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

By:

Ahmad Alshaiban

Supervised By:

Prof. João B.P. Soares

Institute for Polymer Research, Department of Chemical Engineering

University of Waterloo

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

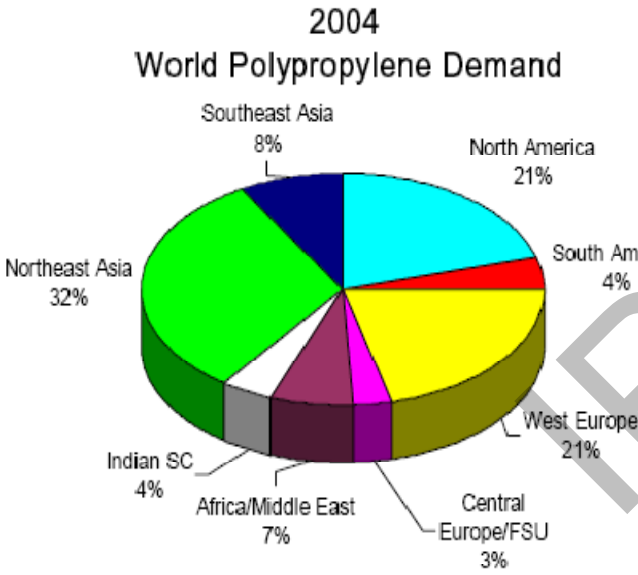
OBJECTIVES

- **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**

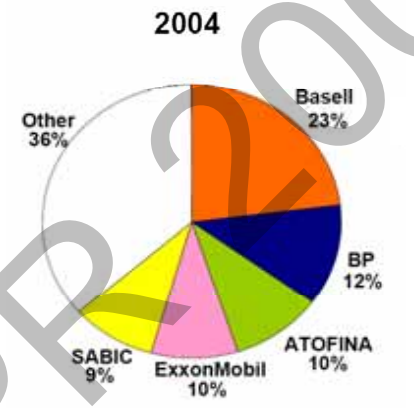
- **Describe, for the first time, site transformation by electron donors, with a mathematical model and quantify its effect on polymer chain microstructure**

INTRODUCTION

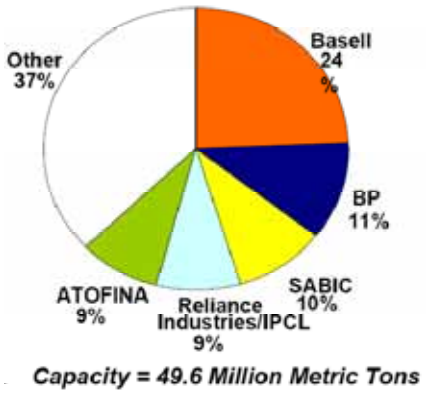
- **SABIC is the world's fourth largest producer of polyolefins. It is the world's third largest producer of polyethylene and the fifth largest producer of polypropylene.**
- **Overall polypropylene demand is forecasted to grow globally at a rate of 5.8% in 2004-2009 timeframe**



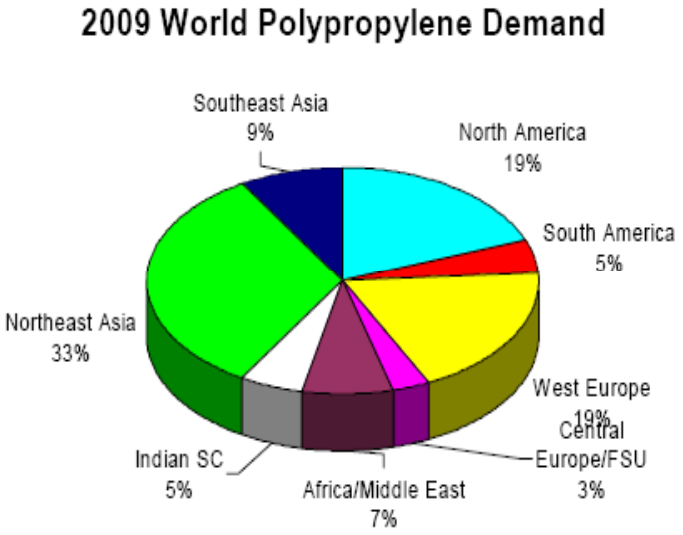
2004 Total Demand = 38.6 Million Metric Tons



Capacity = 41.3 Million Metric Tons



Capacity = 49.6 Million Metric Tons

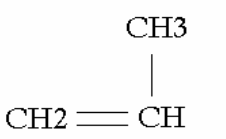


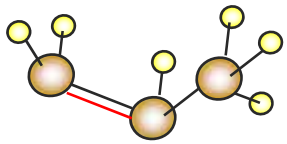
2009 Total Demand = 51.3 Million Metric Tons

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

INTRODUCTION

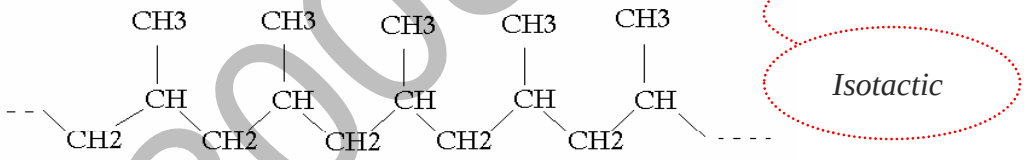
Propylene

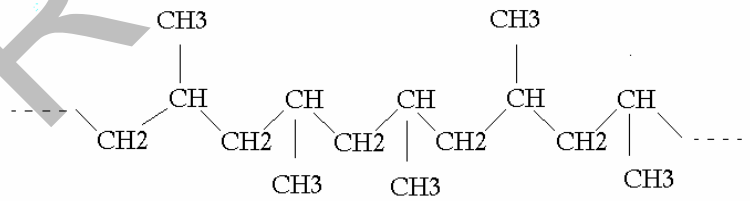


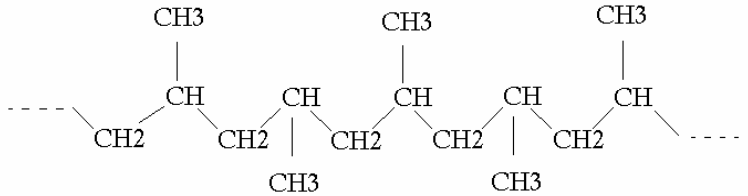


Polypropylene

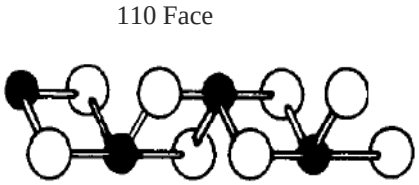
Commercial PP

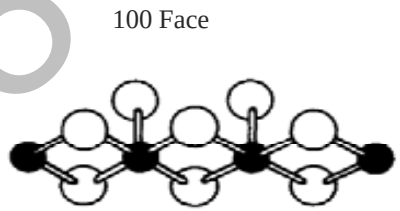


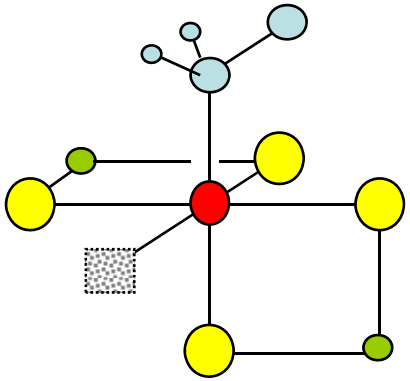




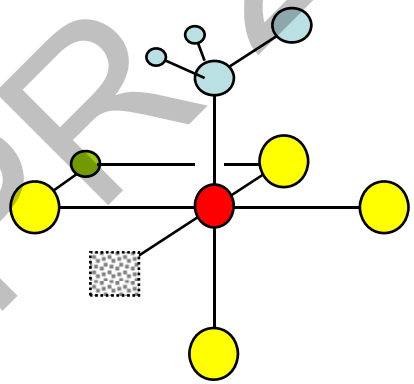
Z-N Multiple Site Catalyst



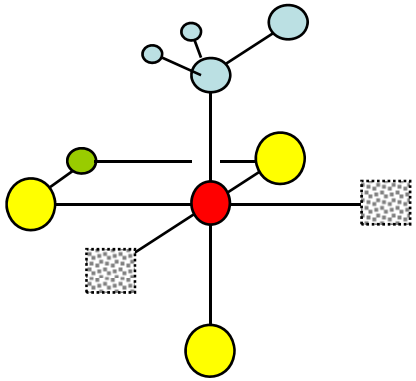




Highly isotactic



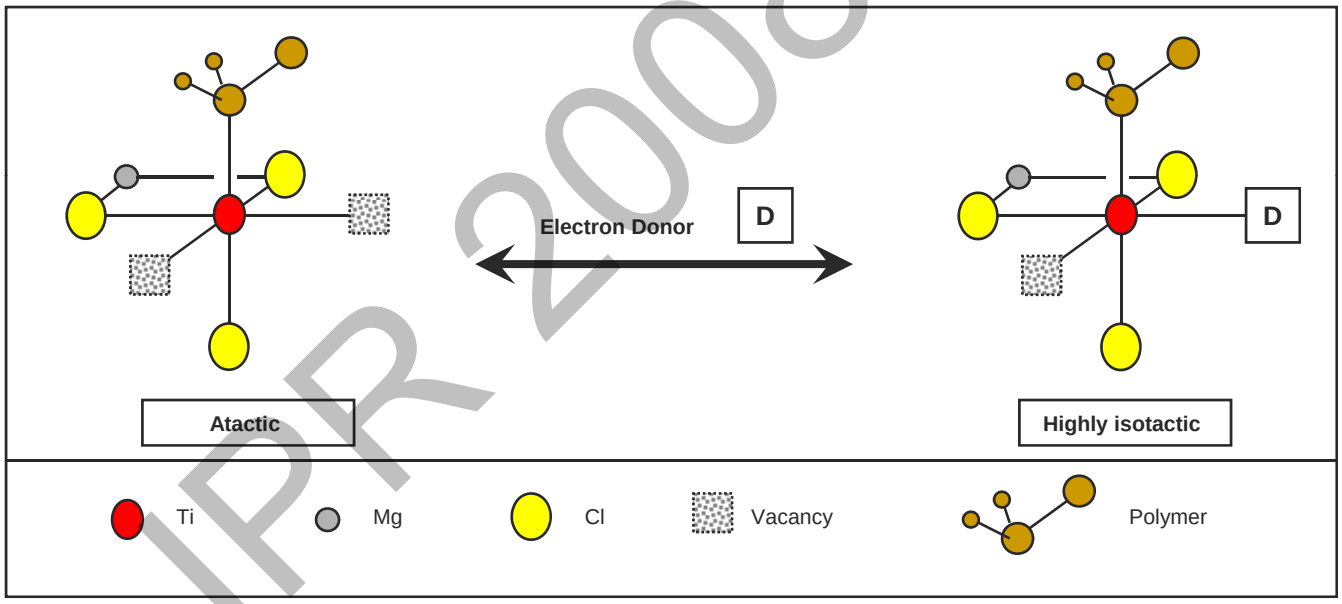
Low isotactic



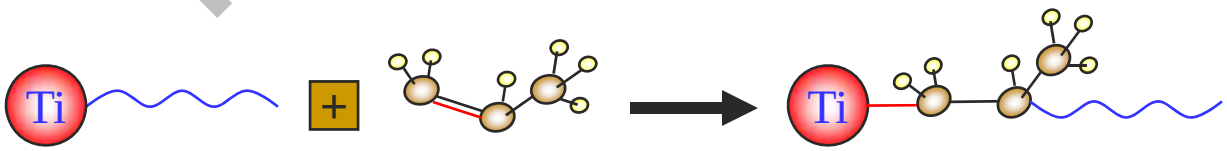
Atactic

Reaction Mechanism:

- **Site Transformation:**

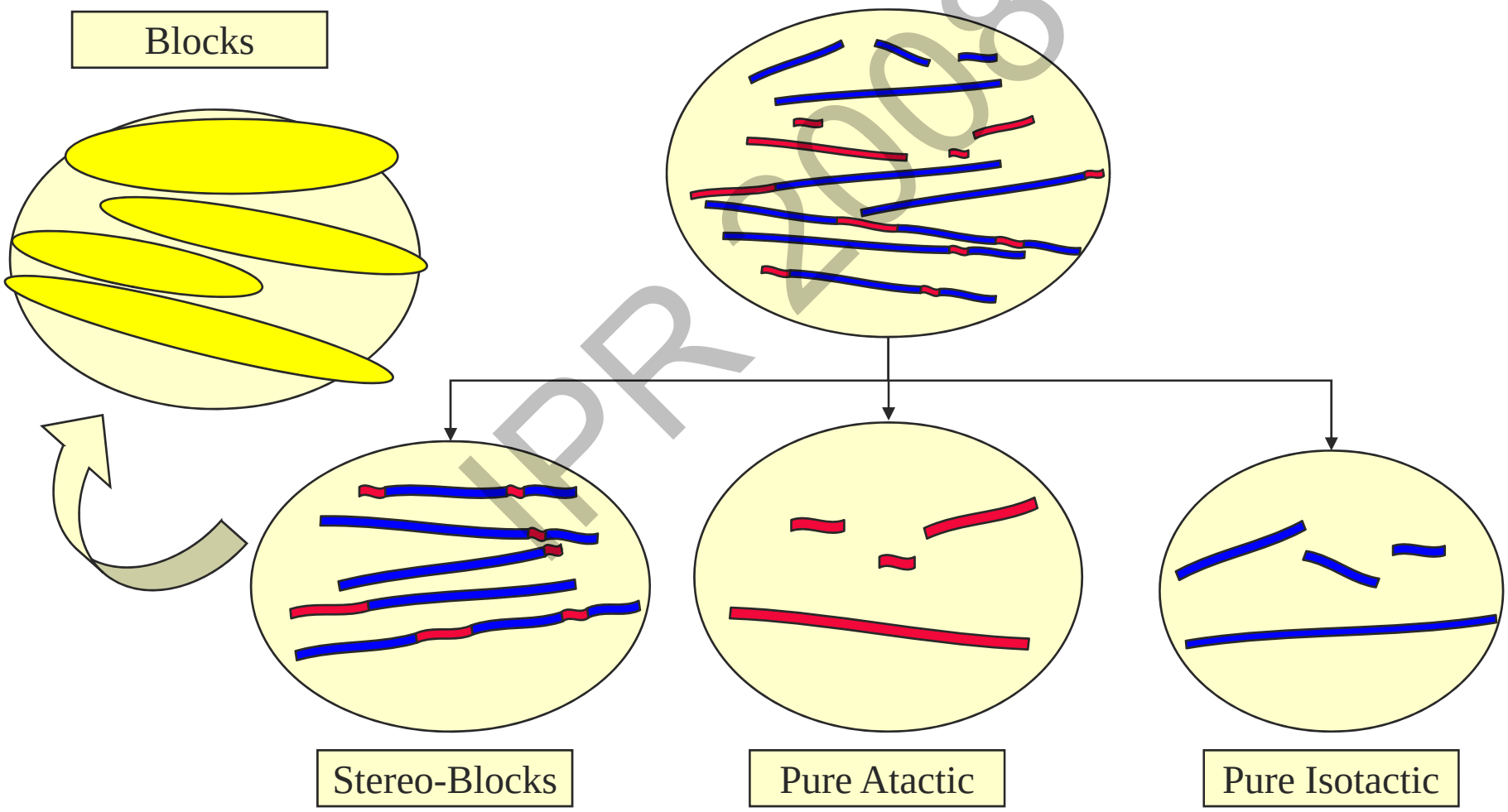


- **Propagation:**



- **Termination:**

Species Classification

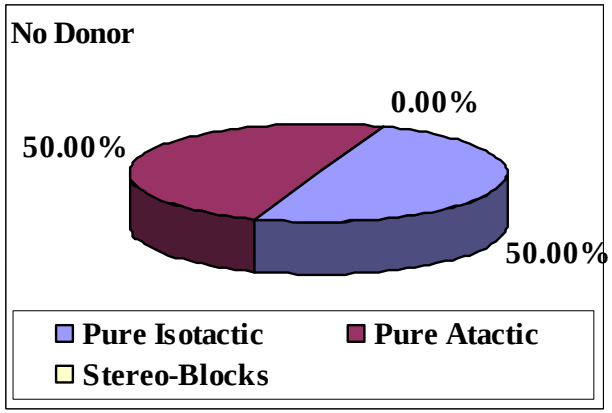


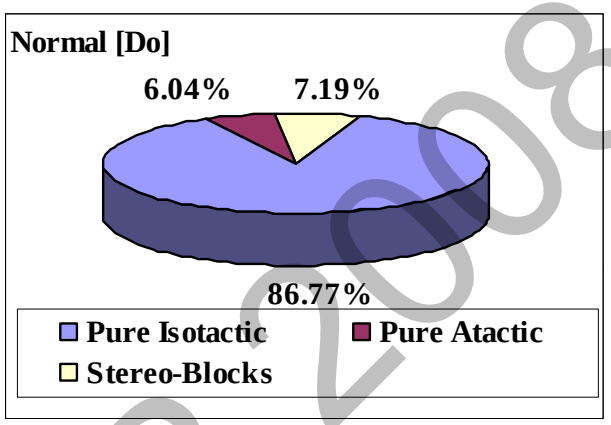
Single Site

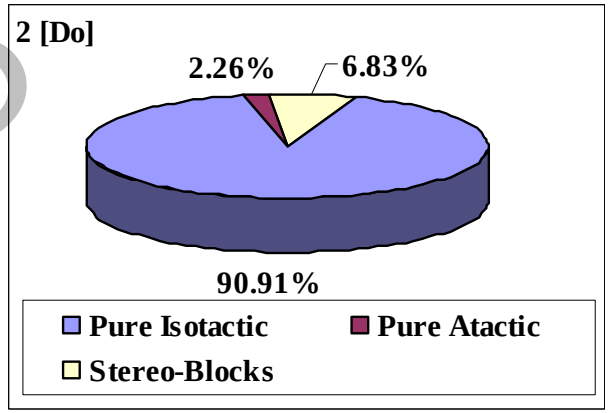
Steady State
Simulation Results

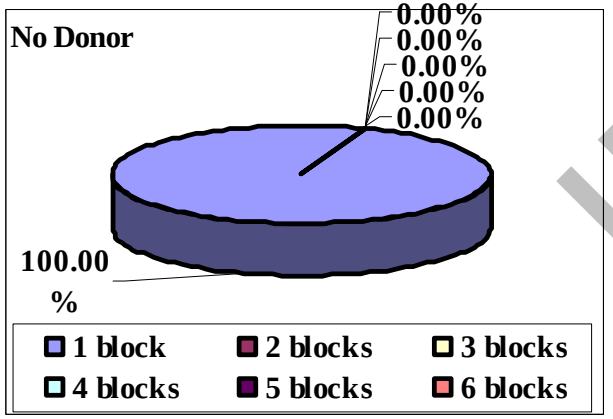
Steady State Solution for One Site Type:
$R_{P1}/R_{P2} = 1$, $R_{P1}/R_{T1} = 1364$, $R_{P2}/R_{T2} = 1364$

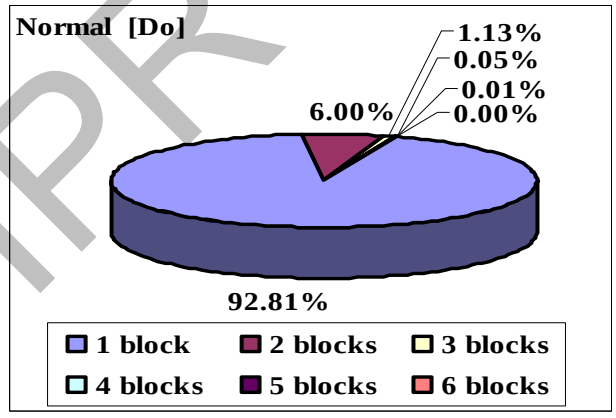
Effect of Changing the Electron Donor Concentration 1/2

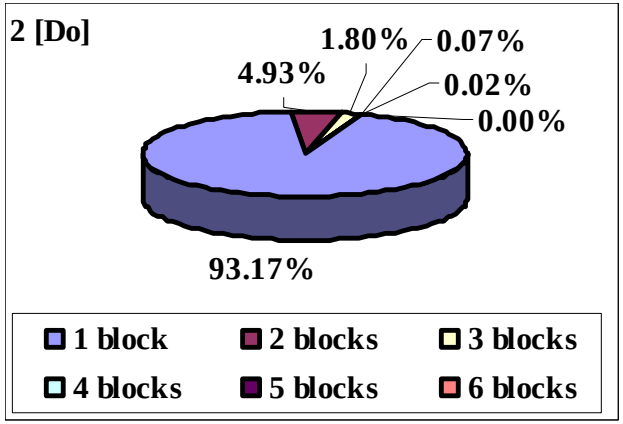








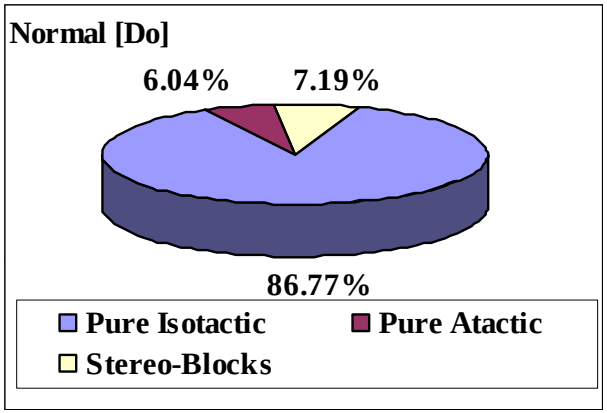


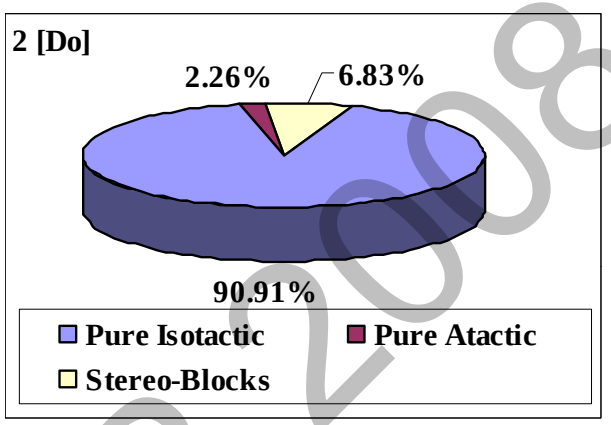


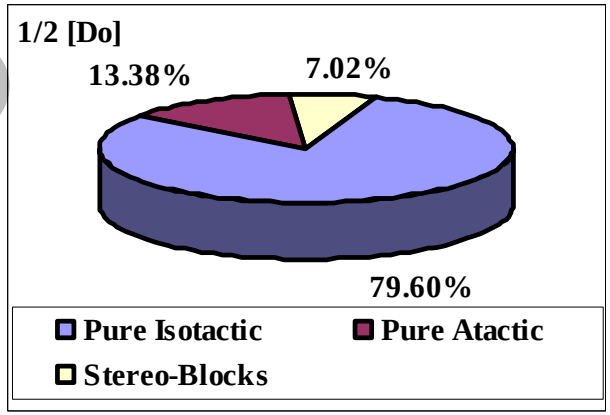
M_n (g/mol)	57,000	57,000	57,000
M_w (g/mol)	114,000	114,000	114,000
PDI	2.00	2.00	2.00

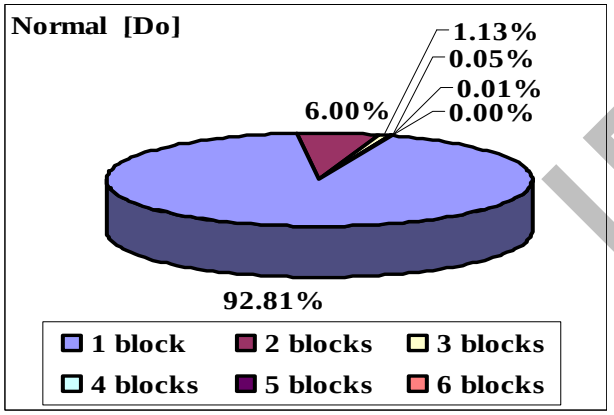
Steady State Solution for One Site Type:
$R_{P1}/R_{P2} = 1$, $R_{P1}/R_{T1} = 1364$, $R_{P2}/R_{T2} = 1364$

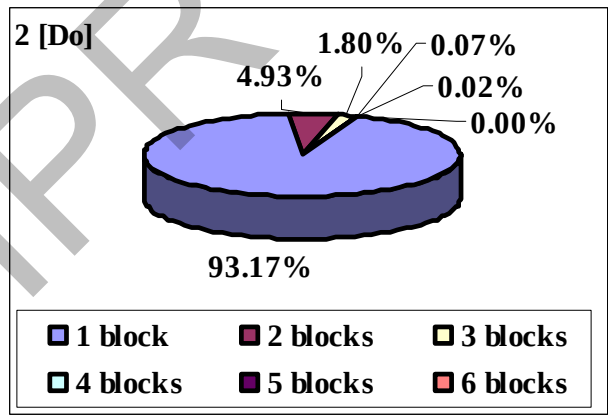
Effect of Changing the Electron Donor Concentration 2/2

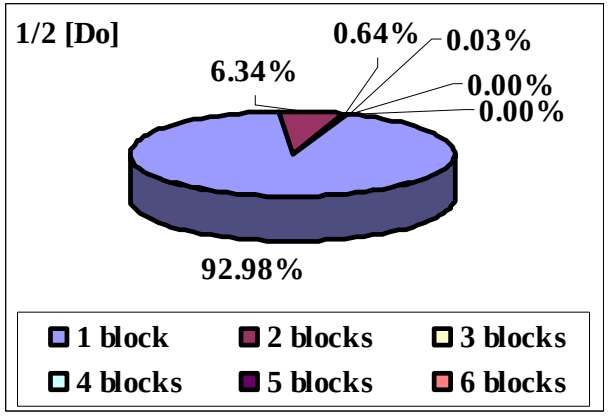








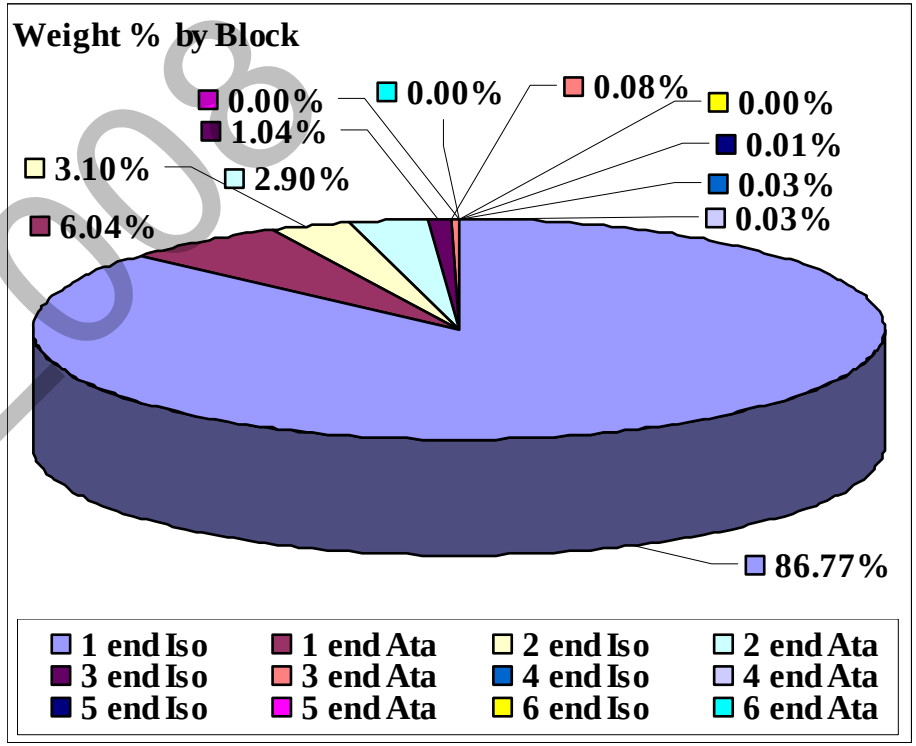




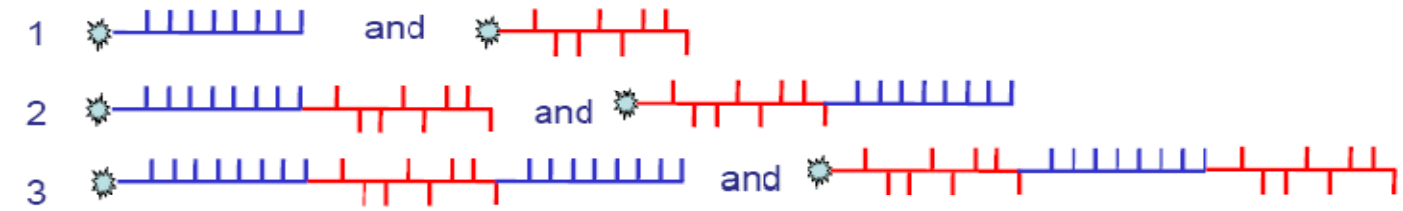
M_n (g/mol)	57,000	57,000	57,000
M_w (g/mol)	114,000	114,000	114,000
PDI	2.00	2.00	2.00

Block's Properties and Their Weight Distribution

	End Iso			End Ata		
i	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



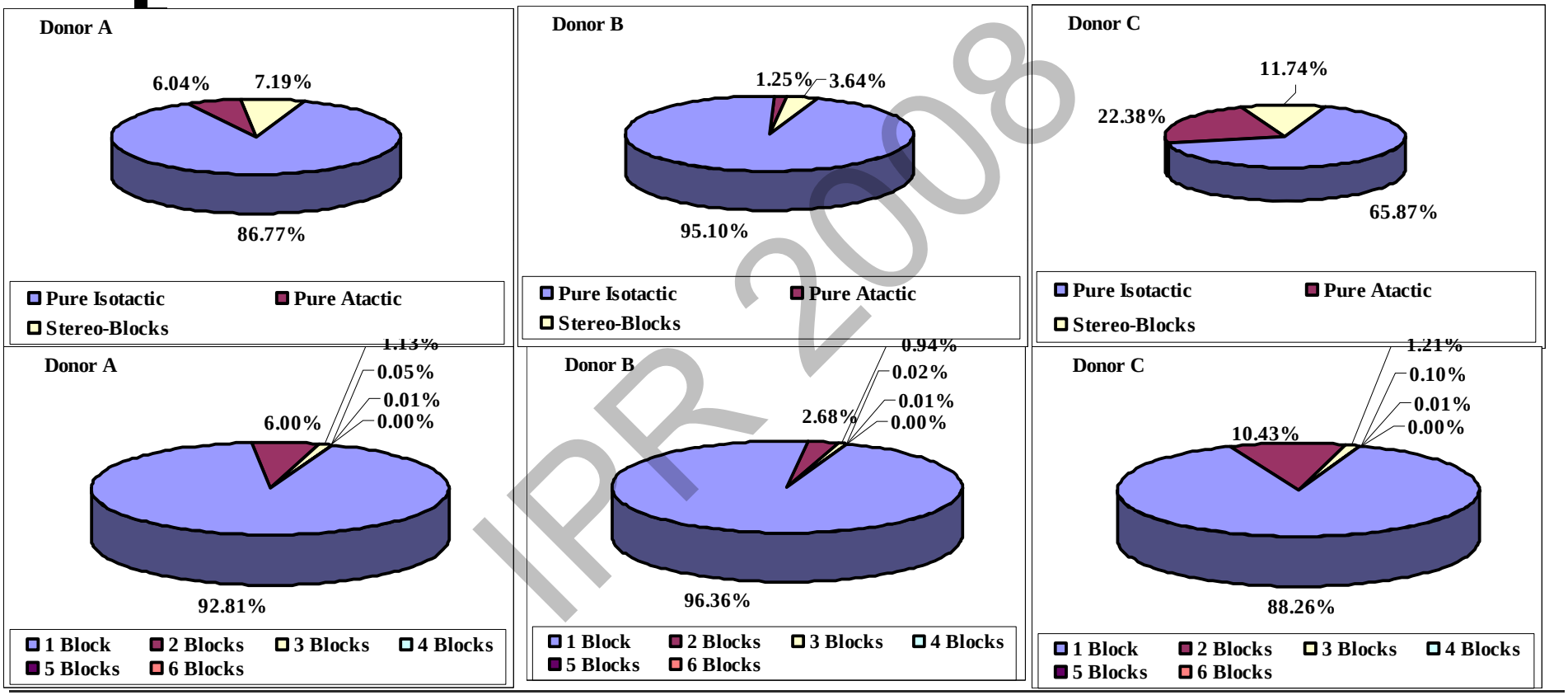
i = Block #



etc.

Steady State Solution for One Site Type

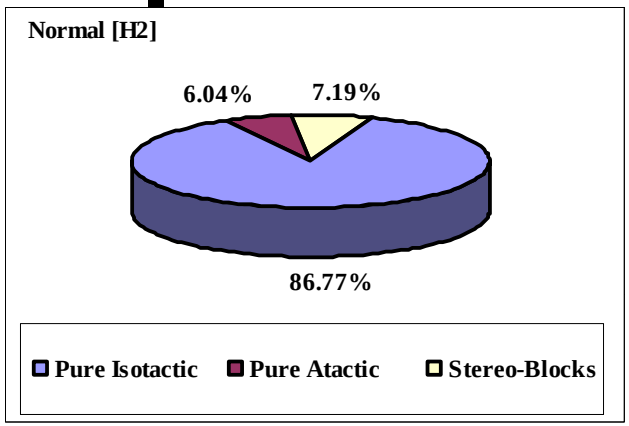
Effect of Changing the Donor Type

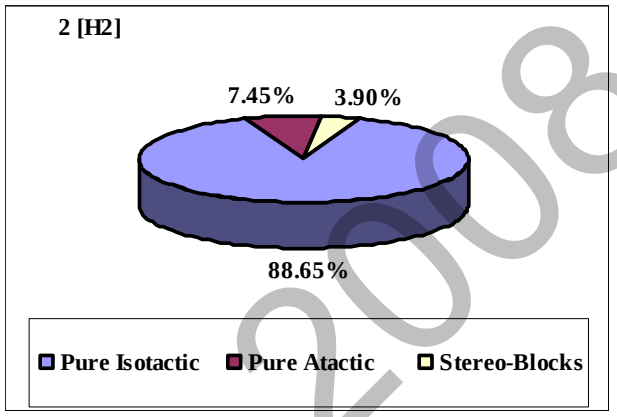


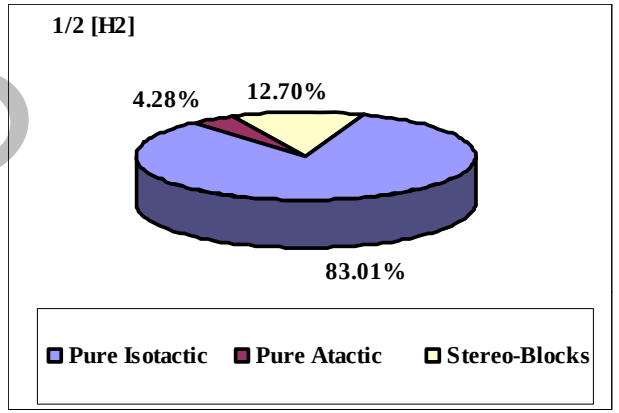
K^+ / K_A^+	1	2	0.5
K^- / K_A^-	1	0.5	2
M_n g/mol	57,000	57,000	57,000
M_w g/mol	114,000	114,000	114,000
PDI	2.00	2.00	2.00

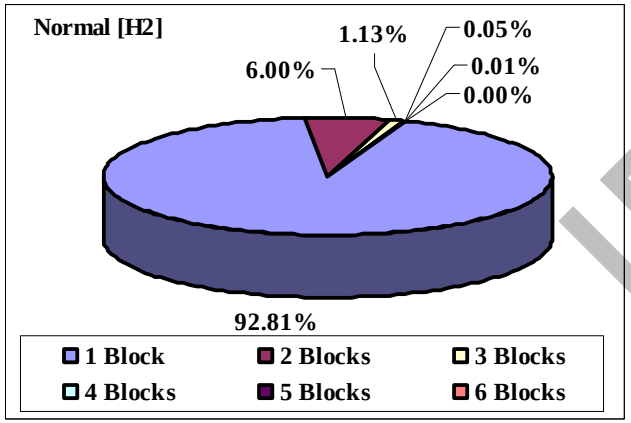
Steady State Solution for One Site Type

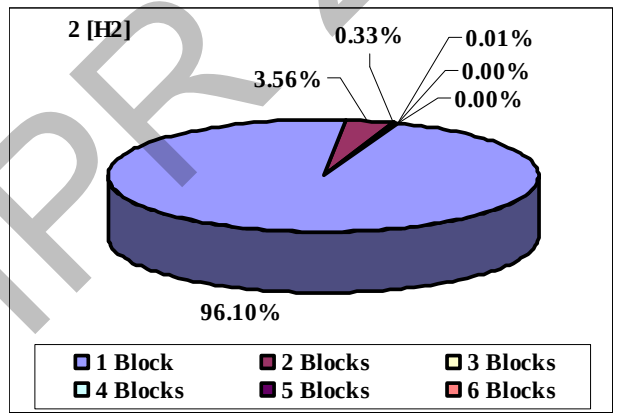
Effect of Changing the Hydrogen Concentration

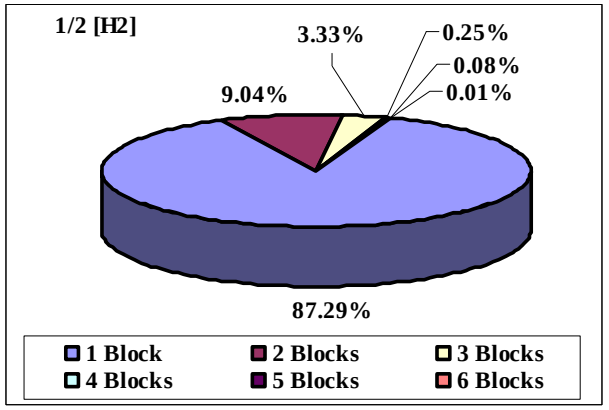












	R_{P1}/R_{T1} =1364 , R_{P2}/R_{T2} =1364	R_{P1}/R_{T1} =682 , R_{P2}/R_{T2} =682	R_{P1}/R_{T1} =2727 , R_{P2}/R_{T2} =2727
M_n g/mol	57,000	29,000	114,000
M_w g/mol	114,000	58,000	228,000
PDI	2.00	2.00	2.00

Multiple Sites

Steady State Simulation Results

Summary Results for a 4-Site Model of Propylene Polymerization

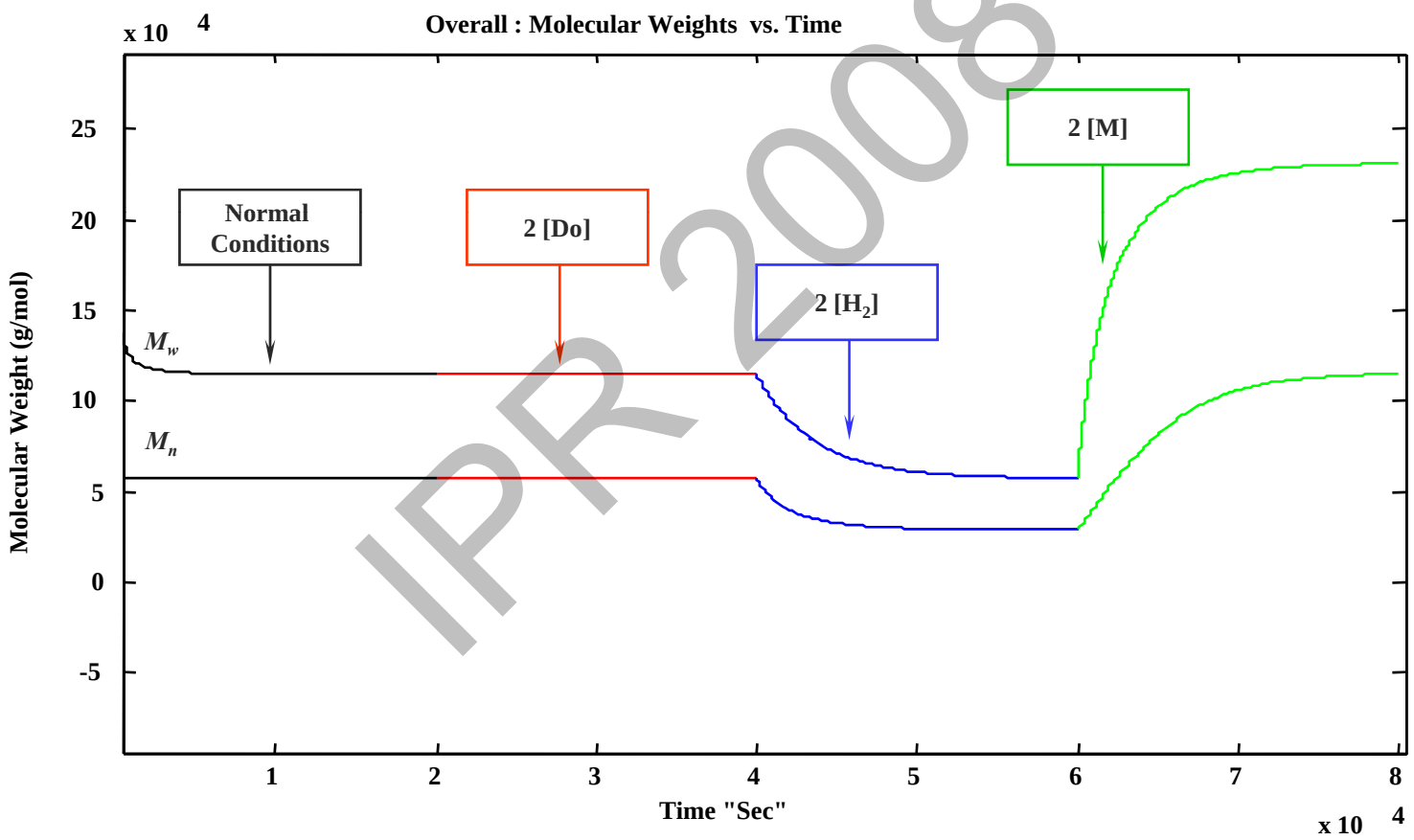
Site		Overall	1	2	3	4
		Mass %	Mass %	Mass %	Mass %	Mass %
Pure Isotactic		98.22%	100 %	100 %	93.40%	86.47%
Pure Atactic		0.30%	0.0 %	0.0 %	2.84%	0.88%
Stereo-Blocks		1.48%	0.0 %	0.0 %	3.76%	12.64%
Block weight %:			Single-state stereospecific sites		Two-state sites	
	1 block	97.98%	100 %	100 %	96.24%	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

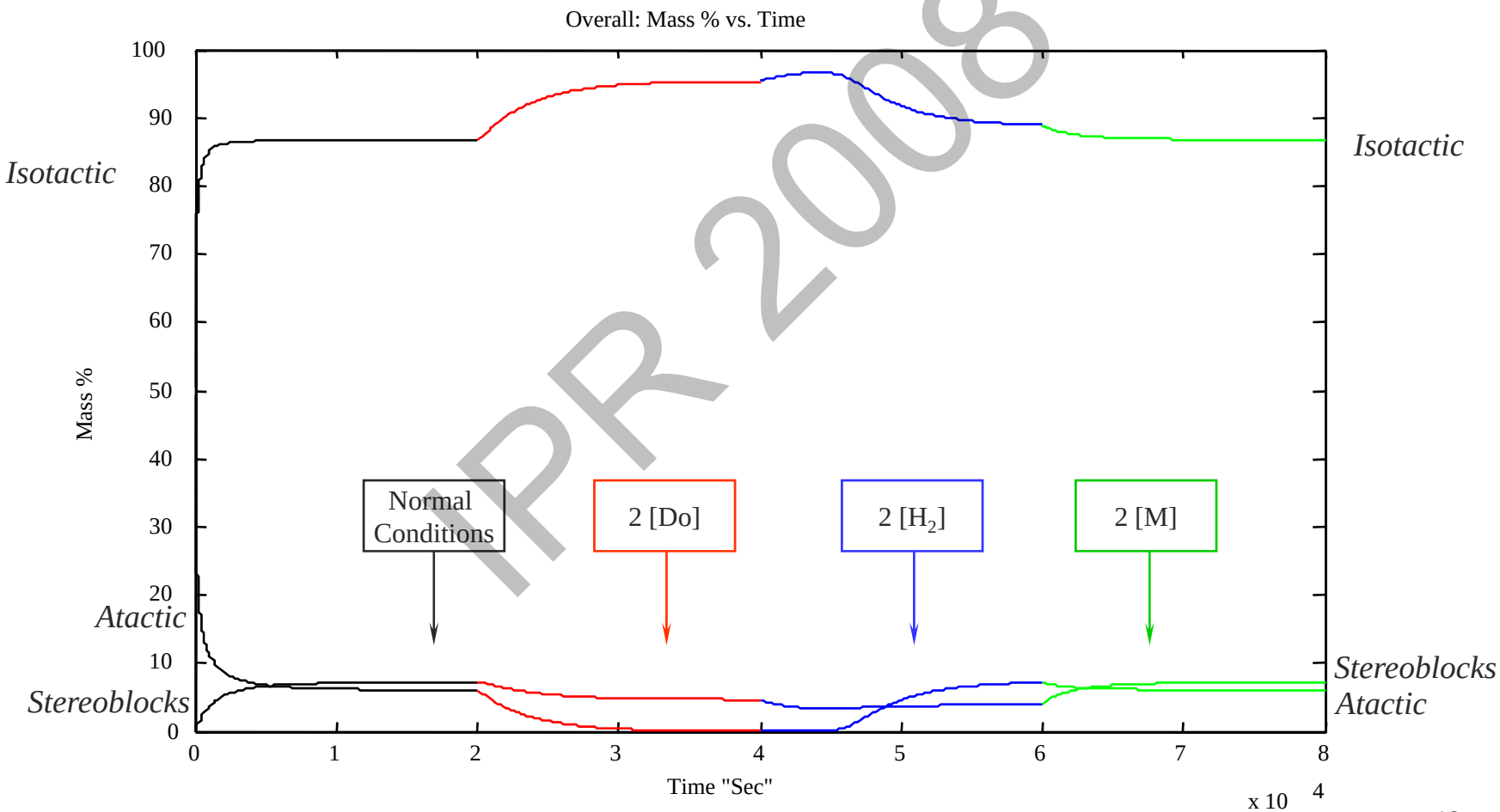
Dynamic Solution Simulation

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



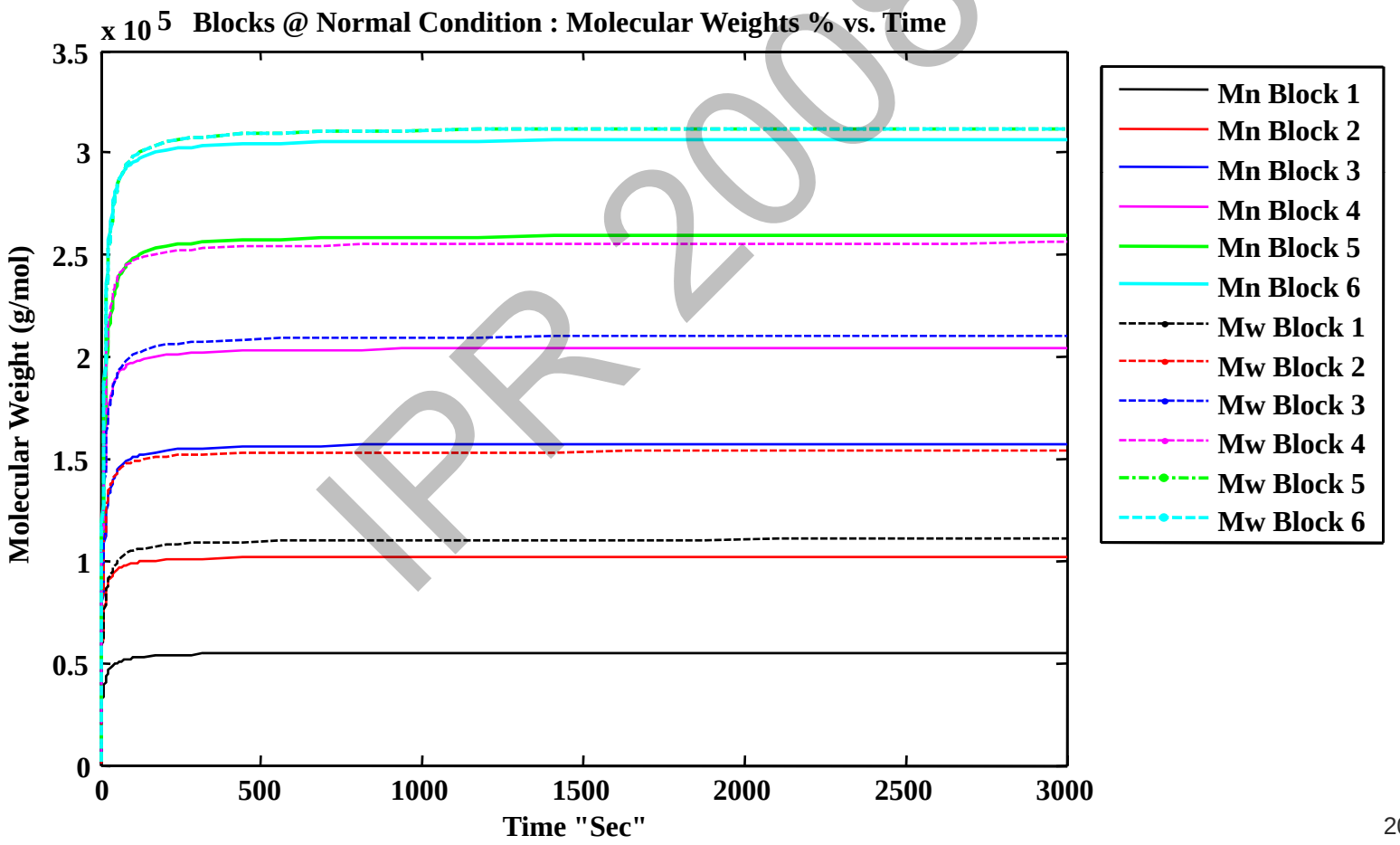
Dynamic Solution Simulation

Effect of Donor, Hydrogen, & Monomer Concentrations on Tacticity



Dynamic Solution Simulation

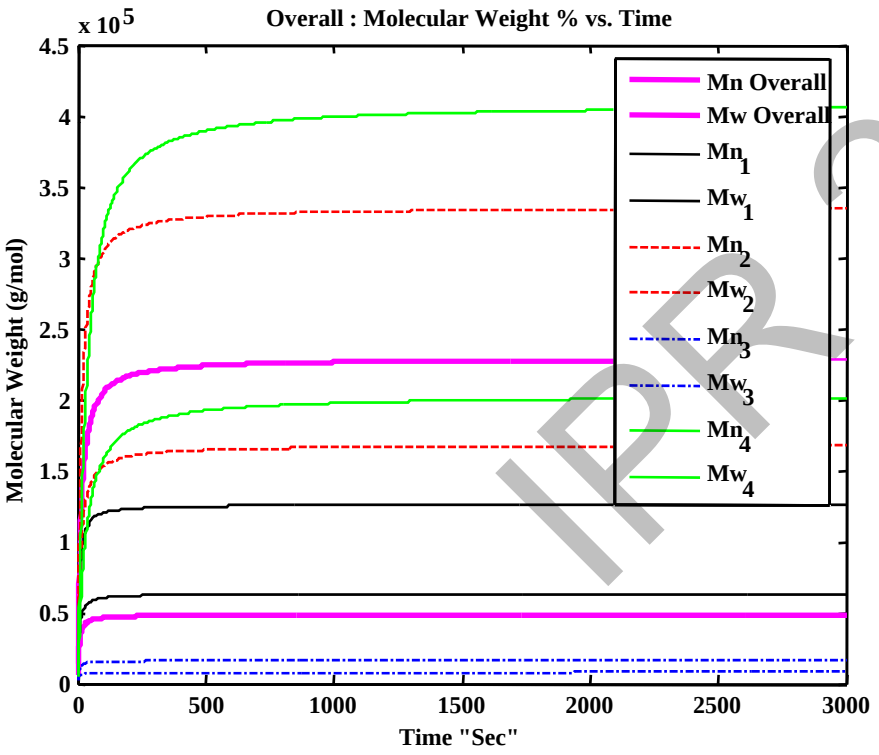
Molecular Weights by Block Number

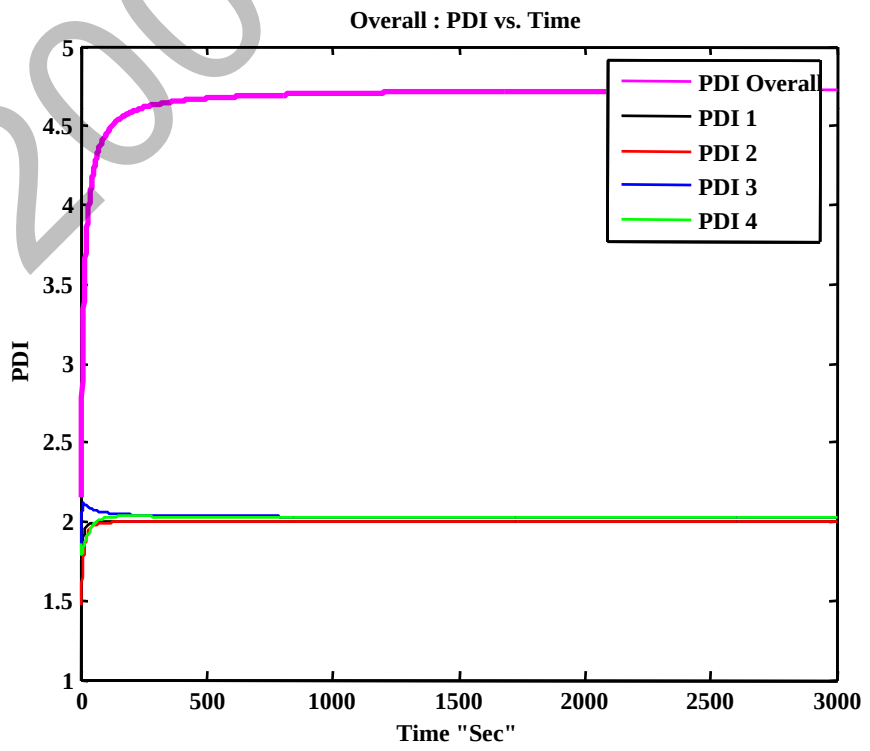


Multiple Sites

Dynamic Simulation Results

Dynamic Solution Simulation for a 4-Site Model
Molecular Weight & Polydispersity Index





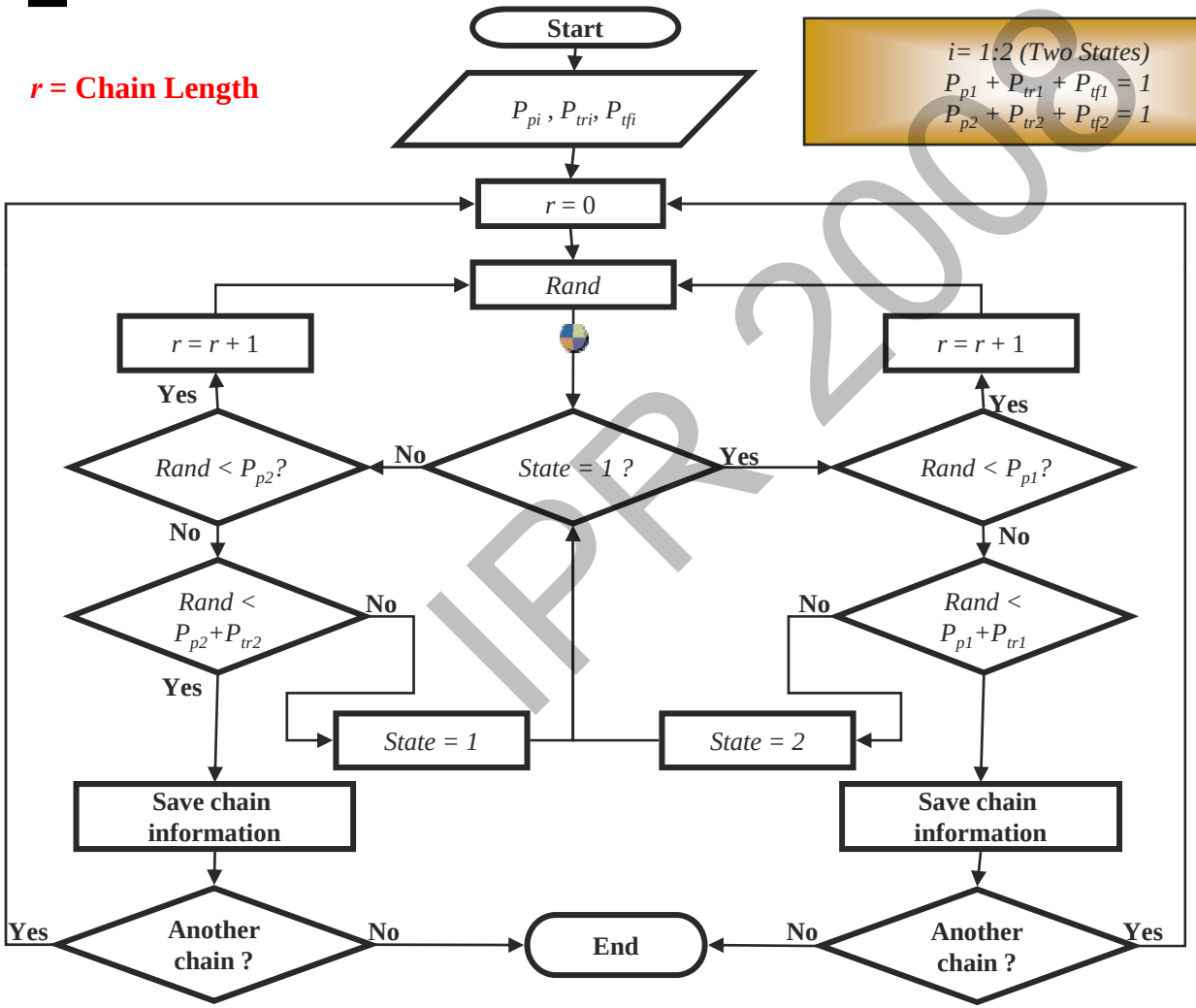
Monte Carlo Simulation

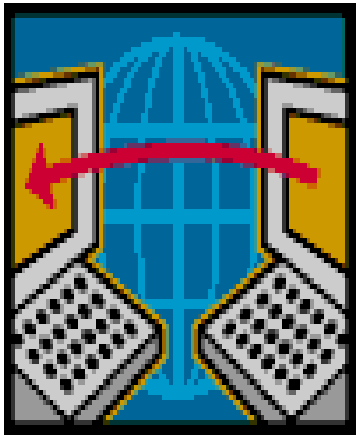
$$P_p = \frac{R_p}{R_p + R_{tr} + R_{tf}} \qquad P_{tr} = \frac{R_{tr}}{R_p + R_{tr} + R_{tf}} \qquad P_{tf} = \frac{R_{tf}}{R_p + R_{tr} + R_{tf}}$$

Can have the whole distribution

Monte Carlo Approach

***r* = Chain Length**





Monte Carlo Approach

- **Donor Effect:**

$$P_{p1} + P_{tr1} + P_{tf1} = 1$$
$$P_{p2} + P_{tr2} + P_{tf2} = 1$$

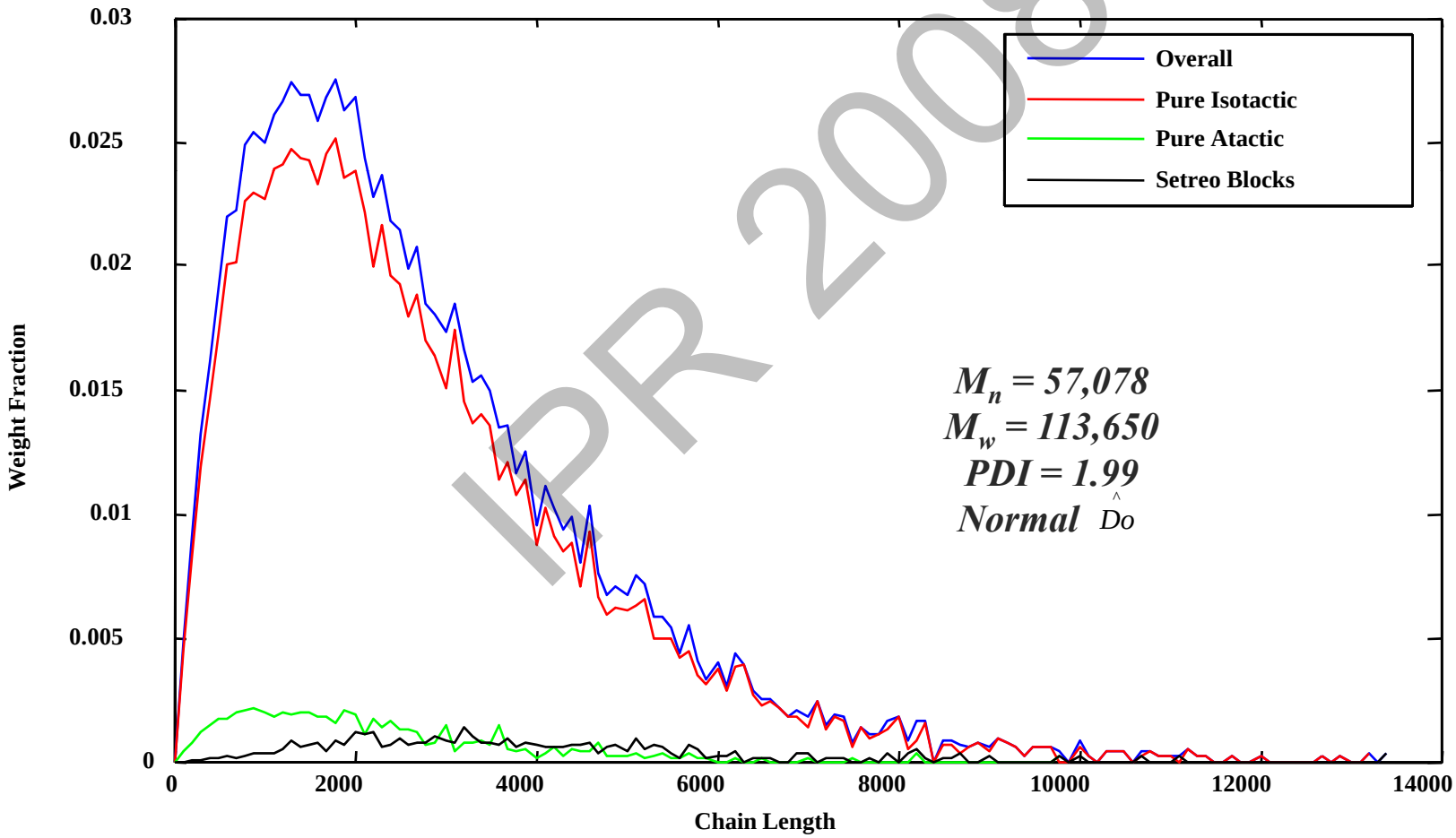
$$P_{tf} = \frac{R_{tf}}{R_p + R_{tr} + R_{tf}}$$

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

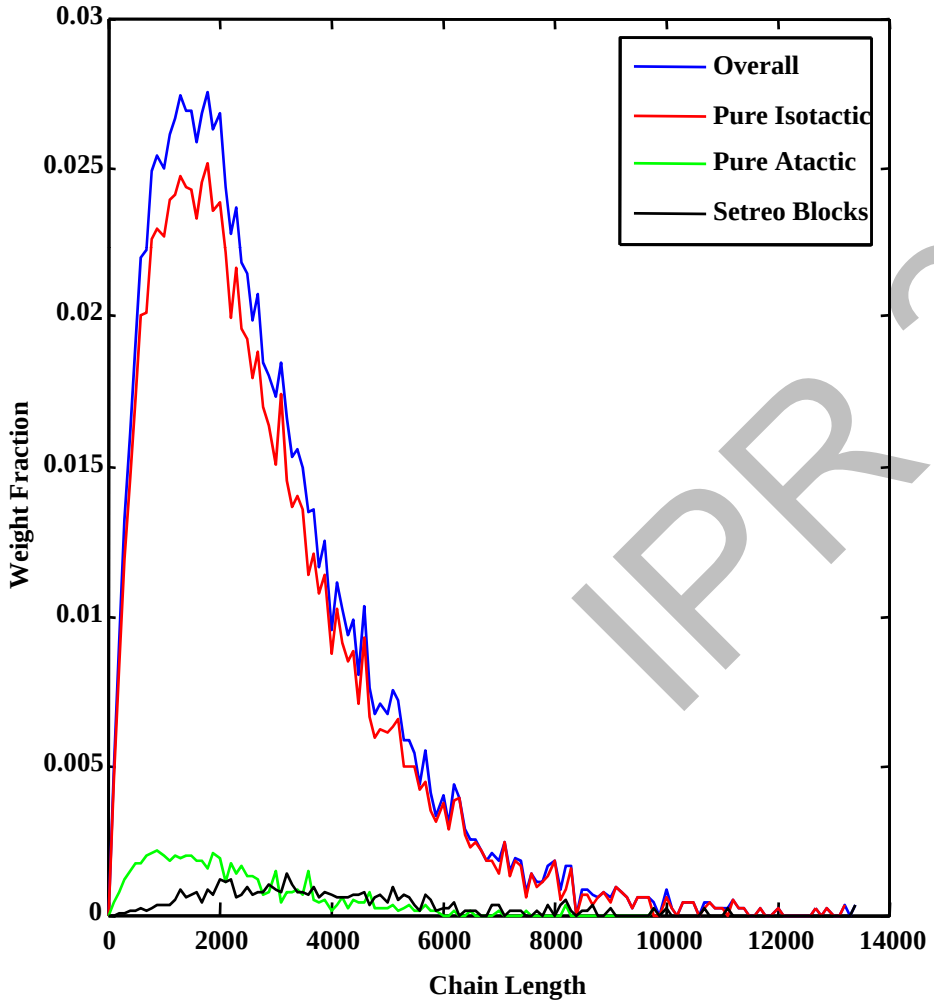
Donor Type

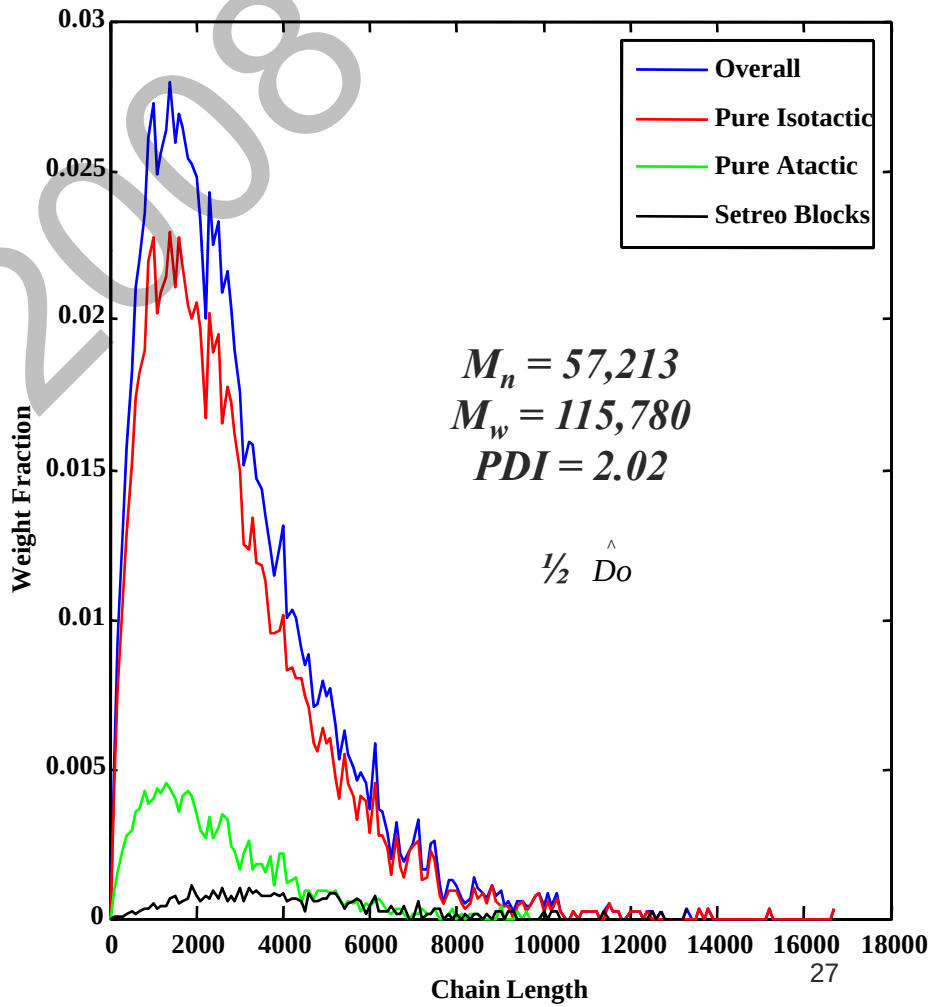
Donor Concentration

Chain Length vs. Weight Fraction @ Normal [Do]

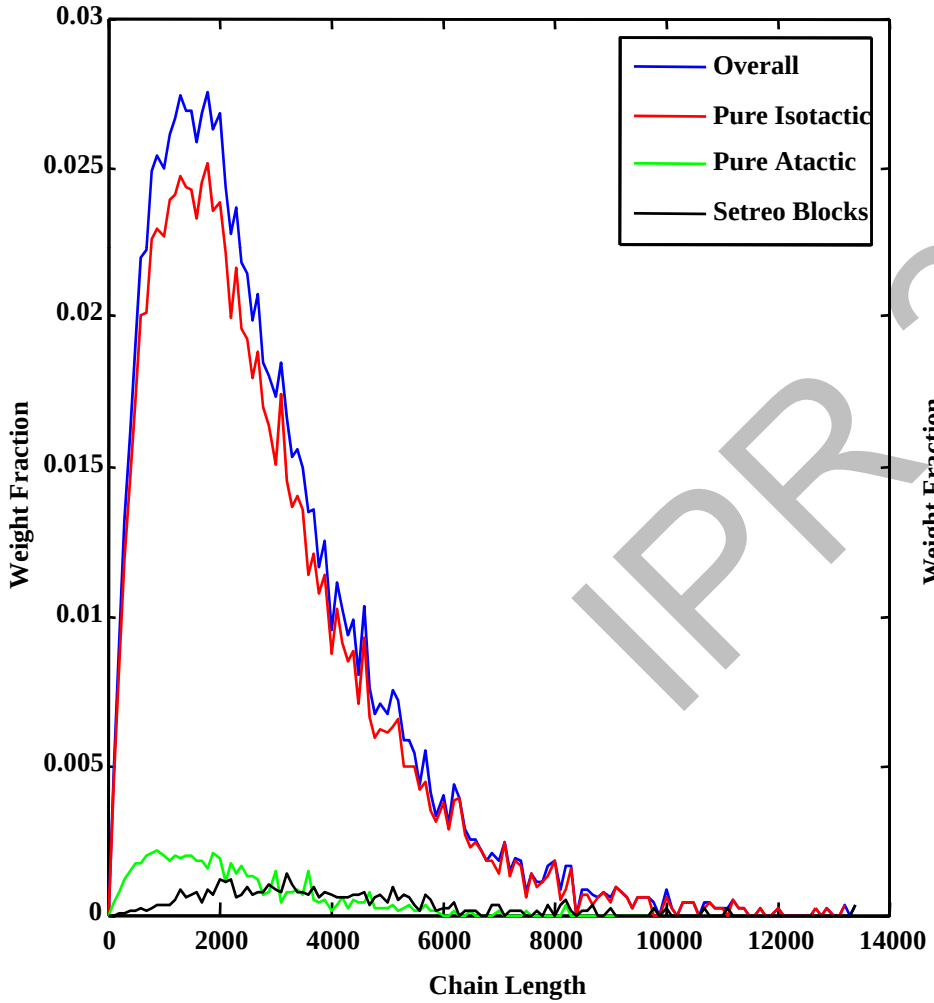


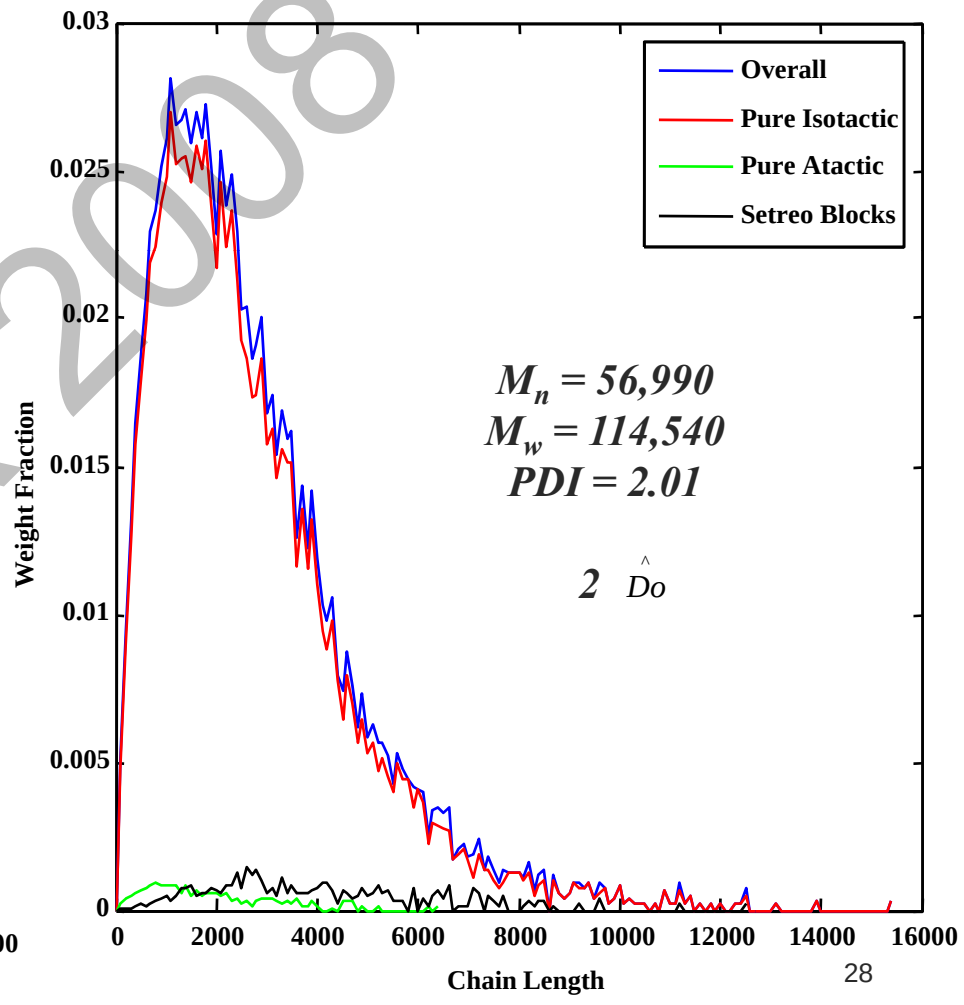
Chain Length vs. Weight Fraction @ 1/2 [Do]





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%
PDI		2.00	2.00	0.00%

Steady State vs. Dynamic Solution Simulations

	Steady State			Dynamic			Error %		
i	***Mn***	***Mw***	**PD**	***Mn***	***Mw***	**PD**	***Mn***	***Mw***	**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%

	Steady State			Dynamic			Error %		
	Mn	**Mw**	**PD**	**Mn**	**Mw**	**PD**	**Mn**	**Mw**	**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%