



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

**Mingxiao Zhou  
Neil McManus & Alex Penlidis**

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# Outline

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



# Radical Polymerization (RP)

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## □ Advantages:

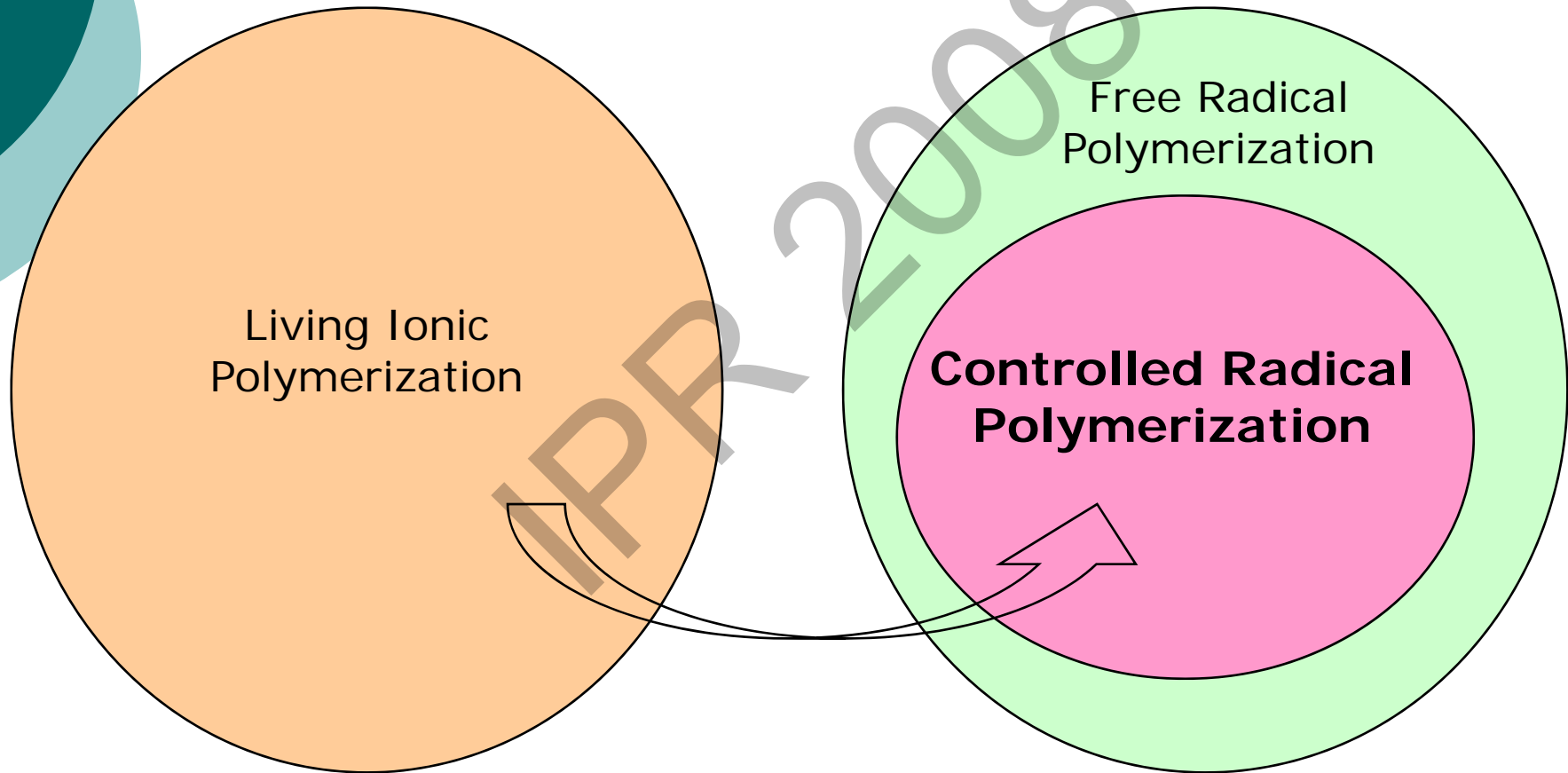
- Versatility
- Synthetic ease
- Compatibility with many monomer families and functional groups
- Wide range of operating conditions

## □ Disadvantages:

- Limited control of microstructure

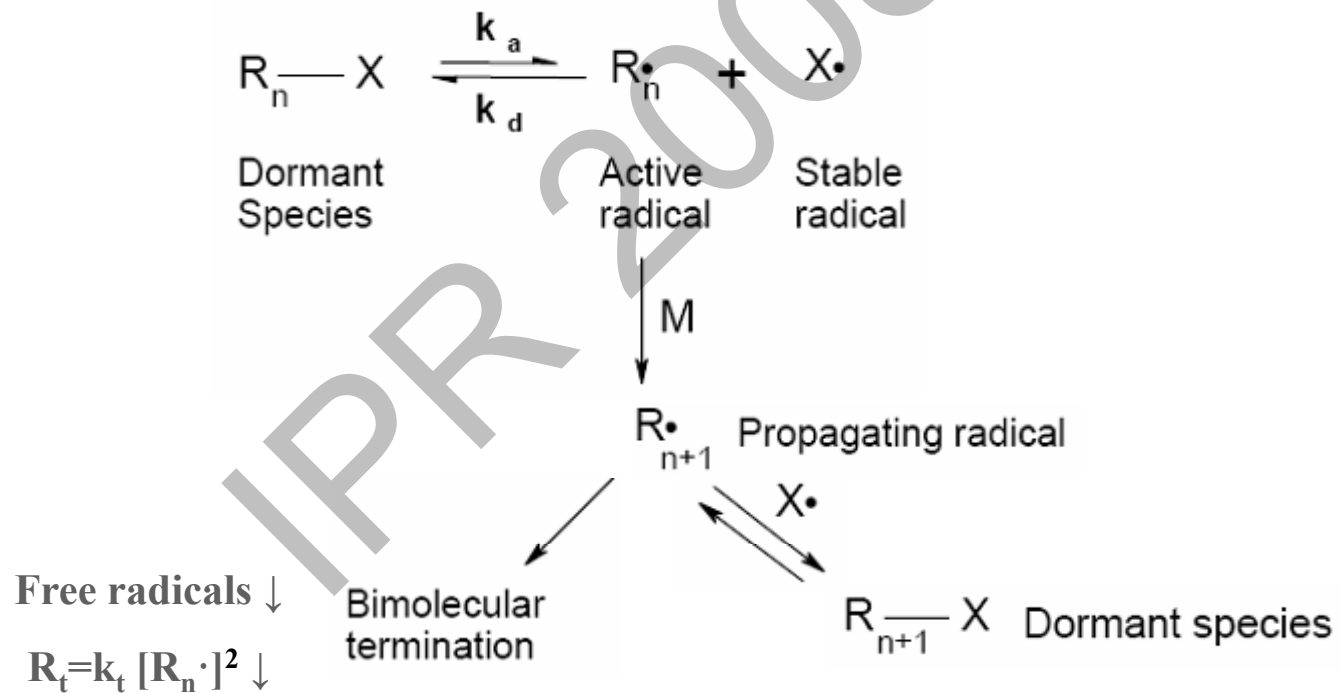
# Controlled Radical Polymerization (CRP)

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# Mechanism Differences in CRP

## Reversible Activation Process

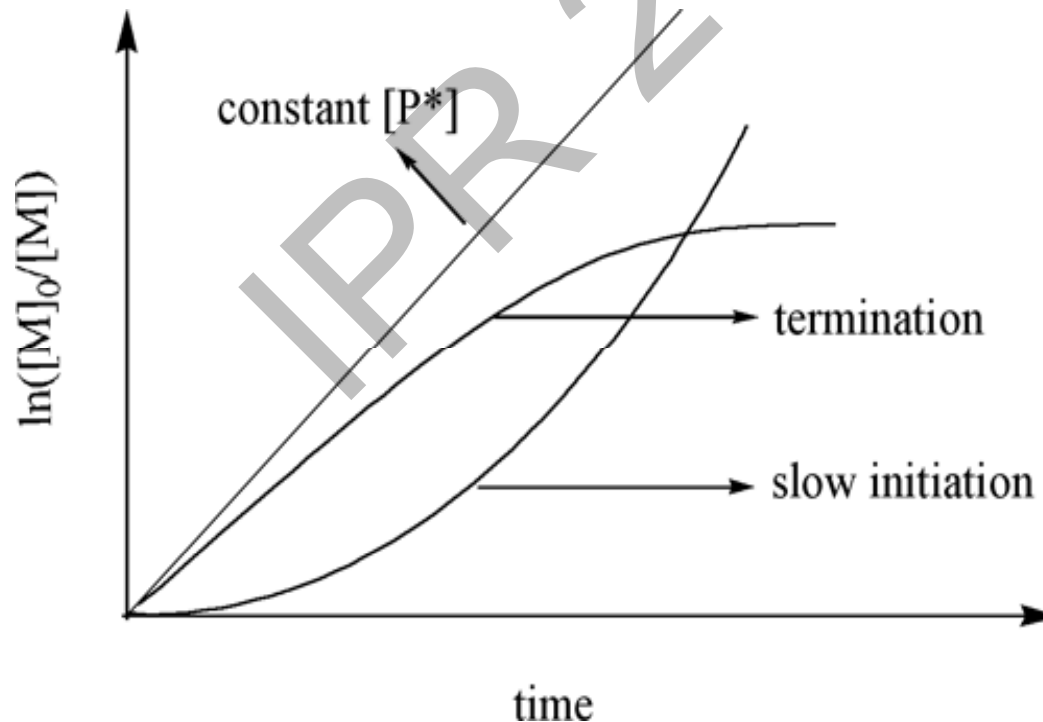


# Features of CRP

## □ *First-order Kinetics Behavior*

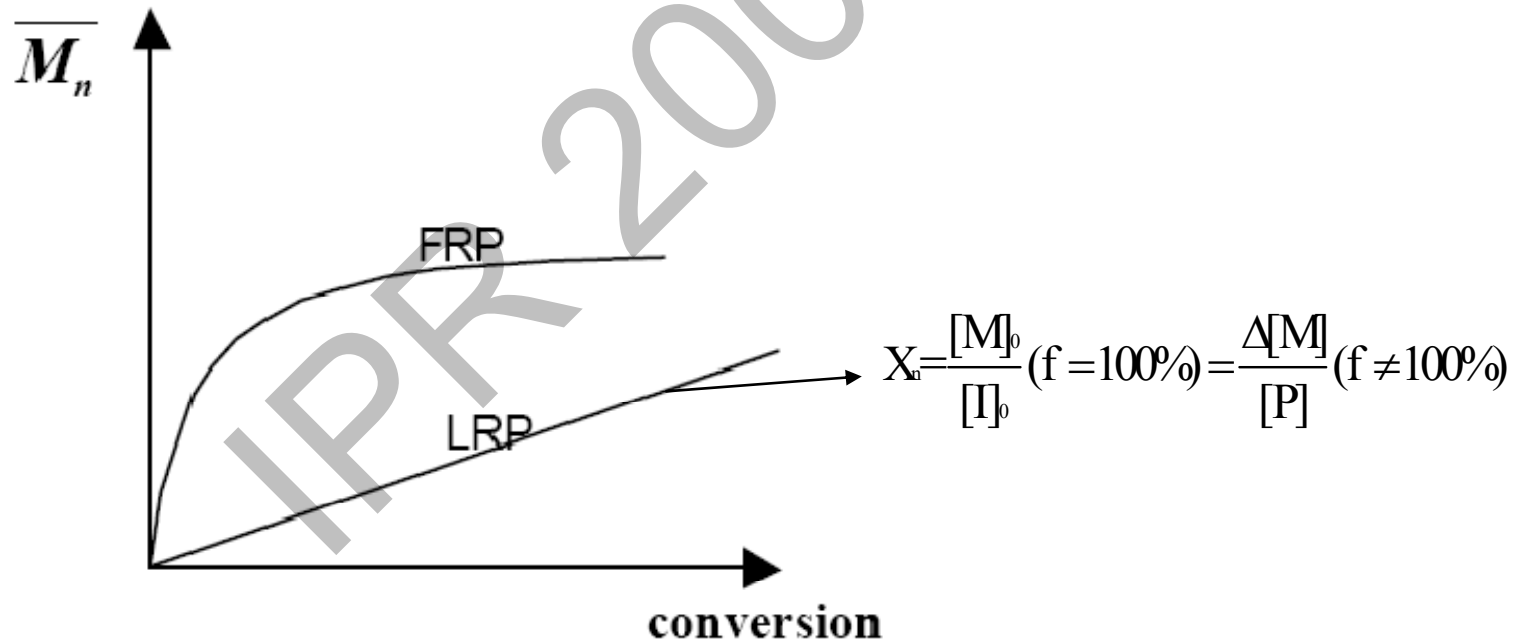
$$R_p = - d[M]/dt = k_p [R_{n+1} \cdot] [M]$$

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



# Features of CRP

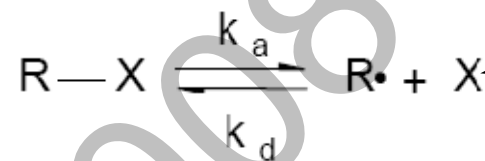
- *MW increases linearly with conversion*



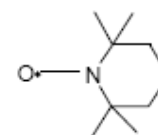
- *Narrow molecular weight distribution*

# Main Types of CRP: NMRP, ATRP, RAFT

□ Nitroxide Mediated Radical Polymerization (NMRP)

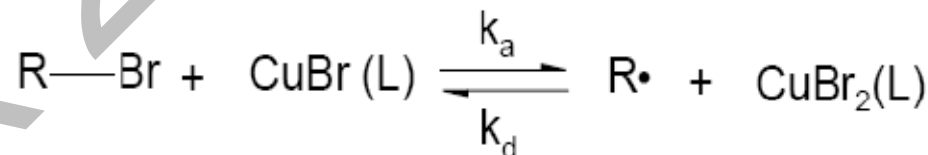


Nitroxide

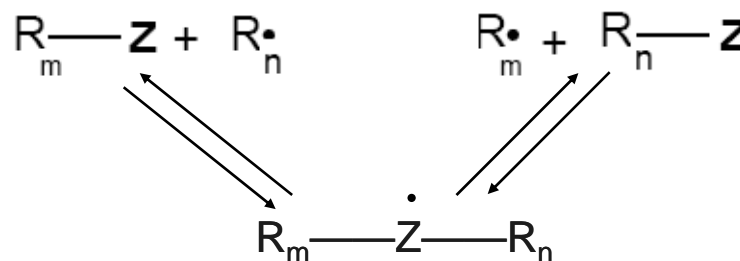


TEMPO

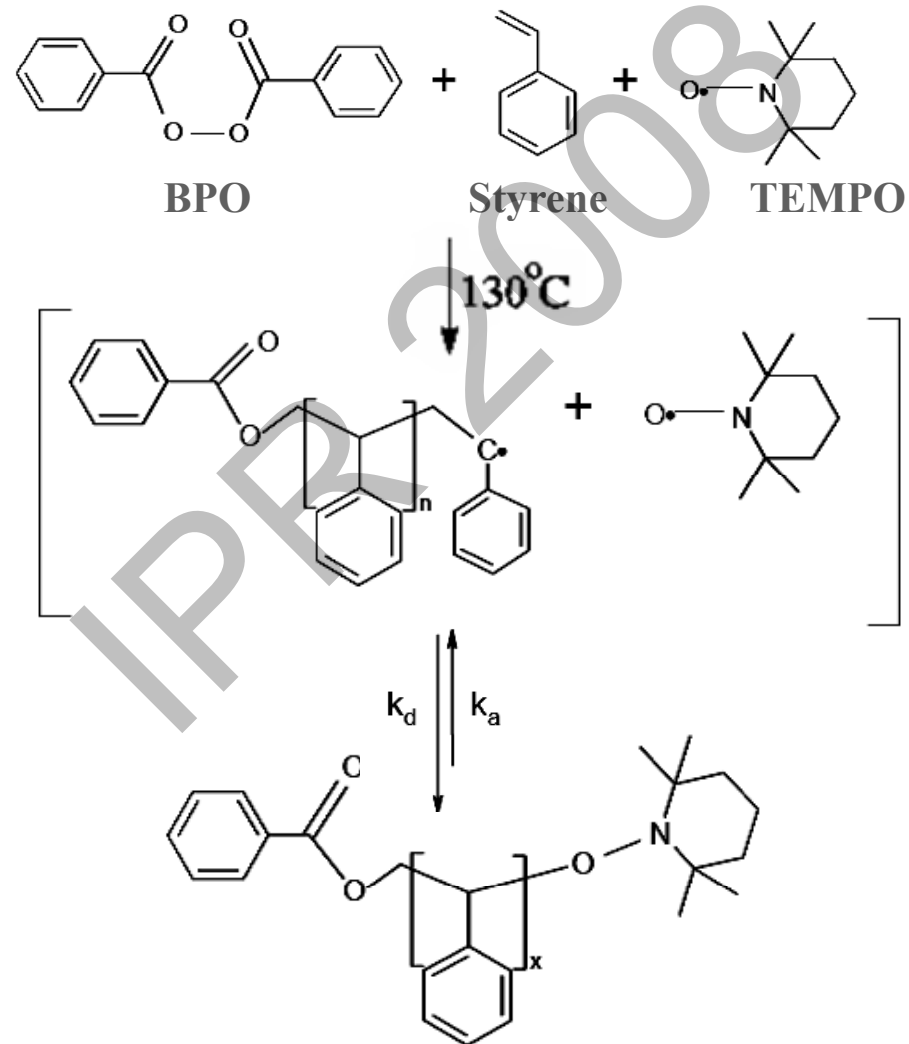
□ Atom Transfer Radical Polymerization (ATRP)



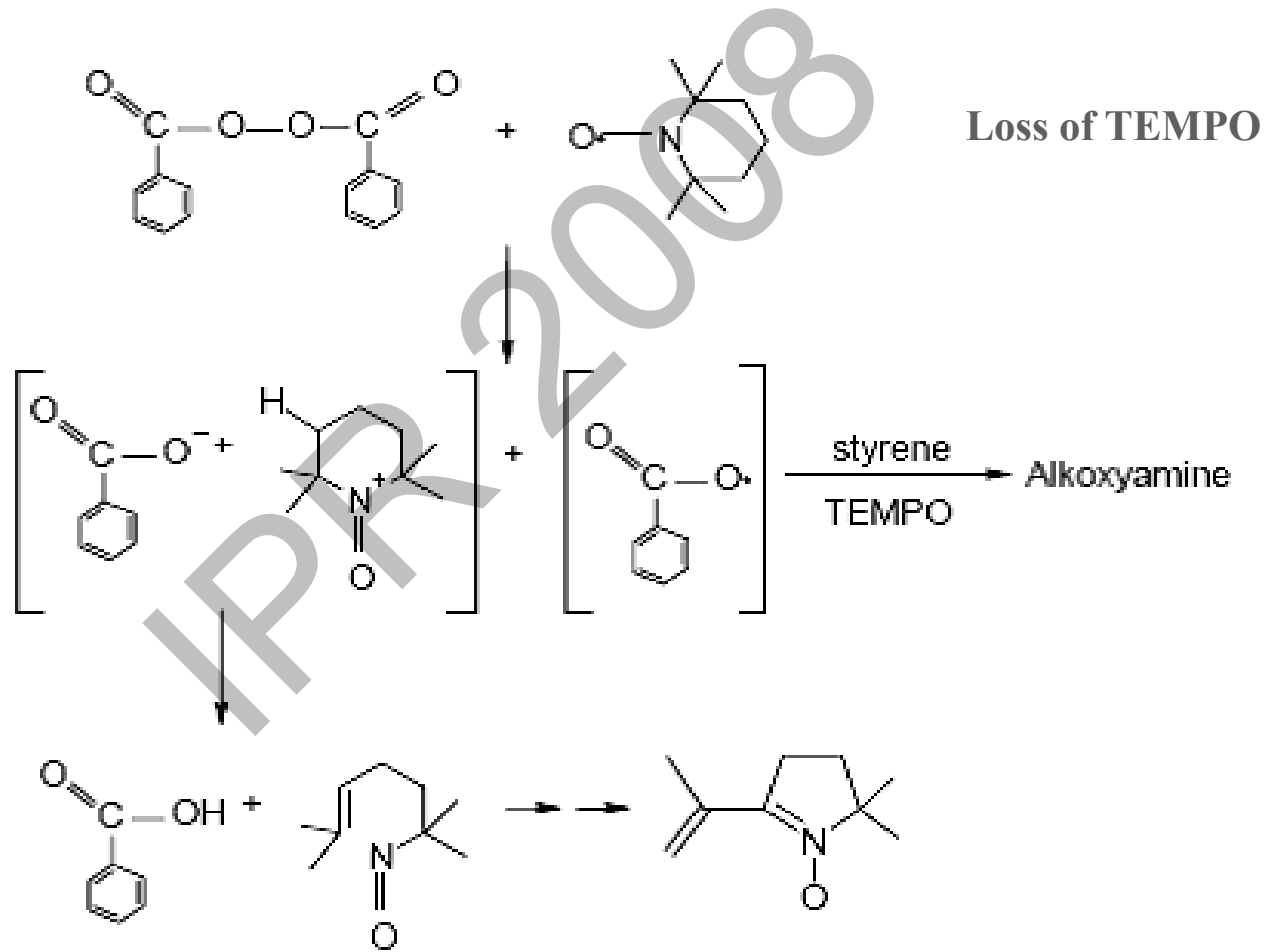
□ Reversible Addition-Fragmentation Transfer Polymerization (RAFT)



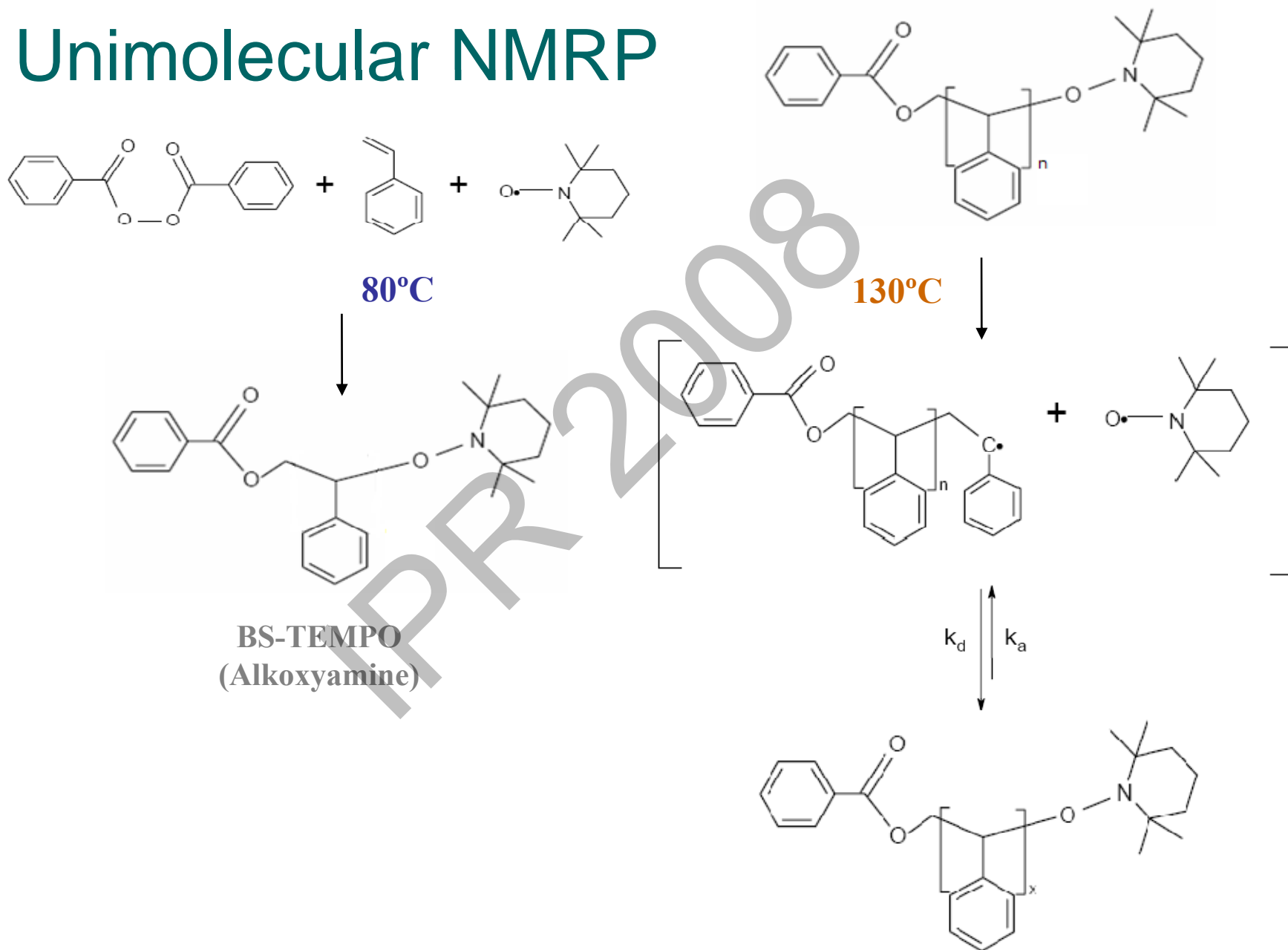
# Bimolecular NMRP



# “Promoted Dissociation” of BPO



# Unimolecular NMRP





## Advantages of Unimolecular System

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



# Research Objectives

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- 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

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

# Data Collection

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□ Monomer Conversion - Gravimetry

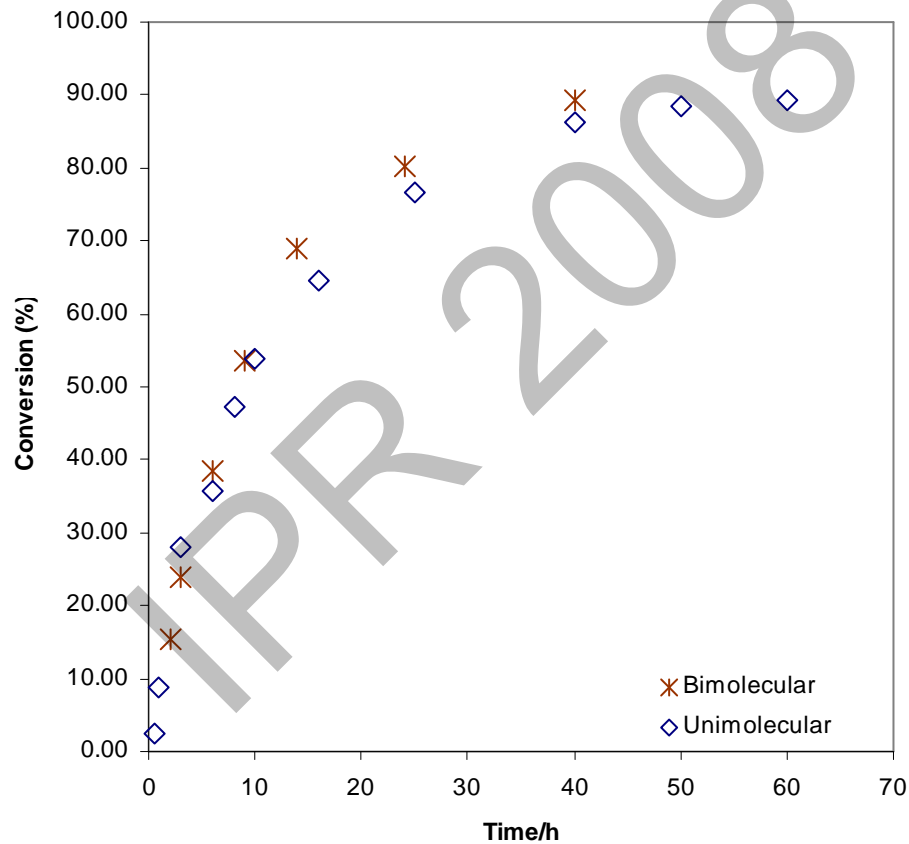
□ Molecular Weight ( $M_n$ ,  $M_w$ )

□ Polydispersity Index ( $PDI = M_w / M_n$ )

**GPC**

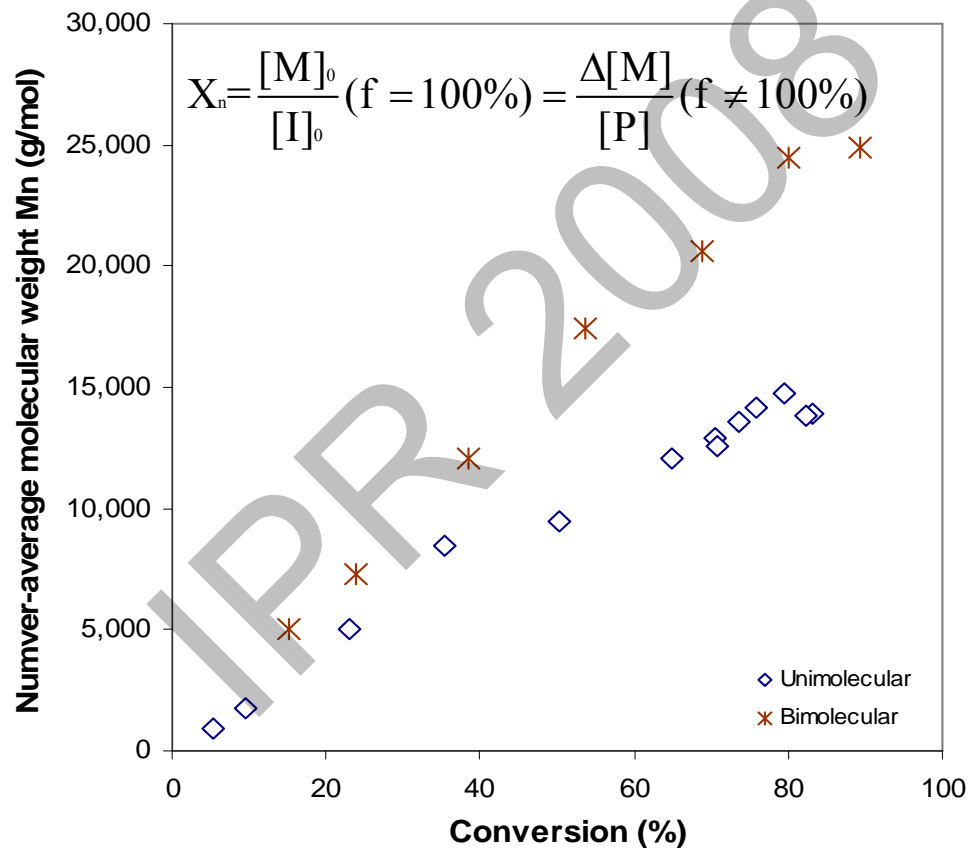
```
graph LR; A[Molecular Weight (Mn, Mw)] --- B[ ]; C[Polydispersity Index (PDI = Mw / Mn)] --- B; B --- D[GPC]
```

# Bimolecular vs. Unimolecular



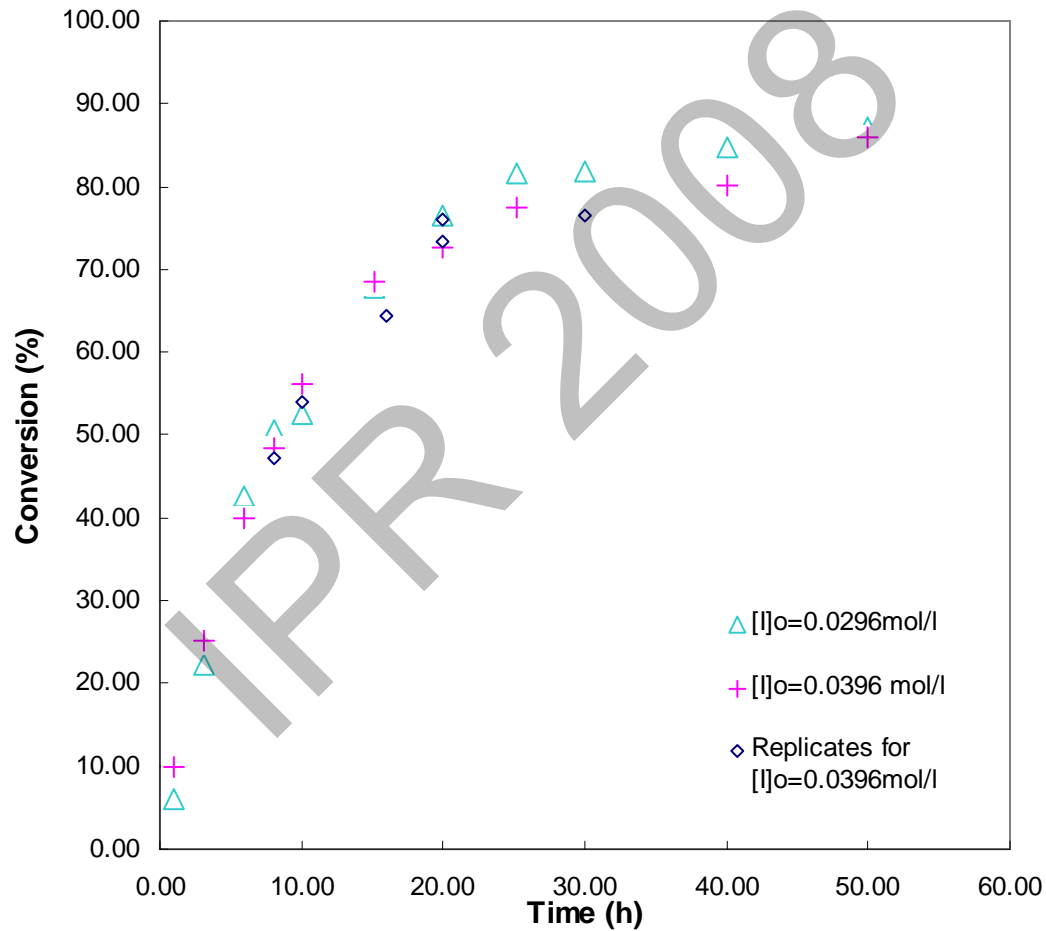
Conversion vs. time for NMRP of styrene at 120°C,  $[I]_0=0.0396M$

# Bimolecular vs. Unimolecular



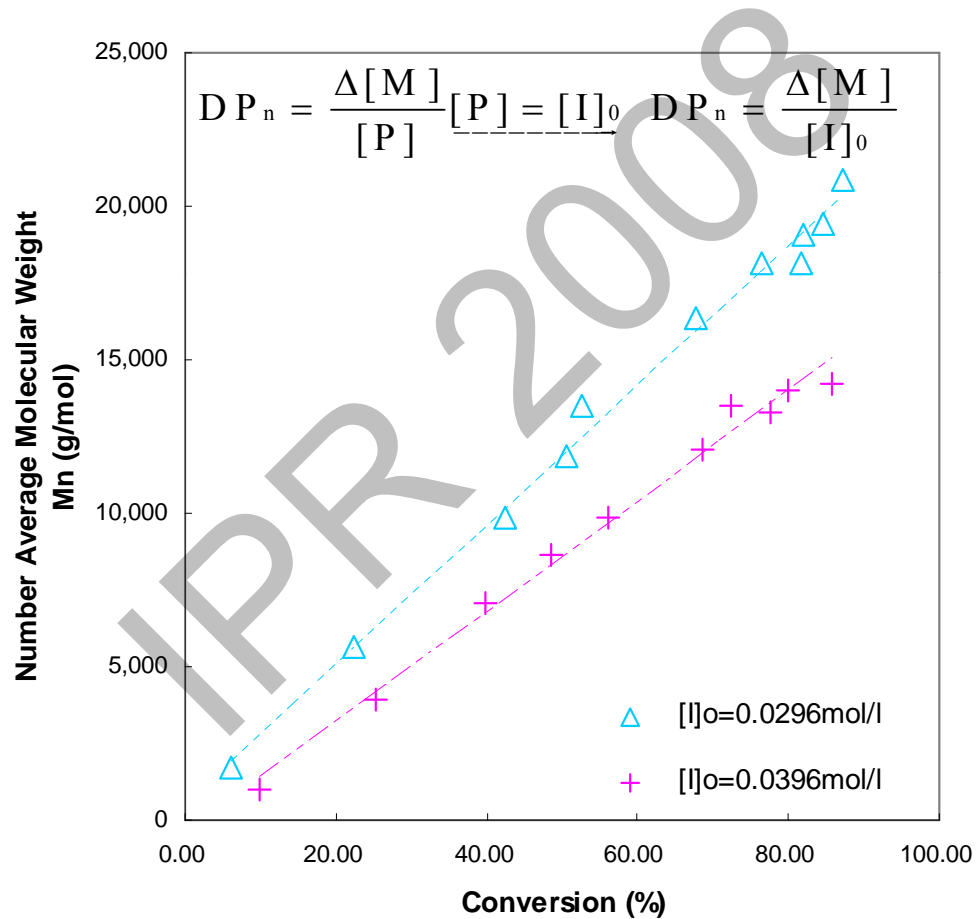
Molecular weight vs. conversion for NMRP of styrene at 120°C,  $[M]=0.0396M$

# Unimolecular Effect of Initiator Concentration



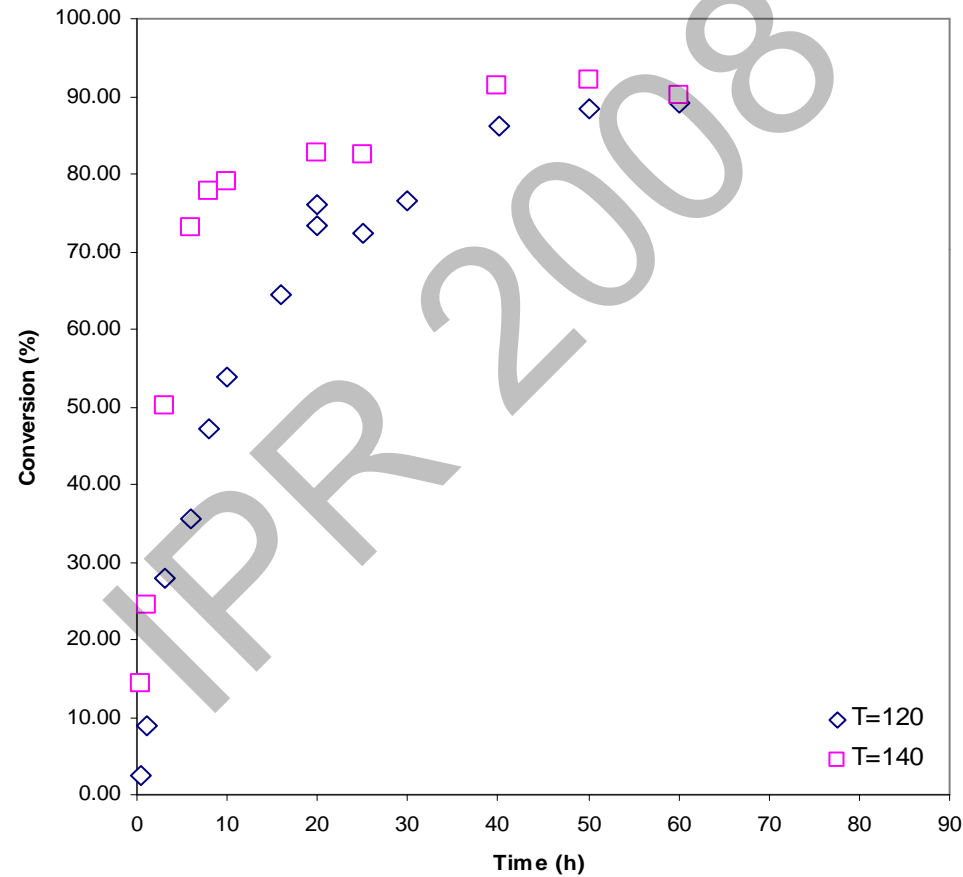
Effect of initiator concentration on polymerization rate at 120°C

# Effect of Initiator Concentration



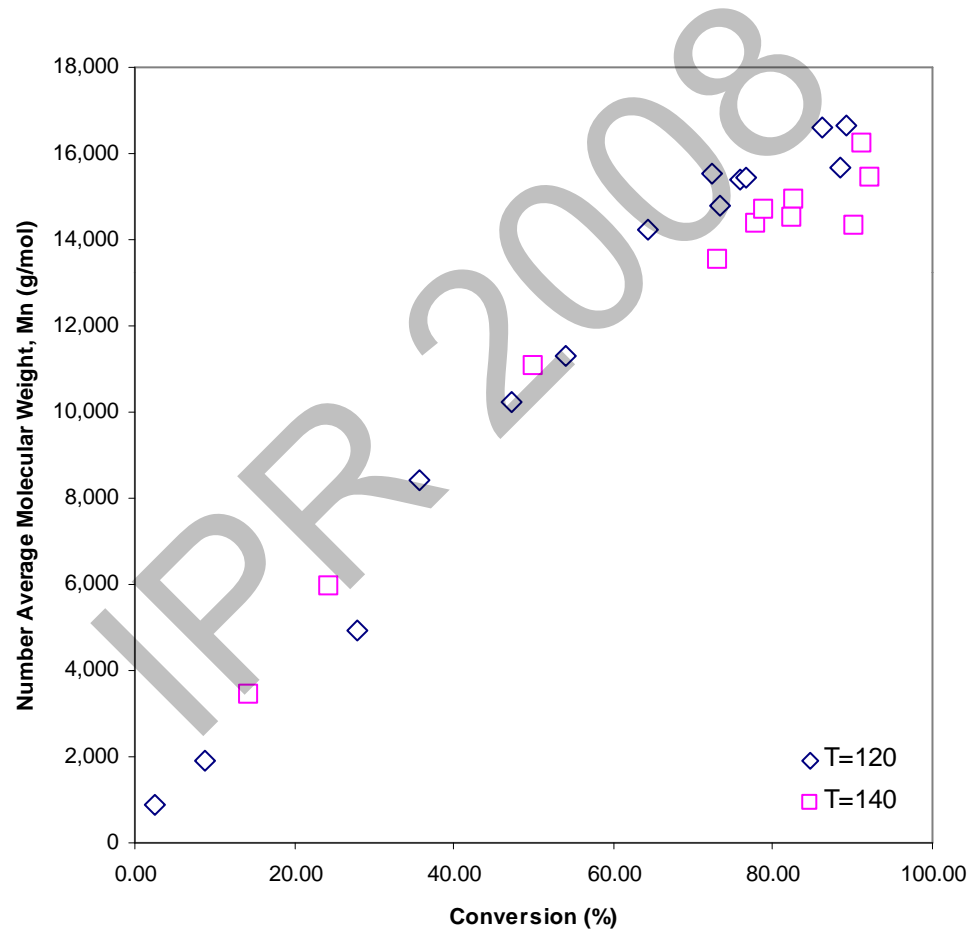
Effect of initiator concentration on molecular weight at 120°C

# Effect of Temperature



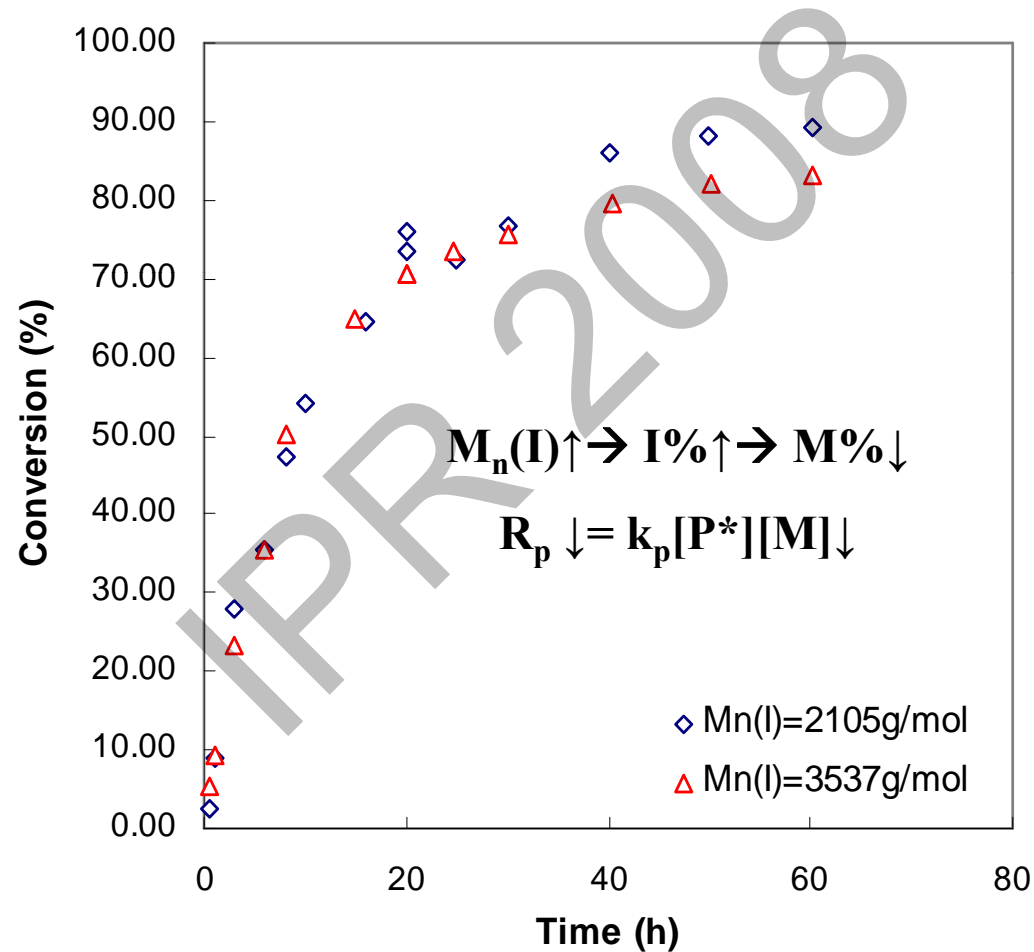
Effect of temperature ( $^{\circ}\text{C}$ ) on polymerization rate,  $[I]_0=0.0396\text{M}$

# Effect of Temperature



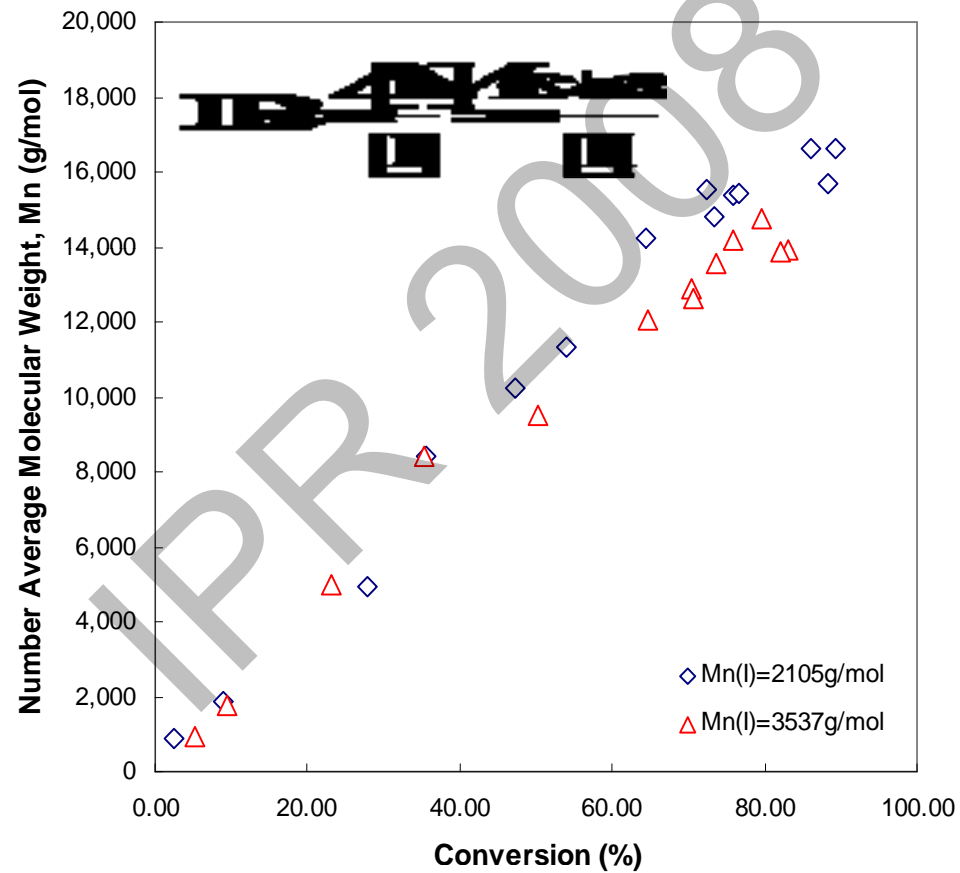
Effect of temperature ( $^{\circ}\text{C}$ ) on molecular weight,  $[I]_0=0.0396\text{M}$

# Effect of Initiator Molecular Weight



Effect of initiator molecular weight on polymerization rate at 120°C

# Effect of Initiator Molecular Weight



Effect of initiator molecular weight on molecular weight at 120°C

# Effect of Initiator Molecular Weight



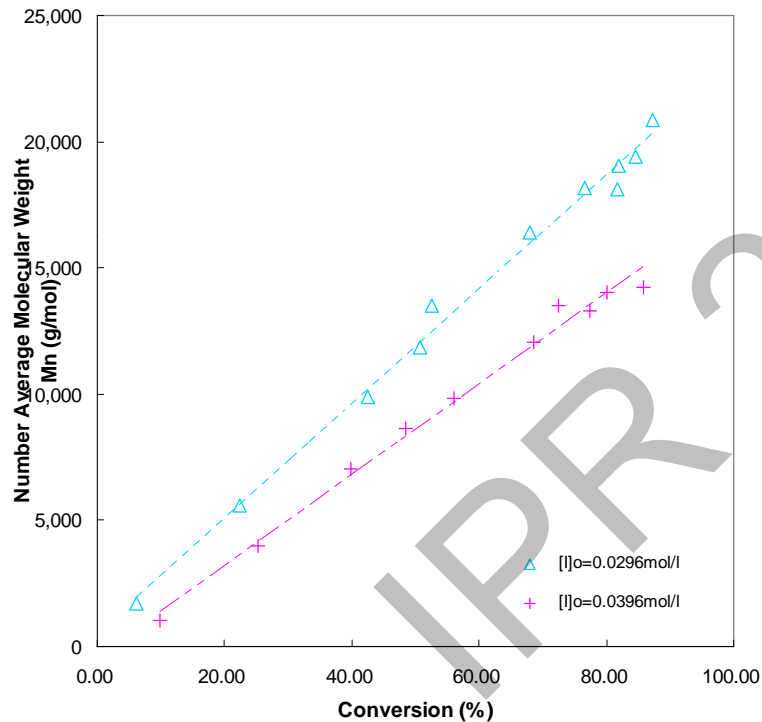


## Summary of experimental factors

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	Polymerization Rate	Molecular Weight
<i>Initiator Concentration</i>	0	—
<i>Temperature</i>	+	0/—
<i>Initiator Molecular Weight</i>	0/—	0/—

# Prediction of Molecular Weight



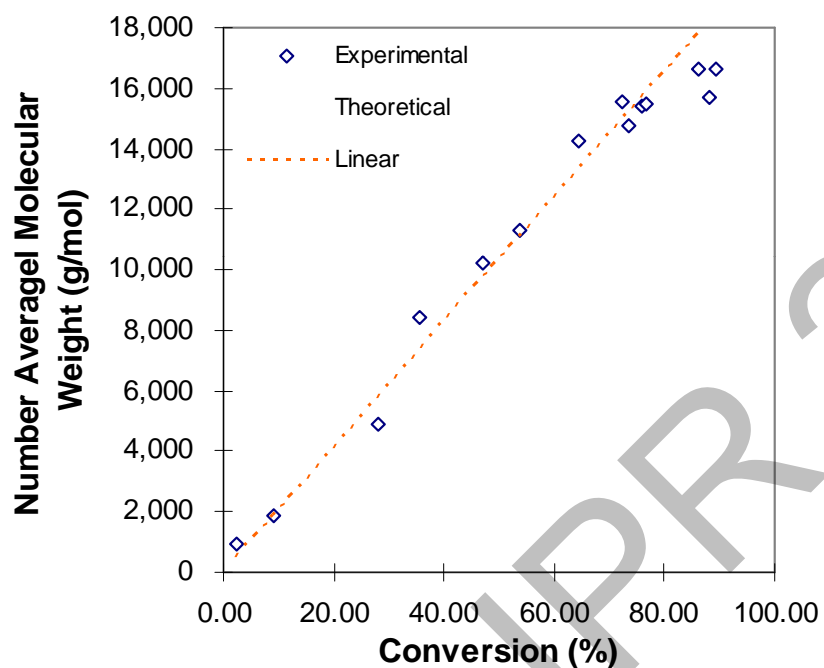
Same  $[I]_0$ , Conversion  $\uparrow \rightarrow M_n \uparrow$

Same Conversion,  $[I]_0 \uparrow \rightarrow M_n \downarrow$

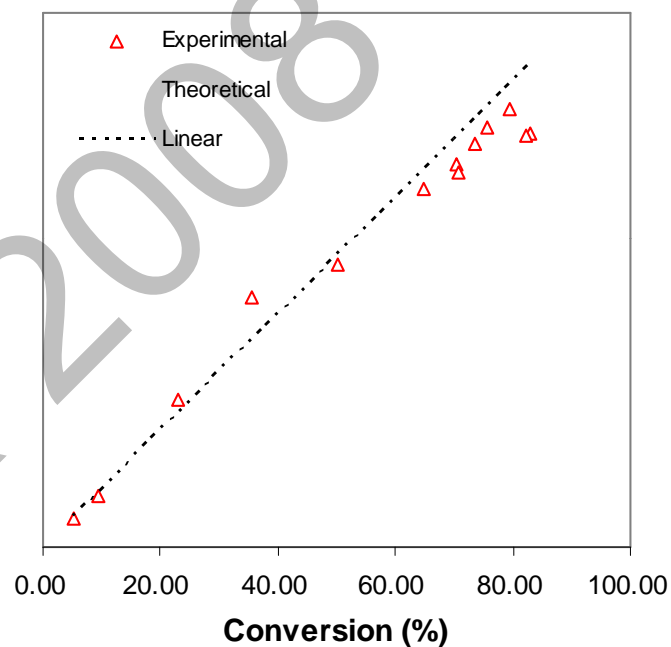
$$M_n(\text{Theoretical}) = M_0 \frac{\Delta[M]}{[I]_0}$$

$$[P] = [I]_0$$

# Prediction of Molecular Weight



**Mn(I)=2193g/mol, T=120°C, [I]=0.0396M**



**Mn(I)=3537g/mol, T=120°C, [I]=0.0396M**



## Future Work

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



# Acknowledgements

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*Many thanks to*  
*Prof. Neil McManus*  
*Prof. Alex Penlidis*

*Ms. Afsaneh Nabifar*  
*Ms. Joy Cheng*

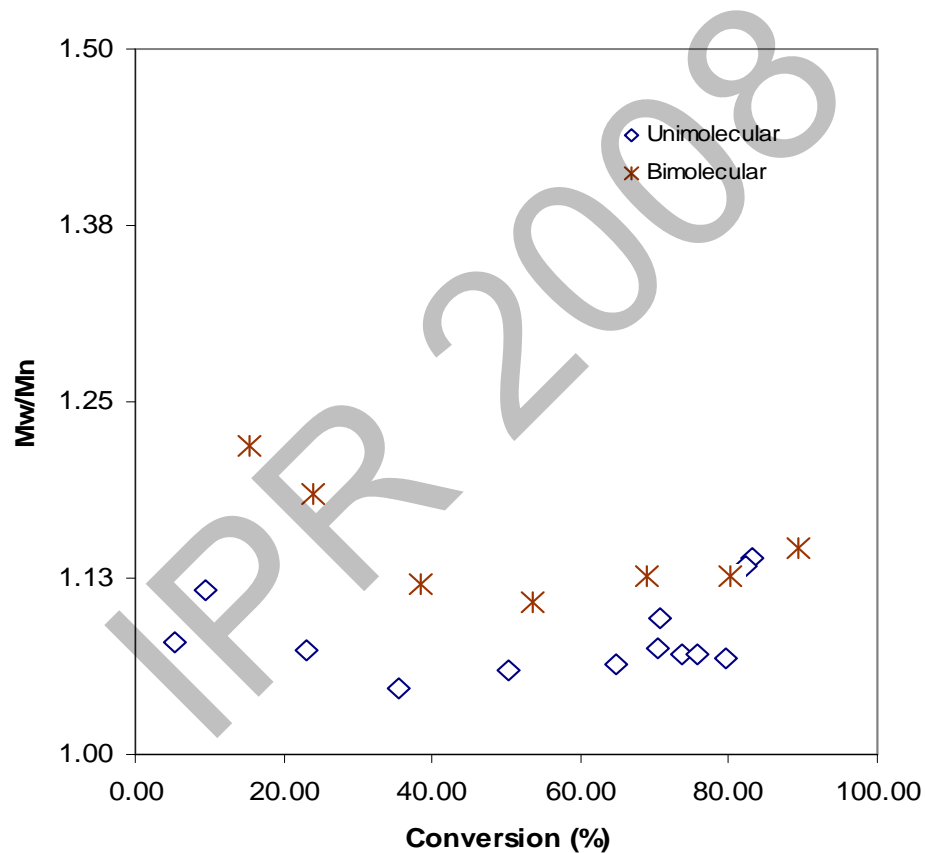


*Thank you!*

# Comparisons of NMRP, ATRP, RAFT

	<b>NMRP</b>	<b>ATRP</b>	<b>RAFT</b>
Range of polymerizable monomers	Styrene, Acrylates	<b>Nearly all vinyl monomers</b>	<b>Nearly all vinyl monomers</b>
Reaction Conditions	Elevated T > 120°C; Waterborne system OK; Sensitive to O <sub>2</sub>	<b>Large T range (-30~150°C); Waterborne system OK; Some tolerance to O<sub>2</sub></b>	Elevated T; <b>Waterborne system OK;</b> Sensitive to O <sub>2</sub>
Nature of transferable group	<b>Alkoxyamines Easy to handle; Some are commercially available</b>	<b>Alkyl halides thermally and photo-stable; inexpensive</b>	Dithioesters, iodides, and methacrylates; Less thermally stable; Relatively expensive
Additives	<b>No additional additives</b>	<b>Transition metal catalyst</b>	Conventional radical initiator

# Bimolecular vs. Unimolecular



PDI vs. conversion plots for NMRP of styrene at 120°C

# 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 (° 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

