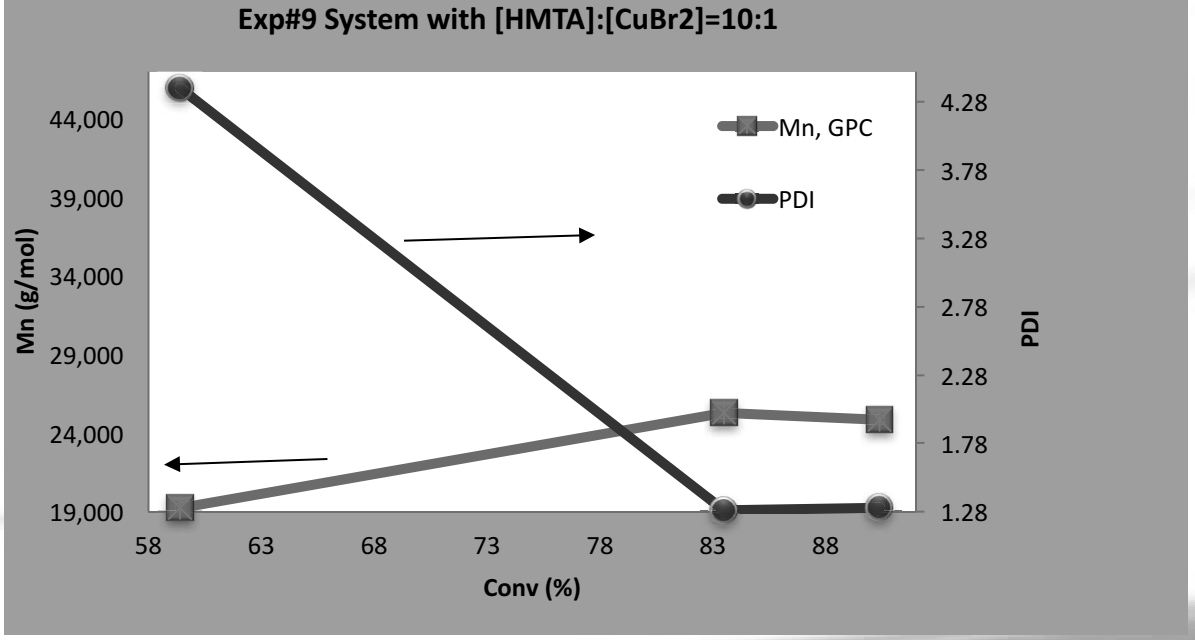
# Molar Ratios for Each Run Using HMTA Ligand

| ExP# | MMAI(g) | MMAII(g) | EBiB (g) | CuBr2 (g) | HMTA (g) | AA (g) | Brij 98 (g) | Water (g) |
|---|---|---|---|---|---|---|---|---|
| E1 | 54.88001076 | 164.6400323 | 1 | 0.146833781 | 0.855645274 | 0.133324663 | 5.106682654 | 7580.364816 |
| E2 | 54.88001076 | 164.6400323 | 1 | 0.146833781 | 0.295078974 | 0.133324663 | 5.106682654 | 7580.364816 |
| E5 | 350.669197 | 1052.007591 | 1 | 0.499344481 | 1.000713064 | 0.24989372 | 32.63039276 | 49276.36784 |
| E6 | 350.669197 | 1052.007591 | 1 | 0.499344481 | 1.000713064 | 0.24989372 | 32.63039276 | 49276.36784 |
| E7 | 54.88001076 | 164.6400323 | 1 | 0.078147812 | 0.156612398 | 0.039108568 | 5.106682654 | 7711.791115 |
| E8 | 54.88001076 | 164.6400323 | 1 | 0.146833781 | 0.295078974 | 0.078217136 | 5.106682654 | 7820.407892 |
| E9 | 124.2450386 | 372.7351158 | 1 | 0.196045376 | 1.967078833 | 0.598945177 | 12.98556446 | 20438.57396 |

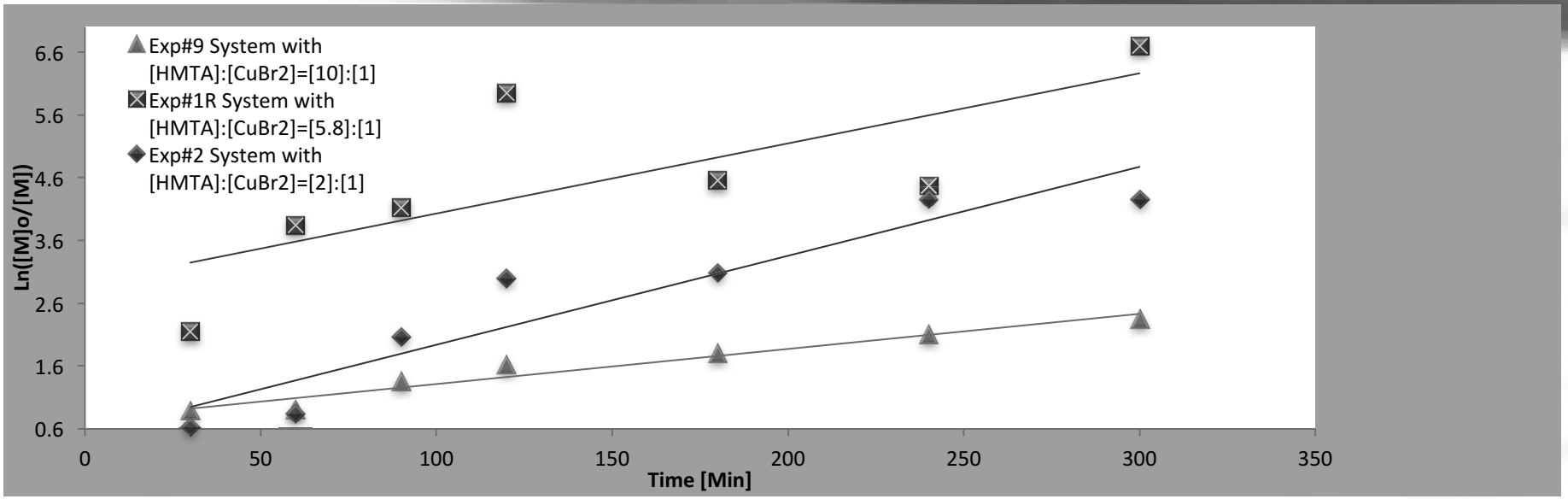
# 4- RESULTS AND DISCUSSION/ Ligand Ratio Effect

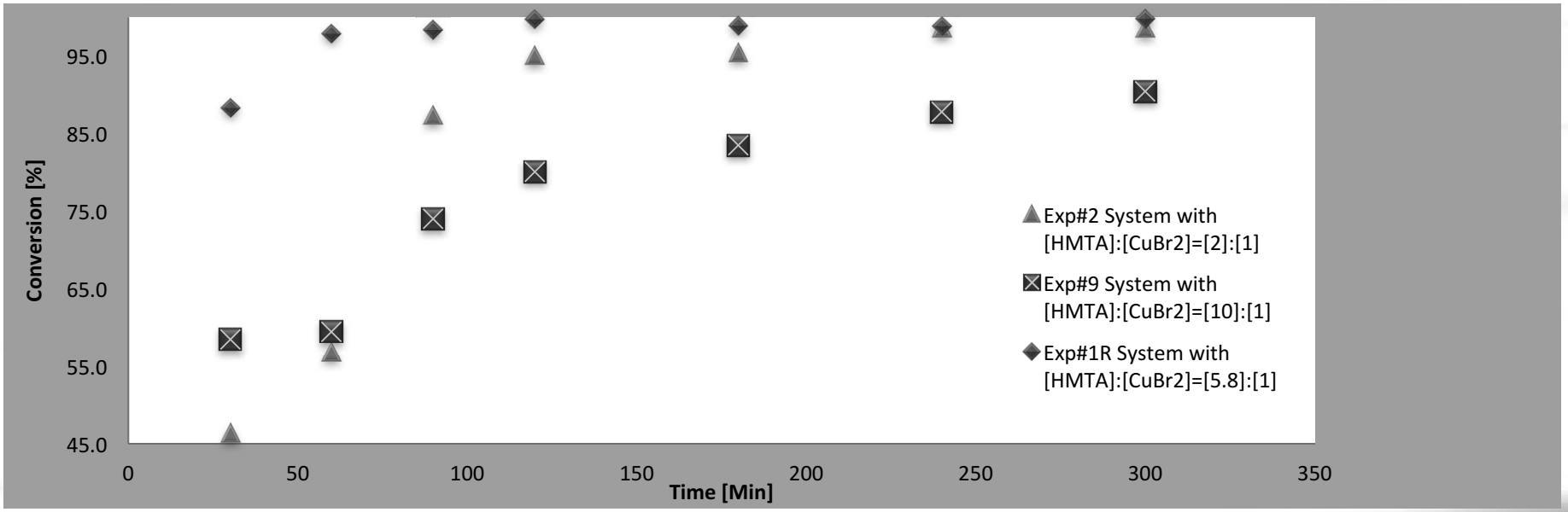


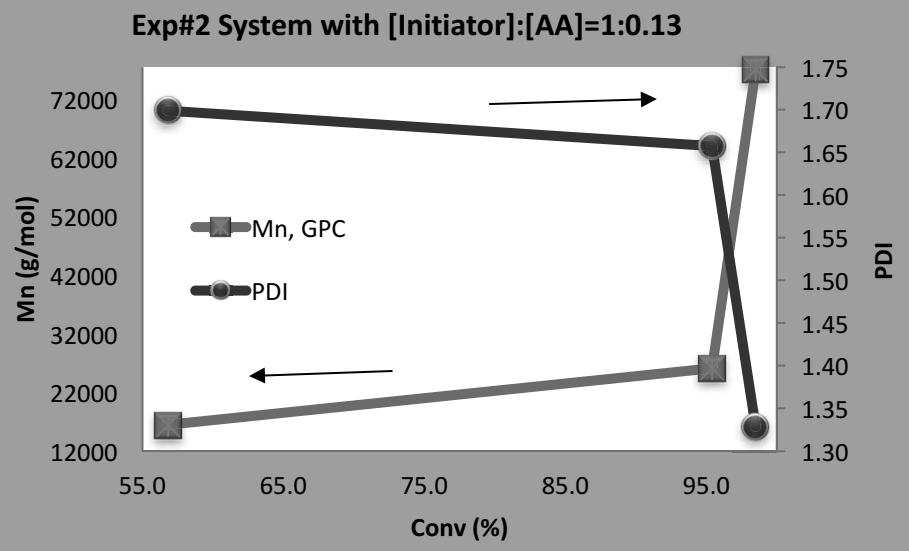



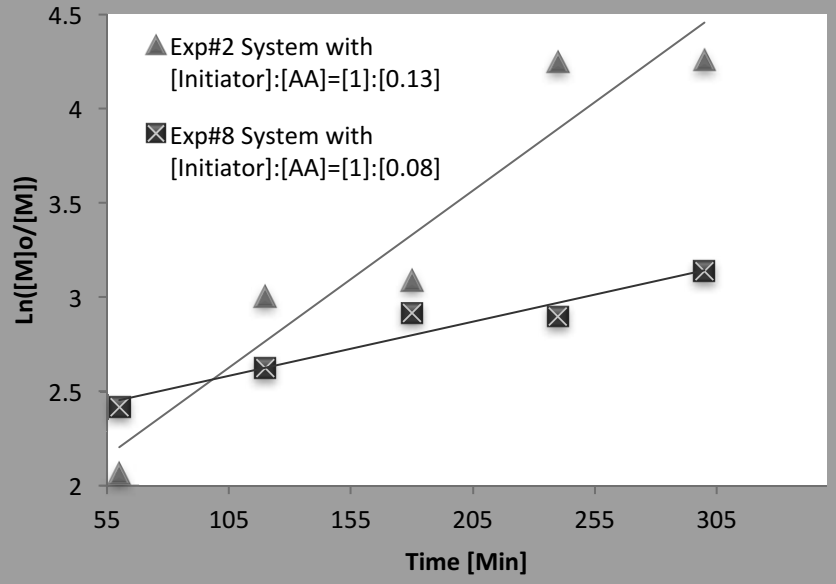
# 4- RESULTS AND DISCUSSION/ Ligand Ratio Effect

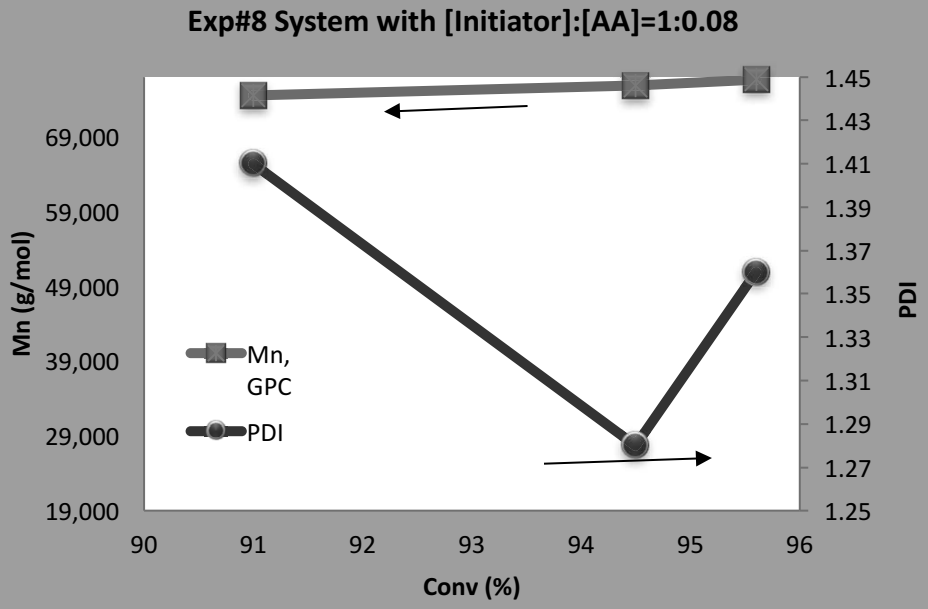


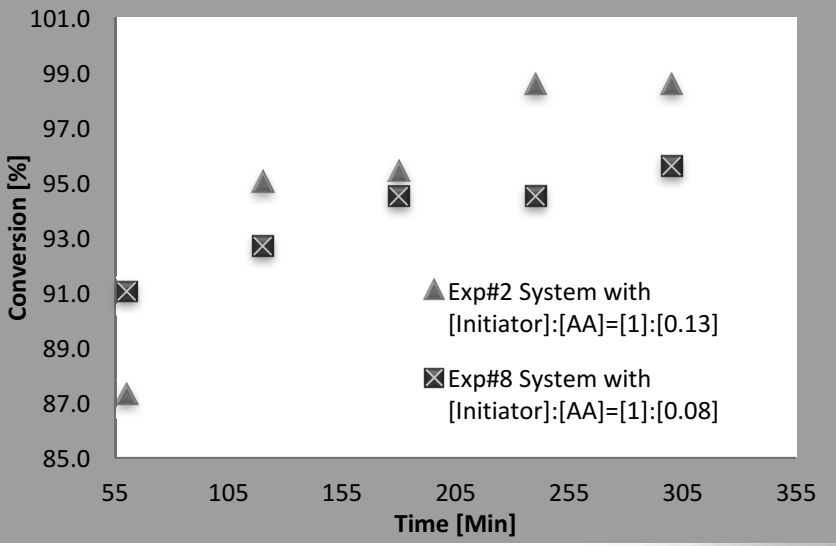



# 4- RESULTS AND DISCUSSION/ Reducing Agent Effect



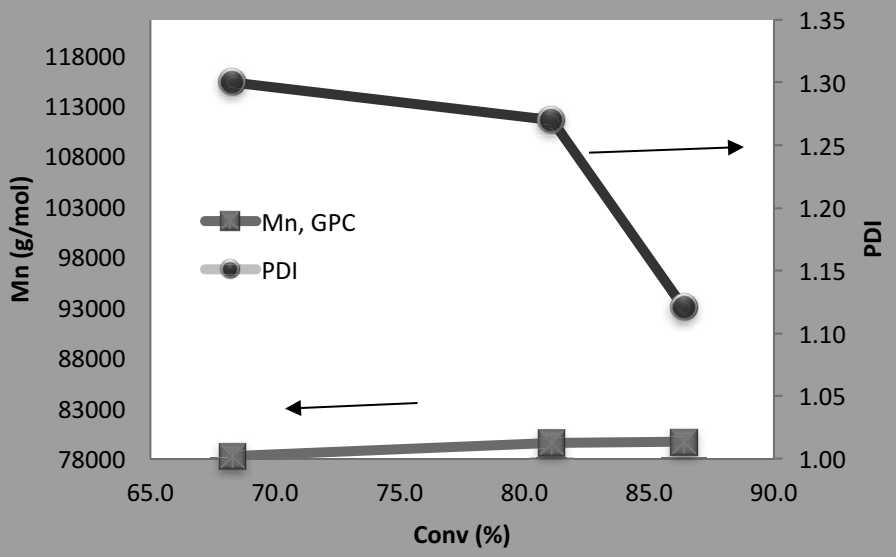



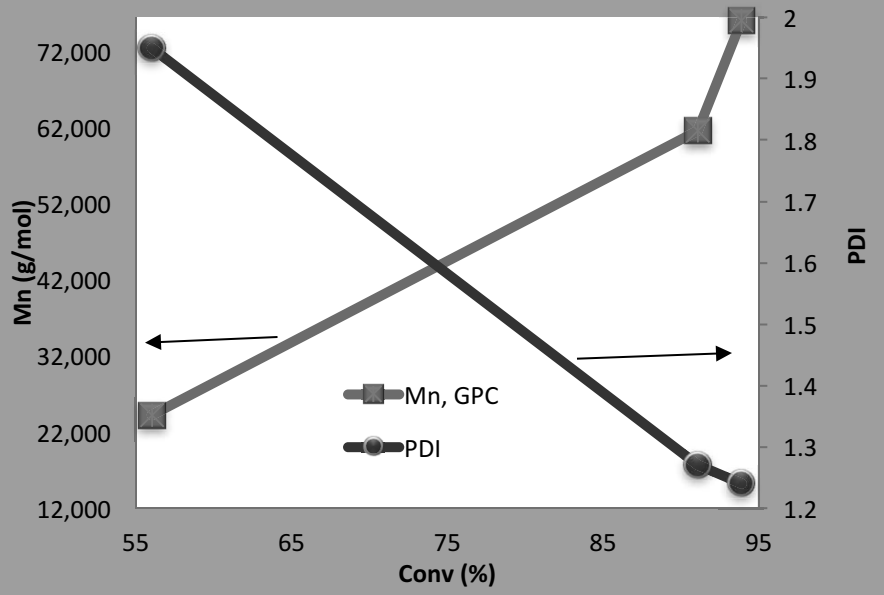



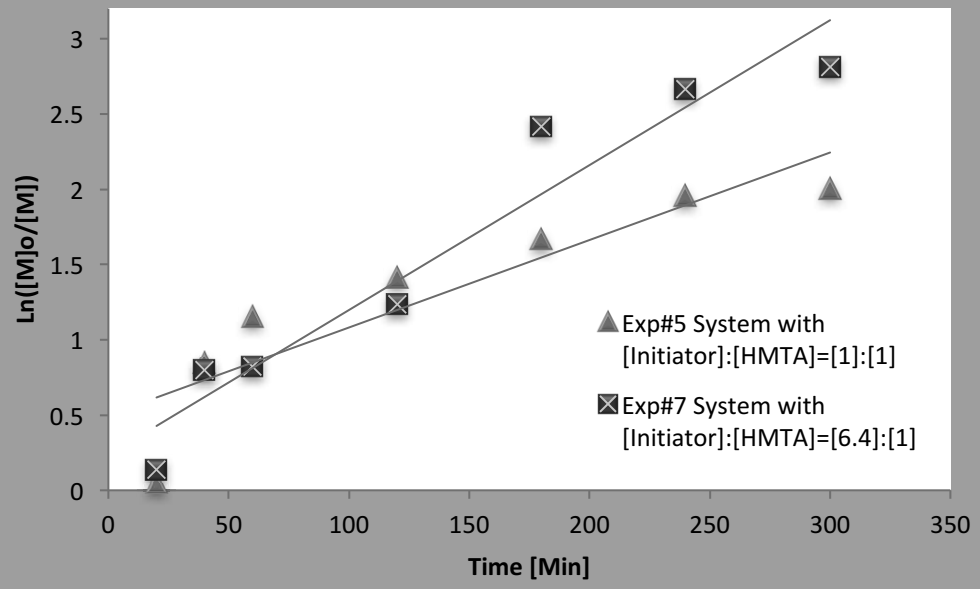
# 4- RESULTS AND DISCUSSION/ Initiator Effect

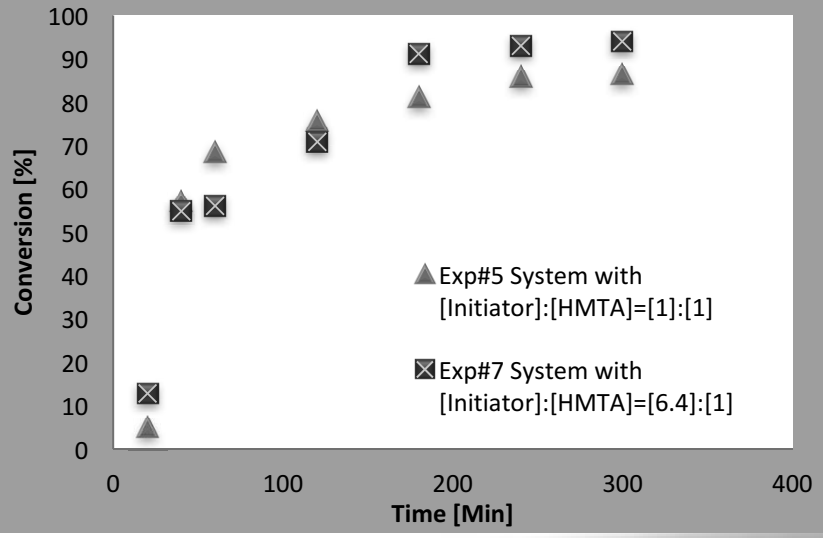
**Exp#5 System with [Initiator]:[HMTA]=1: 1**



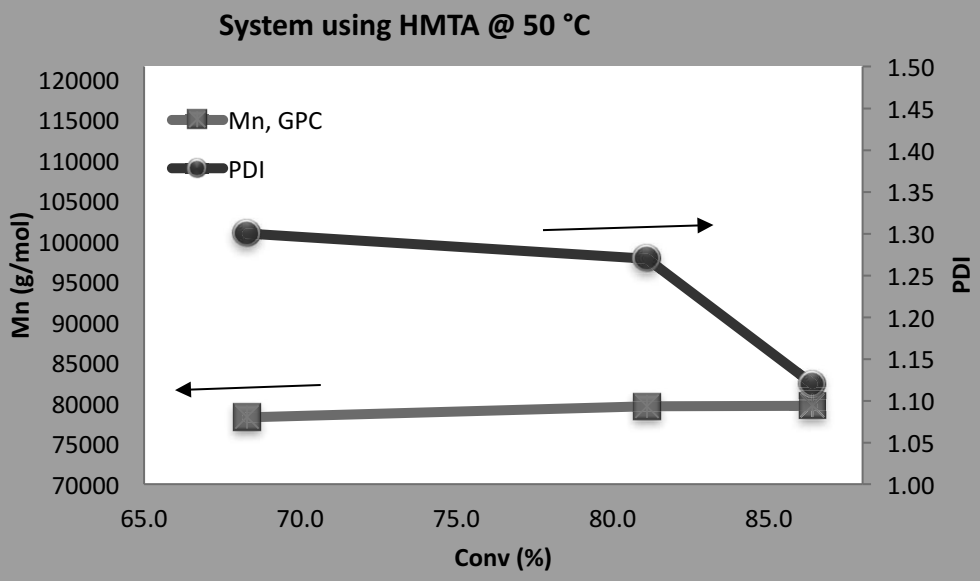

**Exp#7 System with [Initiator]:[HMTA]=6.4:1**

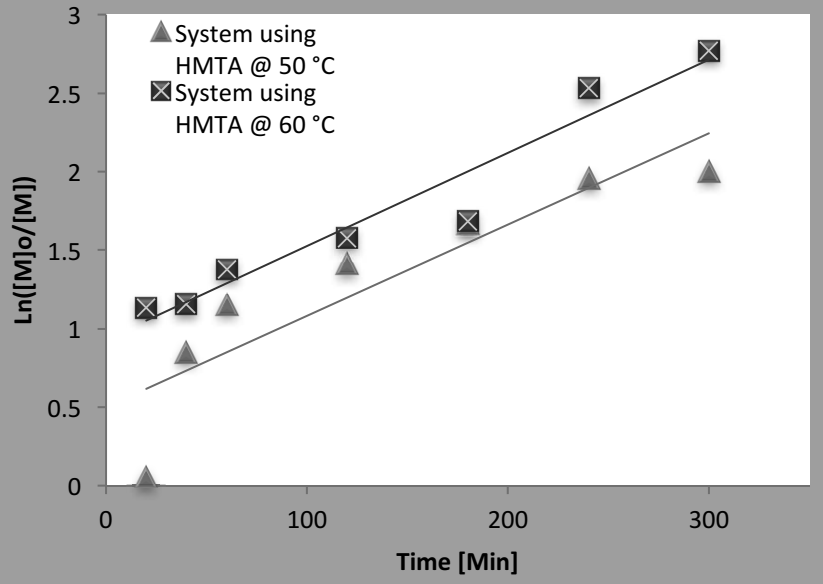


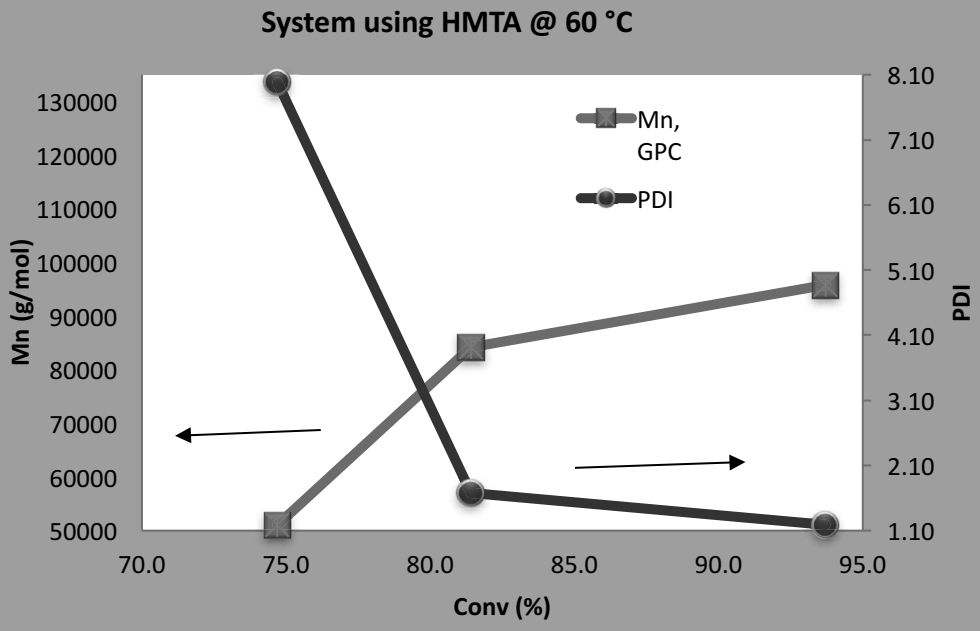



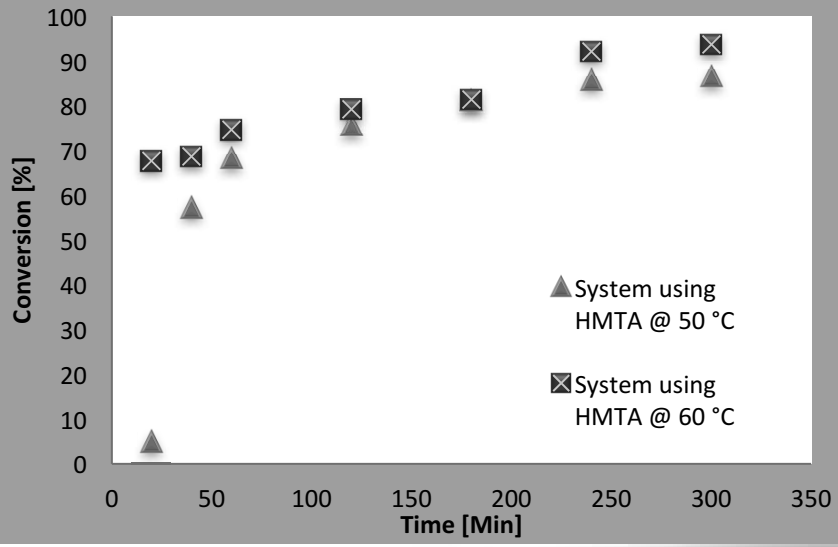



# 4- RESULTS AND DISCUSSION/ Temperature Effect

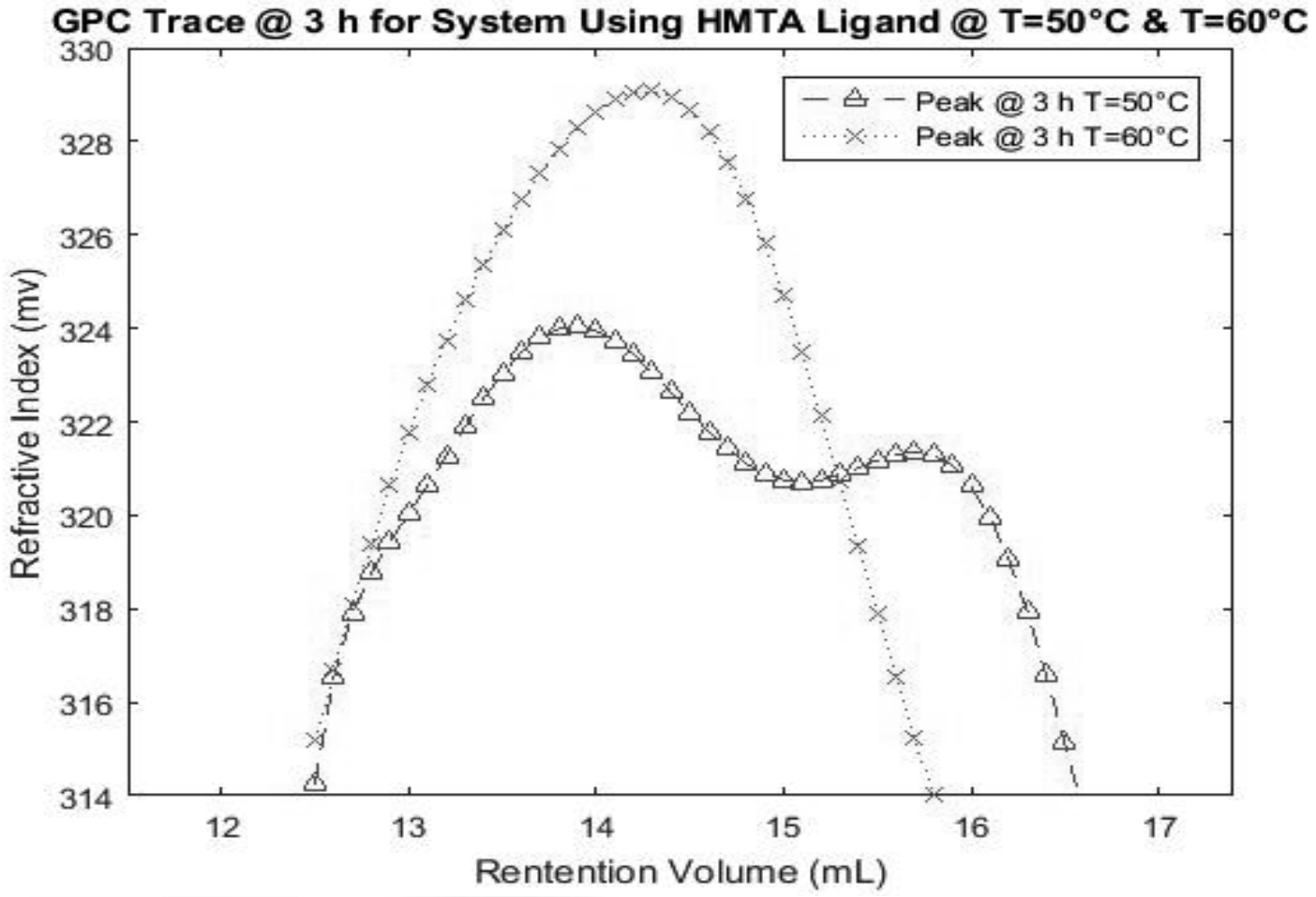


# 5- RESULTS AND DISCUSSION/ Temperature Effect

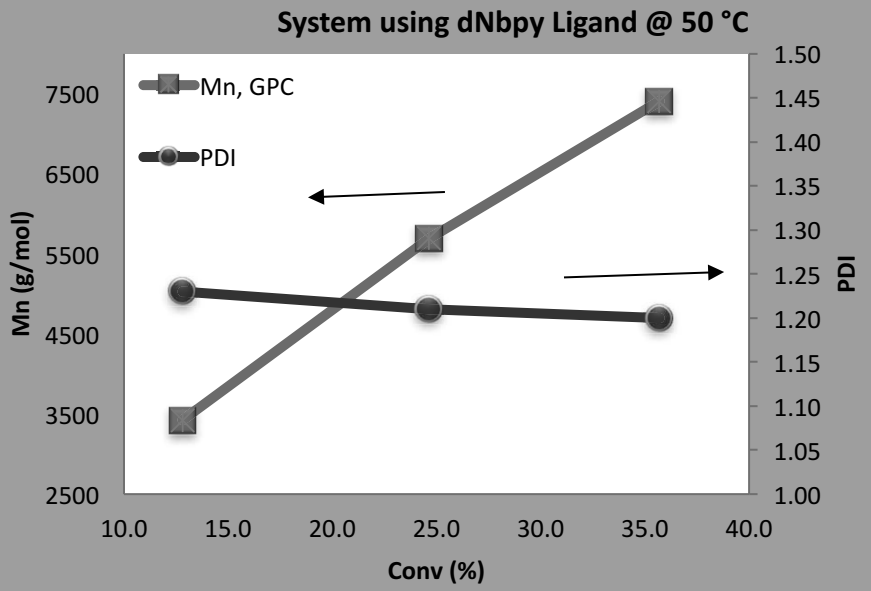


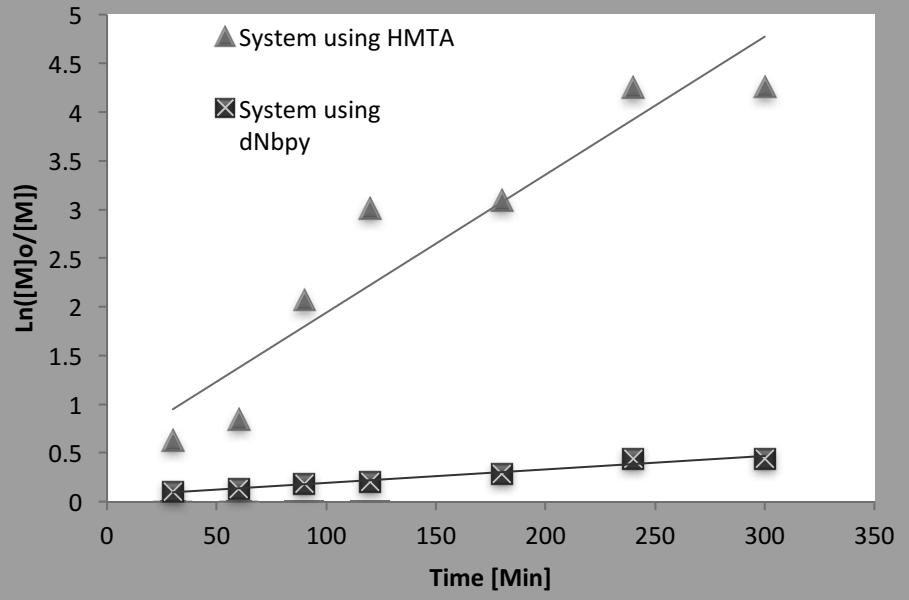
# 5- RESULTS AND DISCUSSION/ Temperature Effect

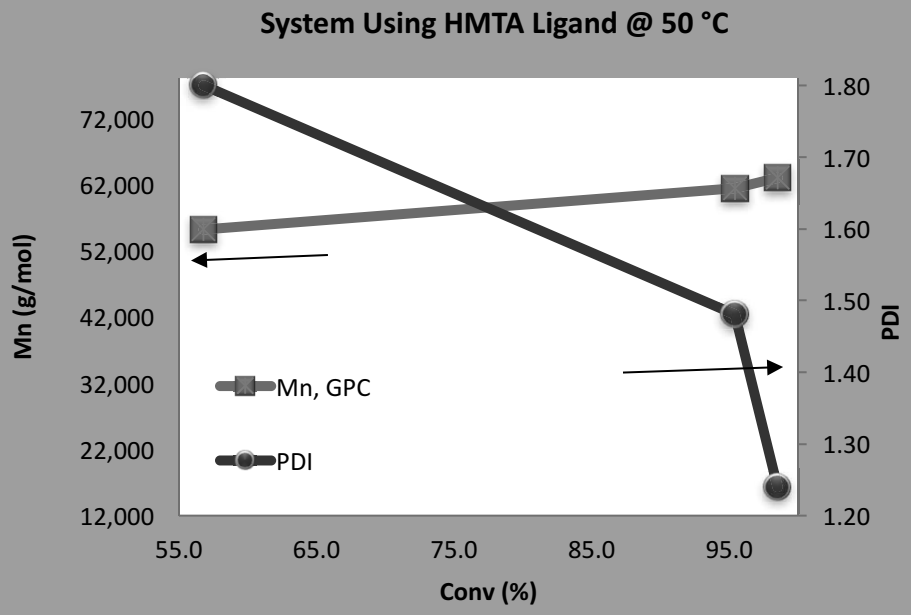
Slight Coagulation occurred @ 50°C

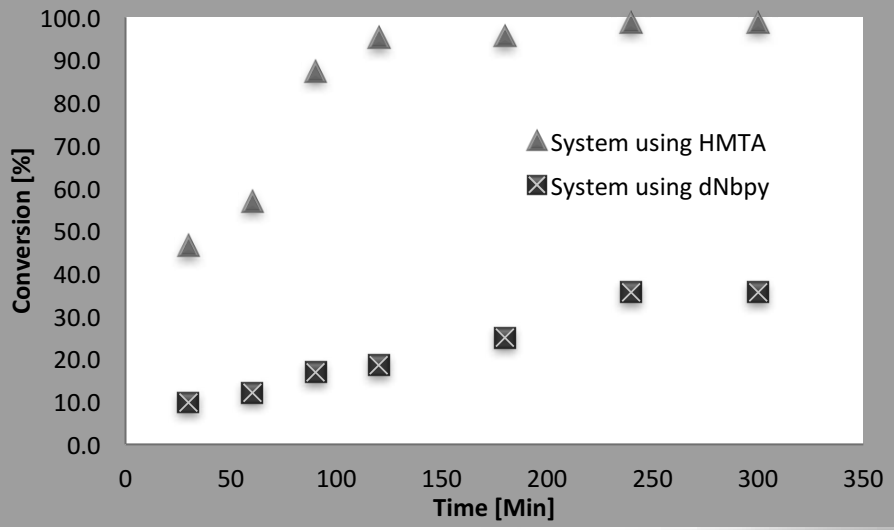
Slight Coagulation occurred @ 60°C

# 4- RESULTS AND DISCUSSION/ Different Ligands Effect

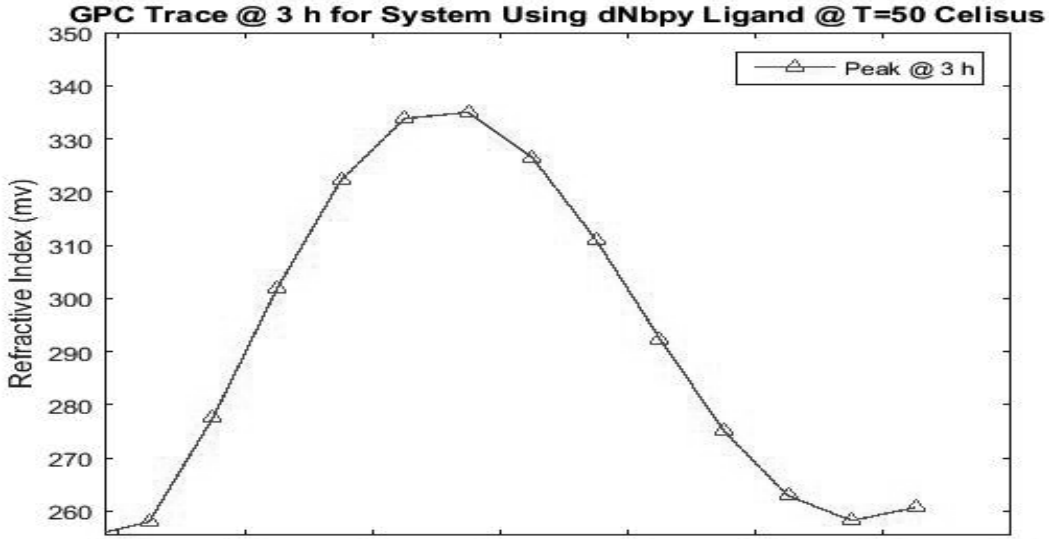


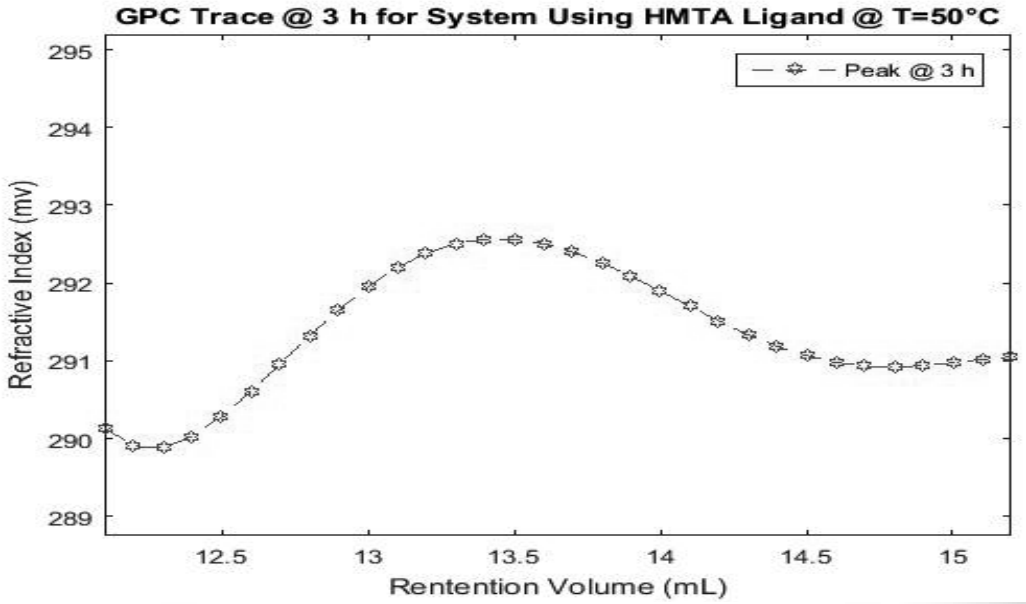



# 4- RESULTS AND DISCUSSION/ Different Ligands Effect



# 4- RESULTS AND DISCUSSION/ Results Summary

| Exp# | t/hr | Conversion | Mn, th(gmol-1) | Mn, GPC (gmol-1) | PDI |
|---|---|---|---|---|---|
| E1 | 1 | 97.8 | 21509.9614 | 16,440 | 1.41 |
| | 3 | 98.9 | 21750.5812 | 19,438 | 1.43 |
| | 5 | 99.8 | 21953.44 | 24,516 | 1.27 |
| E2 HMA Used | 1 | 56.8 | 12489 | 55,180 | 1.80 |
| | 3 | 95.4 | 20982 | 61,418 | 1.48 |
| | 5 | 98.5 | 21676 | 62,985 | 1.24 |
| E2 dNbpy Used | 1 | 12.8 | 2672 | 3426 | 1.23 |
| | 3 | 24.7 | 5515 | 5699 | 1.21 |
| | 5 | 35.7 | 7836 | 7410 | 1.20 |
| E5 | 1 | 68.3 | 95989.7952 | 78249 | 1.30 |
| | 3 | 81.1 | 113897.815 | 79584 | 1.27 |
| | 5 | 86.4 | 121440.103 | 79677 | 1.12 |
| E6 | 1 | 74.7 | 104902.668 | 51065 | 7.98 |
| | 3 | 81.4 | 114309.608 | 84245 | 1.68 |
| | 5 | 93.7 | 131612.224 | 95794 | 1.19 |
| E7 | 1 | 56.03 | 12315 | 24,238 | 1.95 |
| | 3 | 91.1 | 20024 | 61,637 | 1.27 |
| | 5 | 93.9 | 20660 | 76,106 | 1.24 |
| E8 | 1 | 91 | 20015 | 74,461 | 1.41 |
| | 3 | 94.5 | 20792 | 75,746 | 1.28 |
| | 5 | 95.6 | 21027 | 76,569 | 1.36 |
| E9 | 1 | 59.4 | 29579.9171 | 19,229 | 4.38 |
| | 3 | 83.5 | 41544.1527 | 25,283 | 1.29 |
| | 5 | 90.4 | 44983.9556 | 24,820 | 1.31 |

# 5- CONCLUSION

- **Experimental investigations were carried out on HMTA system by observing the effects of reducing agent, initiator, ligand and temperature. In addition to that comparison between two different ligands HMTA and dNbpy has been studied.**

- **HMTA Ligand was chosen because of its environmental friendly characteristics which is the most important and can be noticed by treating the catalyst complex which contains HMTA as a ligand with acids to purify it from the residual catalyst, also it's commercially available with cheap prices.**

- **Good enhancement with systems using HMTA ligand especially the conversion rate while GPC results showed a controlled radical behavior. Increasing the temperature was the main reason of creating coagulation.**

- **Development of AGET Mechanism still under process and interpretation.**

# 6- FUTURE WORKS

- **Ligand solubility should be carefully investigated to avoid the formation of dust that occurred in organic phase during heating before poured to aqueous phase, where that dust cause radicals to be poorly controlled**

- **Particle size of both systems will be determined using SEM technique to obtain an empirical model to the system which obviously has lack of data.**

# 7- Acknowledgment.


- My Supervisors: Dr. T. Duever and Dr. R. Dhib
- NSERC
- Department of Chemical Engineering, Ryerson University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NSERC CRSNG

# THANK YOU