Kinetic Study of Nitroxide-Mediated Radical Polymerization of Styrene with a Unimolecular Initiator

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Outline

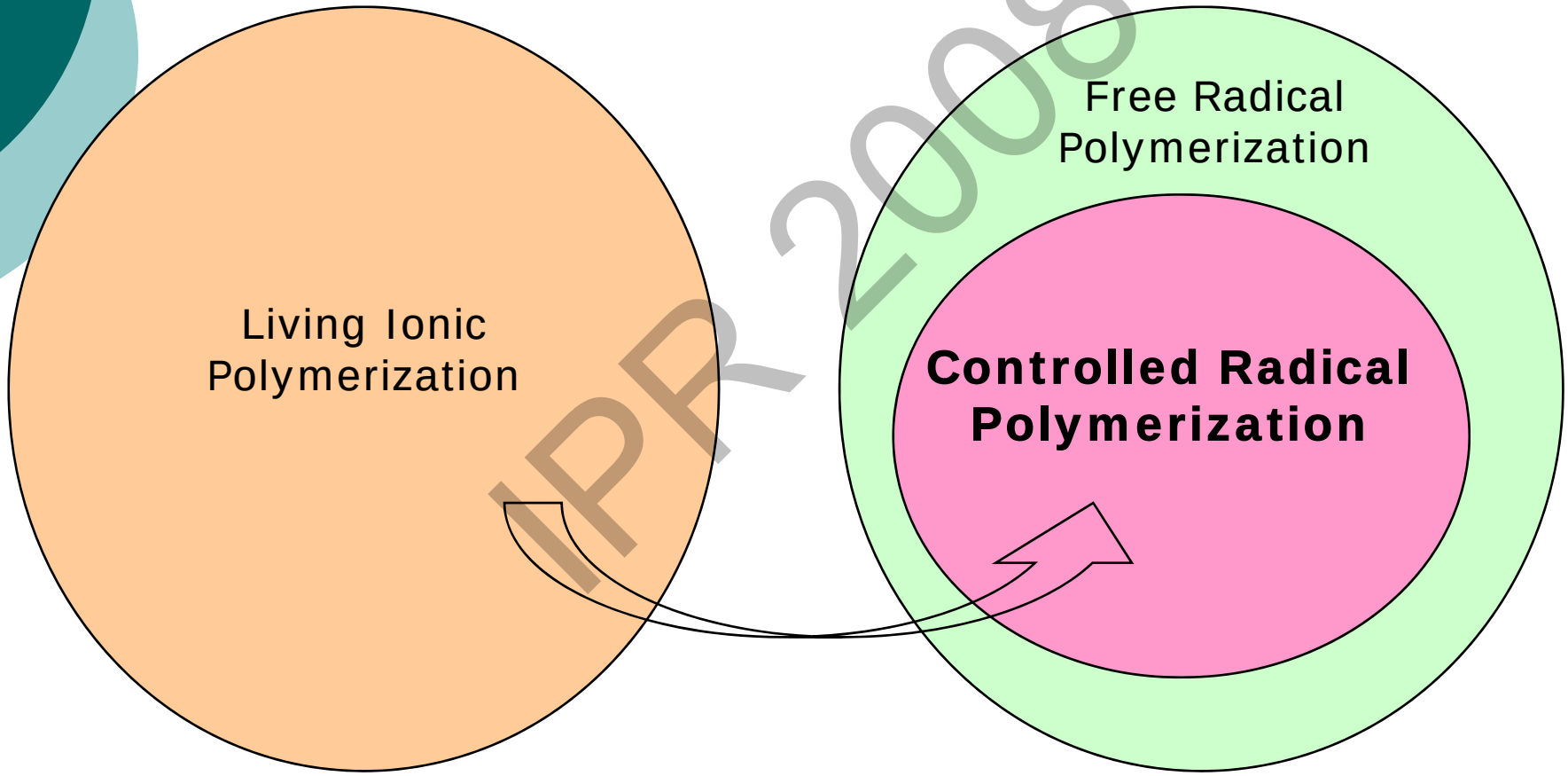
- Background
- Research Objectives
- Experimental
- Discussion
- Future Work

Radical Polymerization (RP)

- Advantages:
  - Versatility
  - Synthetic ease
  - Compatibility with many monomer families and functional groups
  - Wide range of operating conditions

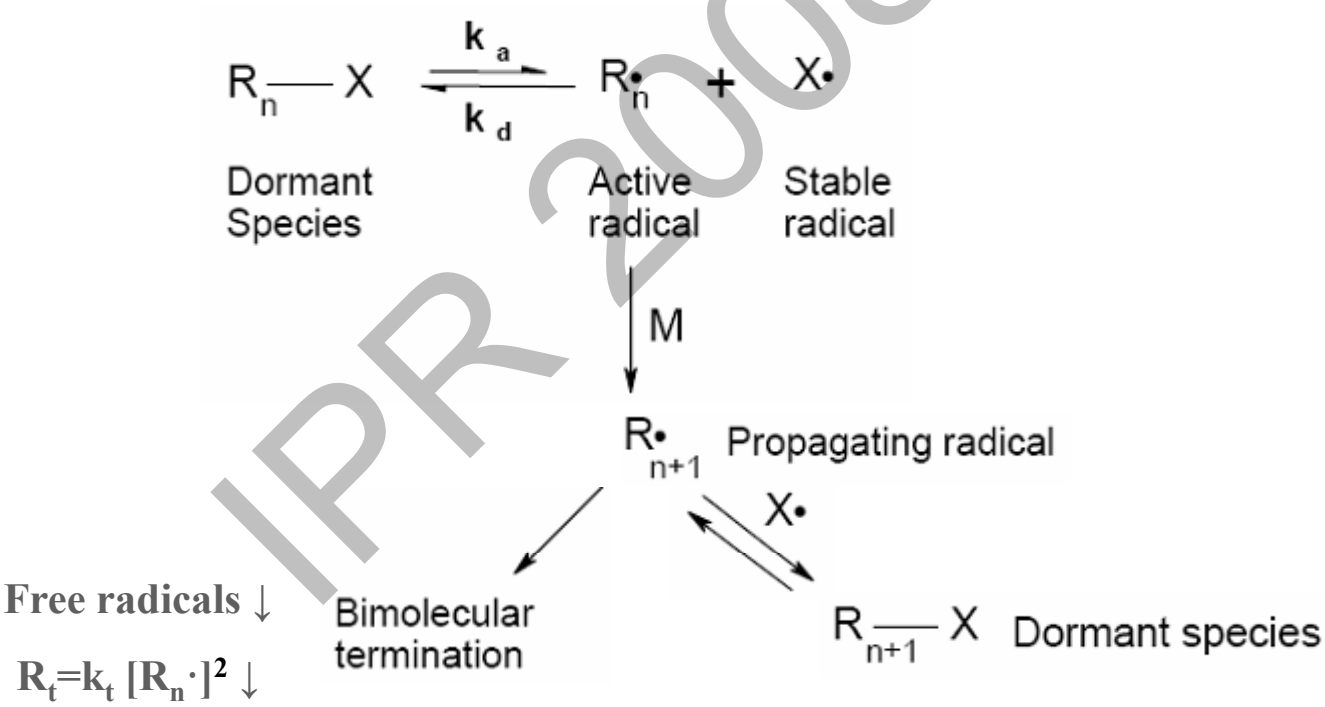
- Disadvantages:
  - Limited control of microstructure

Controlled Radical Polymerization (CRP)



Mechanism Differences in CRP

Reversible Activation Process

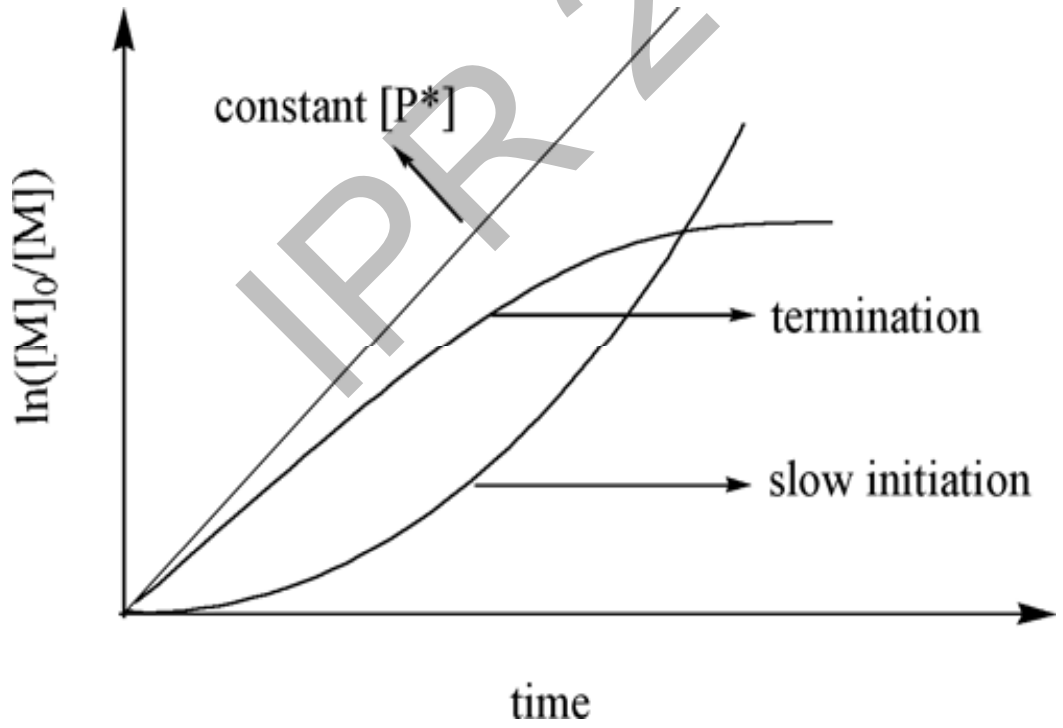


Features of CRP

- ***First-order Kinetics Behavior***

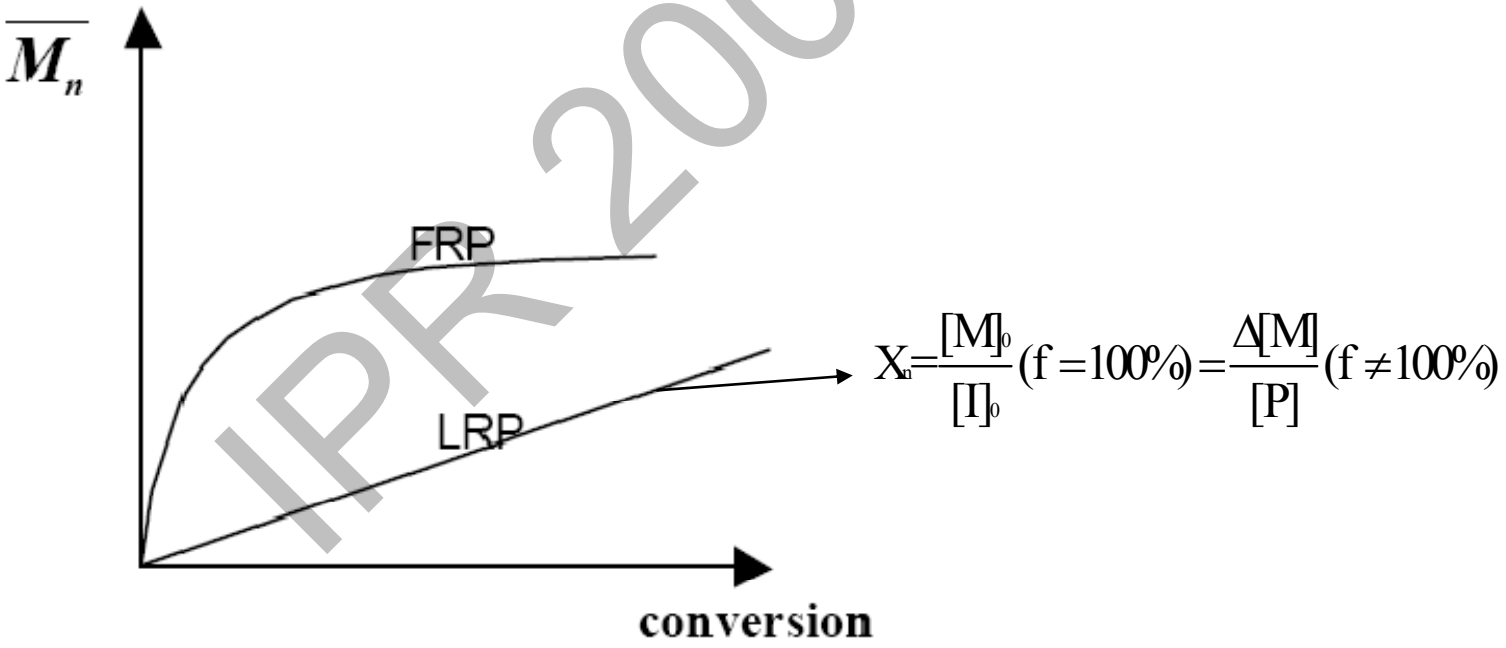
$$R_p = -d[M]/dt = k_p [R_{n+1}\cdot][M]$$

$$Ln([M]_0/[M]) = k_p [R_{n+1}\cdot]t$$



Features of CRP

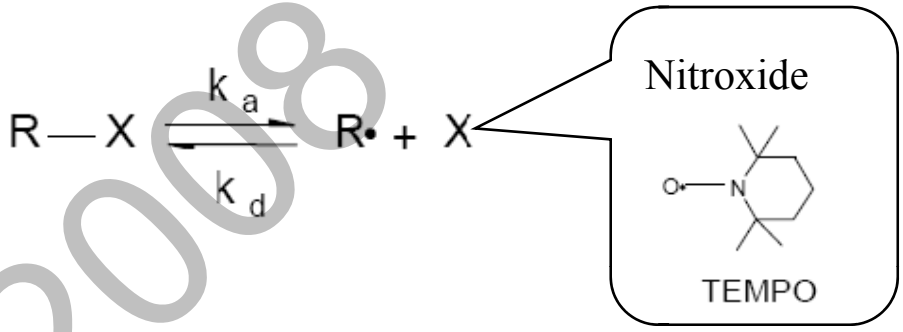
- ***MW increases linearly with conversion***



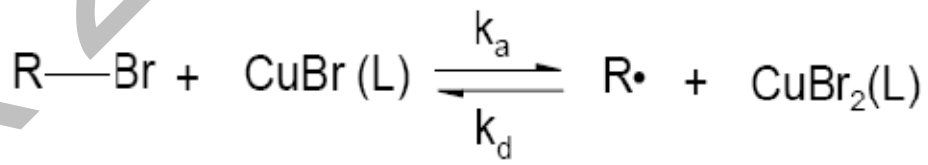
- ***Narrow molecular weight distribution***

Main Types of CRP: NMRP, ATRP, RAFT

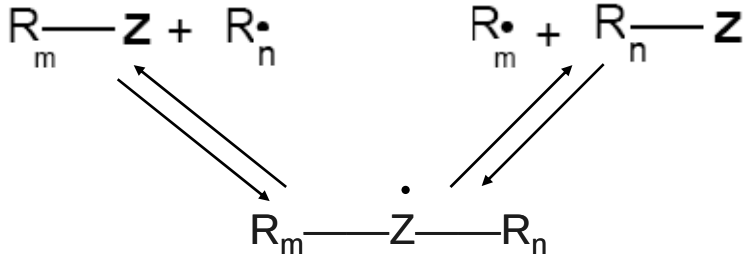
- Nitroxide Mediated Radical Polymerization (NMRP)



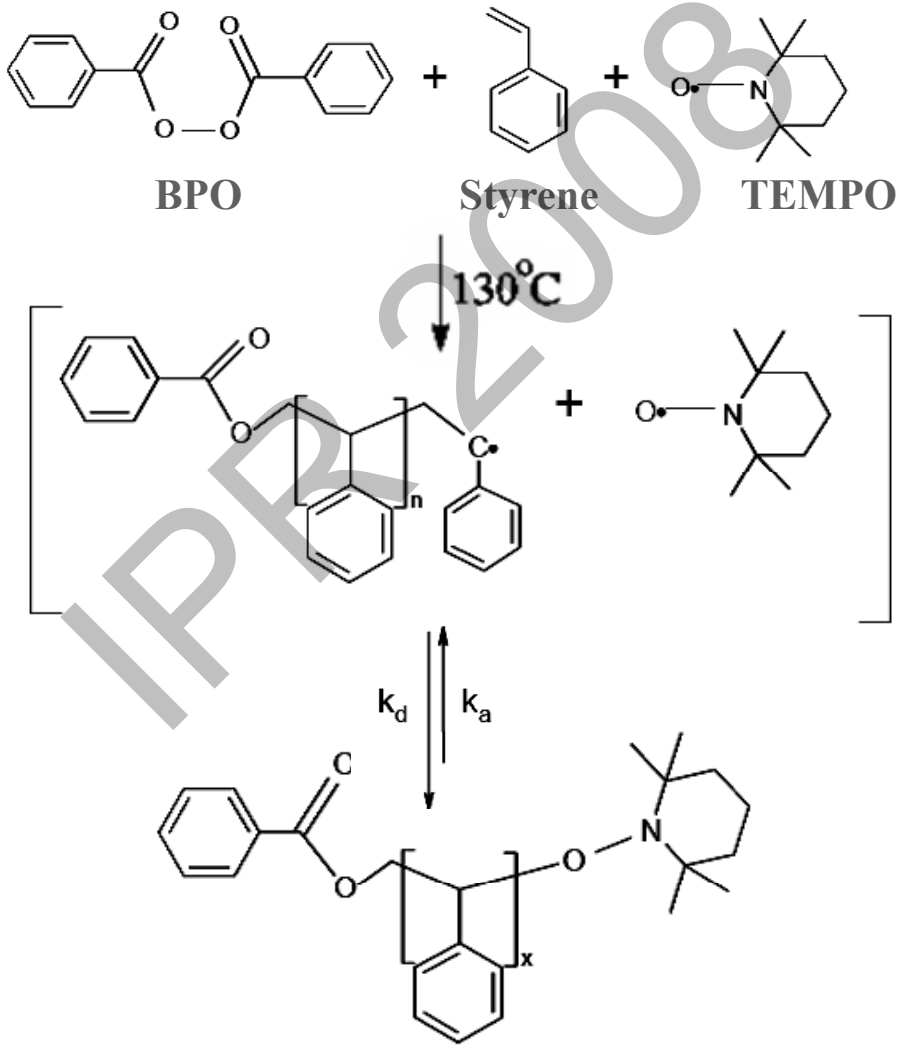
- Atom Transfer Radical Polymerization (ATRP)



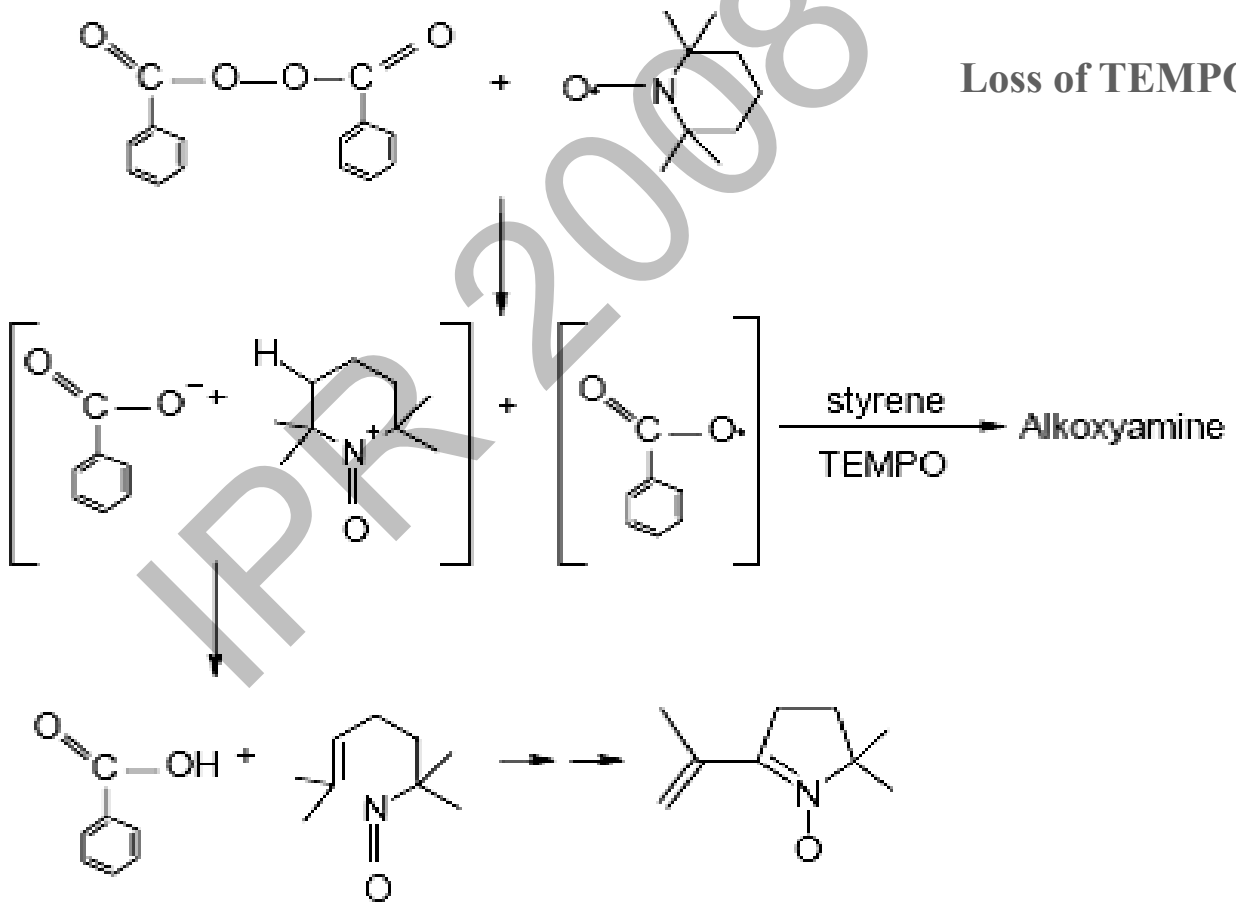
- Reversible Addition-Fragmentation Transfer Polymerization (RAFT)



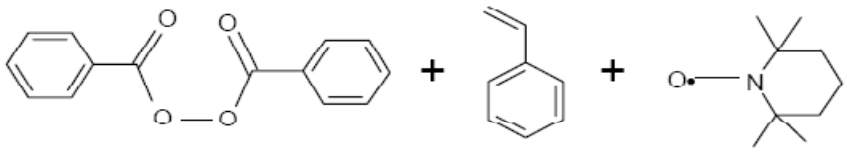
Bimolecular NMRP



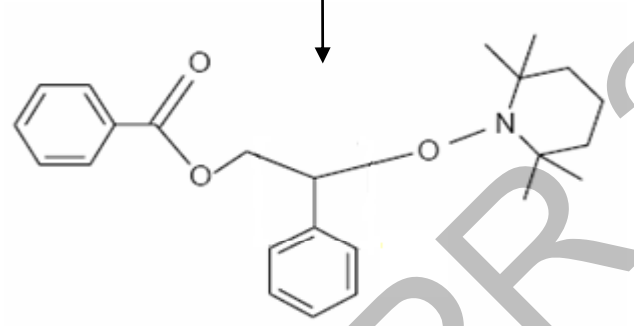
“Promoted Dissociation” of BPO



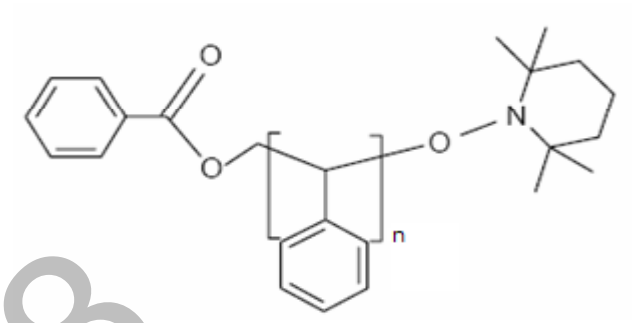
Unimolecular NMRP



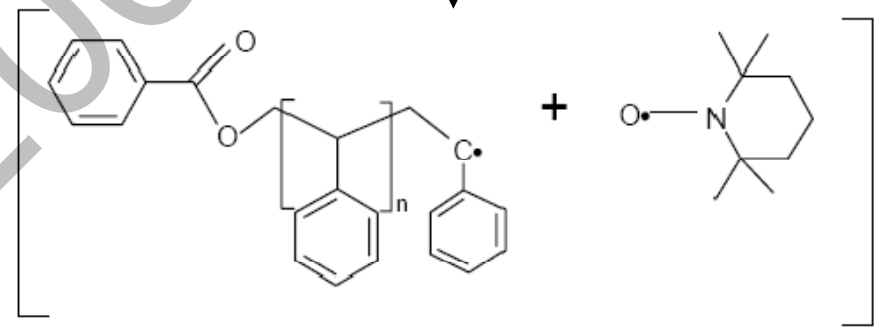
80ºC



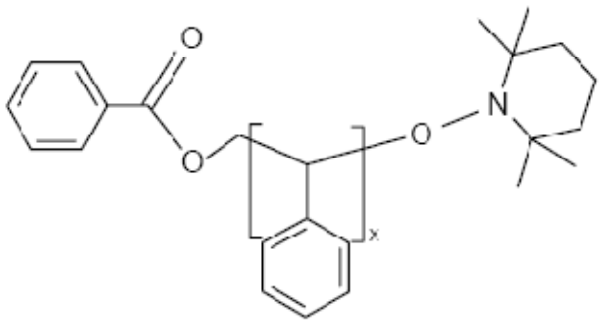
BS-TEMPO
(Alkoxyamine)



130ºC



k_d k_a



Advantages of Unimolecular System

- Avoidance of side reactions of bimolecular system
- Molecular weight is more predictable

Research Objectives

- Study the differences between unimolecular system and bimolecular system
- Investigate the experimental factors affecting the unimolecular system
- Use data to refine the kinetic model for unimolecular system

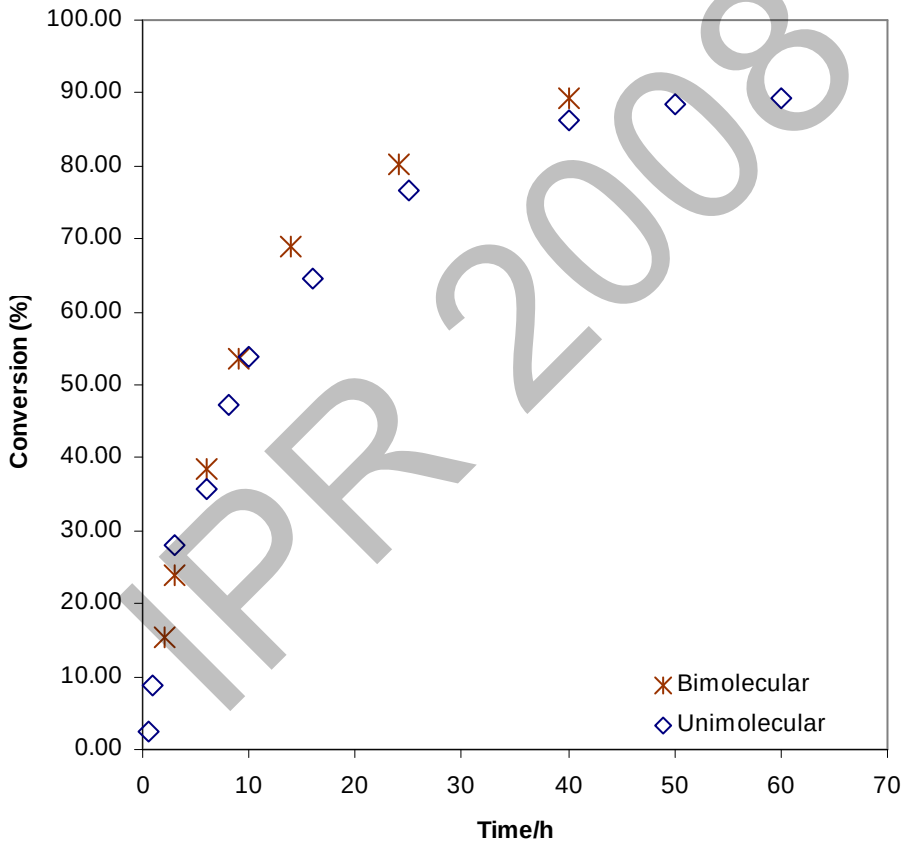
Experimental

- Bimolecular vs. Unimolecular
- Unimolecular System:
  - Effect of Initiator Concentration
  - Effect of Temperature
  - Effect of Initiator Molecular Weight
  - Molecular Weight Prediction

Data Collection

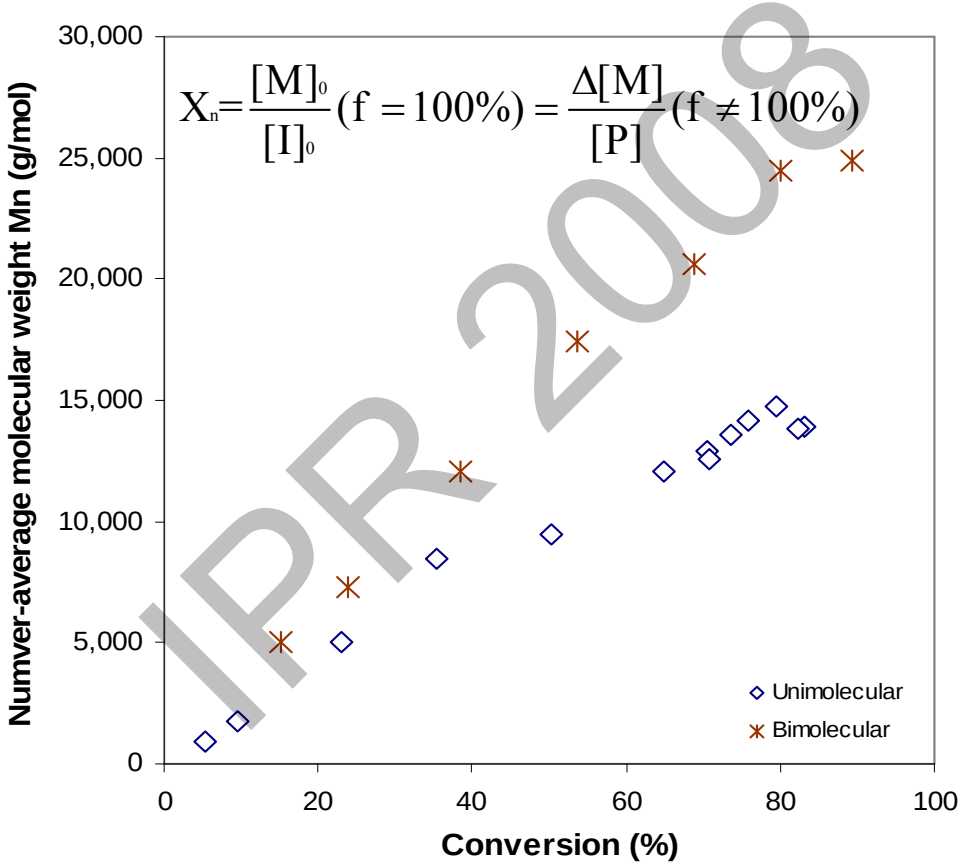
- Monomer Conversion - Gravimetry
- Molecular Weight (M_n, M_w) — ***GPC***
- Polydispersity Index (PDI= M_w/ M_n) — ***GPC***

Bimolecular vs. Unimolecular



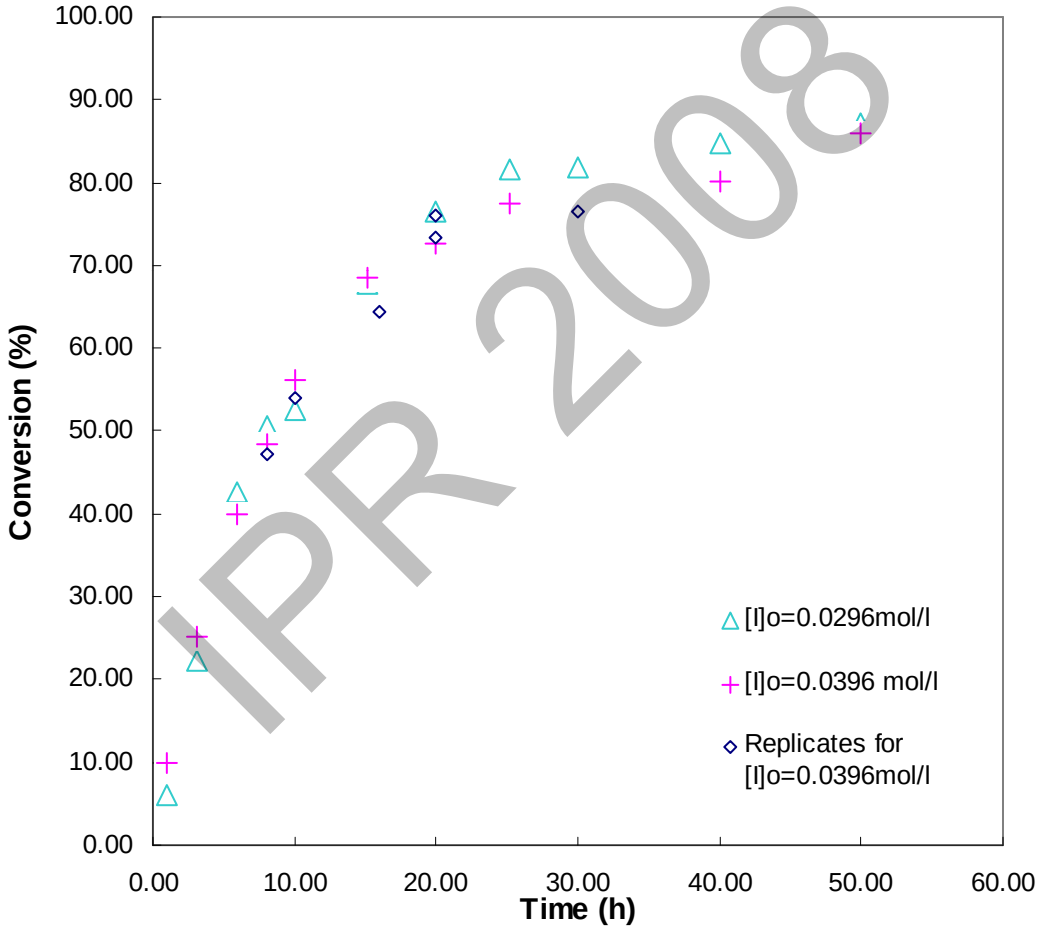
Conversion vs. time for NMRP of styrene at 120ºC, $[I]_0$=0.0396M

Bimolecular vs. Unimolecular



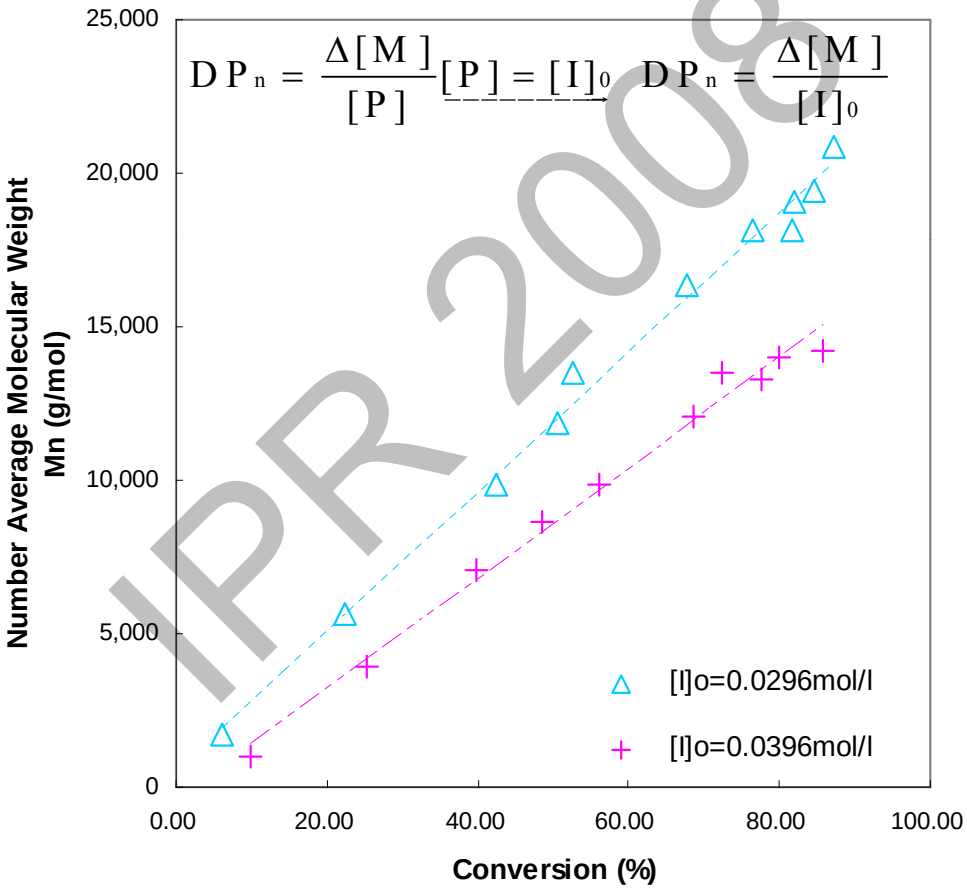
Molecular weight vs. conversion for NMRP of styrene at 120ºC, [M]=0.0396M

Unimolecular
Effect of Initiator Concentration



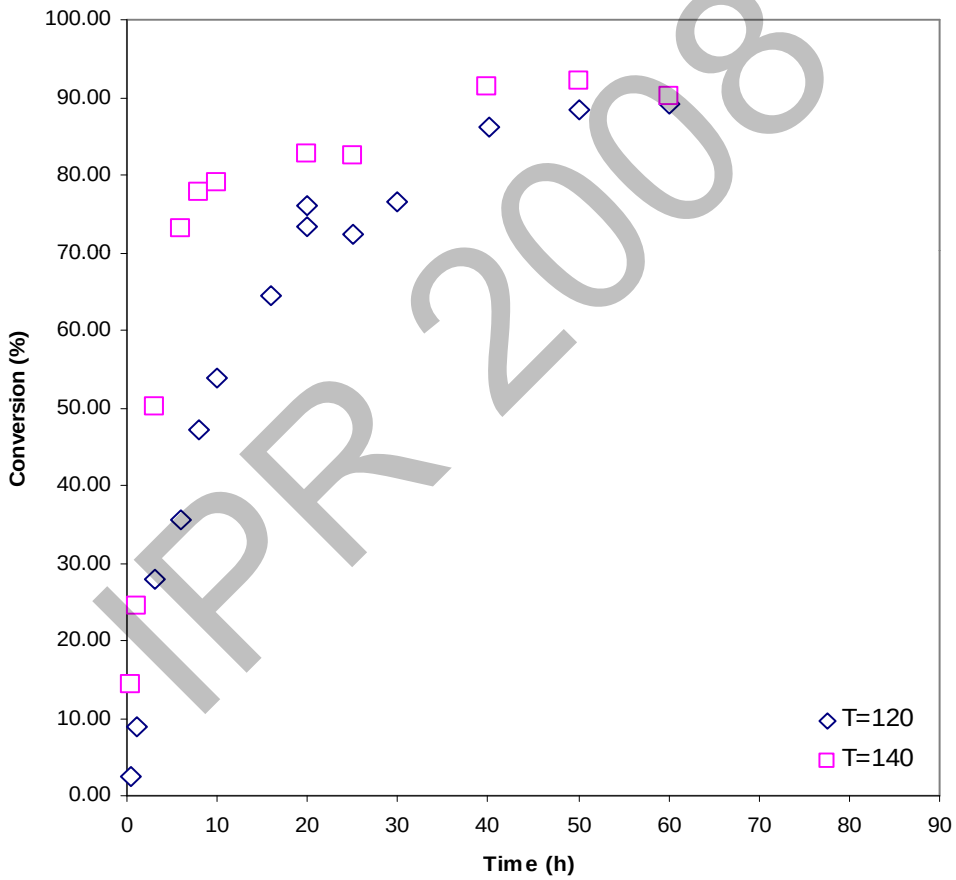
Effect of initiator concentration on polymerization rate at 120ºC

Effect of Initiator Concentration



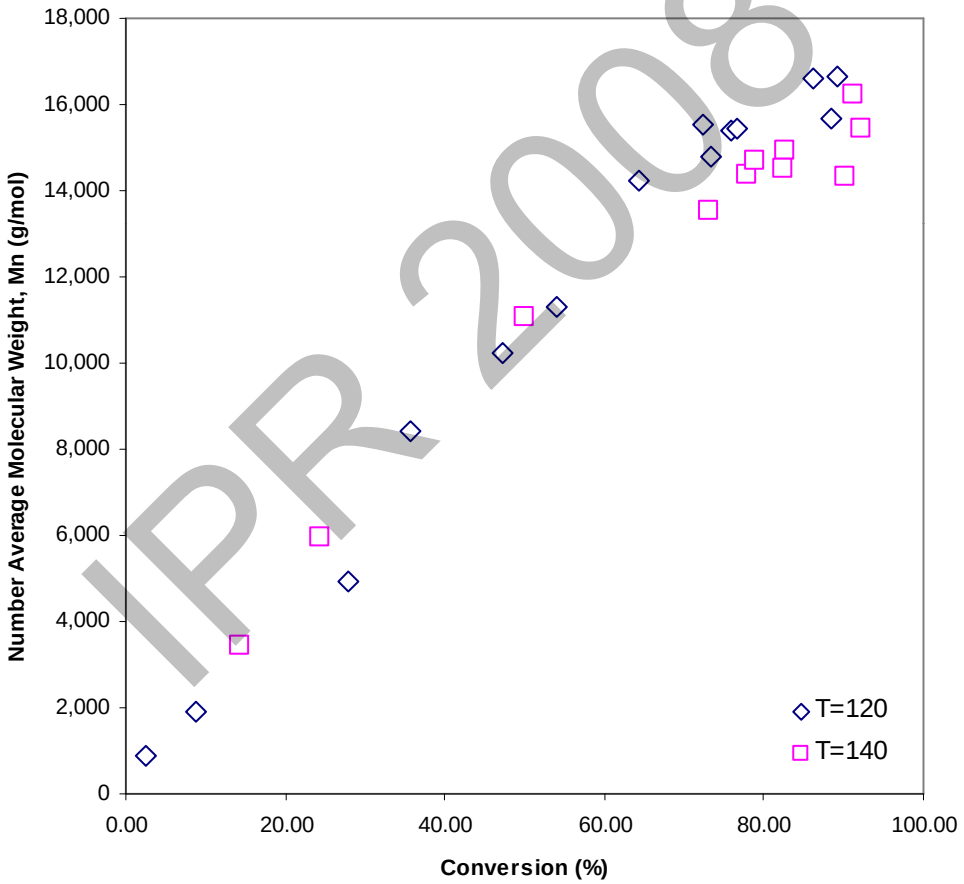
Effect of initiator concentration on molecular weight at 120ºC

Effect of Temperature



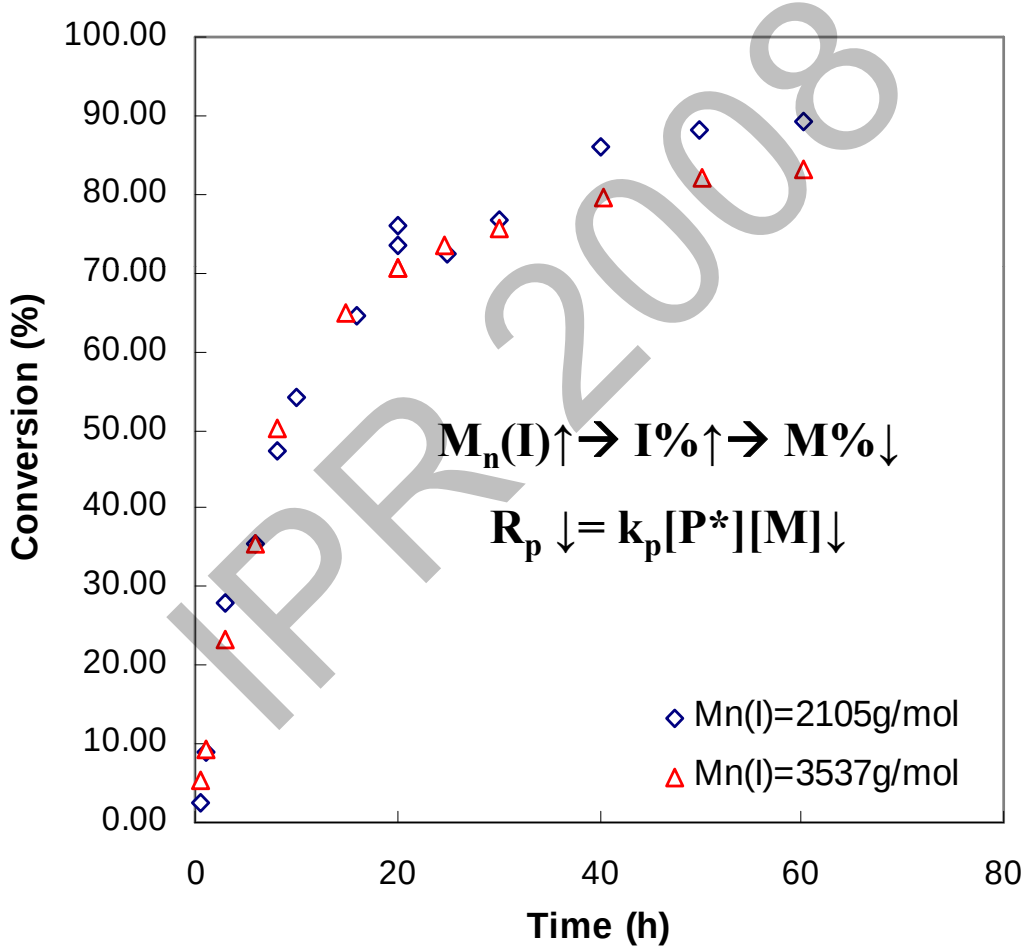
Effect of temperature (ºC) on polymerization rate, $[I]_0$=0.0396M

Effect of Temperature



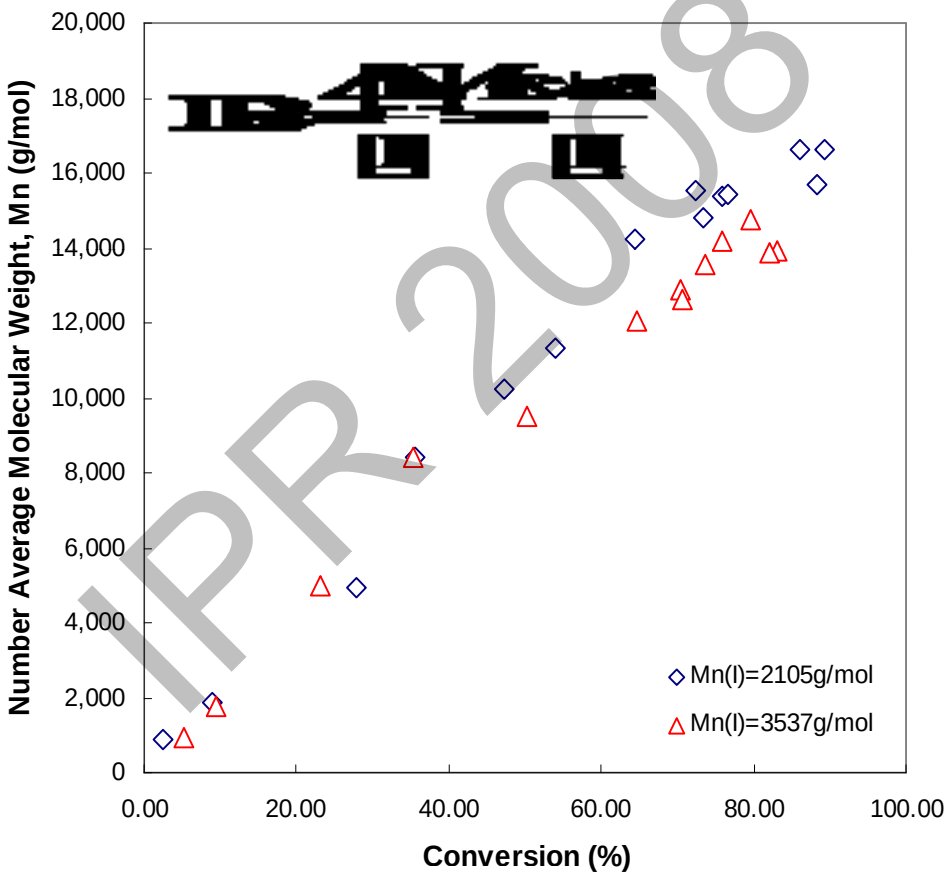
Effect of temperature (ºC) on molecular weight, $[I]_0$=0.0396M

Effect of Initiator Molecular Weight



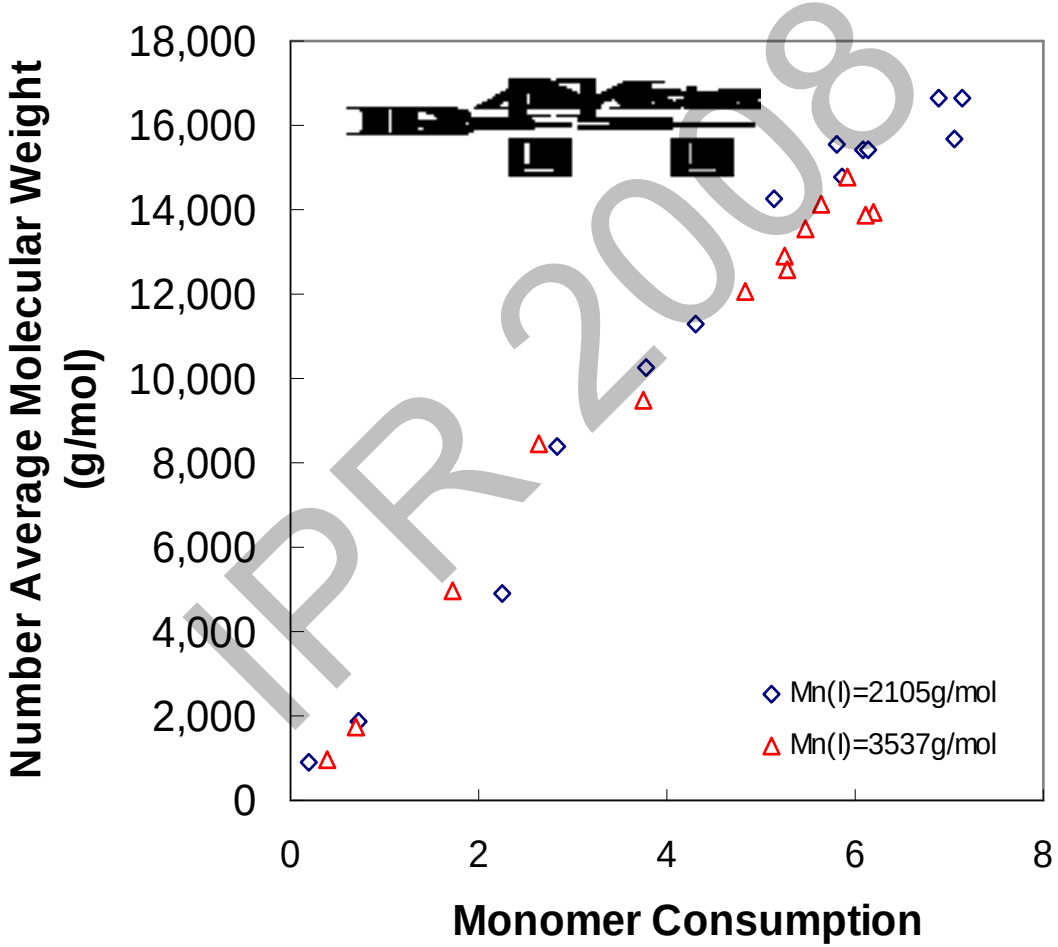
Effect of initiator molecular weight on polymerization rate at 120ºC

Effect of Initiator Molecular Weight



Effect of initiator molecular weight on molecular weight at 120ºC

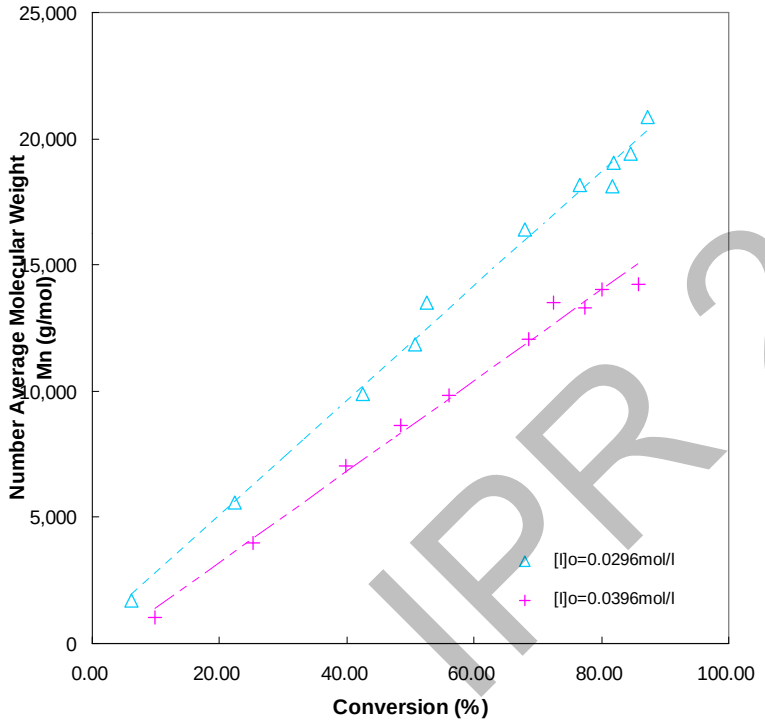
Effect of Initiator Molecular Weight



Summary of experimental factors

	Polymerization Rate	Molecular Weight
Initiator Concentration	0	—
Temperature	+	0/—
Initiator Molecular Weight	0/—	0/—

Prediction of Molecular Weight



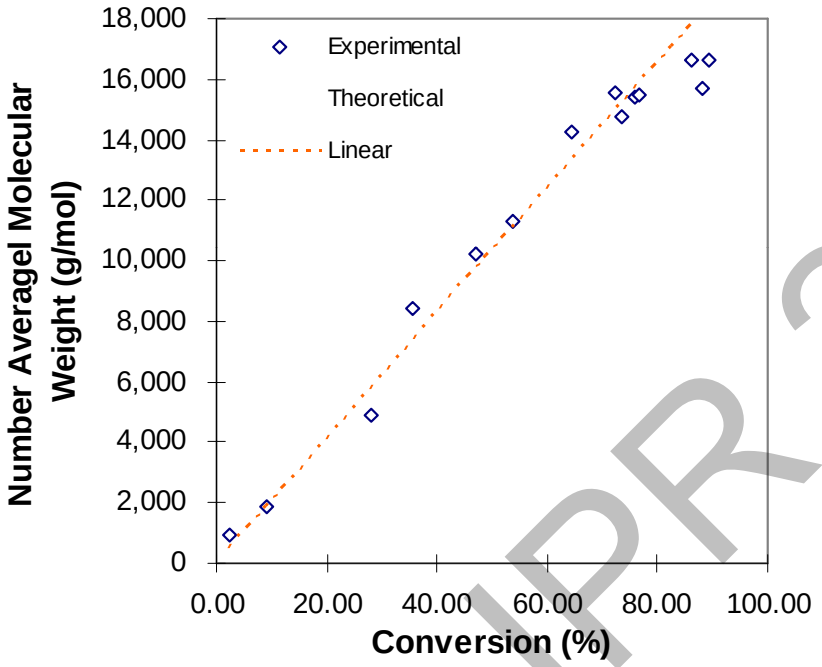
Same $[I]_0$, Conversion↑→ M_n↑

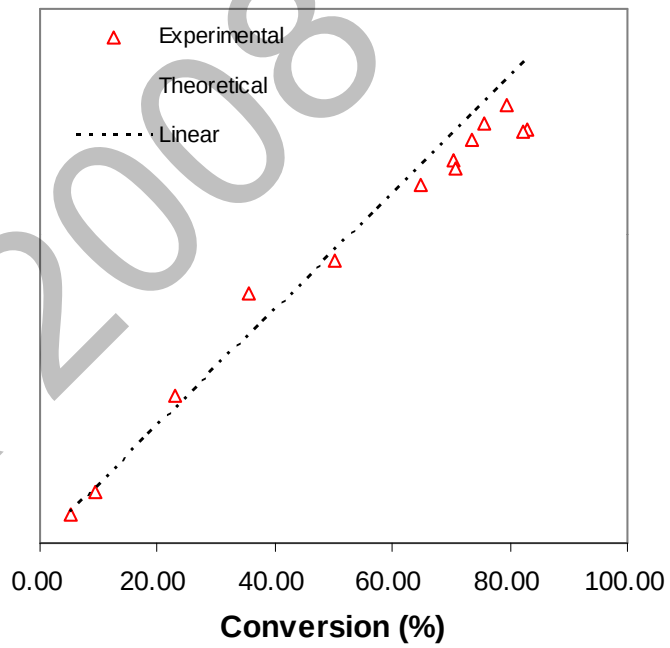
Same Conversion, $[I]_0$↑→ Mn↓

$$Mn(Theoretical)=M_0\frac{\Delta[M]}{[I]_0}$$

$$\mathbf{[P]=[I]_0}$$

Prediction of Molecular Weight





Mn(I)=2193g/mol, T=120ºC, [I]=0.0396M

Mn(I)=3537g/mol, T=120ºC, [I]=0.0396M

Future Work

- *Effect of ratio of* $\Delta[M]/[I]_0$
- *Effect of Temperature*
- *Refine the kinetic model for unimolecular system*

Acknowledgements

Many thanks to

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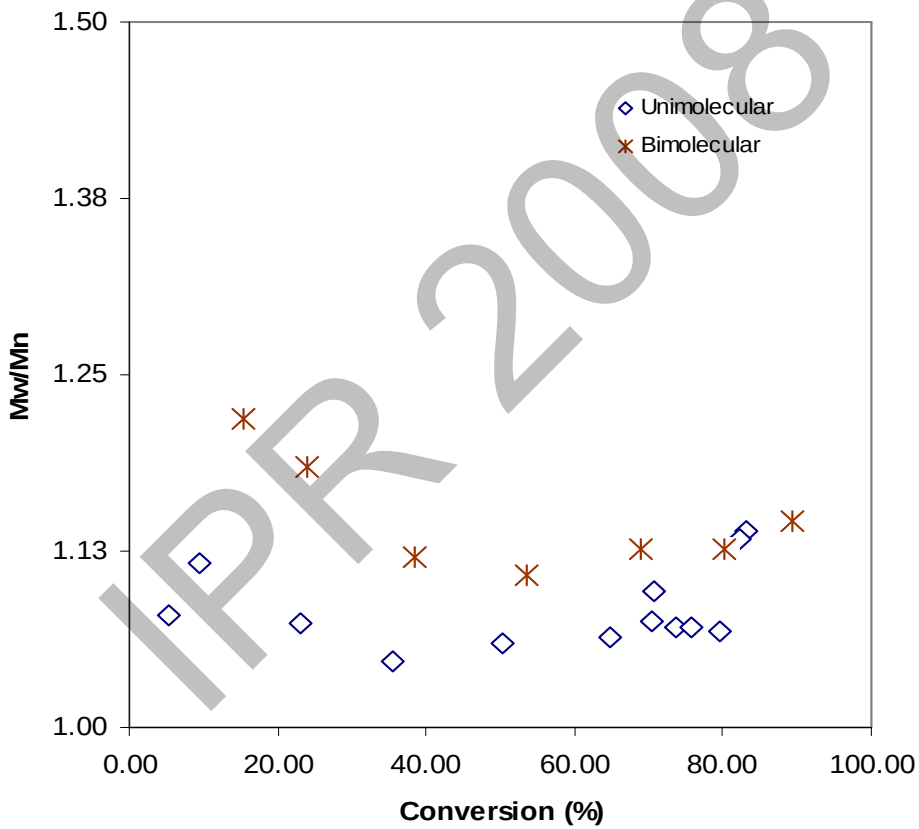
Ms. Joy Cheng

Thank you!

Comparisons of NMRP, ATRP, RAFT

	NMRP	ATRP	RAFT
Range of polymerizable monomers	Styrene, Acrylates	**Nearly all vinyl monomers**	**Nearly all vinyl monomers**
Reaction Conditions	Elevated T>120ºC; Waterborne system OK; Sensitive to O_2	**Large T range (-30~150ºC); Waterborne system OK; Some tolerance to O_2**	Elevated T; **Waterborne system OK;** Sensitive to O2
Nature of transferable group	**Alkoxyamines Easy to handle; Some are commercially available**	**Alkyl halides thermally and photo-stable; inexpensive**	Dithioesters, iodides, and methacrylates; Less thermally stable; Relatively expensive
Additives	**No additional additives**	**Transition metal catalyst**	Conventional radical initiator

Bimolecular vs. Unimolecular



PDI vs. conversion plots for NMRP of styrene at 120ºC

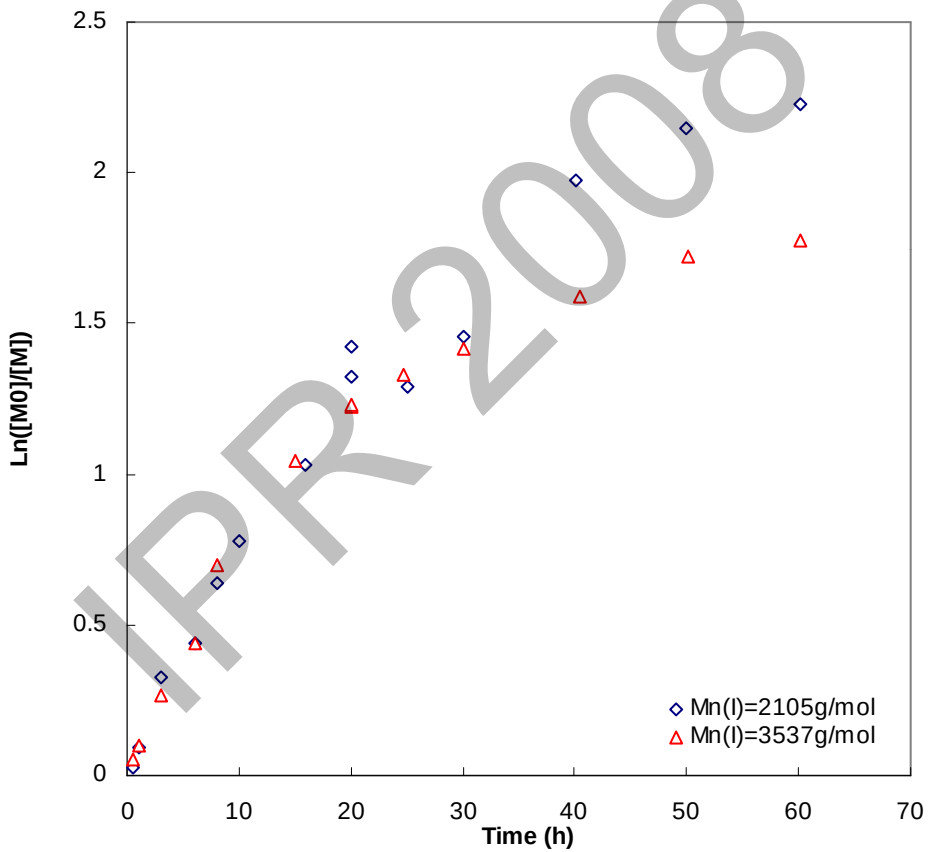
Effect of Initiator Concentration

	[I] (mol/l)	0.0296M	0.0396M	Deviation	Variance
Replicates for 0.0396M		75.93	73.34		3.35
Time (h)	25	81.7	77.48	4.22	
	30	81.96	76.62	5.34	
	40	84.68	80.04	4.64	

Effect of monomer concentration

Experiment	M_0%weight	Temperature (^{o} C)	$[I]_0$ (mol/l)	Mn(I) (g/mol)
1	9.2363	120	0.0396	2105
2	8.8546	120	0.0296	2193
3	9.6283	120	0.0396	2193
4	9.2426	140	0.0396	2105
5	16.2722	120	0.0396	3537

Effect	Experiment	$\Delta[M]_0$ (%)
Initiator concentration	2 vs. 3	**8.74**
Temperature	1 vs. 4	—
Initiator molecular weight	1 vs. 5	**76.18**


2.5
2
1.5
1
0.5
0
Ln([M0]/[M])
0
10
20
30
40
50
60
70
Time (h)
Mn(I)=2105g/mol
Mn(I)=3537g/mol