

Active Site Identification and Mathematical Modeling of Polypropylene Made with Ziegler-Natta Catalysts

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OUTLINE

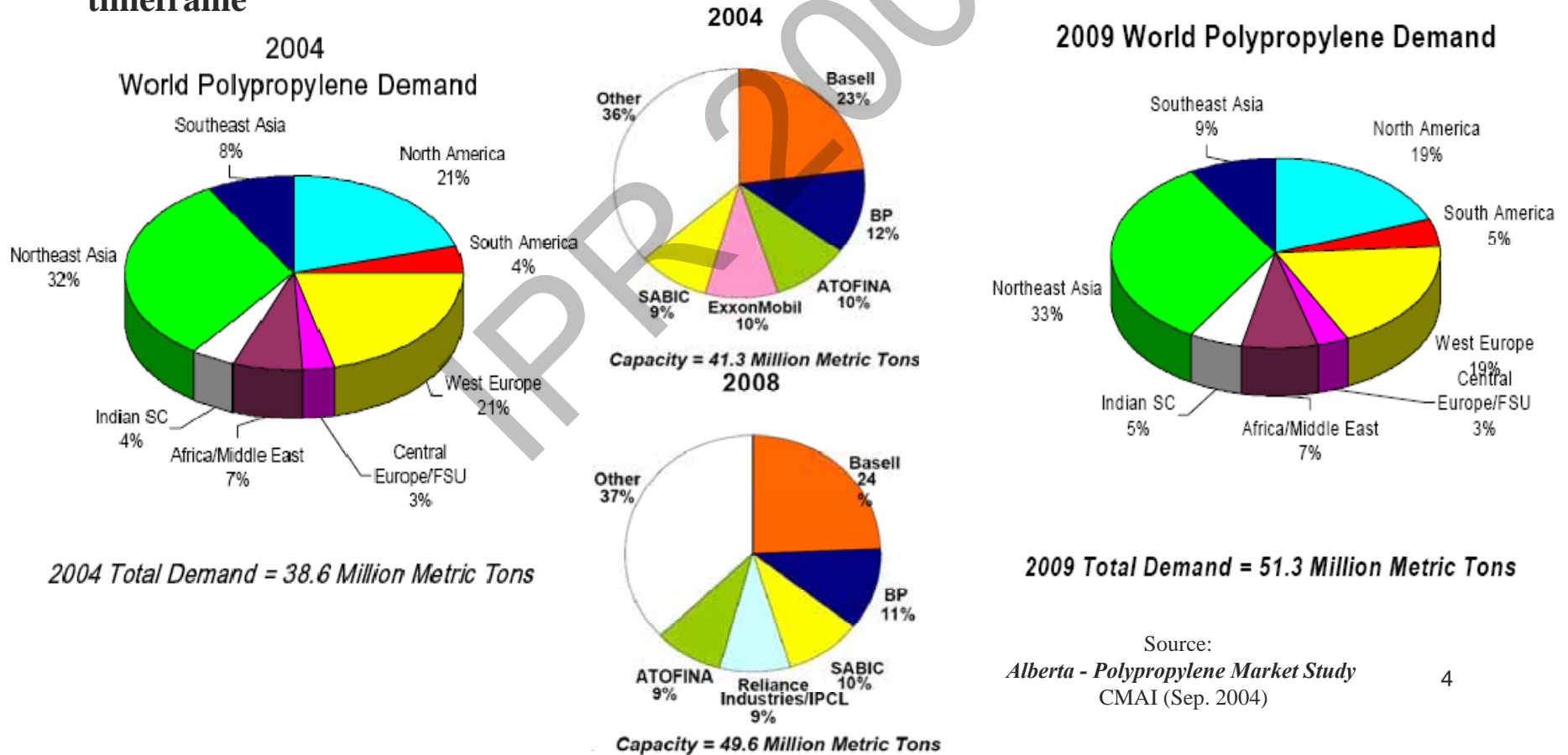
- **OBJECTIVES**
- **INTRODUCTION**
 - **Saudi Basic Industries Corporation “SABIC”**
 - **Polypropylene Facts & Figures**
 - **Polypropylene Structure**
- **MODEL & RESULTS**
 - **Population Balance and Method of Moments:**
 - ❖ **Model**
 - ❖ **Results:**
 - **Steady State vs. Dynamic CSTR’s Solutions**
 - **Monte Carlo Approach:**
 - ❖ **Model**
 - ❖ **Results**
- **CURRENT & FUTURE WORK**
- **CONCLUSION**

OBJECTIVES

- **Develop mathematical models for the steady-state and dynamic simulation of propylene polymerization with Ziegler-Natta catalysts in industrial reactors using different modeling approaches: population balances and method of moments and the Monte Carlo techniques**
- **Describe, for the first time, site transformation by electron donors, with a mathematical model and quantify its effect on polymer chain microstructure**

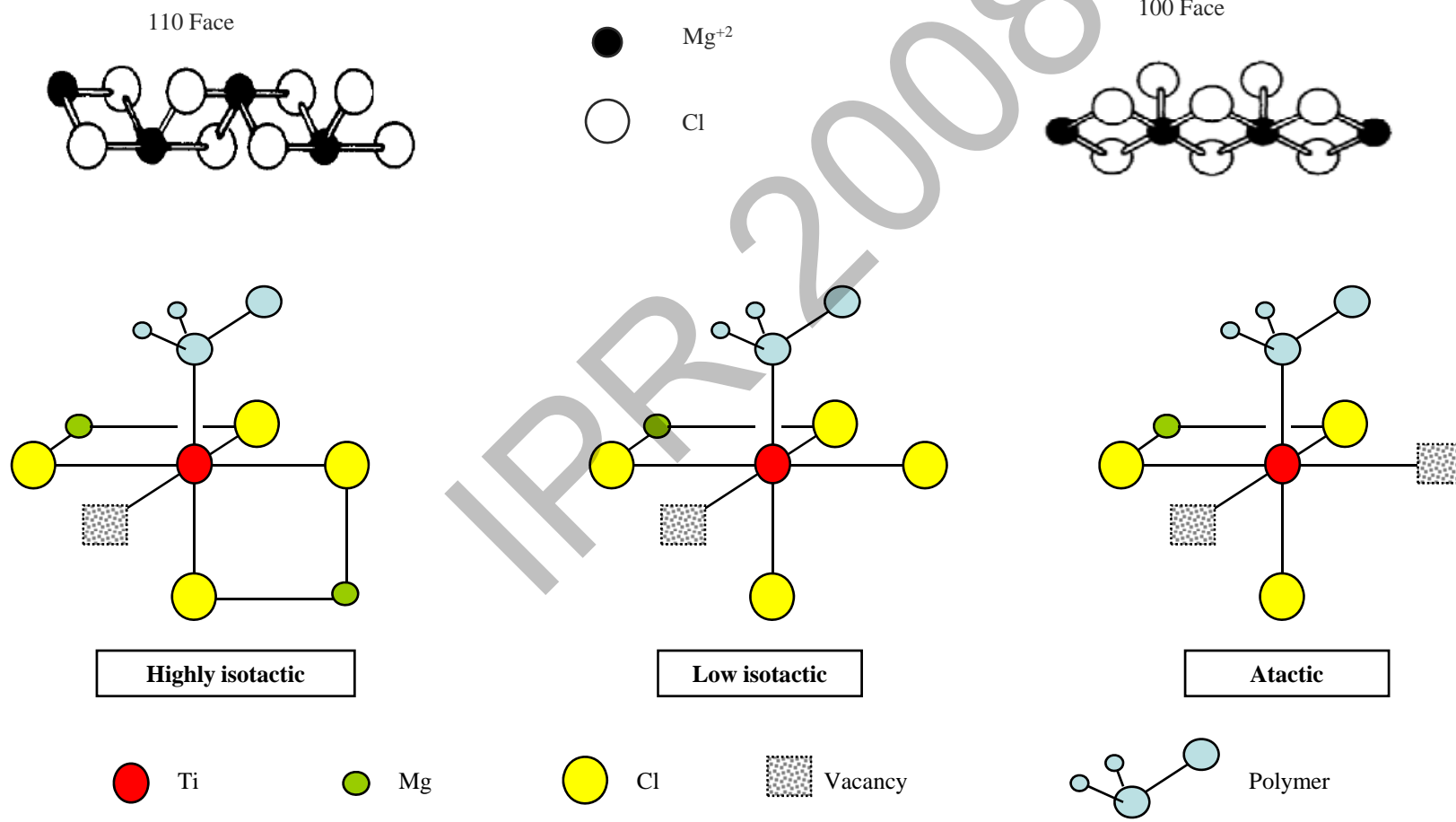
INTRODUCTION

- SABIC is the world's fourth largest producer of polyolefins. It is the world's third largest producer of polyethylene and the fifth largest producer of polypropylene.
- Overall polypropylene demand is forecasted to grow globally at a rate of 5.8% in 2004-2009 timeframe



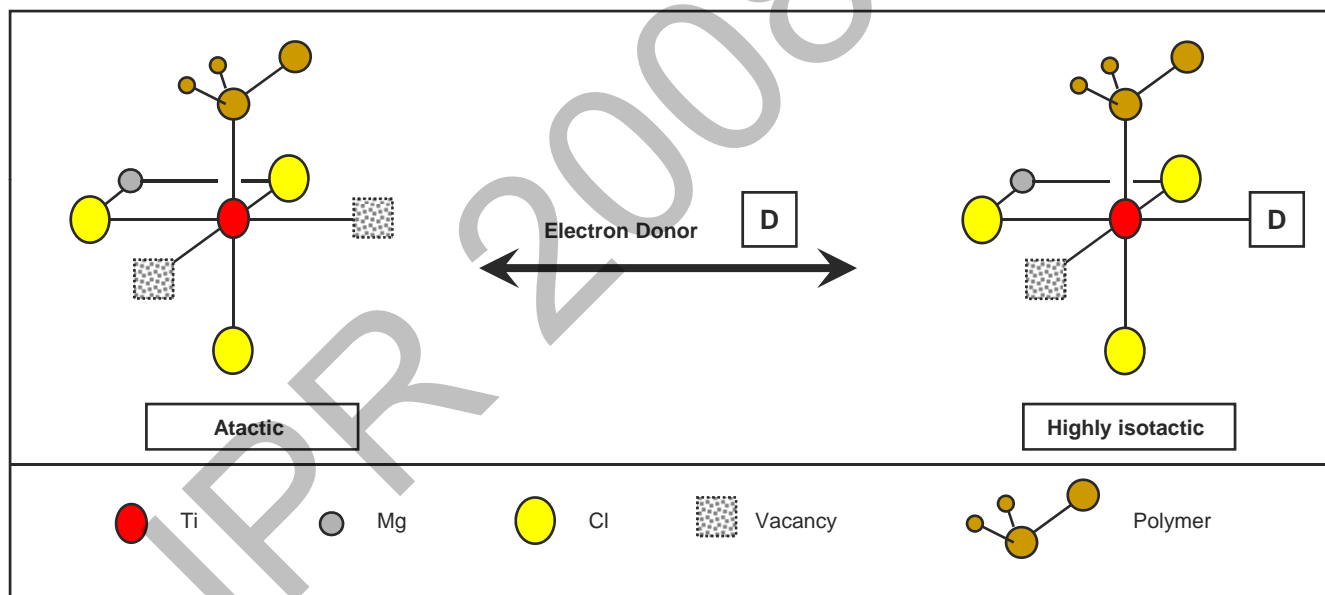
Source:
 Alberta - Polypropylene Market Study
 CMAI (Sep. 2004)

Z-N Multiple Site Catalyst

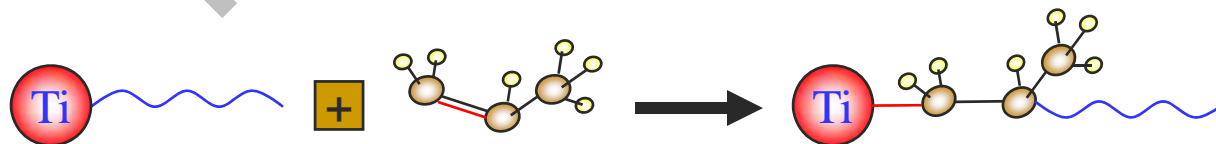


Reaction Mechanism:

➤ **Site Transformation:**



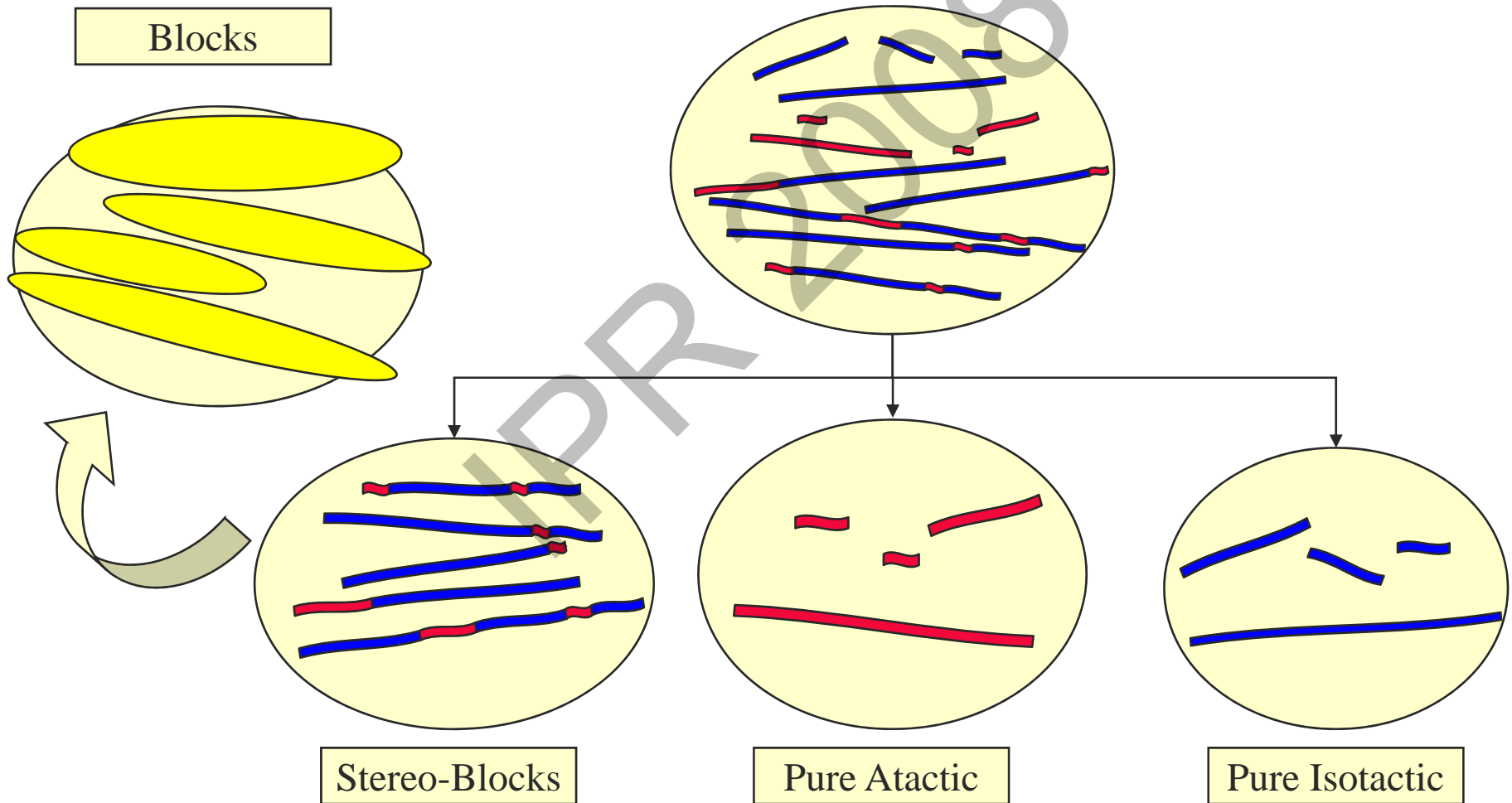
➤ **Propagation:**



➤ **Termination:**



Species Classification



A horizontal line with a gradient from light green to white, flanked by large black and gold brackets.

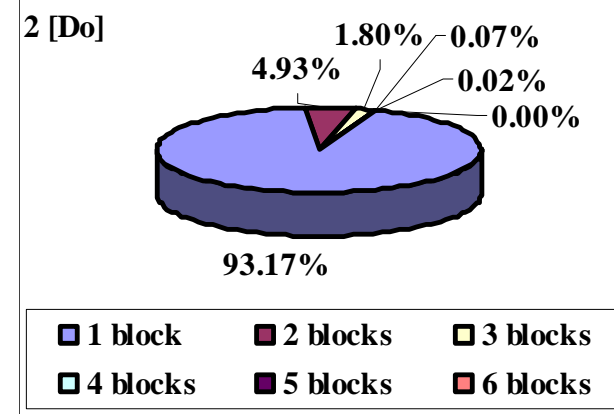
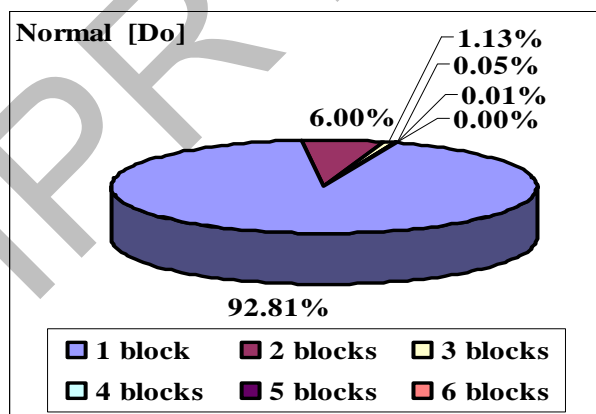
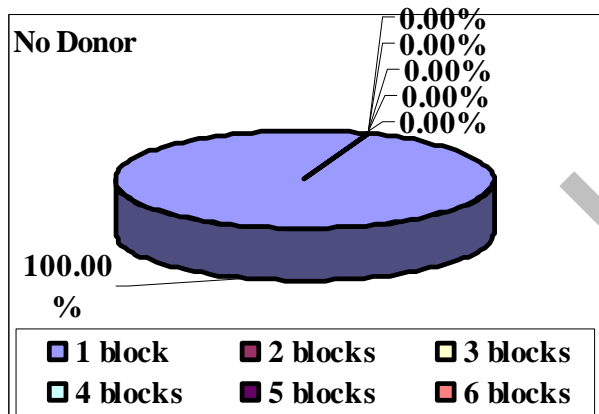
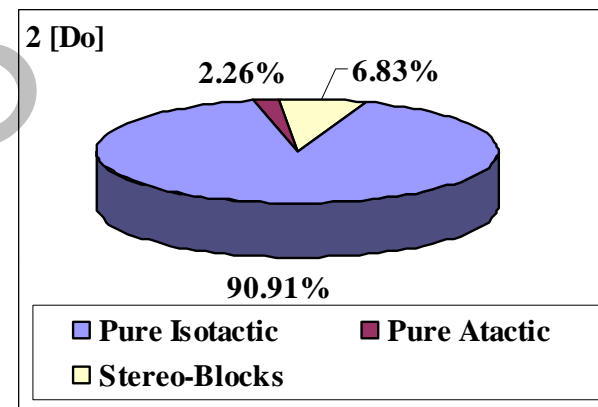
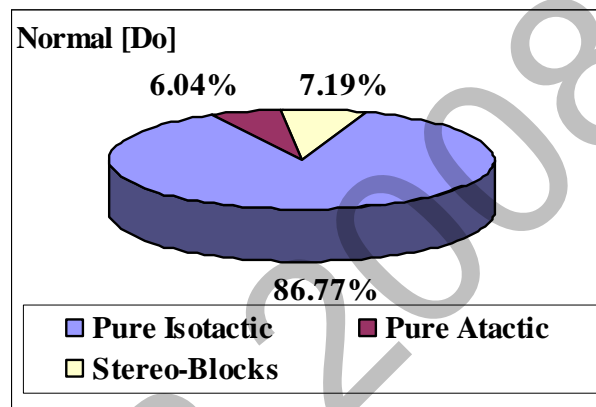
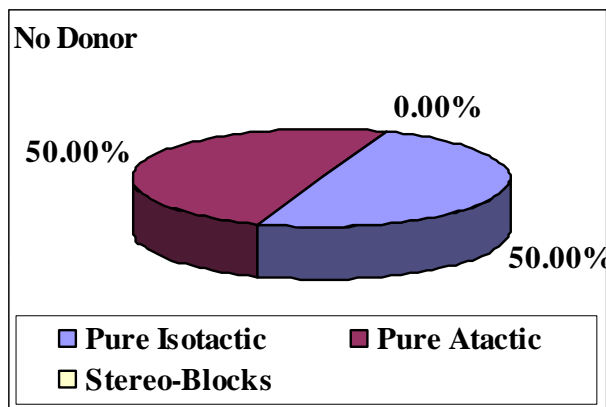
Single Site

Steady State Simulation Results

IPR 2008

Steady State Solution for One Site Type:
 $R_{P1}/R_{P2} = 1$, $R_{P1}/R_{T1} = 1364$, $R_{P2}/R_{T2} = 1364$

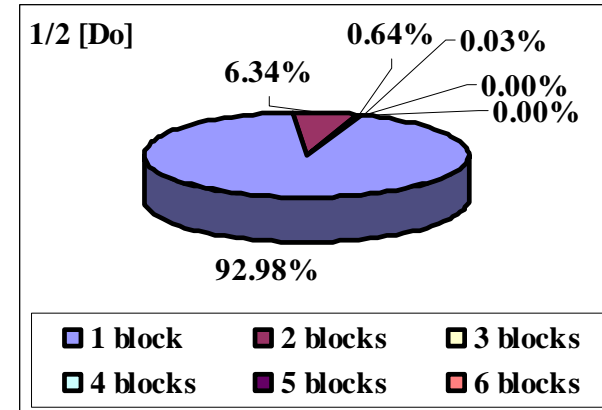
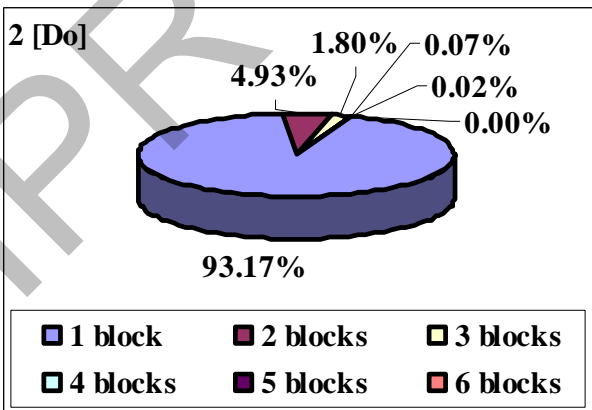
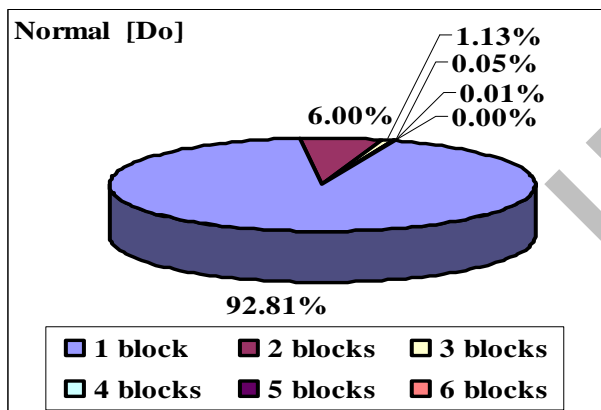
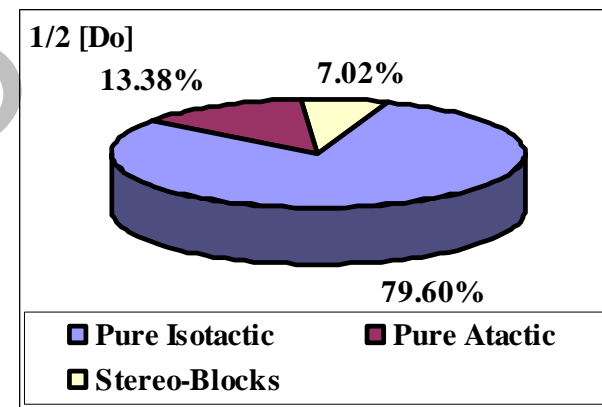
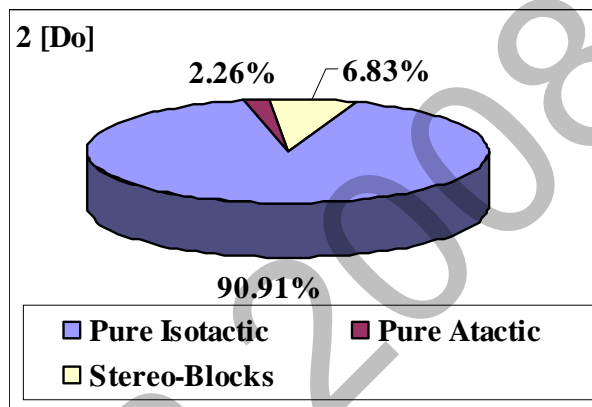
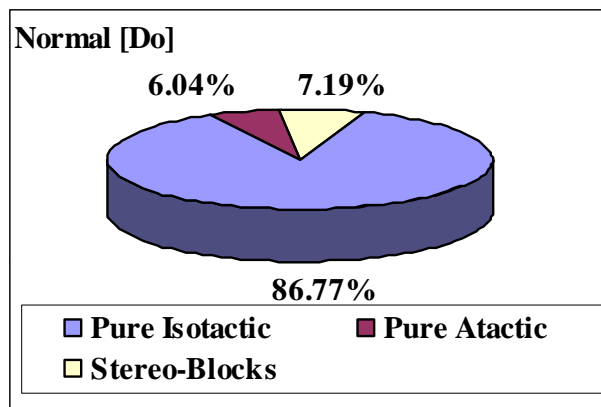
Effect of Changing the Electron Donor Concentration 1/2



M_n (g/mol)	57,000	57,000	57,000
M_w (g/mol)	114,000	114,000	114,000
PDI	2.00	2.00	2.00

Steady State Solution for One Site Type:
 $R_{P1}/R_{P2} = 1$, $R_{P1}/R_{T1} = 1364$, $R_{P2}/R_{T2} = 1364$

Effect of Changing the Electron Donor Concentration 2/2



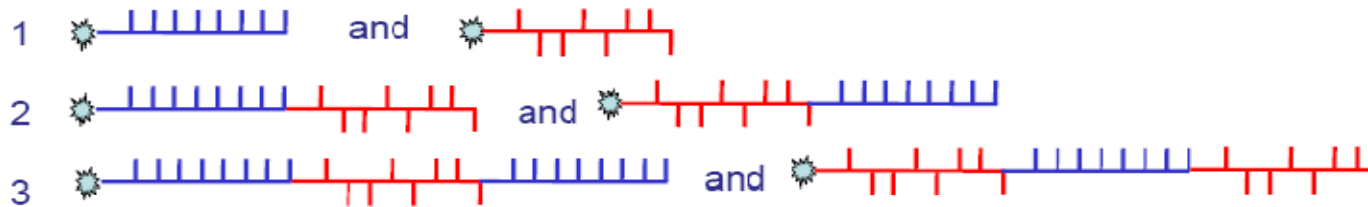
M_n (g/mol)	57,000	57,000	57,000
M_w (g/mol)	114,000	114,000	114,000
PDI	2.00	2.00	2.00

Steady State Solution for One Site Type

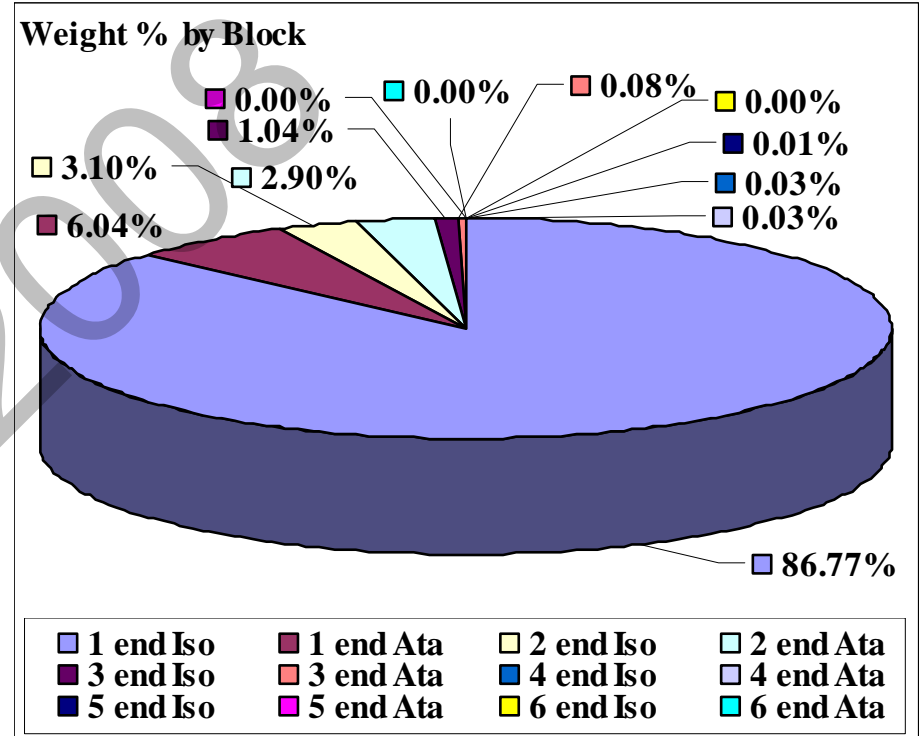
Block's Properties and Their Weight Distribution

<i>i</i>	End Iso			End Ata		
	Mn	Mw	PD	Mn	Mw	PD
1	56,000	112,000	2.00	46,000	92,000	2.00
2	102,000	153,000	1.50	102,000	153,000	1.50
3	158,000	211,000	1.34	148,000	198,000	1.34
4	204,000	256,000	1.25	204,000	256,000	1.25
5	260,000	313,000	1.20	250,000	301,000	1.20
6	307,000	358,000	1.17	307,000	358,000	1.17

i = Block #

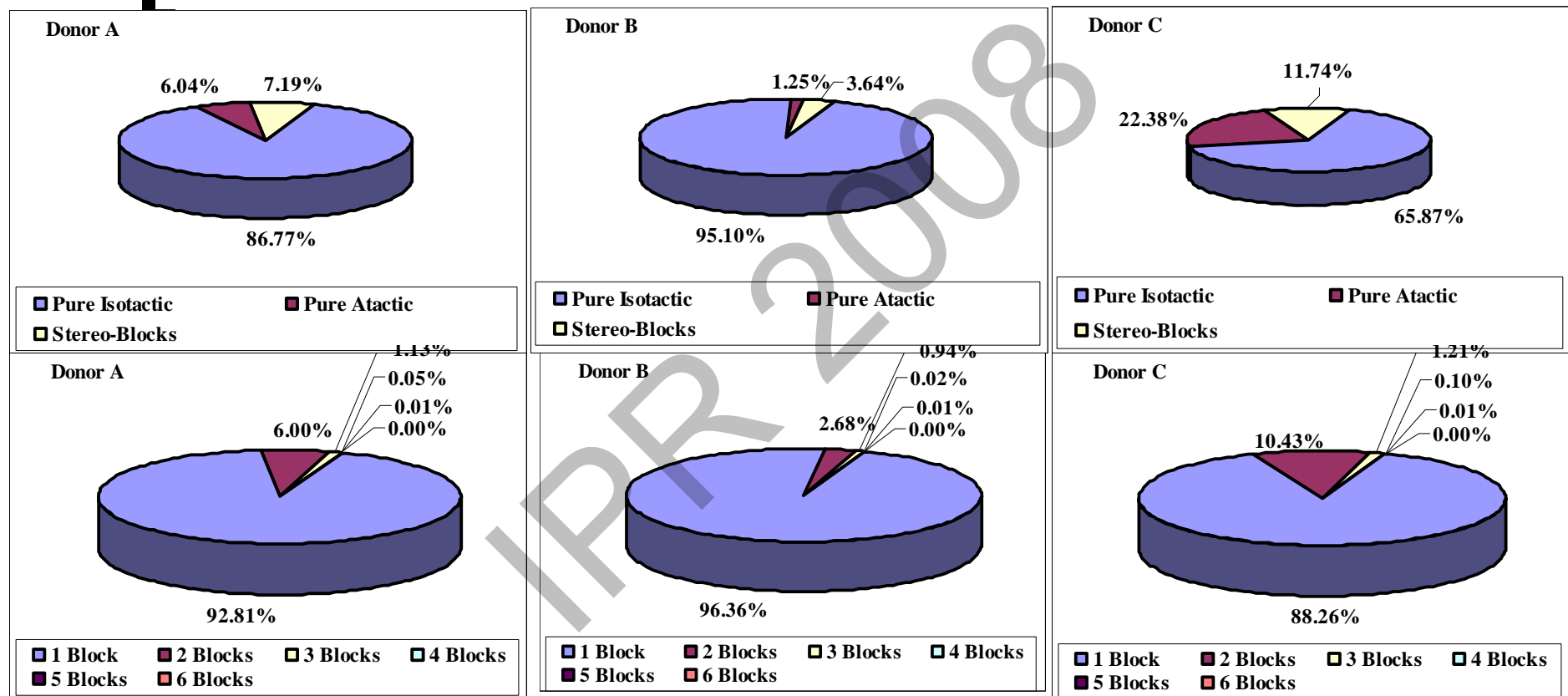


etc.



Steady State Solution for One Site Type

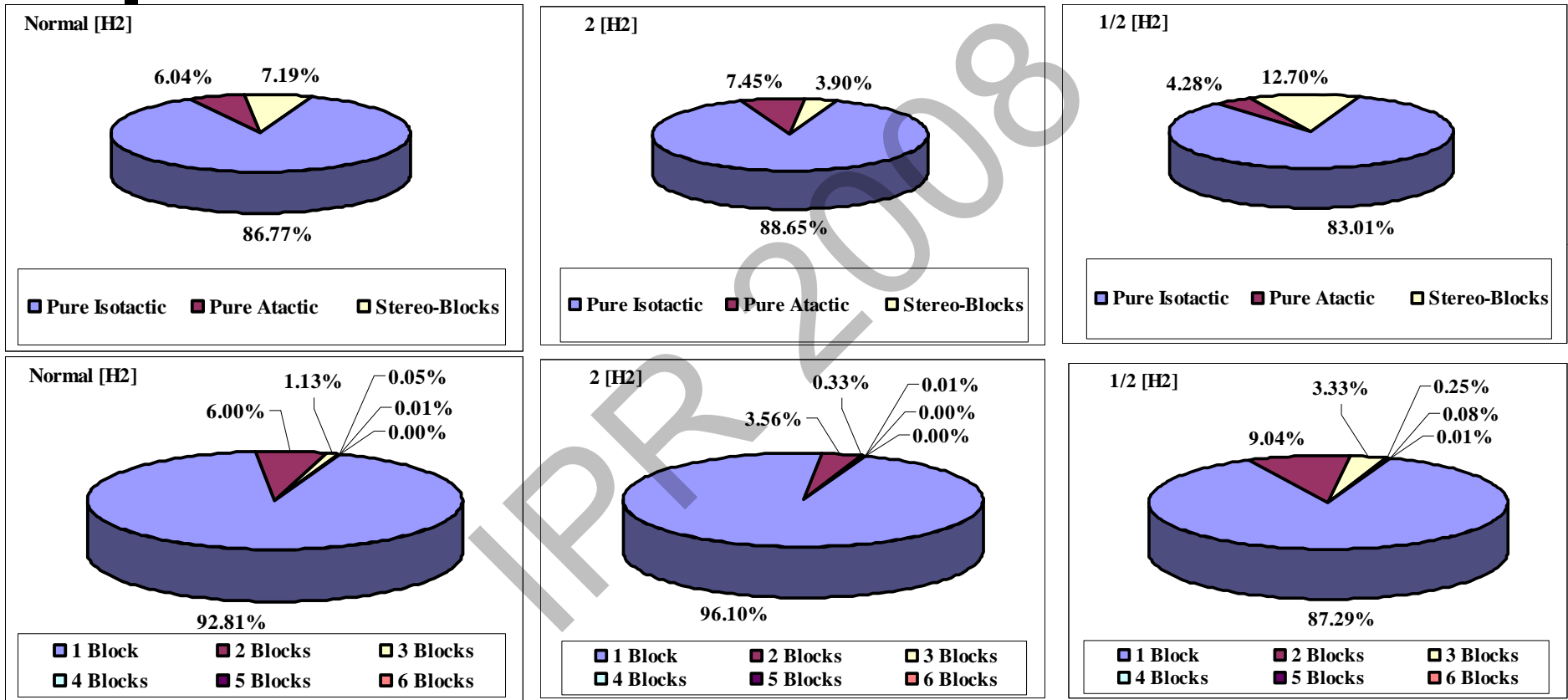
Effect of Changing the Donor Type



K^+ / K_A^+	1	2	0.5	
K^- / K_A^-	1	0.5	2	
M_n g/mol	57,000	57,000	57,000	
M_w g/mol	114,000	114,000	114,000	13
PDI	2.00	2.00	2.00	

Steady State Solution for One Site Type

Effect of Changing the Hydrogen Concentration



$$R_{P1}/R_{T1} = 1364, R_{P2}/R_{T2} = 1364$$

$$R_{P1}/R_{T1} = 682, R_{P2}/R_{T2} = 682$$

$$R_{P1}/R_{T1} = 2727, R_{P2}/R_{T2} = 2727$$

M_n g/mol	57,000	29,000	114,000
M_w g/mol	114,000	58,000	228,000
PDI	2.00	2.00	2.00

Multiple Sites

Steady State Simulation Results

Summary Results for a 4-Site Model of Propylene Polymerization

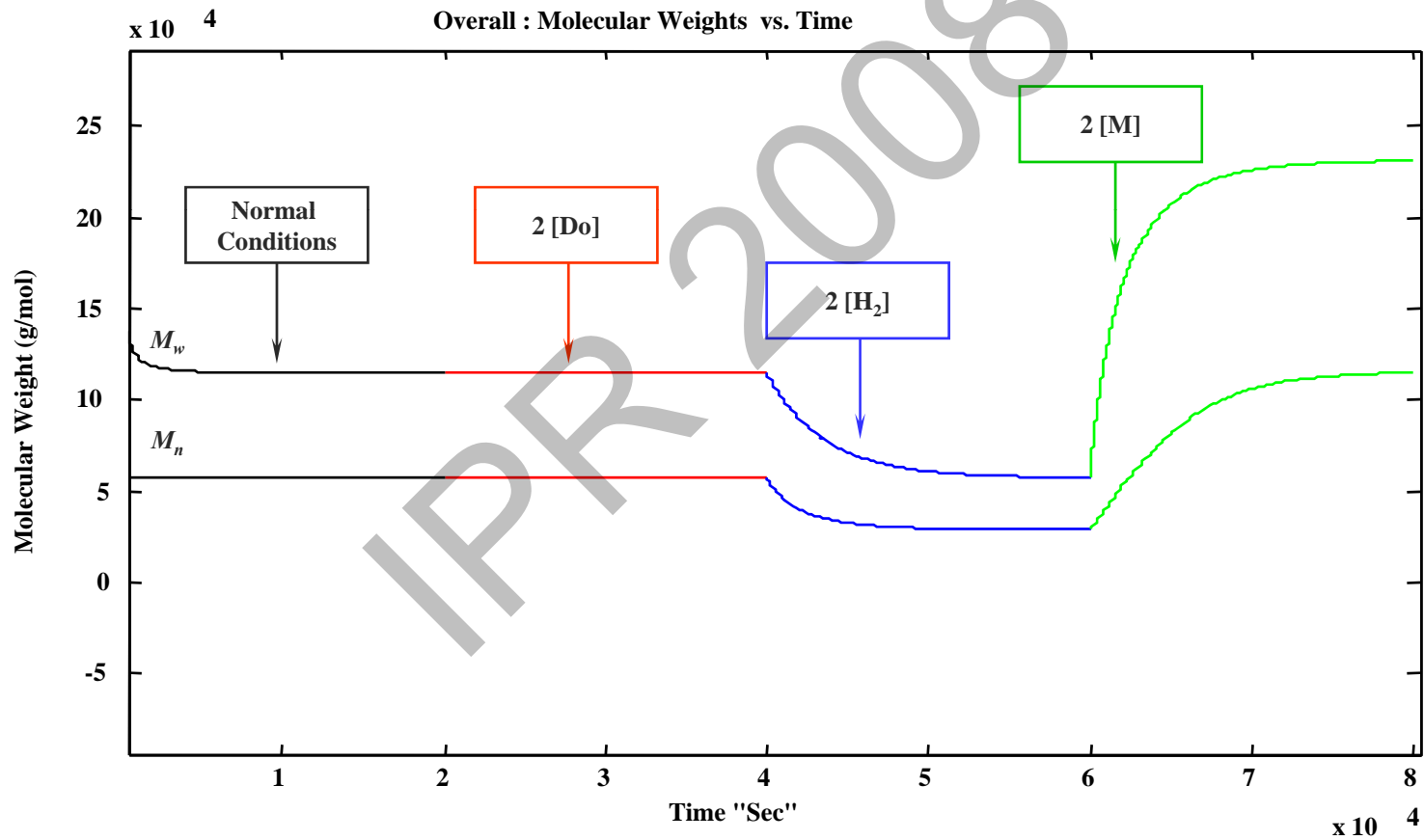
Site	Overall	1	2	3	4
	Mass %	Mass %	Mass %	Mass %	Mass %
Pure Isotactic	98.22%	100 %	100 %	93.40%	86.47%
Pure Atactic	0.30%	0.0 %	0.0 %	2.84%	0.88%
Stereo-Blocks	1.48%	0.0 %	0.0 %	3.76%	12.64%
Block weight %:		Single-state stereospecific sites		Two-state sites	
1 block	97.98%	100 %	100 %	96.24%	87.35%
2 blocks	1.44%	0.0 %	0.0 %	3.24%	7.89%
3 blocks	0.52%	0.0 %	0.0 %	0.50%	4.25%
4 blocks	0.04%	0.0 %	0.0 %	0.01%	0.35%
5 blocks	0.01%	0.0 %	0.0 %	0.00%	0.14%
6 blocks	0.00%	0.0 %	0.0 %	0.00%	0.01%
M_n (g/mol)	52,081	62,957	167,316	7,902	191,523
M_w (g/mol)	231,513	125,890	334,595	16,013	398,055
PDI	4.45	2.00	2.00	2.03	2.08
R_{P1}/R_{P2}				2.50	6.67
R_{P1}/R_{T1}		1500	4000	194	5000
R_{P2}/R_{T2}		0	0	97	1071

Single Site

Dynamic Simulation Results

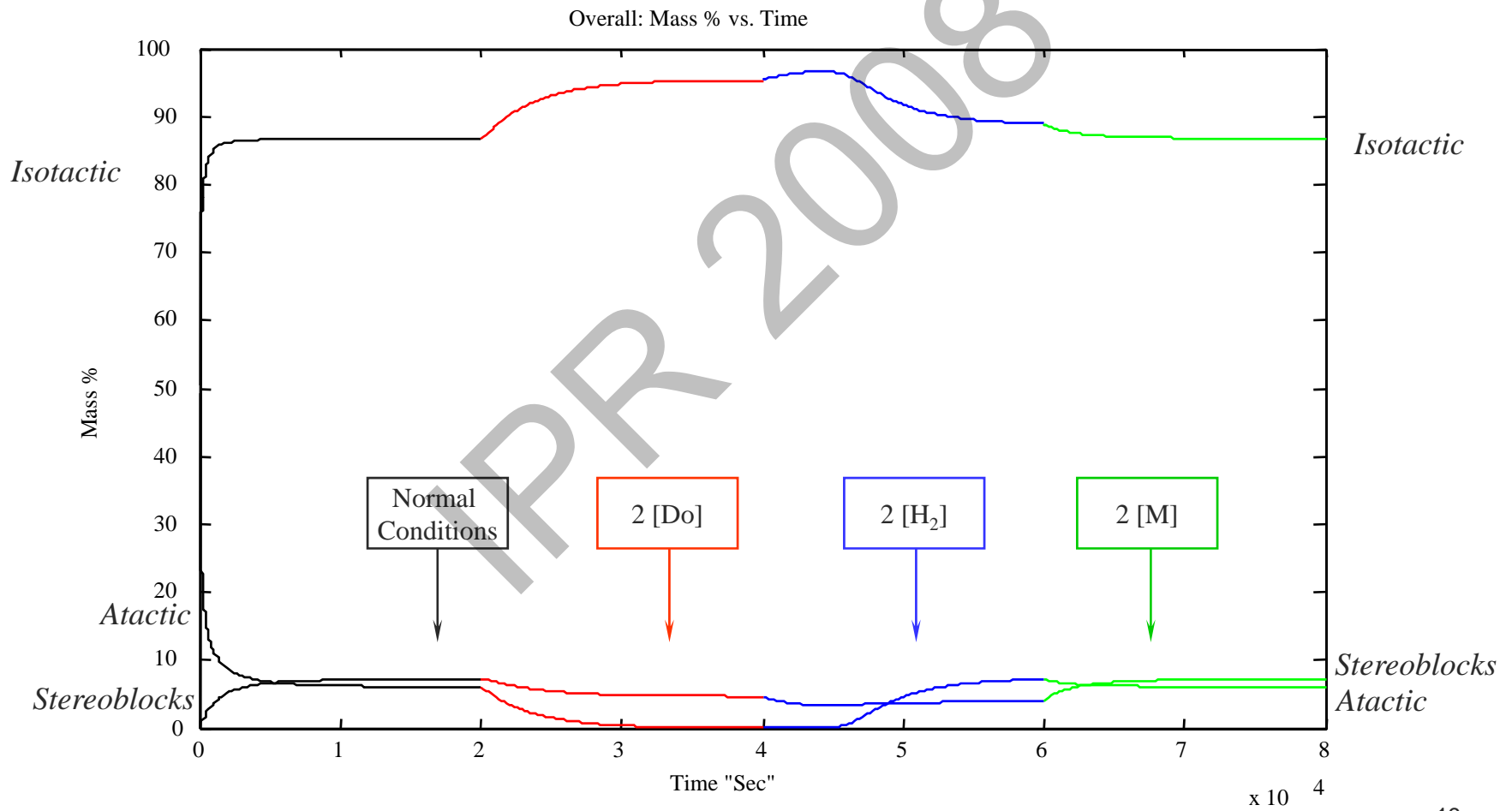
Dynamic Solution Simulation

Effect of Donor, Hydrogen, & Monomer Concentrations on Molecular Weight



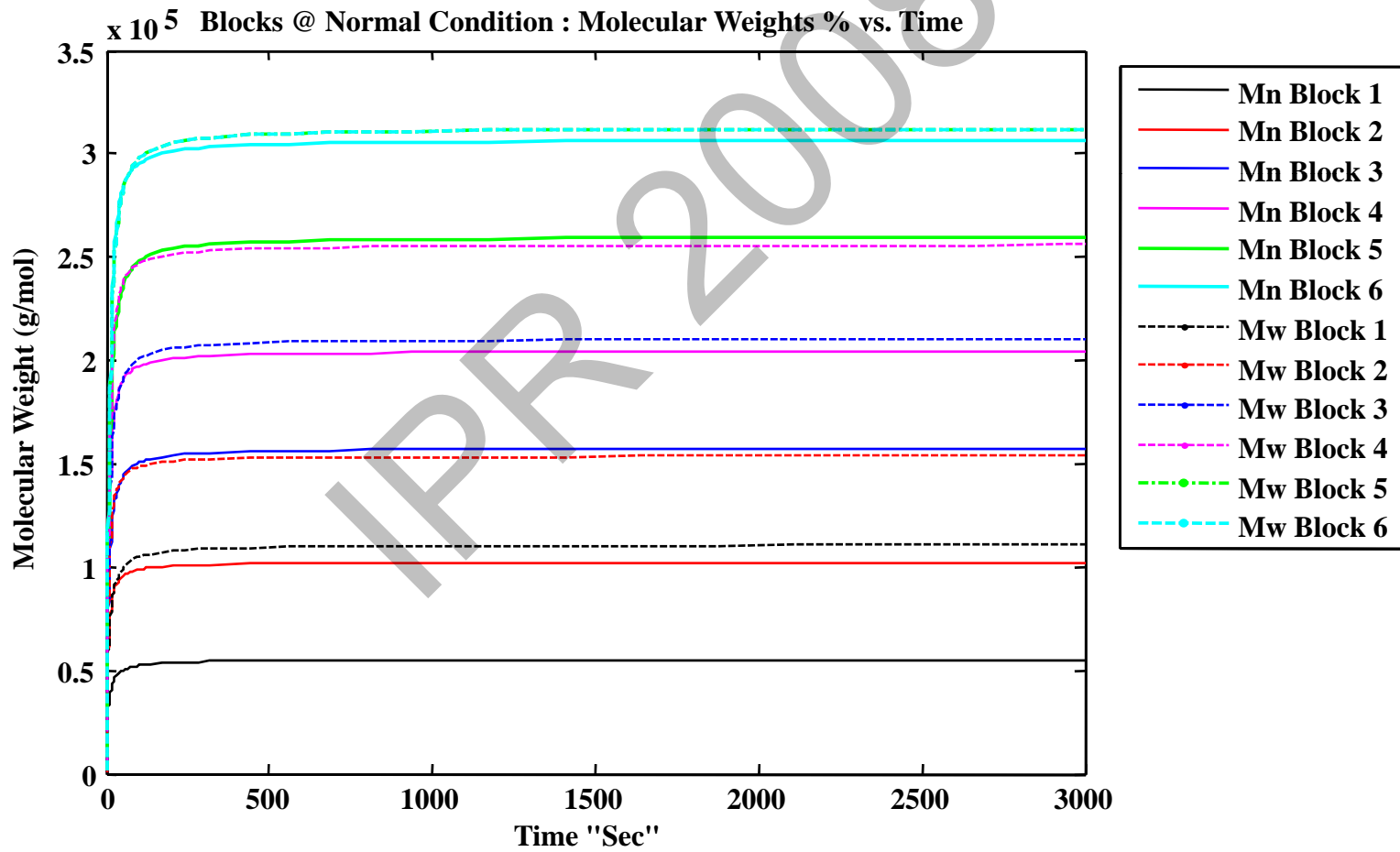
Dynamic Solution Simulation

Effect of Donor, Hydrogen, & Monomer Concentrations on Tacticity



Dynamic Solution Simulation

Molecular Weights by Block Number

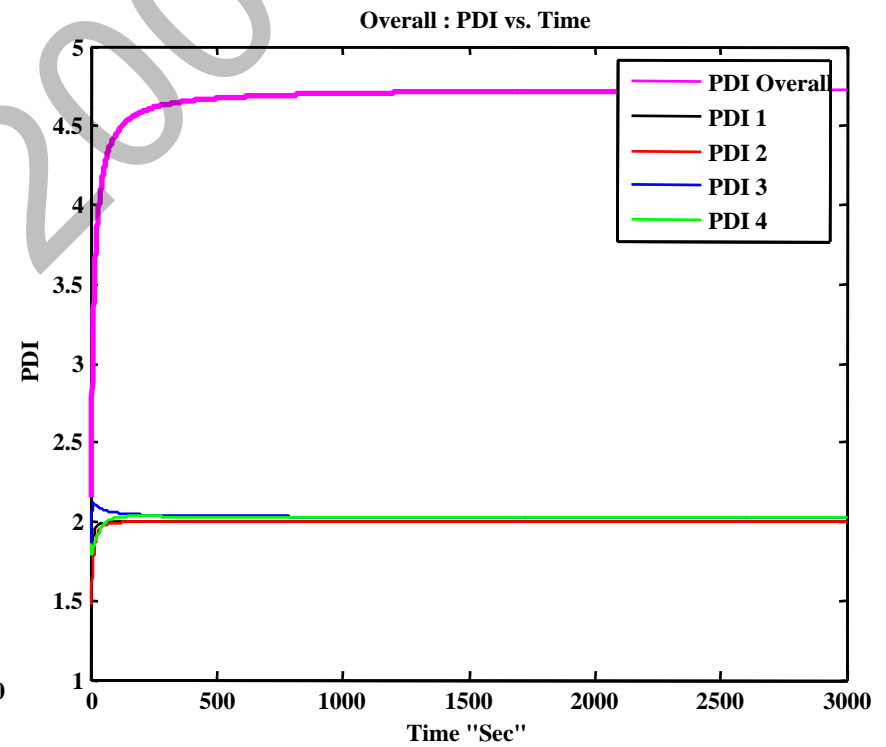
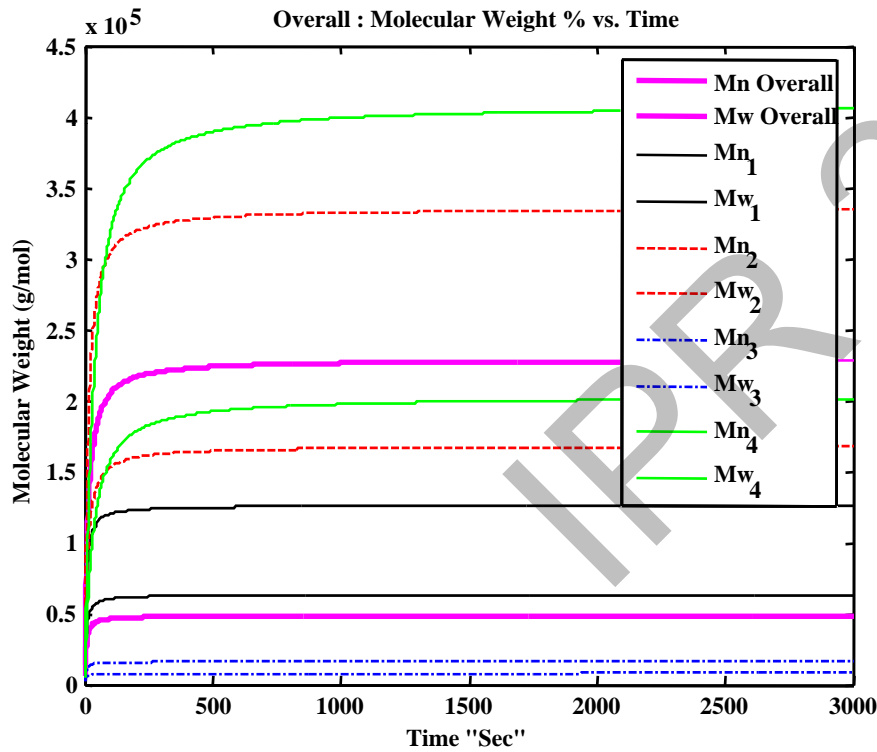


Multiple Sites

Dynamic Simulation Results

Dynamic Solution Simulation for a 4-Site Model

Molecular Weight & Polydispersity Index



Monte Carlo Simulation



$$P_p = \frac{R_p}{R_p + R_{tr} + R_{tf}}$$

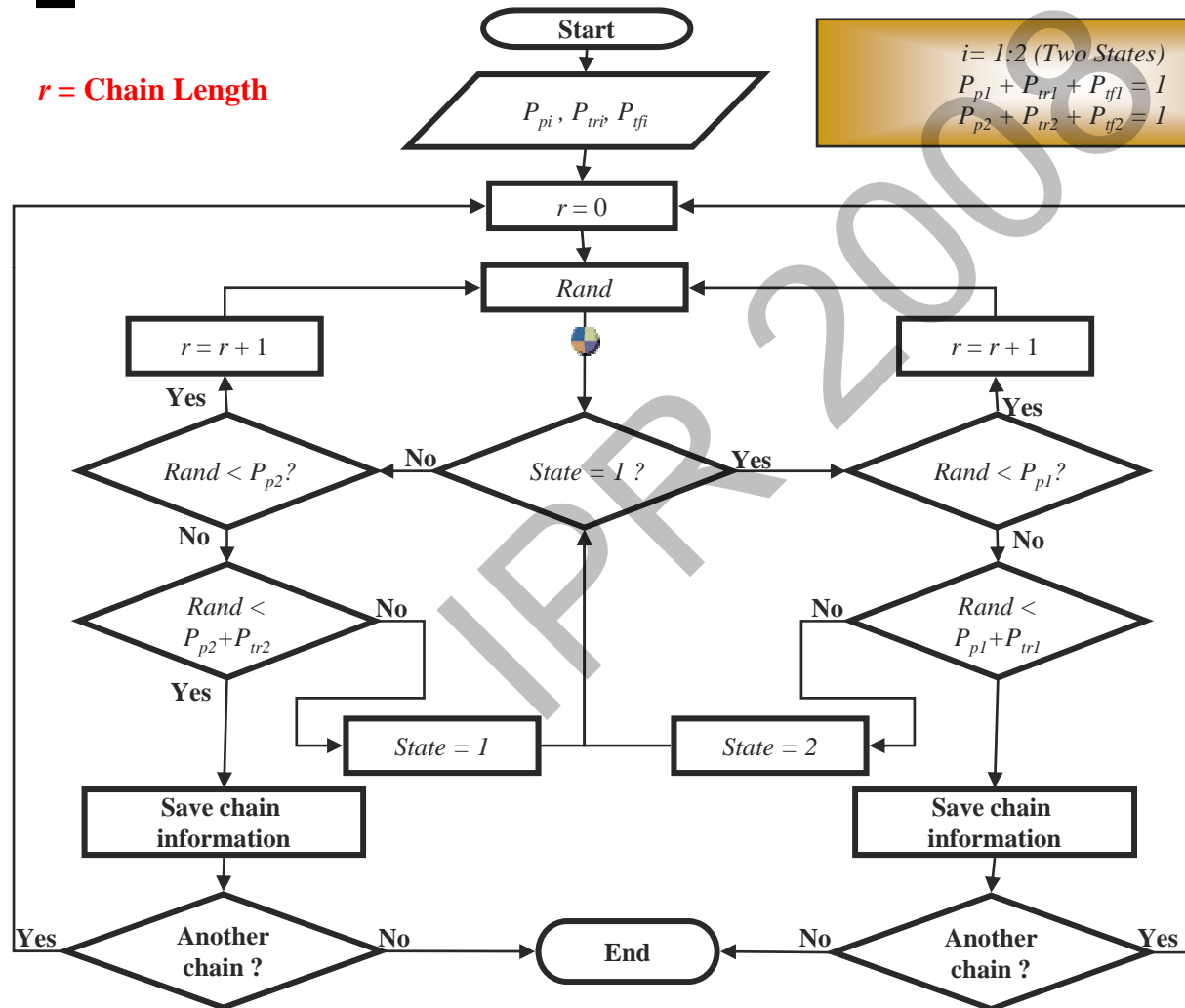
$$P_{tr} = \frac{R_{tr}}{R_p + R_{tr} + R_{tf}}$$

$$P_{tf} = \frac{R_{tf}}{R_p + R_{tr} + R_{tf}}$$

Can have the whole distribution

Monte Carlo Approach

$r = \text{Chain Length}$



$$\begin{aligned}
 & i = 1:2 \text{ (Two States)} \\
 & P_{p1} + P_{tr1} + P_{tf1} = 1 \\
 & P_{p2} + P_{tr2} + P_{tf2} = 1
 \end{aligned}$$



Monte Carlo Approach

■ Donor Effect:

$$\begin{aligned} P_{p1} + P_{tr1} + P_{tf1} &= 1 \\ P_{p2} + P_{tr2} + P_{tf2} &= 1 \end{aligned}$$

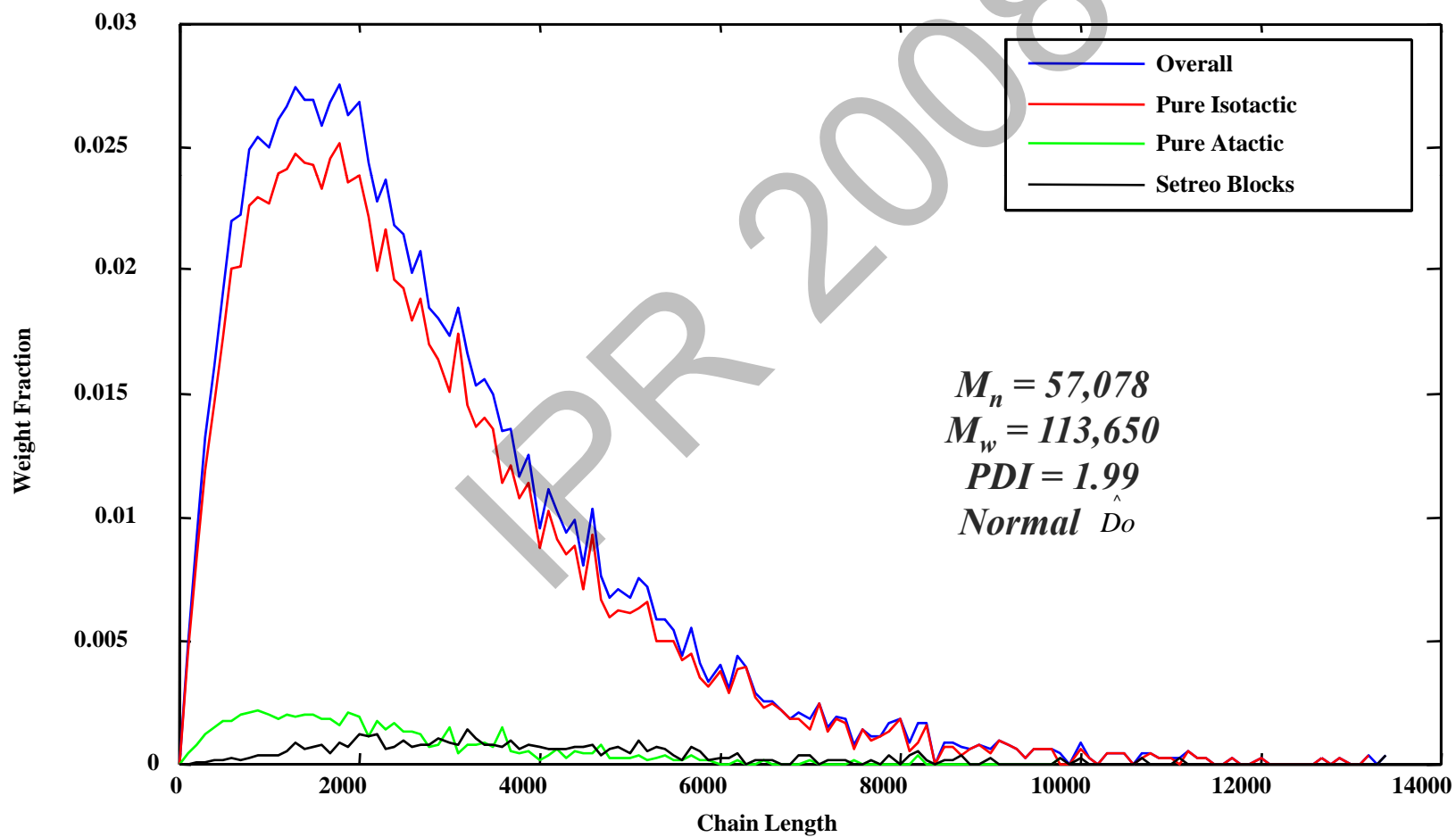
$$P_{tf} = \frac{R_{tf}}{R_p + R_{tr} + R_{tf}}$$

$$R_{tf} = k_{Do}^+ [P_r^{II}] [Do]$$

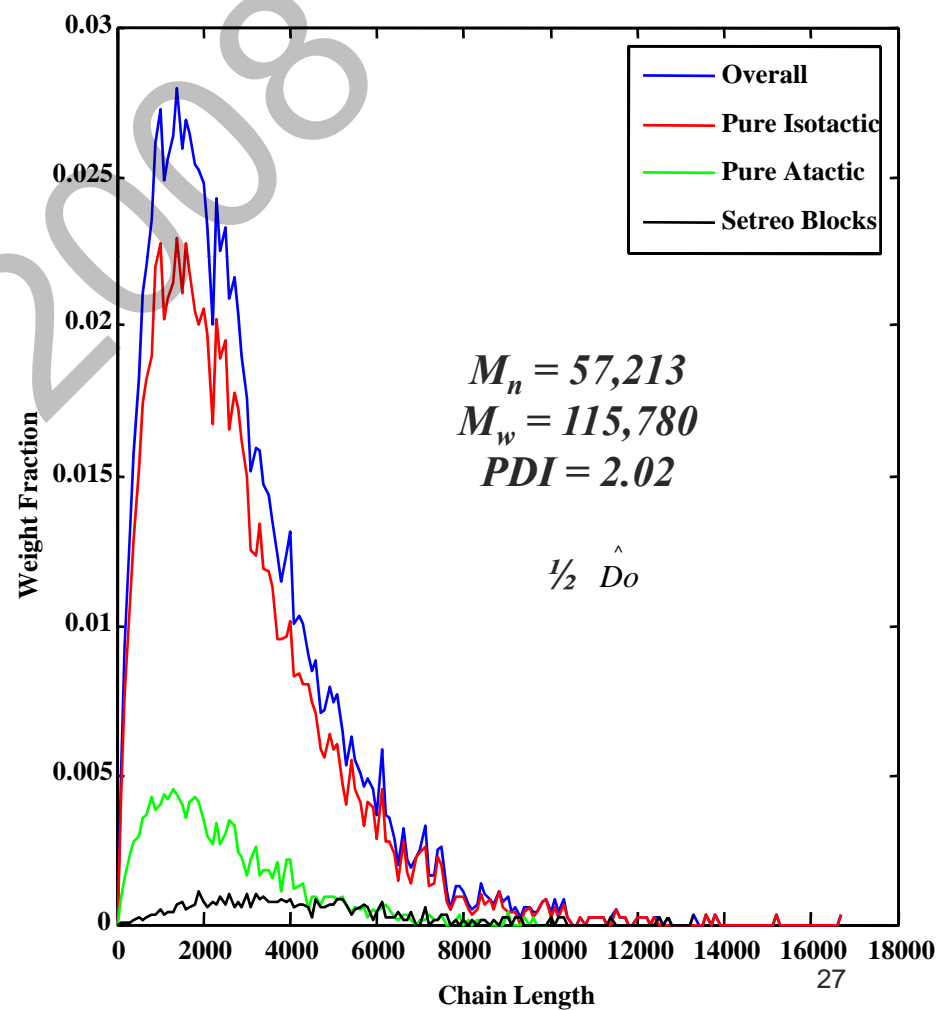
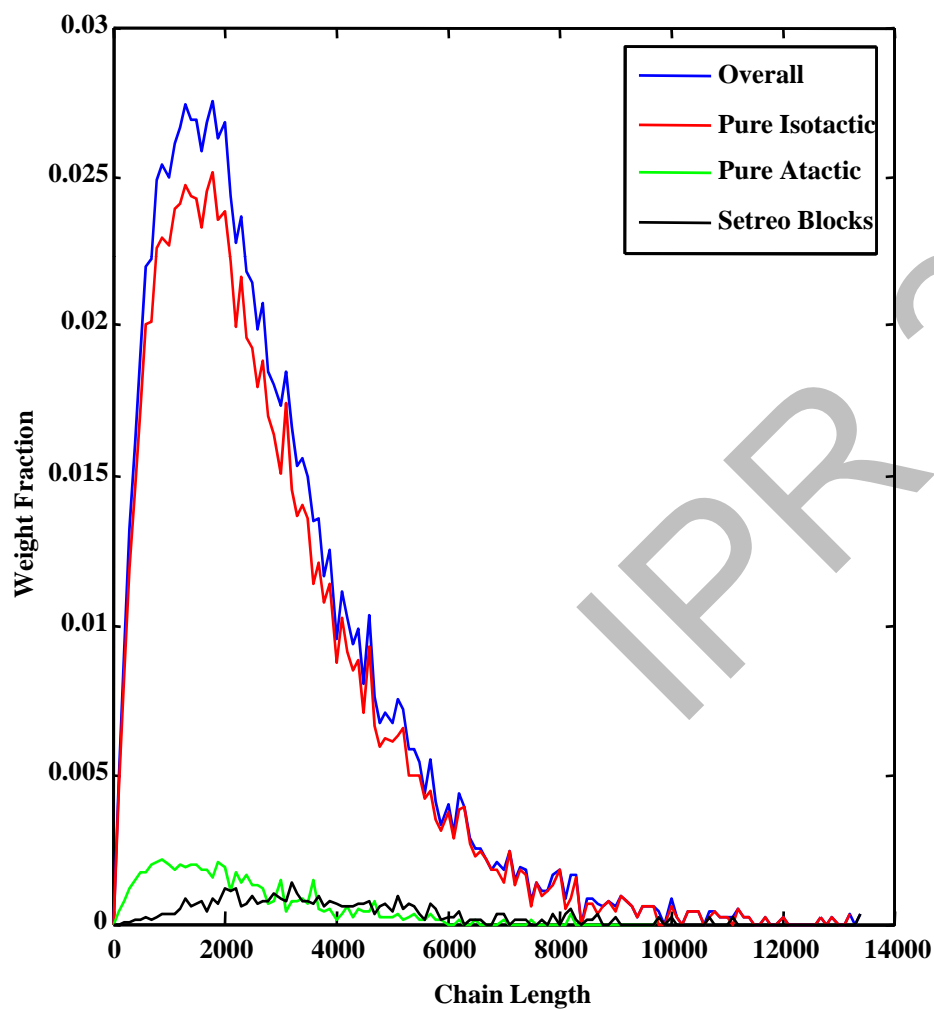
Donor Type

Donor Concentration

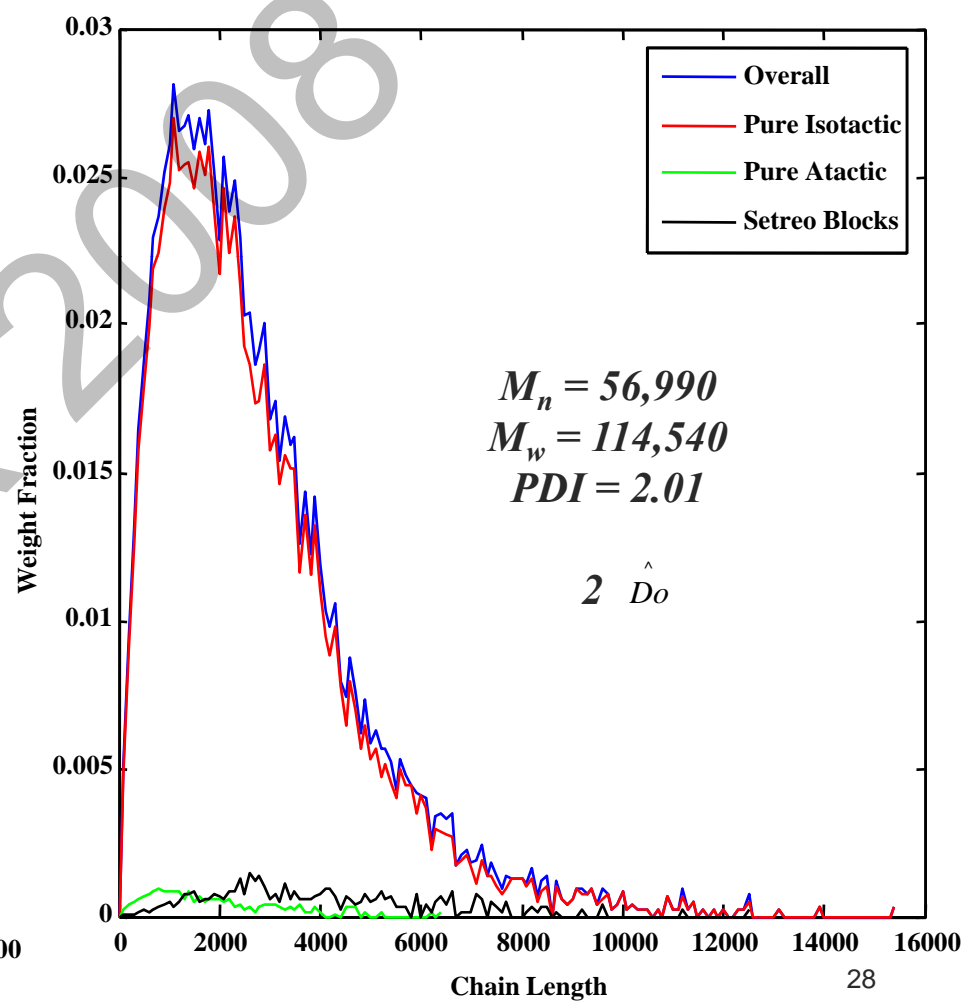
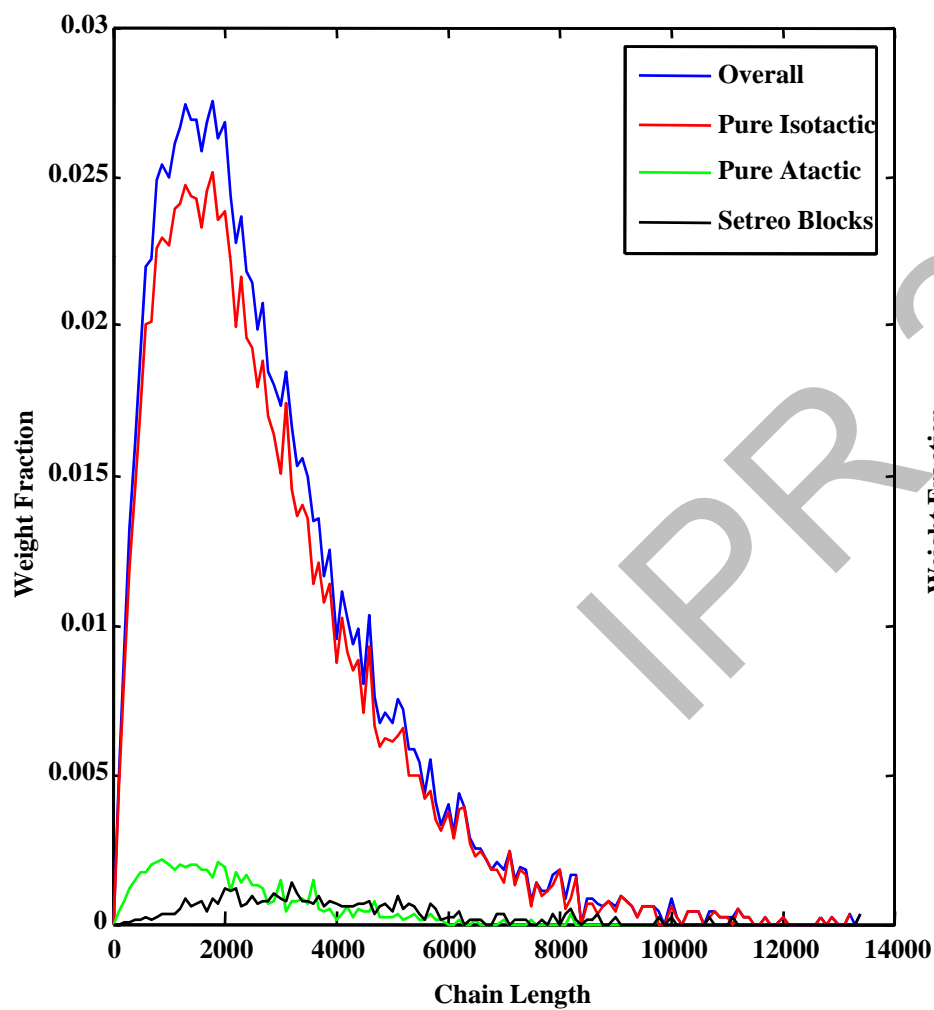
Chain Length vs. Weight Fraction @ Normal [Do]



Chain Length vs. Weight Fraction @ 1/2 [Do]



Chain Length vs. Weight Fraction @ 2 [Do]



[CURRENT & FUTURE WORK]

- Add additional features to the Monte Carlo code such as number of defects per chain and end group determination
- Use the microstructural information obtained by simulation to predict polypropylene fractionation with the temperature rising elution fractionation (TREF) and the nuclear magnetic resonance (^{13}C NMR)
- Plan for the parameter estimation for some known commercial catalyst / donor systems.

CONCLUSION

- The model is able to predict the polypropylene properties taking in consideration site transformation in the presence of the electron donor.
- The model is able to predict the tacticity during propylene polymerization which could enhance and used as a tool for the process control.
- The model will be used for parameter estimation for some commercial catalyst /electron donor systems.
- The microstructural information obtained by simulation can be used to predict polypropylene fractionation with the temperature rising elution fractionation (TREF).

[THE END]

**THANK
YOU**

Steady State vs. Dynamic Solution Simulations

Mass %	Steady State	Dynamic	Error %
Pure Isotactic	86.73%	86.68%	-0.1%
Pure Atactic	6.07%	6.10%	0.5%
Stereo-Blocks	7.20%	7.22%	0.2%
By Block %:			
1 block	92.81%	92.81%	0.0%
2 blocks	6.00%	6.00%	0.0%
3 blocks	1.13%	1.13%	0.0%
4 blocks	0.05%	0.05%	0.0%
5 blocks	0.01%	0.01%	0.0%
6 blocks	0.00%	0.00%	0.0%
M_n (g/mol)	57,270	57,270	0.00%
M_w (g/mol)	114,497	114,500	0.00%
<i>PDI</i>	2.00	2.00	0.00%

Steady State vs. Dynamic Solution Simulations

i	<u>Steady State</u>			<u>Dynamic</u>			<u>Error %</u>		
	<i>Mn</i>	<i>Mw</i>	PD	<i>Mn</i>	<i>Mw</i>	PD	<i>Mn</i>	<i>Mw</i>	PD
1	55,246	110,695	2.00	55,245	110,690	2.00	0.00%	0.00%	0.00%
2	102,229	153,807	1.50	102,230	153,810	1.50	0.00%	0.00%	0.00%
3	157,432	210,382	1.34	157,430	210,380	1.34	0.00%	0.00%	0.00%
4	204,416	256,004	1.25	204,420	256,010	1.25	0.00%	0.00%	0.00%
5	259,619	312,037	1.20	259,620	312,040	1.20	0.00%	0.00%	0.00%
6	306,603	358,194	1.17	306,610	358,200	1.17	0.00%	0.00%	0.00%

	<u>Steady State</u>			<u>Dynamic</u>			<u>Error %</u>		
	<i>Mn</i>	<i>Mw</i>	PD	<i>Mn</i>	<i>Mw</i>	PD	<i>Mn</i>	<i>Mw</i>	PD
Iso-Segments	56,008	111,939	2.00	56,002	111,960	2.00	0.01%	-0.02%	-0.03%
Ata-Segments	46,274	92,507	2.00	46,271	92,500	2.00	0.01%	0.01%	0.00%
Total Segments	55,058	110,377	2.00	55,112	110,470	2.00	-0.10%	-0.08%	0.01%