

Investigating Nitroxide-Mediated Radical Polymerization of Styrene over a Range of Reaction Conditions

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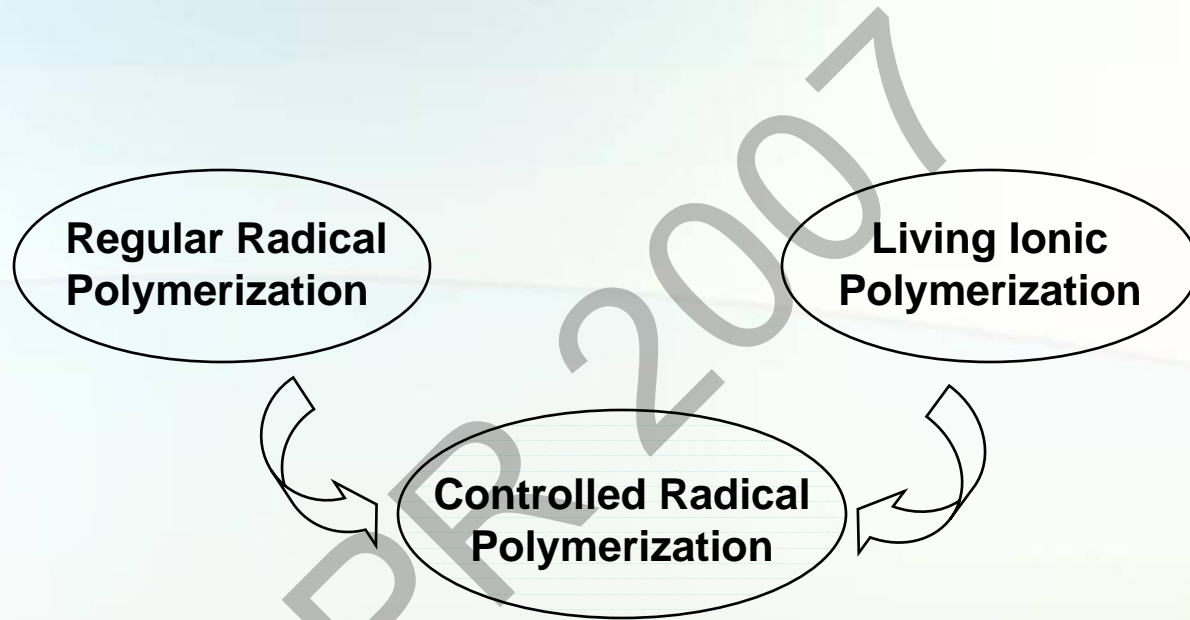
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Controlled Radical Polymerization (CRP)

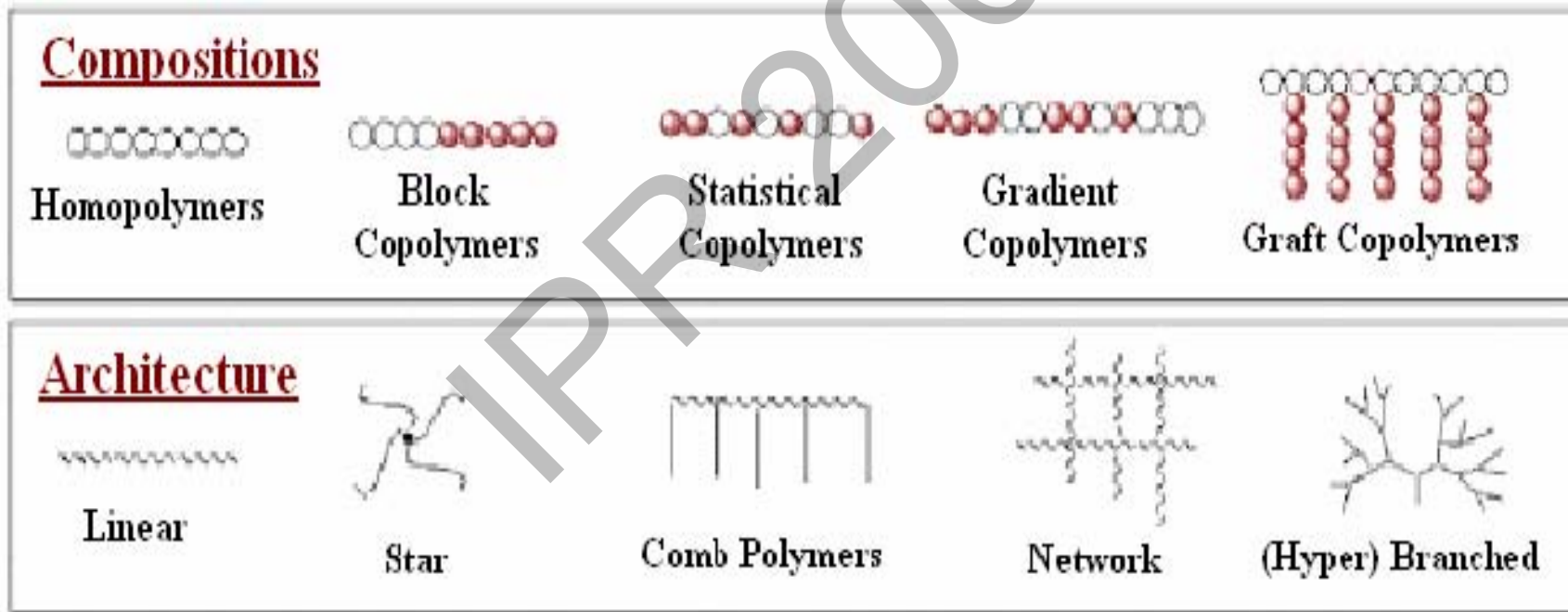
- (Co) polymers with precisely controlled architectures
- Living Ionic Polymerization (good control but stringent conditions; relatively small number of monomers)
- Regular radical polymerization (versatile reaction conditions but poor control over some polymer characteristics)

Controlled Radical Polymerization (CRP)



Controlled Radical Polymerization (CRP)

- Examples of molecular structures attained

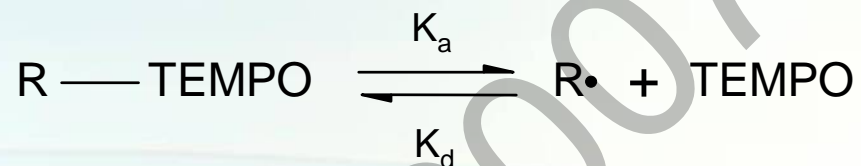


Controlled Radical Polymerization (CRP)

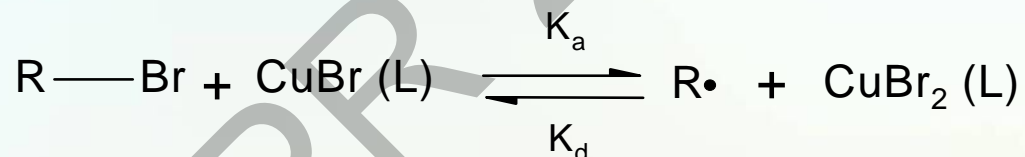
- Applications
 - Acrylic block copolymers as stabilizers in coating, ink applications
 - Additives suitable for use as components of lubricating oils
 - ABC – type block copolymers

Controlled Radical Polymerization (CRP)

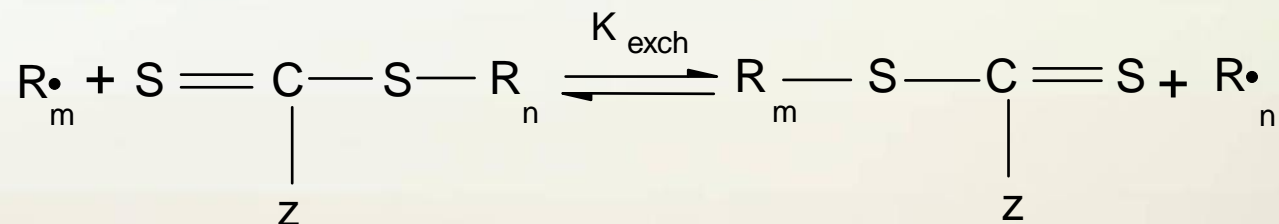
- Nitroxide-Mediated Radical Polymerization (NMRP)



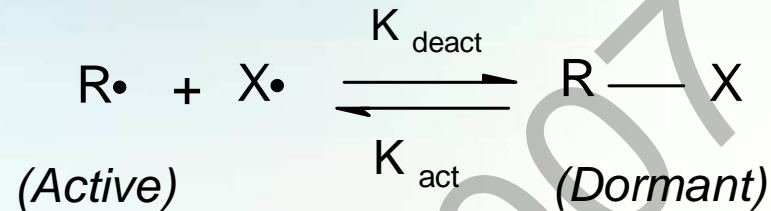
- Atom Transfer Radical Polymerization (ATRP)



- Reversible Addition-Fragmentation Transfer (RAFT)



Controlled Radical Polymerization (CRP)

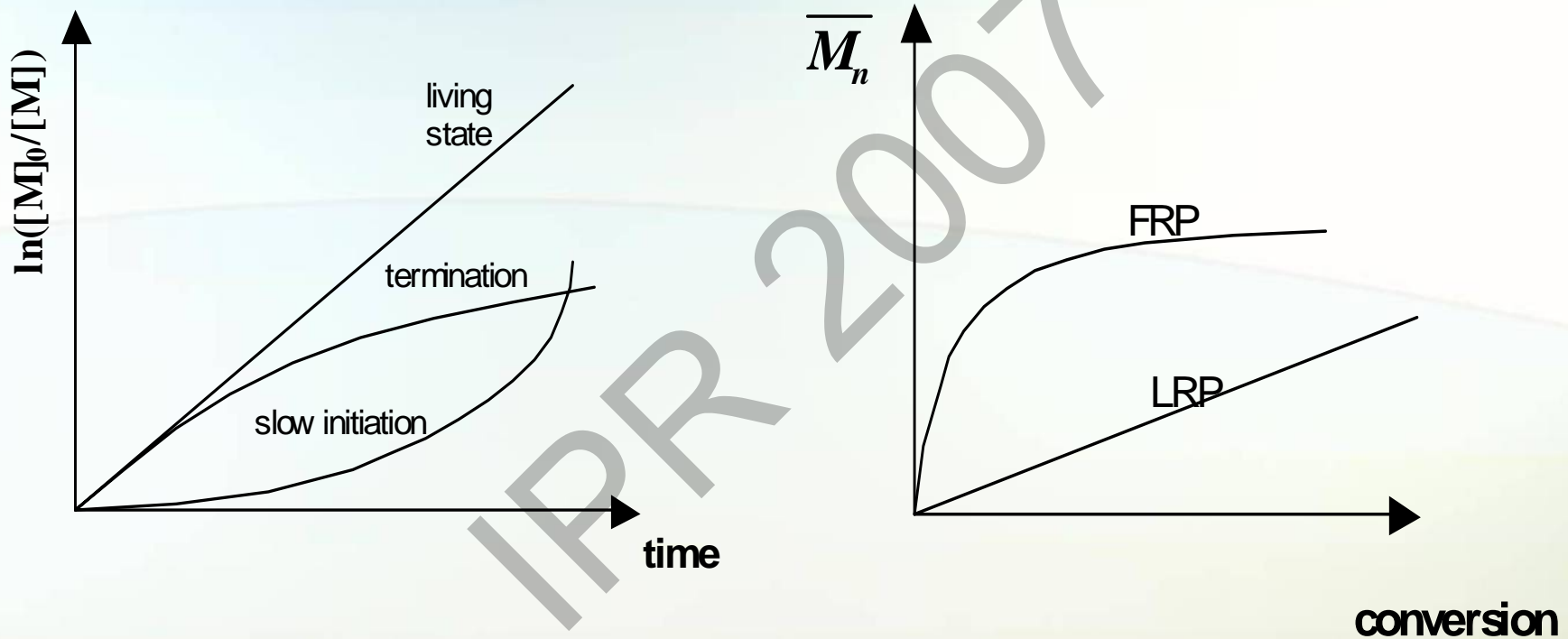


- Exchange equilibrium favours dormant species
- Concentration of radicals is low; bimolecular termination “almost” negligible
- Radicals grow at the same average rate; low polydispersity product

Controlled Radical Polymerization (CRP)

- Prerequisites
 - Small contribution of chain – breaking reactions (termination and transfer reactions)
 - Fast initiation compared to propagation
 - Fast exchange between active and dormant species (provides uniformity in chain length)

Controlled Radical Polymerization (CRP)

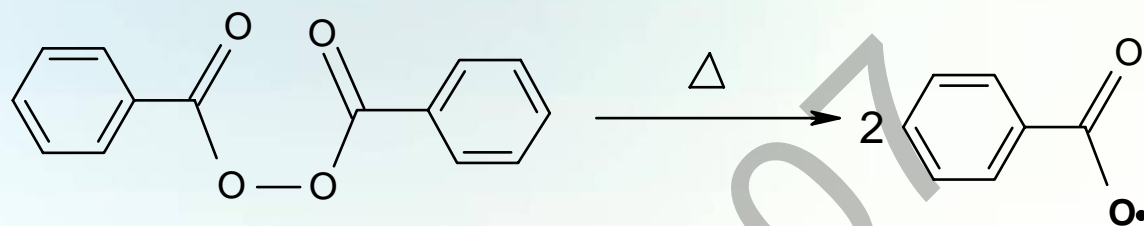


- Deviation from linearity can result from slow initiation or loss of radicals by termination

Nitroxide-Mediated Radical Polymerization (NMRP)

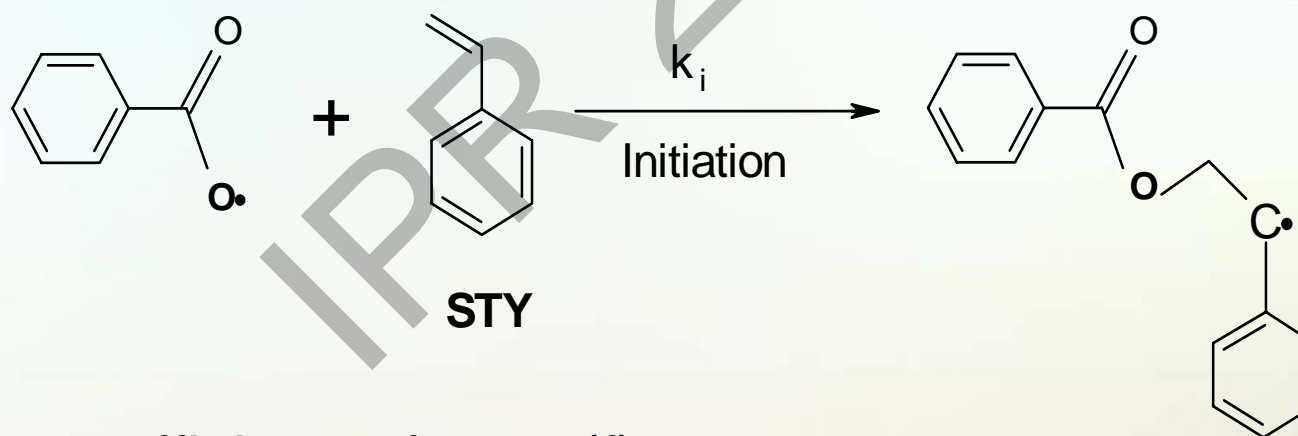
- Addition of a stable nitroxide radical, able to trap the propagating radical in a thermally unstable species
- The most common nitroxide used as trapping agent is TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy)

- **NMRP of Styrene with BPO and TEMPO**



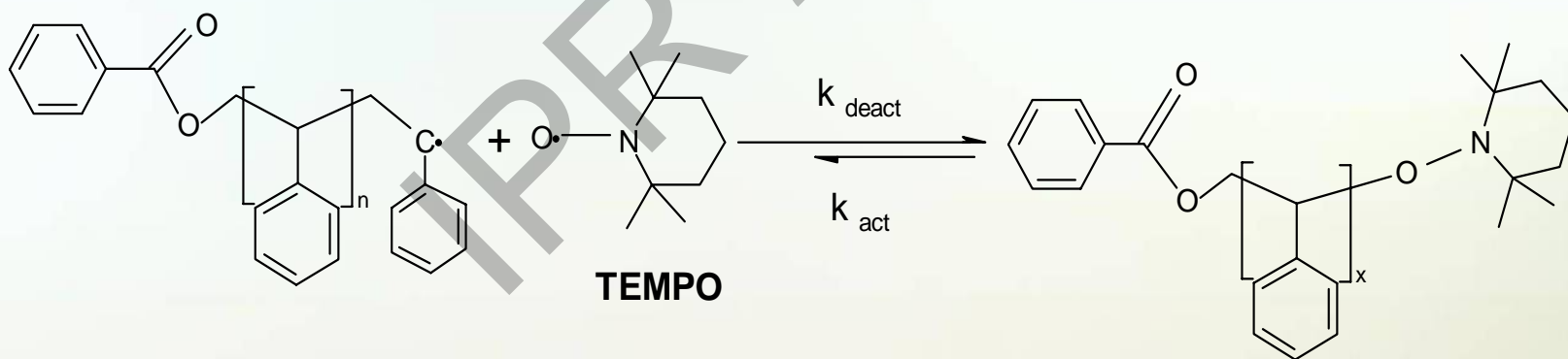
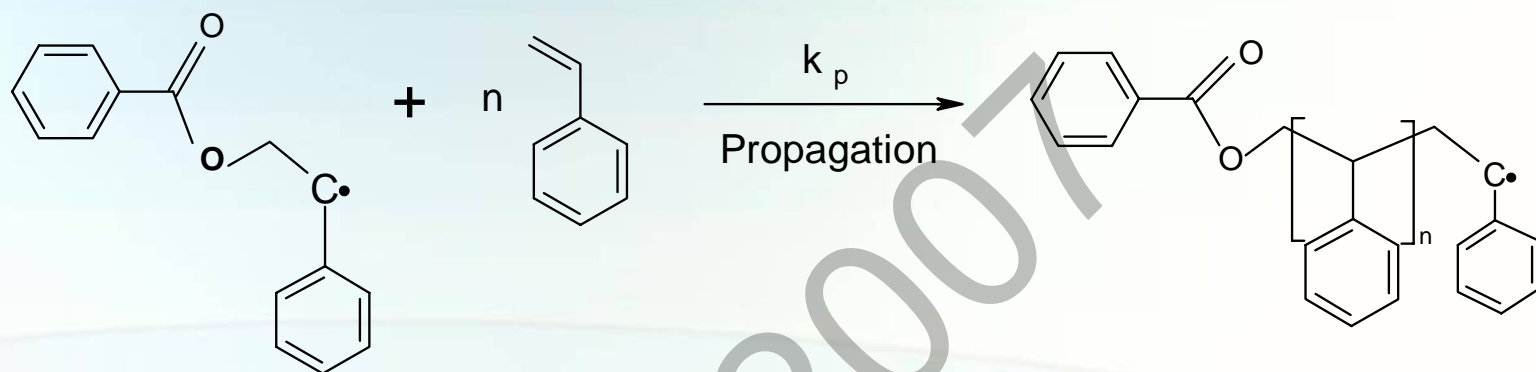
Benzoyl Peroxide

Benzoyloxy radical



- Initiator efficiency factor (f)
- (Thermal) Self initiation of Styrene

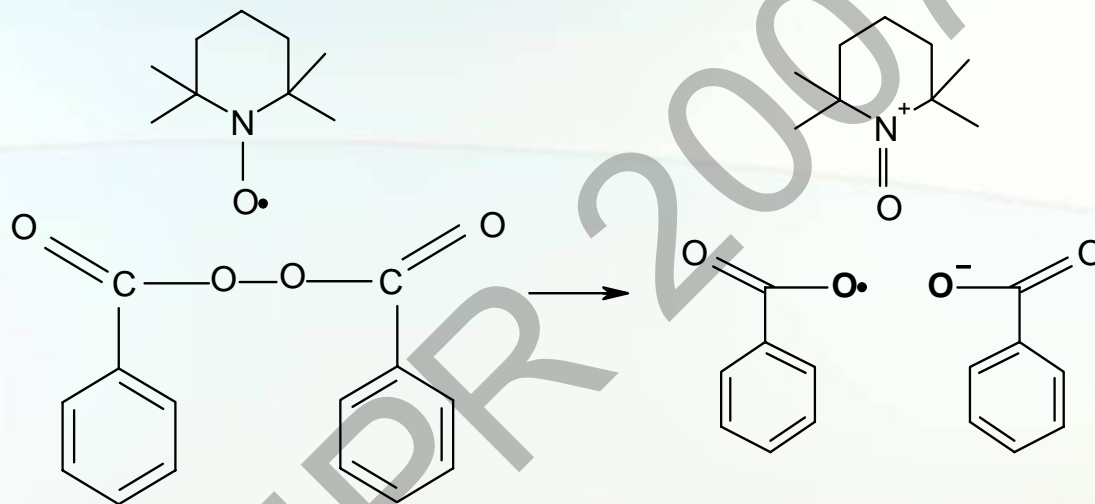
- NMRP of Styrene with BPO and TEMPO**



- $K = k_{deact} / k_{act}$

Side Reactions

- Reaction between TEMPO and BPO



- Nitroxide decomposition

Uncertain Aspects (?)

- Initiator efficiency factor (f)
- Uncertain kinetic constants
- Side reactions

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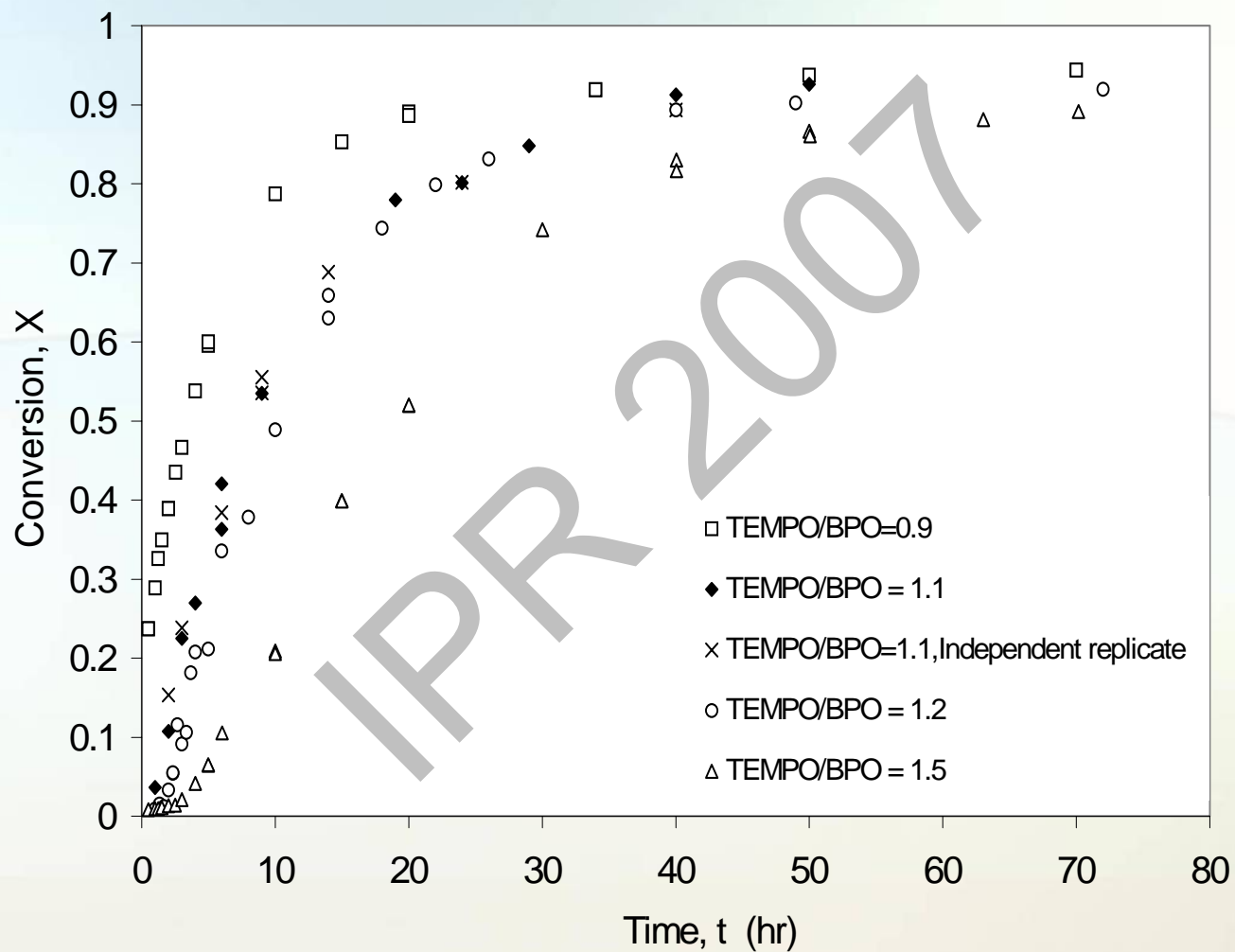
Objectives

- Clarify the effect of polymerization conditions (TEMPO/BPO ratio and temperature)
 - Conversion (rate)
 - Molecular weights
 - Polydispersity
- Generate a source of reliable experimental data
 - Validation of mathematical models
 - Parameter estimation
 - Identification of optimal polymerization conditions

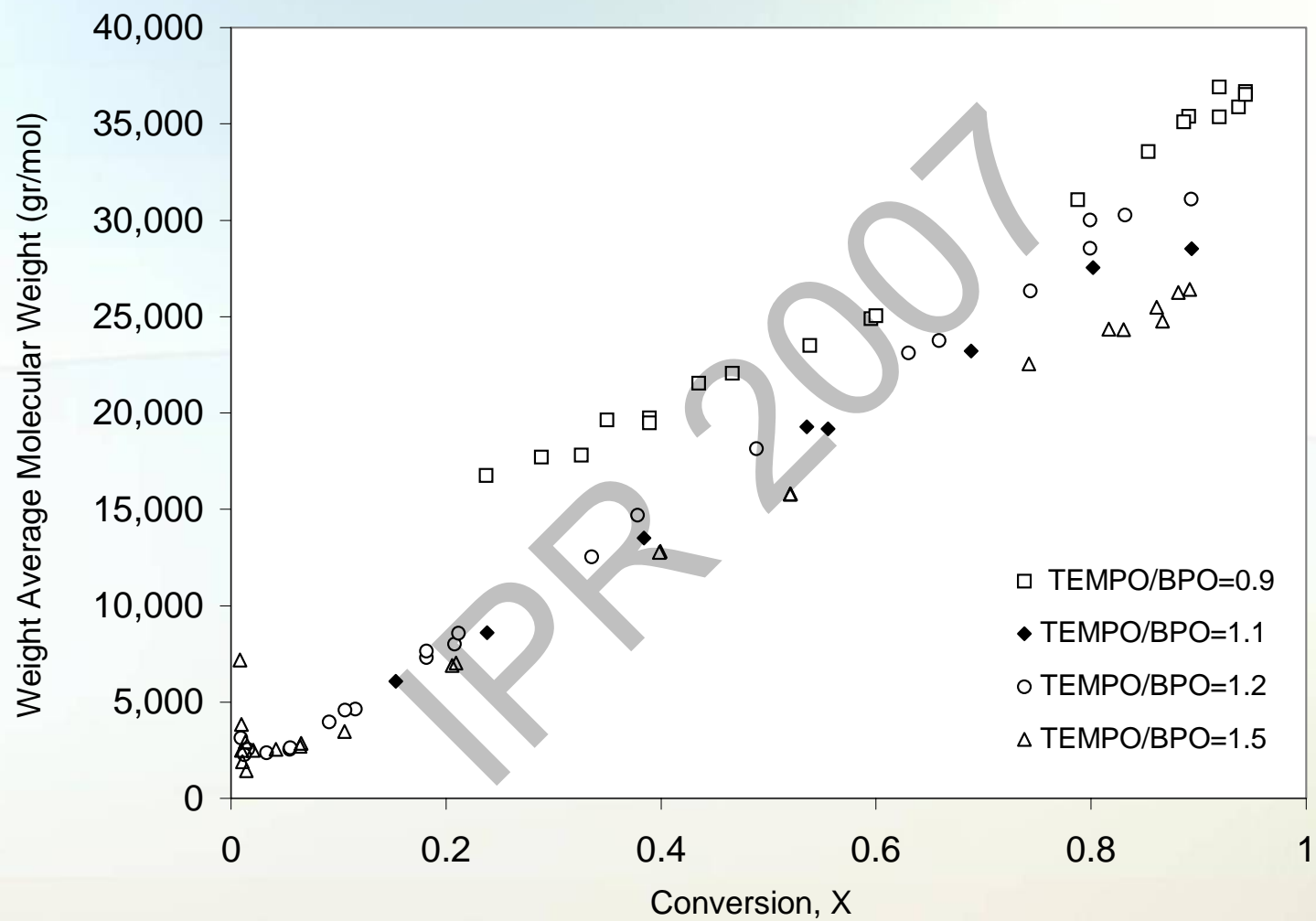
Summary of Runs

Temperature (°C)	[BPO] ₀ M	[TEMPO] / [BPO]	Remarks
120	0.036	0.9	
	0.036	1.1	+ Replicate
	0.036	1.2	
	0.036	1.5	
	Nil	-	Styrene with unimolecular initiator
130	0.036	0.9	
	0.036	1.1	+ Replicate
	0.036	1.3	+ Replicate
	Nil	-	Thermal (self) initiation of styrene + Replicate
	Nil	-	Styrene with TEMPO only

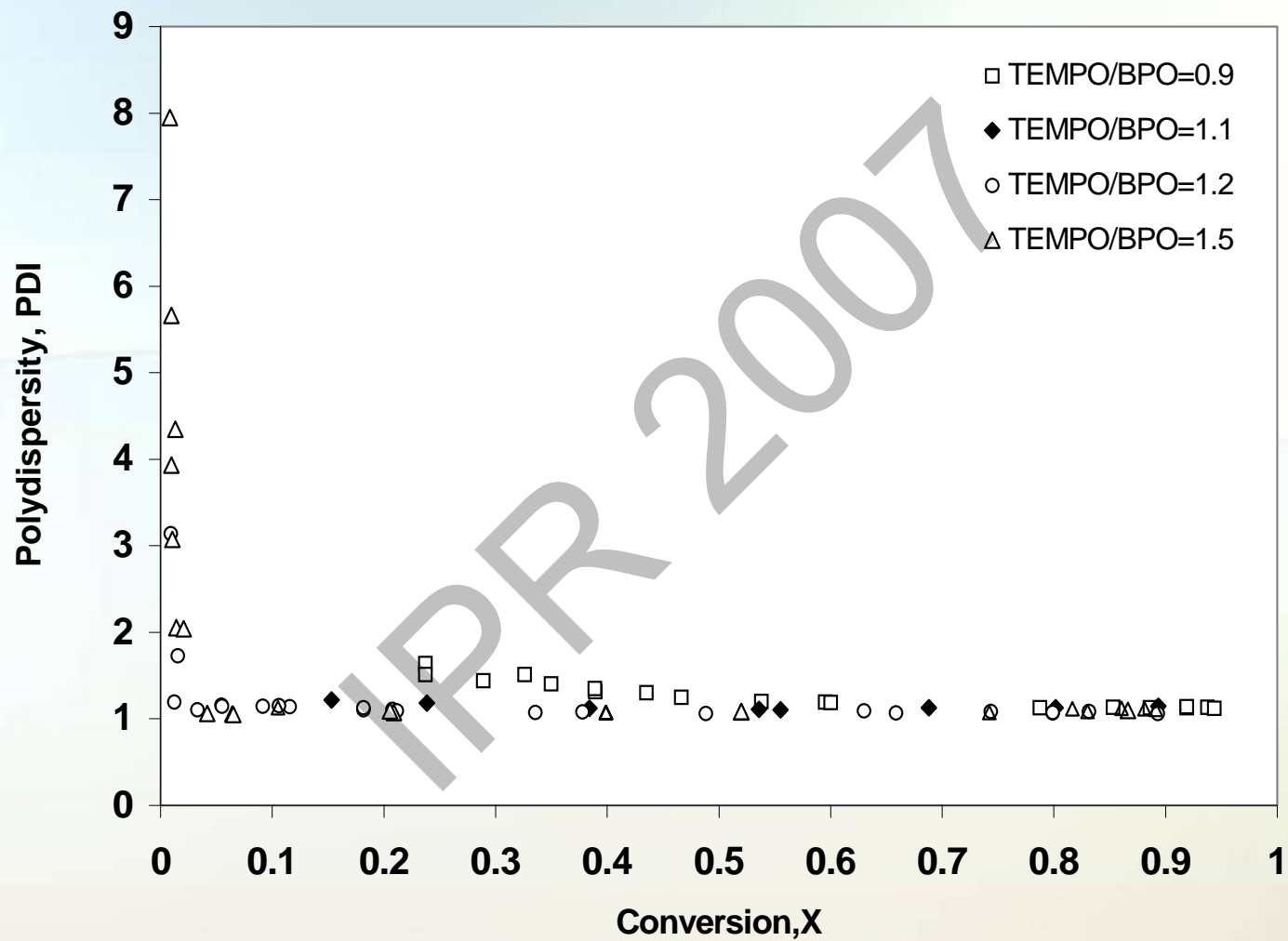
Effect of TEMPO/BPO Ratio



STY polymerization at 120 °C, $[BPO]_0 = 0.036 \text{ M}$



STY polymerization at 120° C, [BPO]₀ = 0.036 M

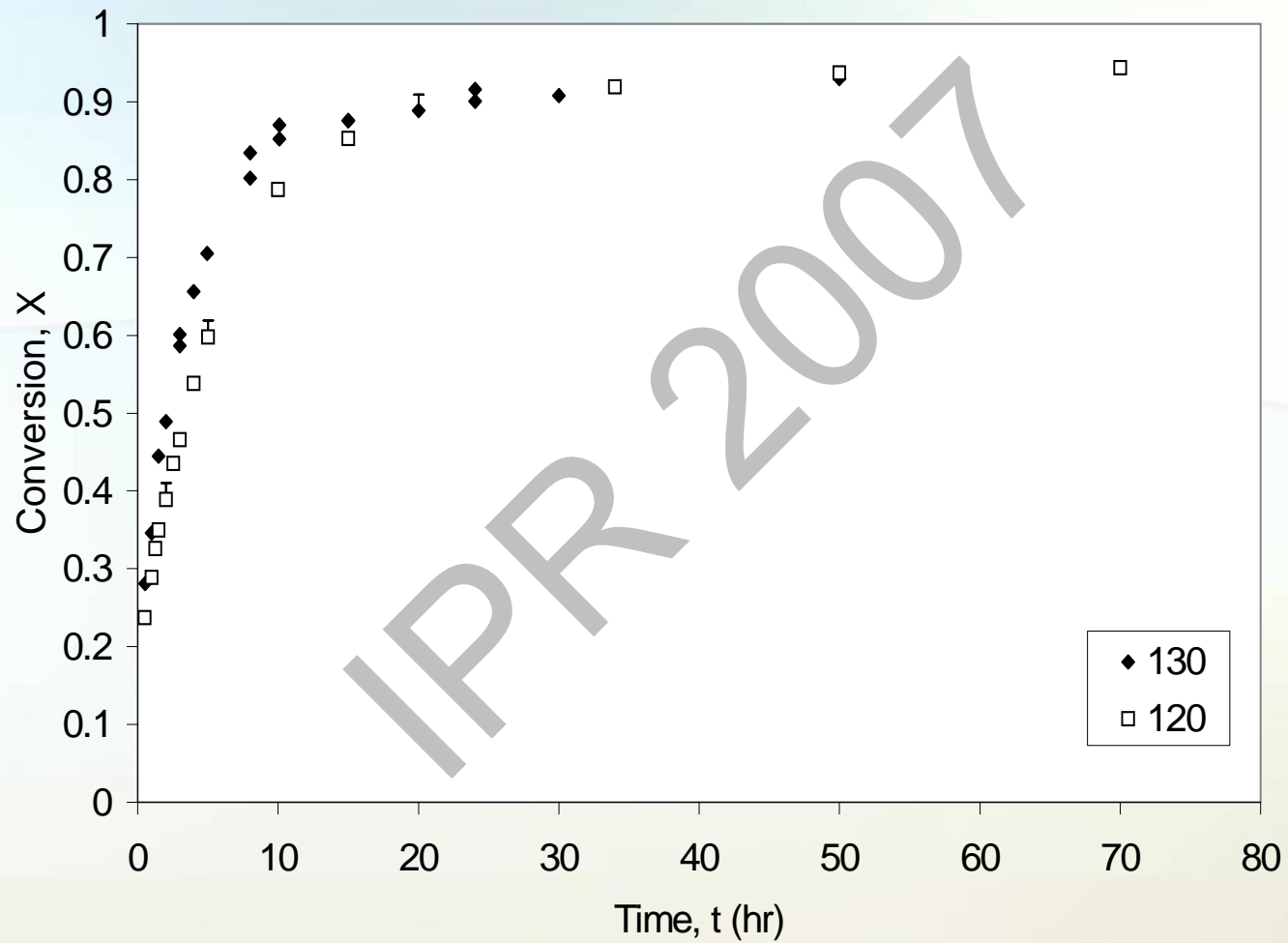


STY polymerization at 120^o C, [BPO]₀ = 0.036 M

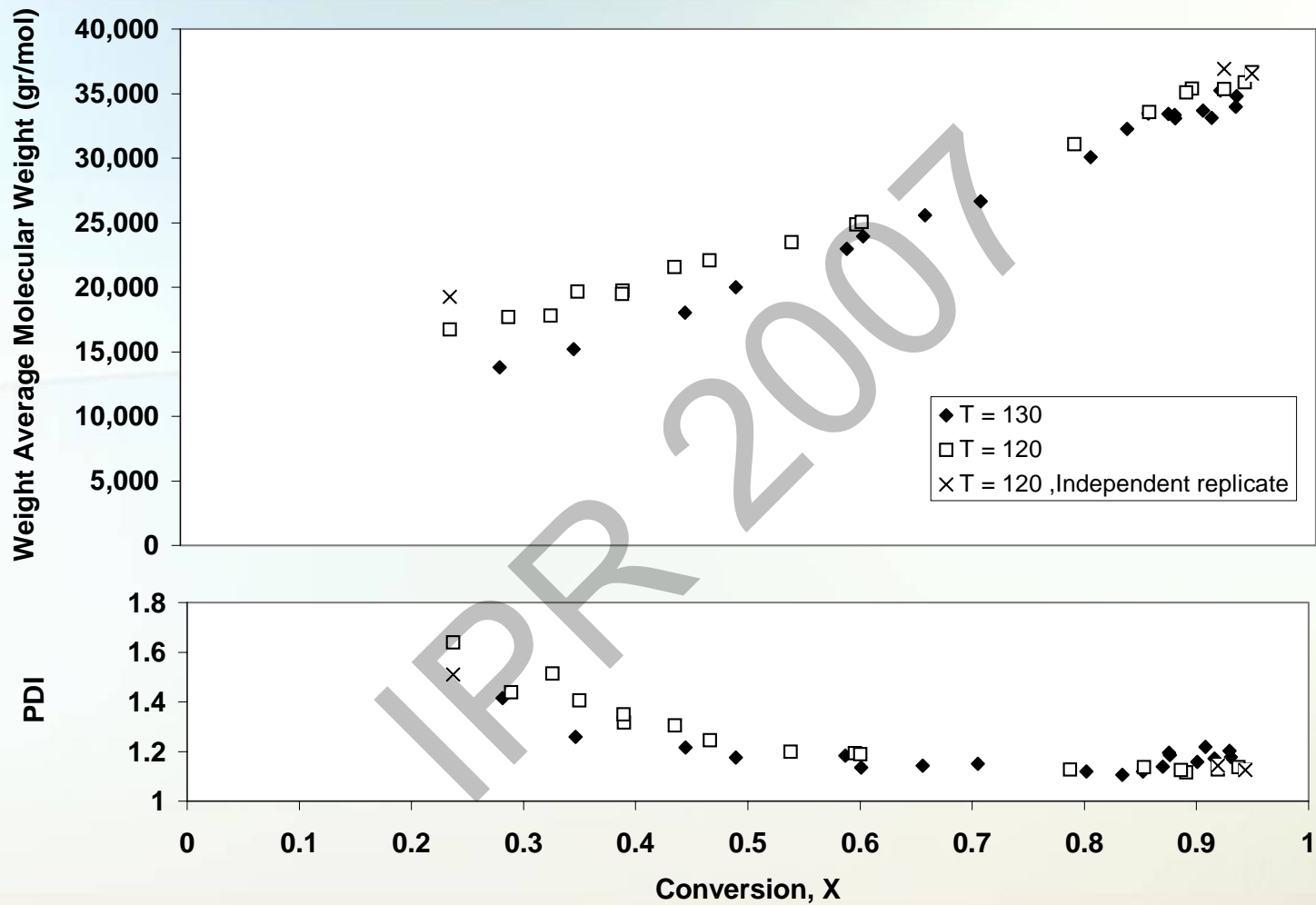
Observations

- The larger the TEMPO/ BPO ratio (the more TEMPO in the recipe), the slower the polymerization
- Higher values of average molecular weights, M_n and M_w , are obtained as TEMPO/BPO ratio decreases
- Low PDI values, below 1.2
- Similar trends with experimental data at 130°C (not shown)

Effect of Temperature



STY polymerization at TEMPO / BPO = 0.9



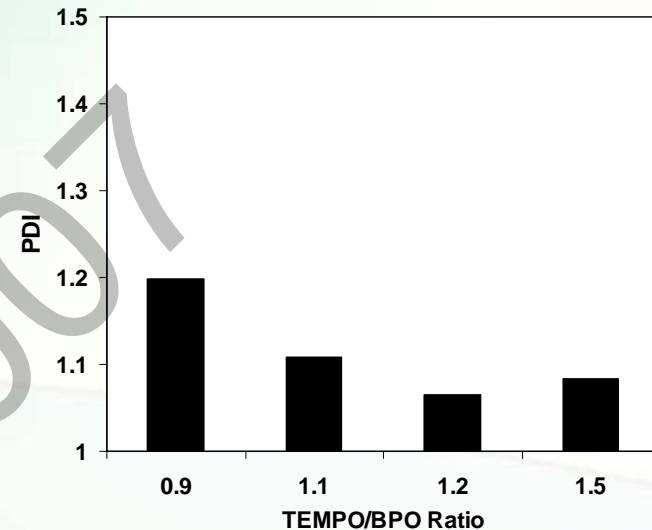
STY polymerization at TEMPO / BPO = 0.9

Mathematical Modeling

- Kinetic model based on a detailed reaction mechanism
- Molar balances; population balances; set of ordinary differential equations
- General trends OK
- Satisfactory prediction of experimental data but more work needs to be done (fine-tuning of key but uncertain parameters)

Concluding Remarks

- “Optimal” ratio to achieve lowest polydispersity seems to be around $[\text{TEMPO}]/[\text{BPO}] = 1.2$



- There is no pronounced temperature effect at studied conditions
- Model trends and preliminary predictions satisfactory for typical polymerization variables (on going work)

Future Steps

- Experimental :
 - Comparison with unimolecular initiator
 - Different initiator (tetrafunctional vs. monofunctional initiator)
- Modeling :
 - More rigorous parameter estimation
 - Using Bayesian design to guide our experimentation for better understanding of the reaction mechanism

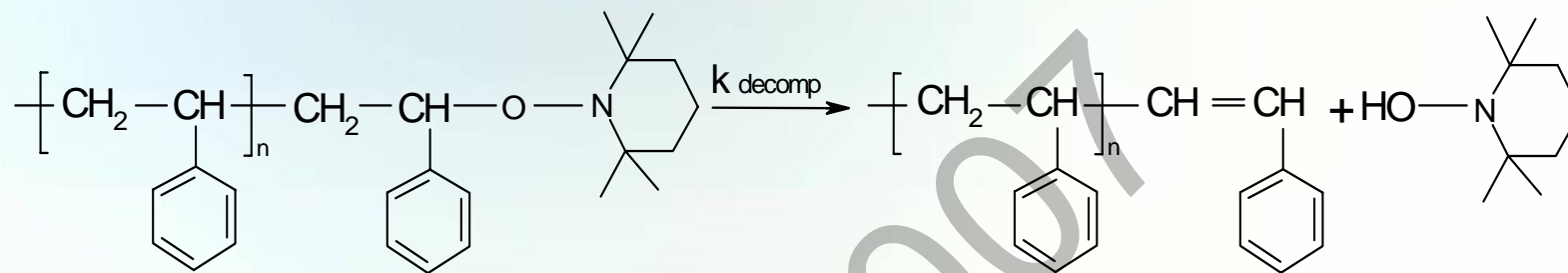
Acknowledgements

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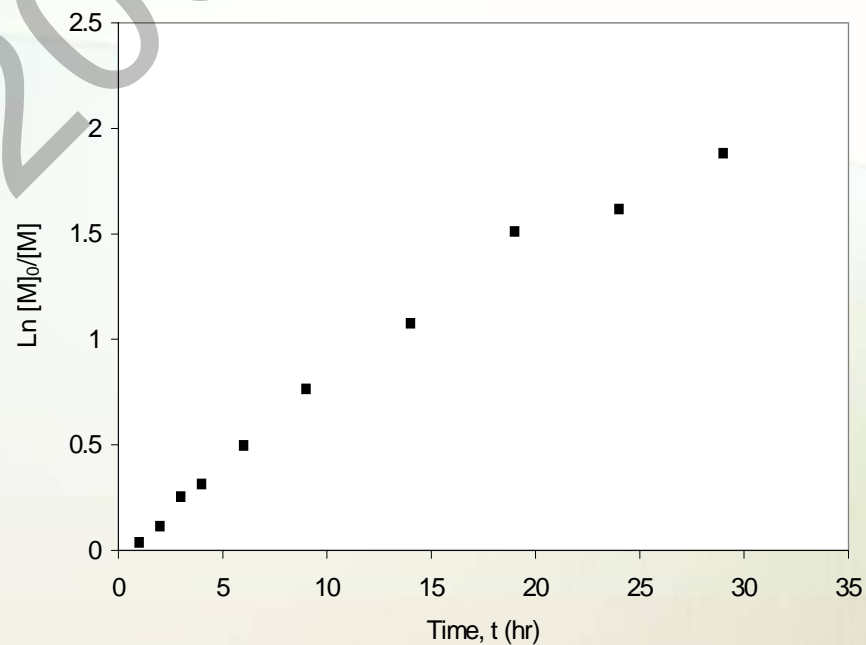
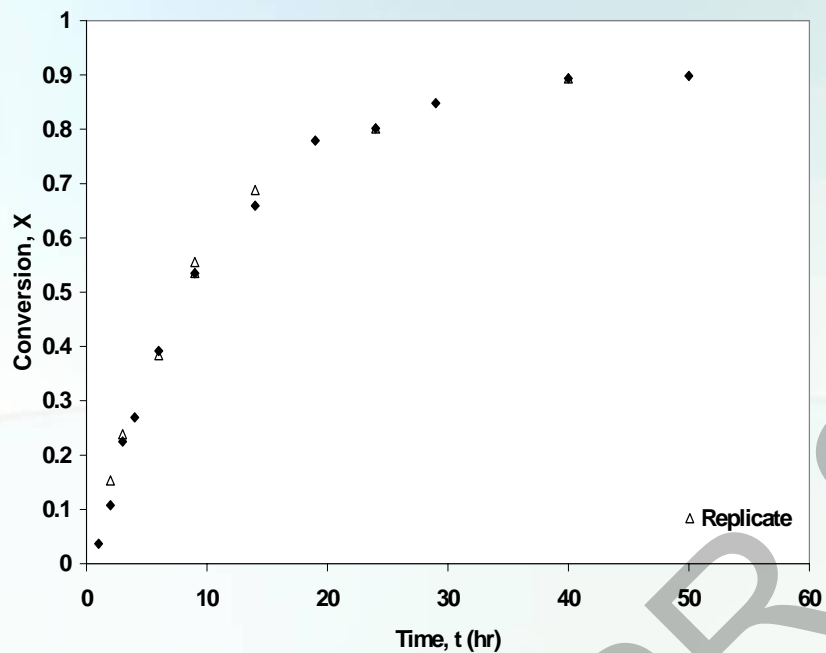


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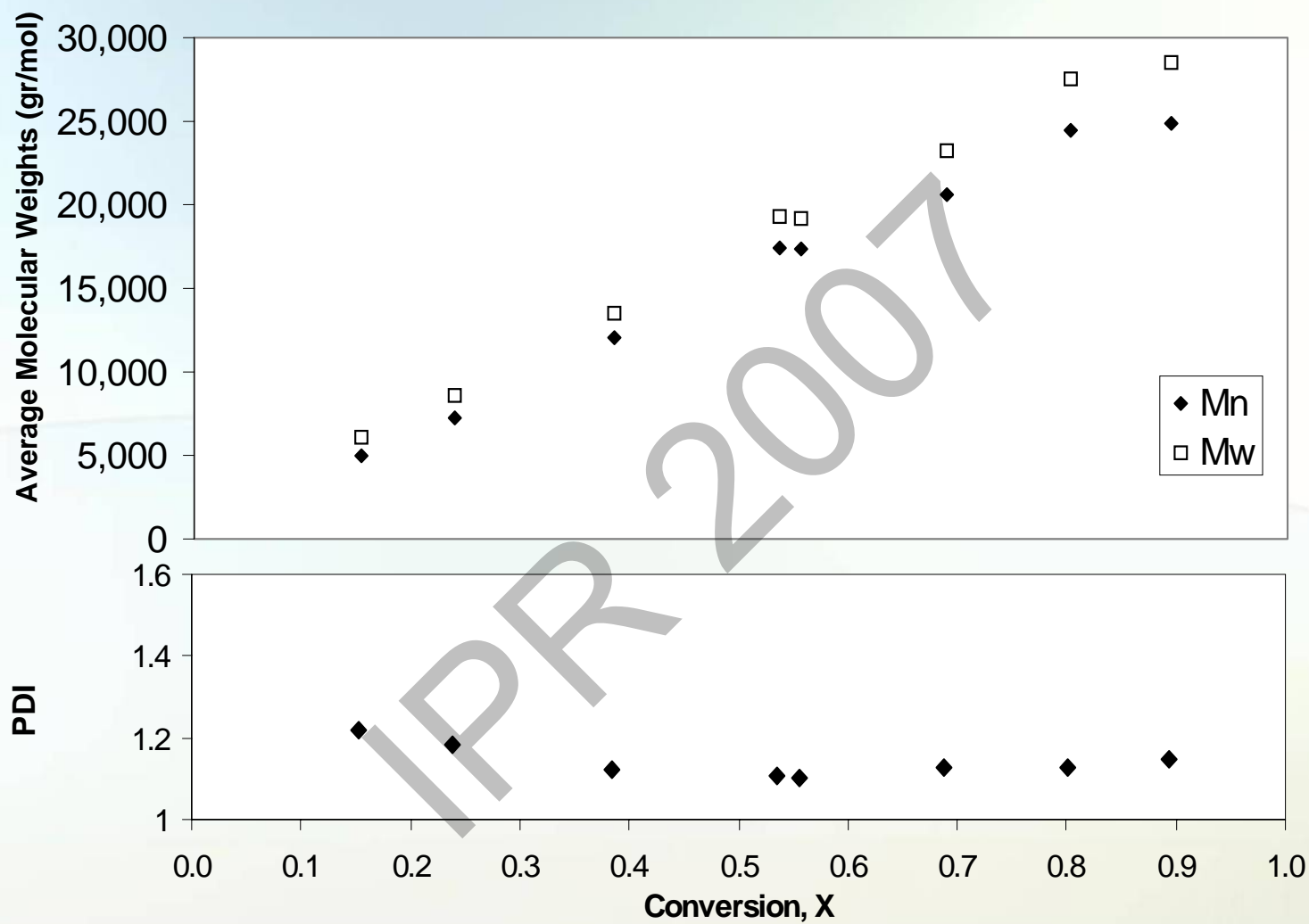
Experimental

- Polymerization
 - Ampoules (~ 4ml volume): degassed , torch-sealed, and then placed in liquid nitrogen until used
 - Isothermal oil bath
- Polymer Characterization
 - Monomer conversion
 - Gravimetry
 - Molecular weight averages and polydispersity
 - Gel permeation chromatography (GPC)

Results



STY polymerization at 120°C, TEMPO/BPO = 1.1

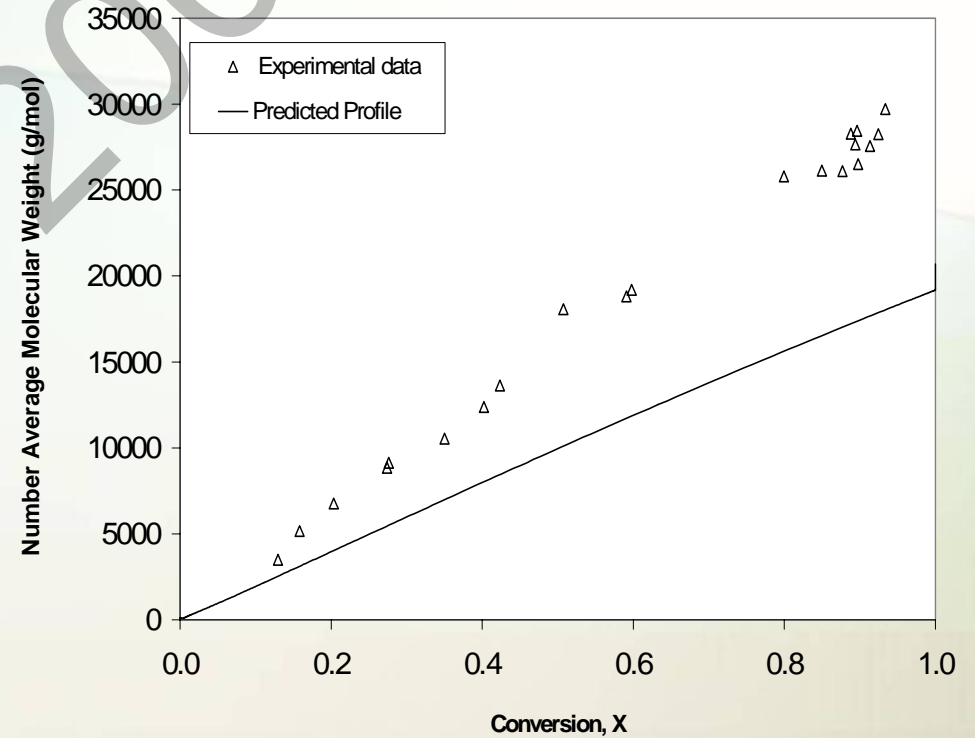
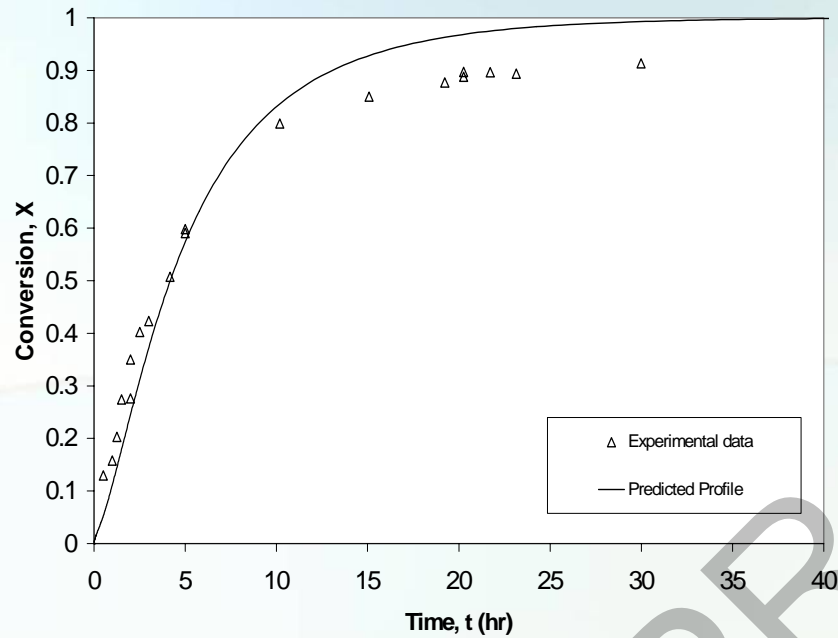


STY polymerization at 120°C, TEMPO/BPO = 1.1

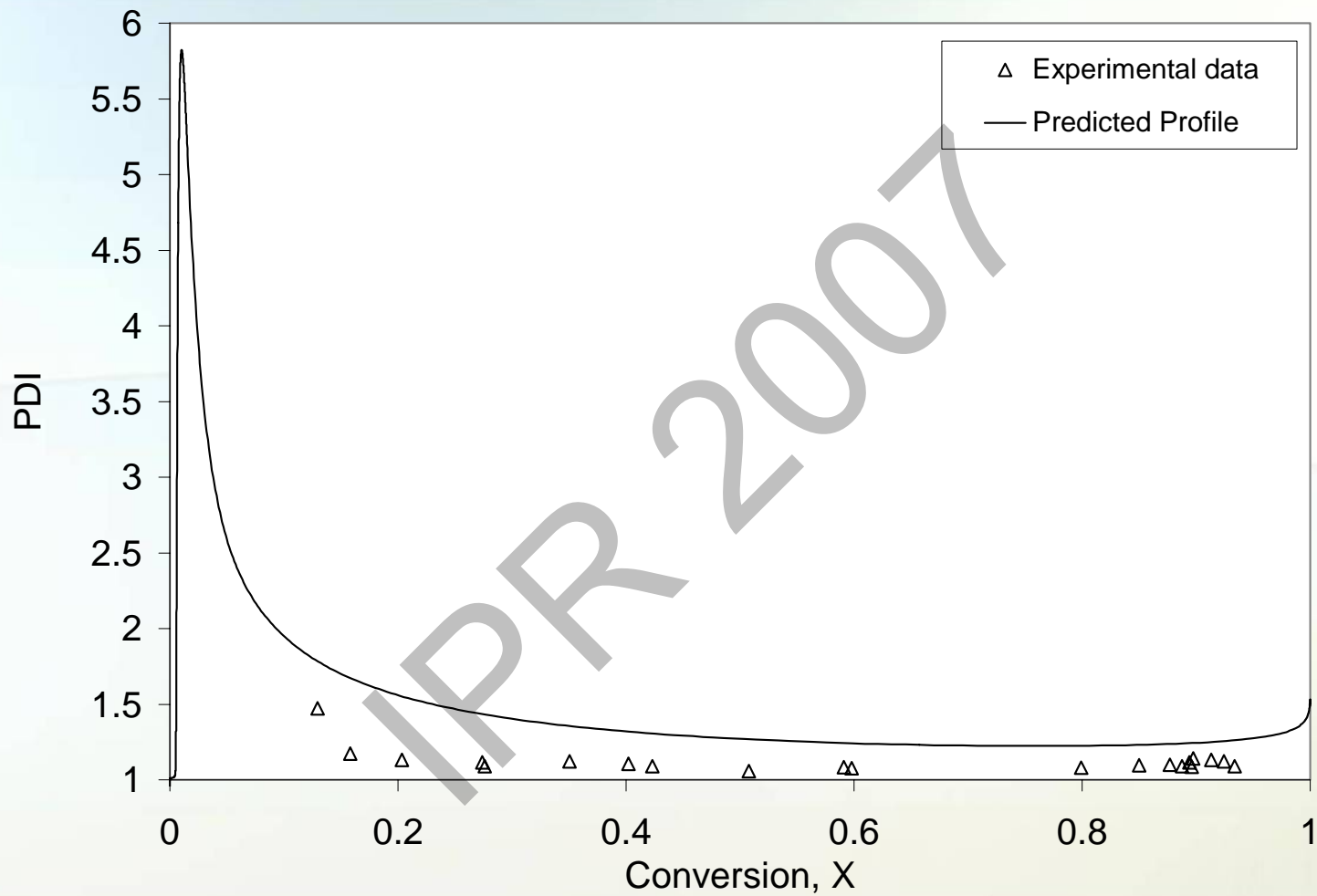
Remarks

- As expected, polymerization proceeds faster at the higher temperature
 - After about 80-85% conversion, rates are almost identical for both temperatures
- A small reduction in molecular weight values as temperature increases
- Experimental data also available for TEMPO/ BPO=1.1

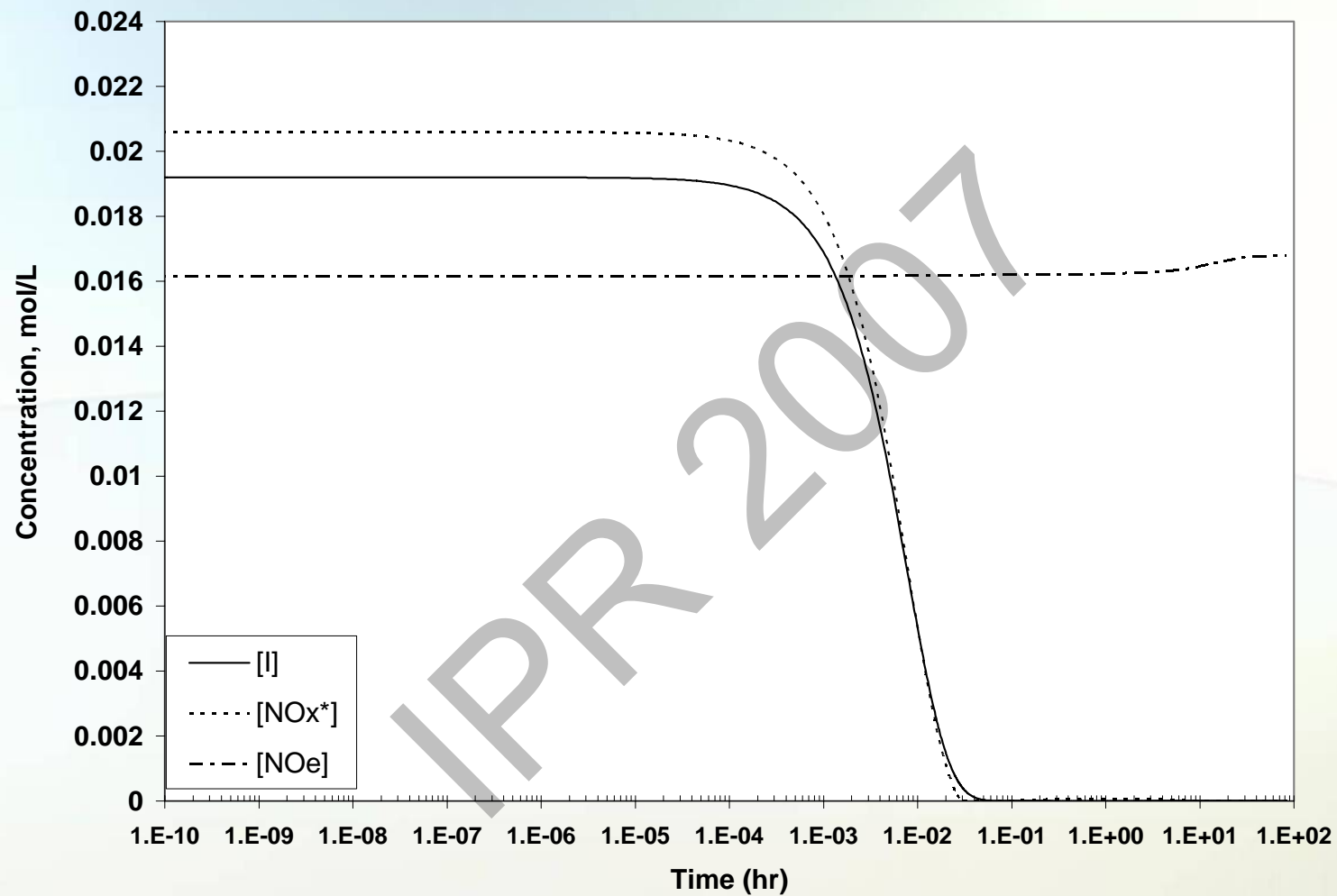
Mathematical Modeling



STY polymerization at $T = 130\text{ }^{\circ}\text{C}$, TEMPO/BPO = 1.1



STY polymerization at $T = 130\text{ }^{\circ}\text{C}$, TEMPO/BPO = 1.1



Typical calculated profiles for concentration of initiator, nitroxyl stable radicals and alcoxyamine

Kinetic Mechanism (Bonilla et al., 2002)

Description	Step
Chemical initiation	$I \xrightarrow{k_d} 2R_{in} \bullet$
Nitroxyl ether decomposition	$NO_E \xrightleftharpoons[k_{d2}]{k_{a2}} R_{in} \bullet + NO_x \bullet$
Mayo dimerization	$M + M \xrightarrow{k_{dim}} D$
Thermal initiation	$M + D \xrightarrow{k_{ia}} D \bullet + M \bullet$
First propagation (primary radicals)	$R_{in} \bullet + M \xrightarrow{k_p} R_1 \bullet$
First propagation (monomeric radicals)	$M \bullet + M \xrightarrow{k_p} R_1 \bullet$
First propagation (dimeric radicals)	$D \bullet + M \xrightarrow{k_p} R_1 \bullet$
Propagation	$R_r \bullet + M \xrightarrow{k_p} R_{r+1} \bullet$
Dormant living exchange (monomeric alkoxyamine)	$M \bullet + NO_x \bullet \xrightleftharpoons[k_{da}]{k_a} MNO_x$
Dormant living exchange (polymeric alkoxyamine)	$R_r \bullet + NO_x \bullet \xrightleftharpoons[k_{da}]{k_a} R_rNO_x$
Alkoxyamine decomposition	$MNO_x \xrightarrow{k_{decomp}} M + HNO_x$
Rate enhancement reaction	$D + NO_x \bullet \xrightarrow{k_{h3}} D \bullet + HNO_x$
Termination by combination	$R_r \bullet + R_s \bullet \xrightarrow{k_{tc}} P_{r+s}$
Termination by disproportionation	$R_r \bullet + R_s \bullet \xrightarrow{k_{td}} P_r + P_s$
Transfer to monomer	$R_r \bullet + M \xrightarrow{k_{fM}} P_r + M \bullet$
Transfer to dimer	$R_r \bullet + D \xrightarrow{k_{fD}} P_r + D \bullet$

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First propagation (dimeric radicals)	$D \bullet + M \xrightarrow{k_p} R_1 \bullet$
Propagation	$R_r \bullet + M \xrightarrow{k_p} R_{r+1} \bullet$
Dormant living exchange (monomeric alkoxyamine)	$M \bullet + NO_x \bullet \xrightleftharpoons[k_{da}]{k_a} MNO_x$
Dormant living exchange (polymeric alkoxyamine)	$R_r \bullet + NO_x \bullet \xrightleftharpoons[k_{da}]{k_a} R_rNO_x$
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Termination by disproportionation	$R_r \bullet + R_s \bullet \xrightarrow{k_{td}} P_r + P_s$
Transfer to monomer	$R_r \bullet + M \xrightarrow{k_{fM}} P_r + M \bullet$
Transfer to dimer	$R_r \bullet + D \xrightarrow{k_{fD}} P_r + D \bullet$



Thermal Self initiation of Styrene

