Propylene Polymerization using Ziegler-Natta Catalysts

Mathematical Modeling, Polymerization Kinetics and Polymer Characterization Study

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University of Waterloo

Waterloo, Ontario

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Outline

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  - Polypropylene
  - Ziegler-Natta Catalysts and Electron Donors
- **Results**
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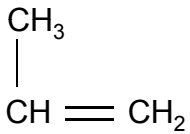
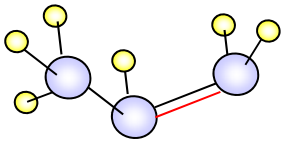
  - Polymerization Experiments: Kinetic
    - Reactor Setup
    - Estimation of Kinetic Constants
  - Polymerization Experiments: Characterization
    - Molecular Weight / GPC
    - Tacticity / ^{13}C NMR
    - Crystallinity / CEF
- **Conclusions**

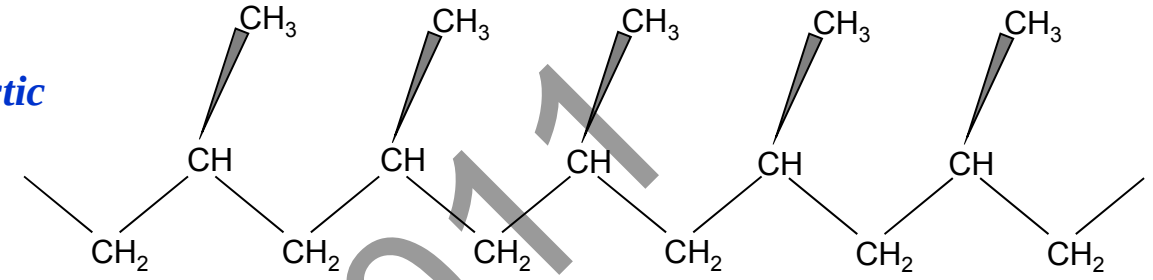
Polypropylene

Propylene

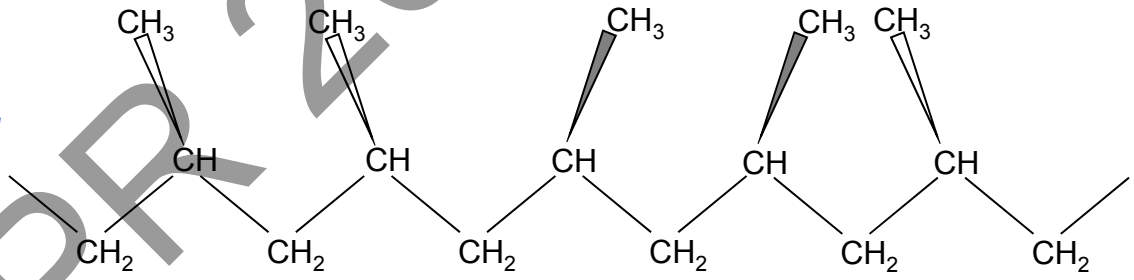




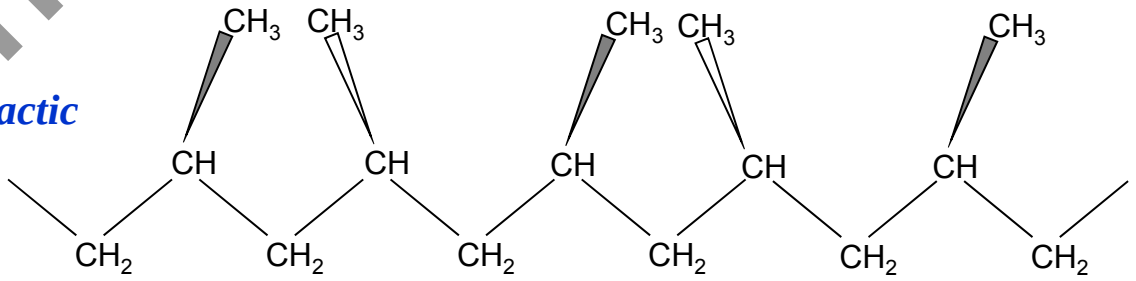
Isotactic



Atactic

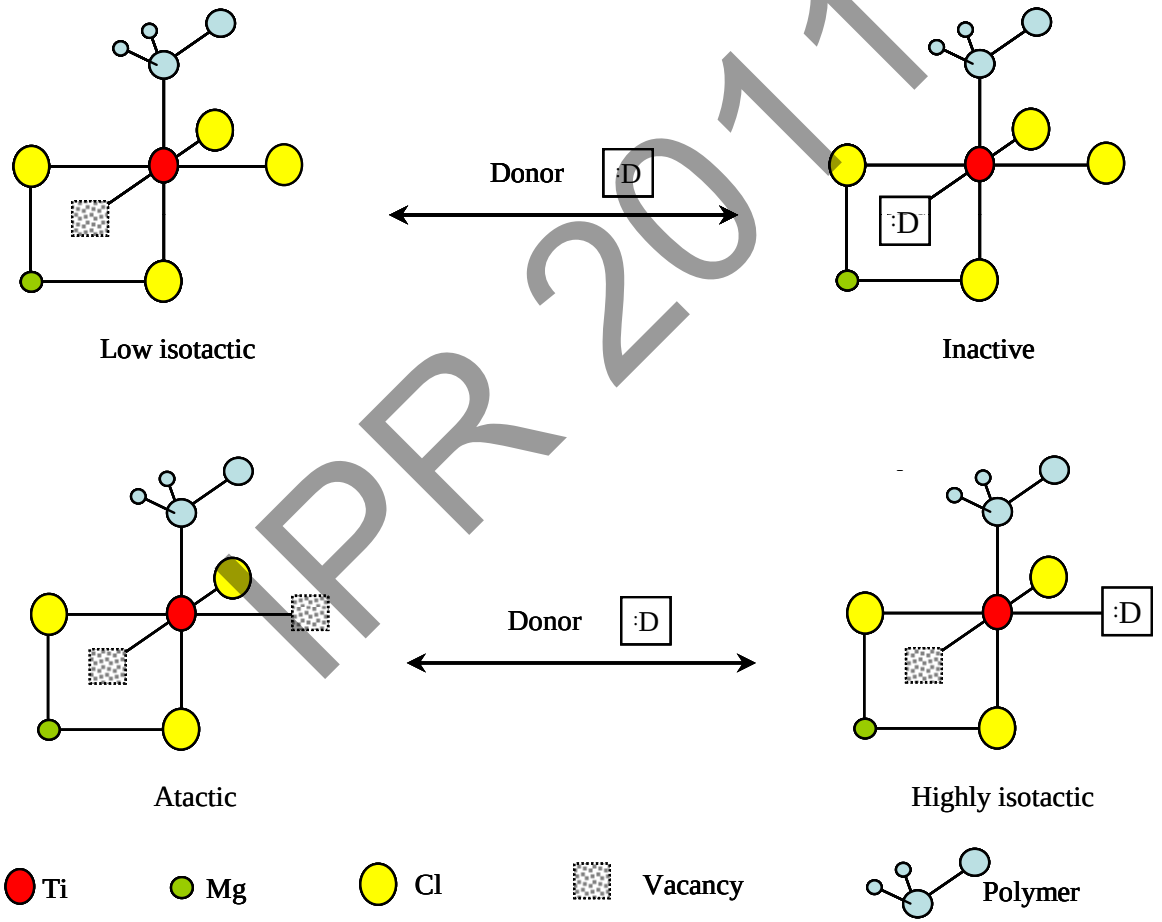


Syndiotactic



Ziegler-Natta Catalyst

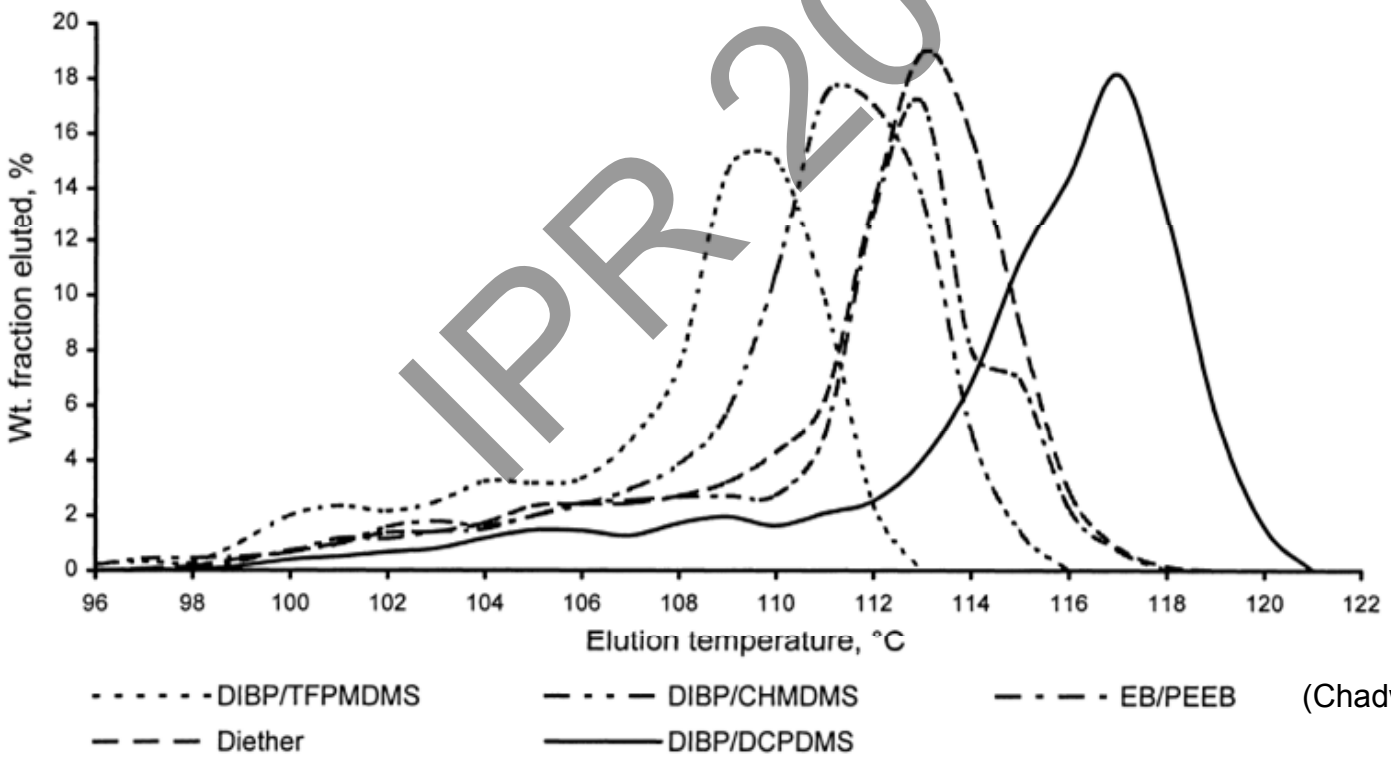
- Electron Donor Functionality



Active site models for **$MgCl_2$·$TiCl_4$** (Kakugo *et al.*, 1988)

Isotacticity and MWD

- Polypropylene tacticity and MWD have a significant effect on its properties.
- Electron donors control polypropylene tacticity.

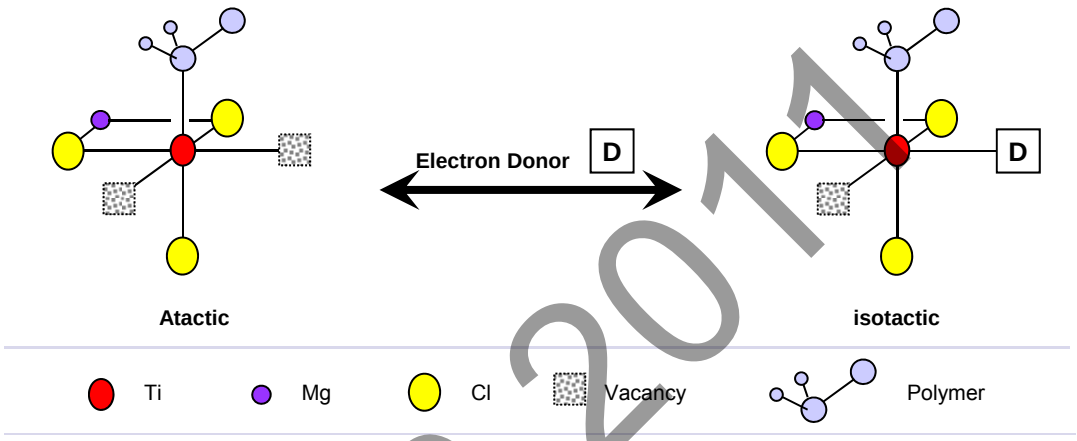


(Chadwick *et al*, 2001)

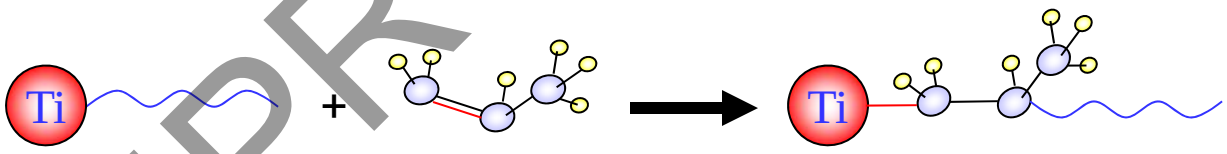
Mathematical Modeling

Modeling

- **Site Transformation:**



- **Propagation:**

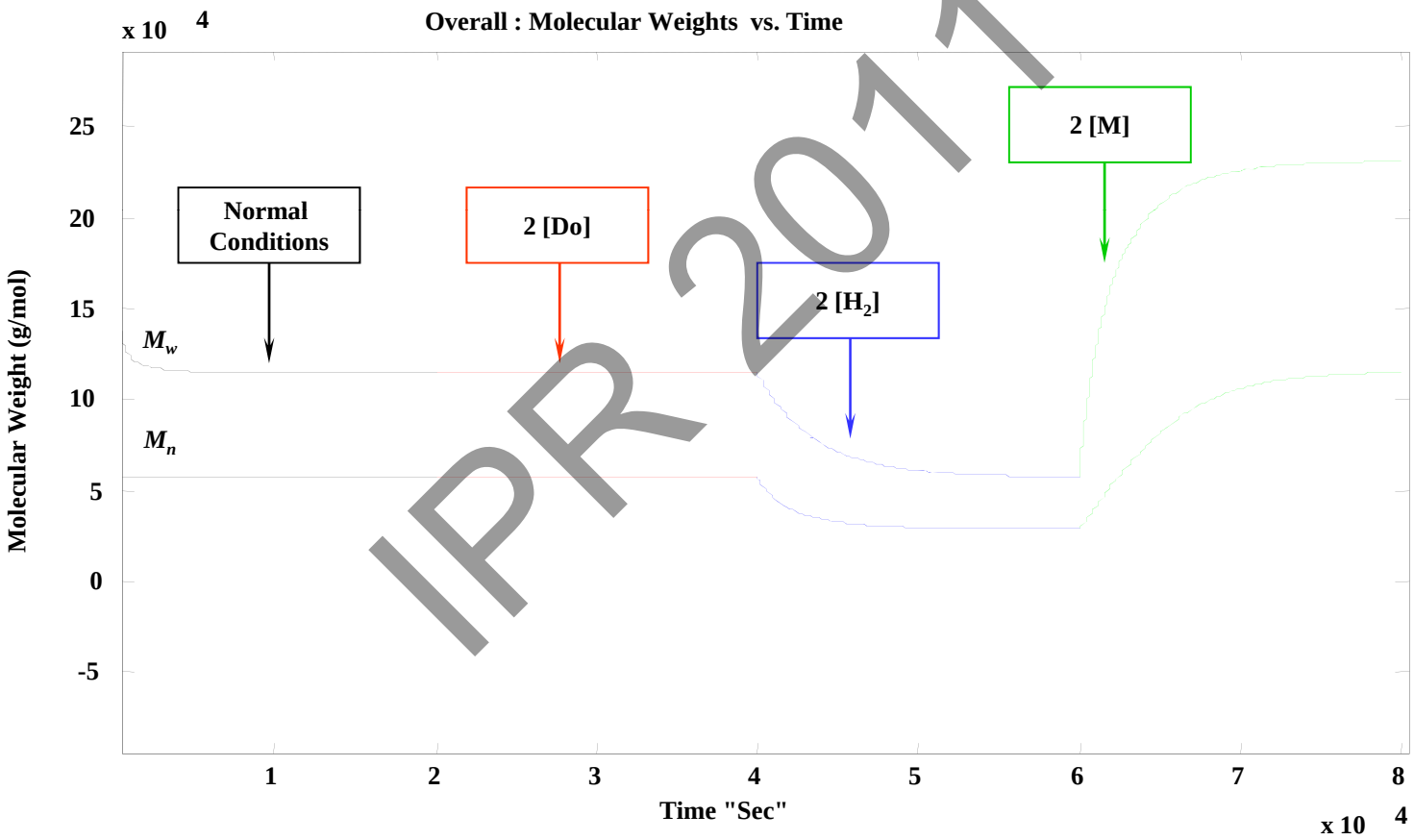


- **Termination:**

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

Dynamic Solution Simulation

Modeling Results



A. Alshaiban and J. B. P. Soares, *Macromol. Symp.*, **285**, 8 (2009)

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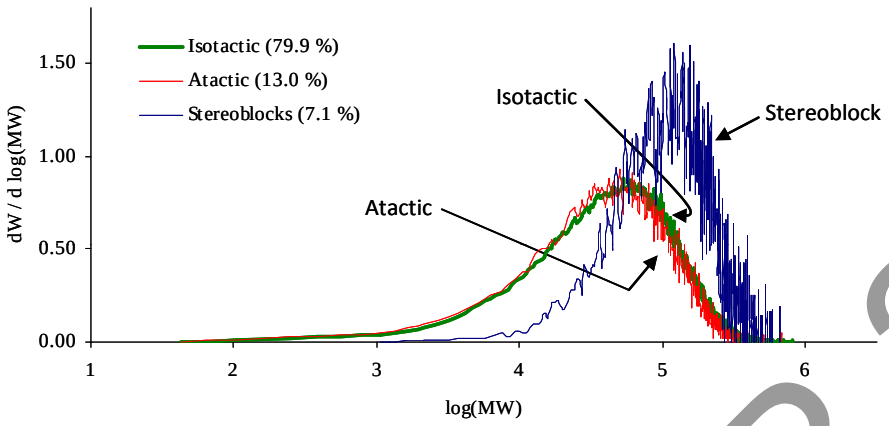
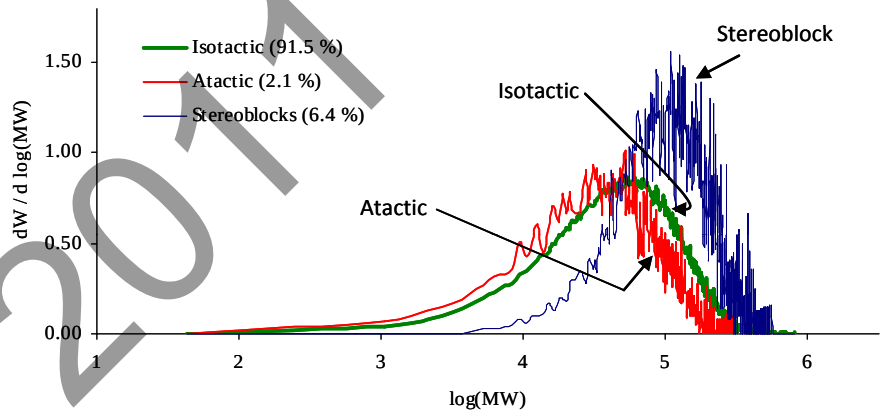
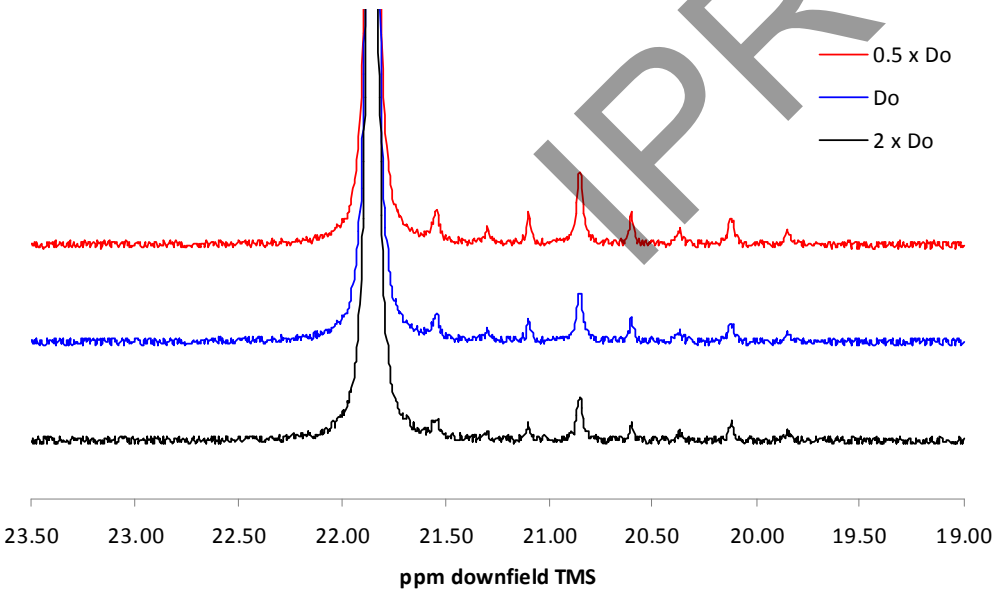
Monte Carlo Simulations







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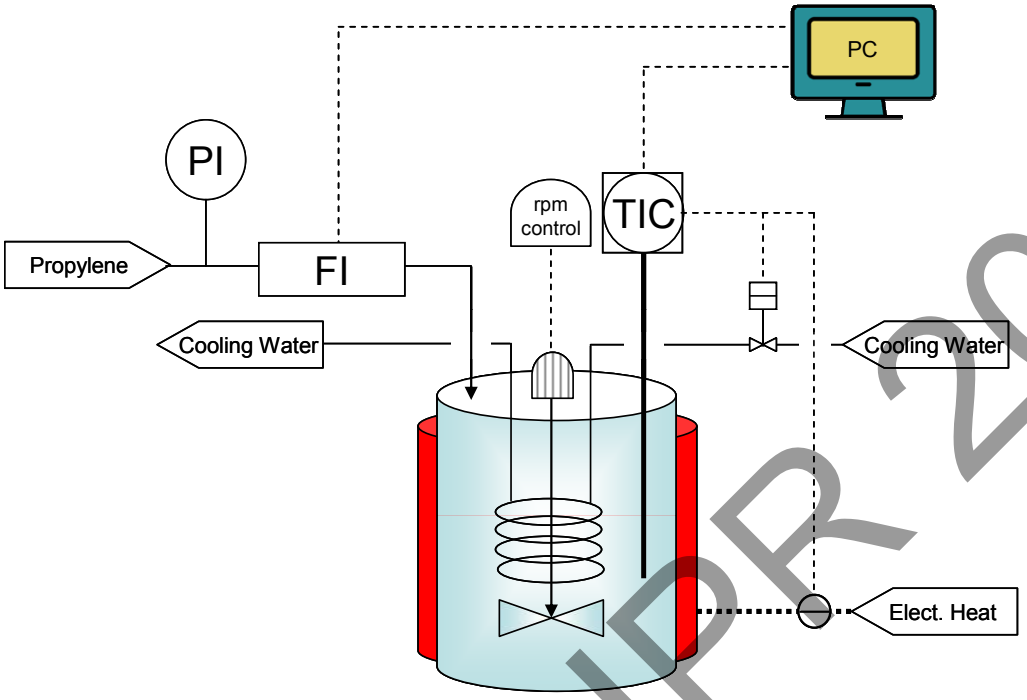
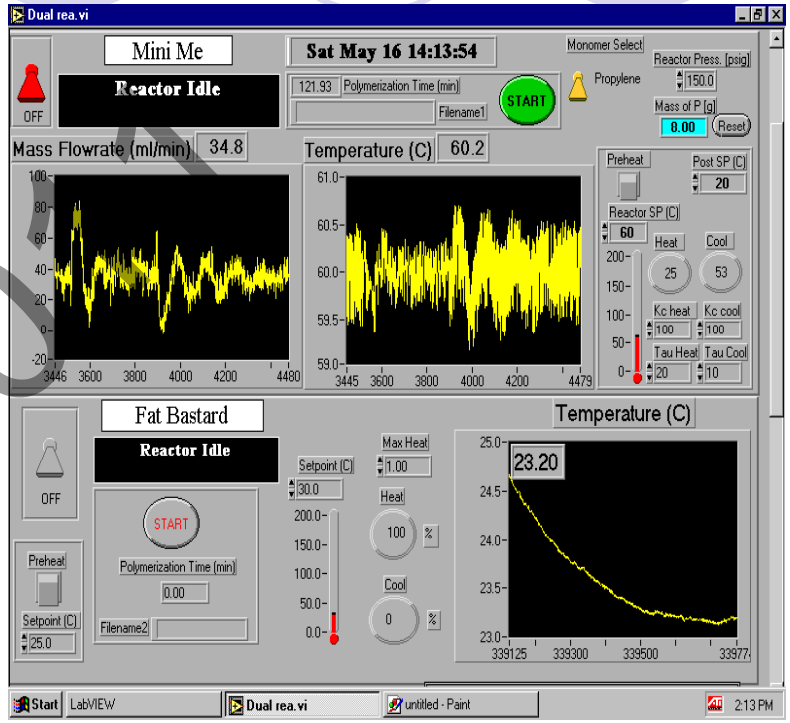
Polymerization Experiments

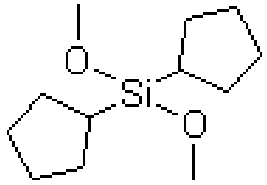
Reactor Set-up





DCPDMS (D-Donor)

Di cyclo pentyl di methoxy silane



	Level-1	Level-2
Do/*Ti* (mol/mol)	**1.5**	**0**
H_2 (psi)	**16**	**0**
T (°C)	**60**	**70**

Estimation of Kinetic Constants

Propylene Uptake

$$R_{p,Exp} = -V\frac{\mathrm{d}M}{\mathrm{d}t}$$

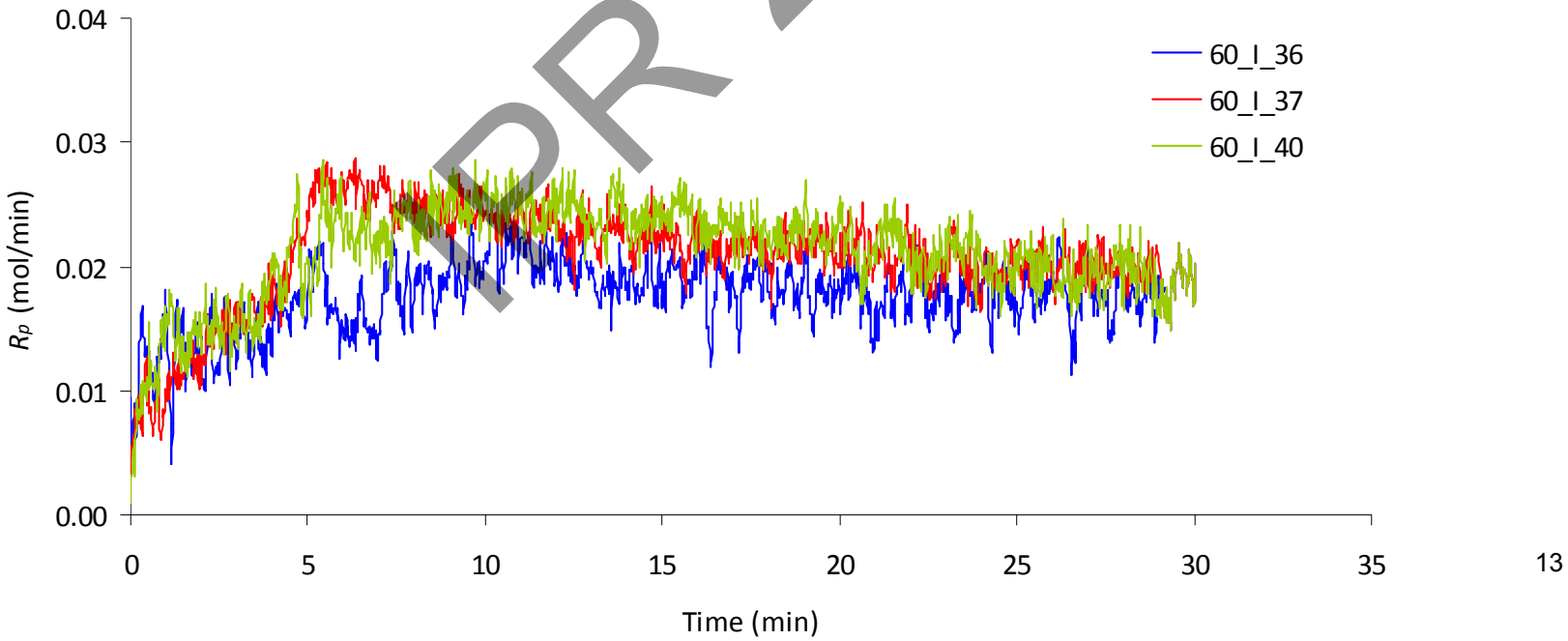
Mathematical Formulation

$$R_p = k_p M C_0 \frac{\left[1 - e^{-K_a t\left(1-{k_d}/{K_a}\right)}\right] e^{-k_d t}}{1-{k_d}/{K_a}} V$$

$$\Delta^2 = \min_{\substack{k_p \\ K_a \\ k_d}} \sum [R_{p,Exp} - R_p]^2$$

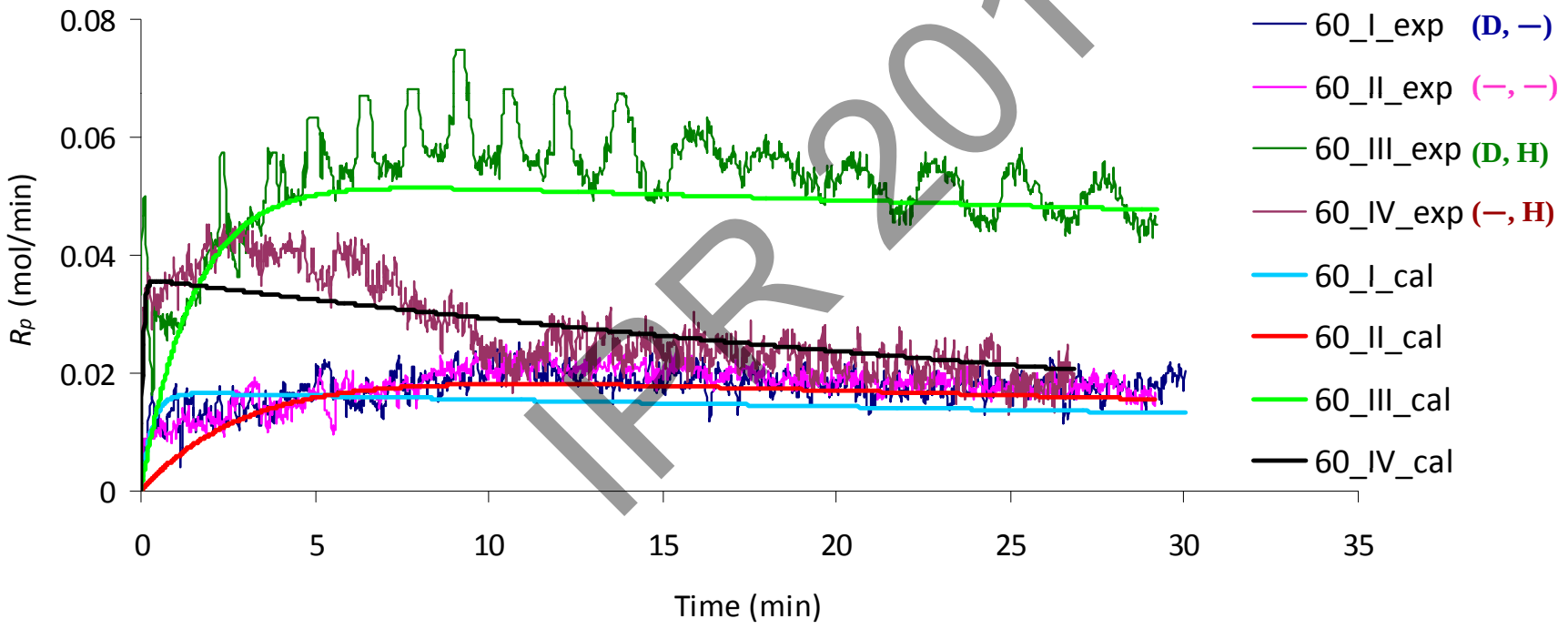
Polymerization Experiments

	60°C			
Factor	**I**	**II**	**III**	**IV**
Al/Ti (mol/mol)	900 (± 7.1%)	900 (± 16%)	900 (± 7.7%)	900 (± 7.2%)
Do/Ti (mol/mol)	1.5 (± 7.1%)	0	1.5 (± 9.6%)	0
H_2 (psi)	0	0	16 (± 10%)	16 (± 10%)
Yield (g-PP·g-cat^{-1}·min^{-1})	7.6 (±15%)	6.1 (±15%)	17.3 (±2.5%)	8.4 (±6.5%)



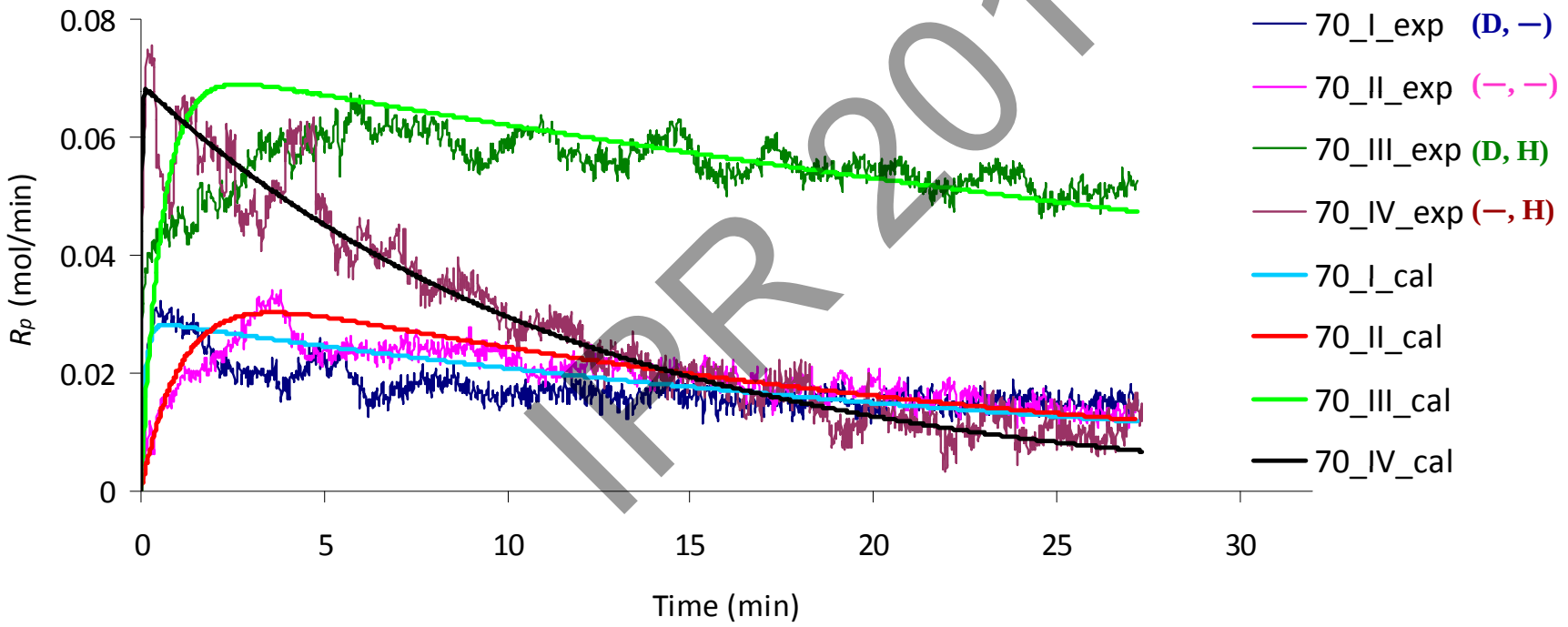
Polymerization Experiments

R_p Experimental vs. Calculated at **60**°C



Polymerization Experiments

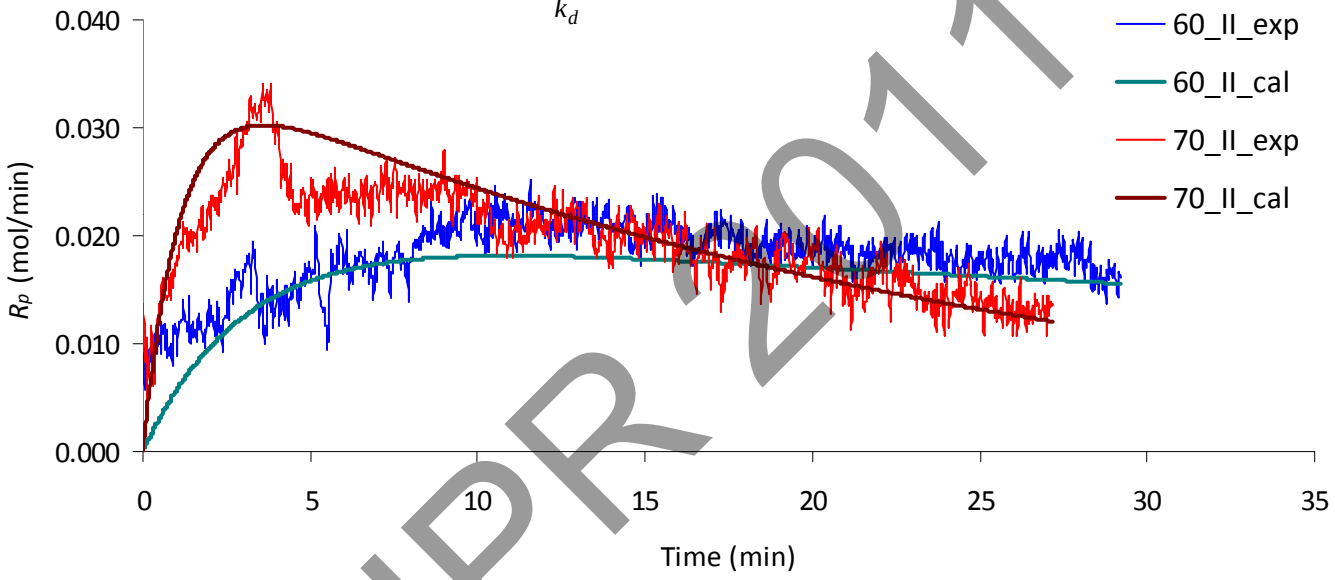
R_p Experimental vs. Calculated at **70**°C



Polymerization Experiments

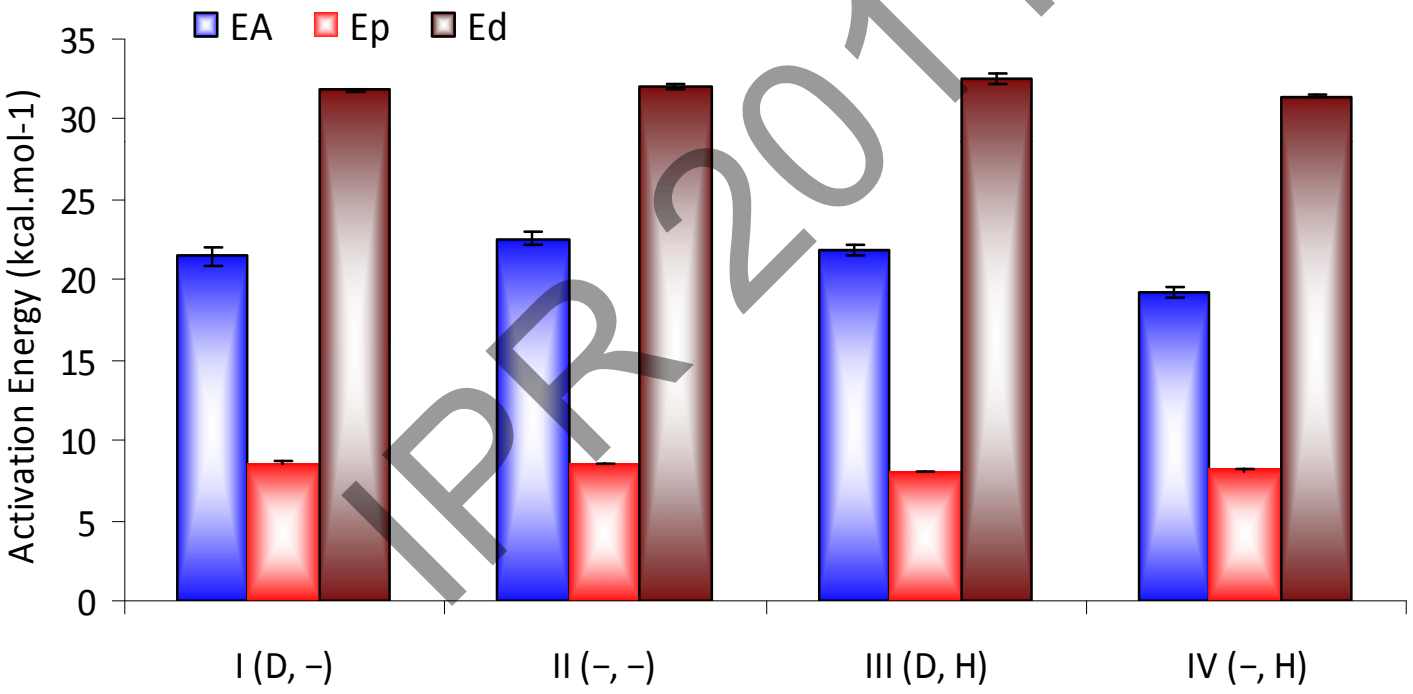
Group II (D, —)

$$\Delta^2 = \min_{\substack{k_p \\ K_a \\ k_d}} \sum [(R_{p,Exp} - R_p)\big|_{60^\circ C} + (R_{p,Exp} - R_p)\big|_{70^\circ C}]^2$$

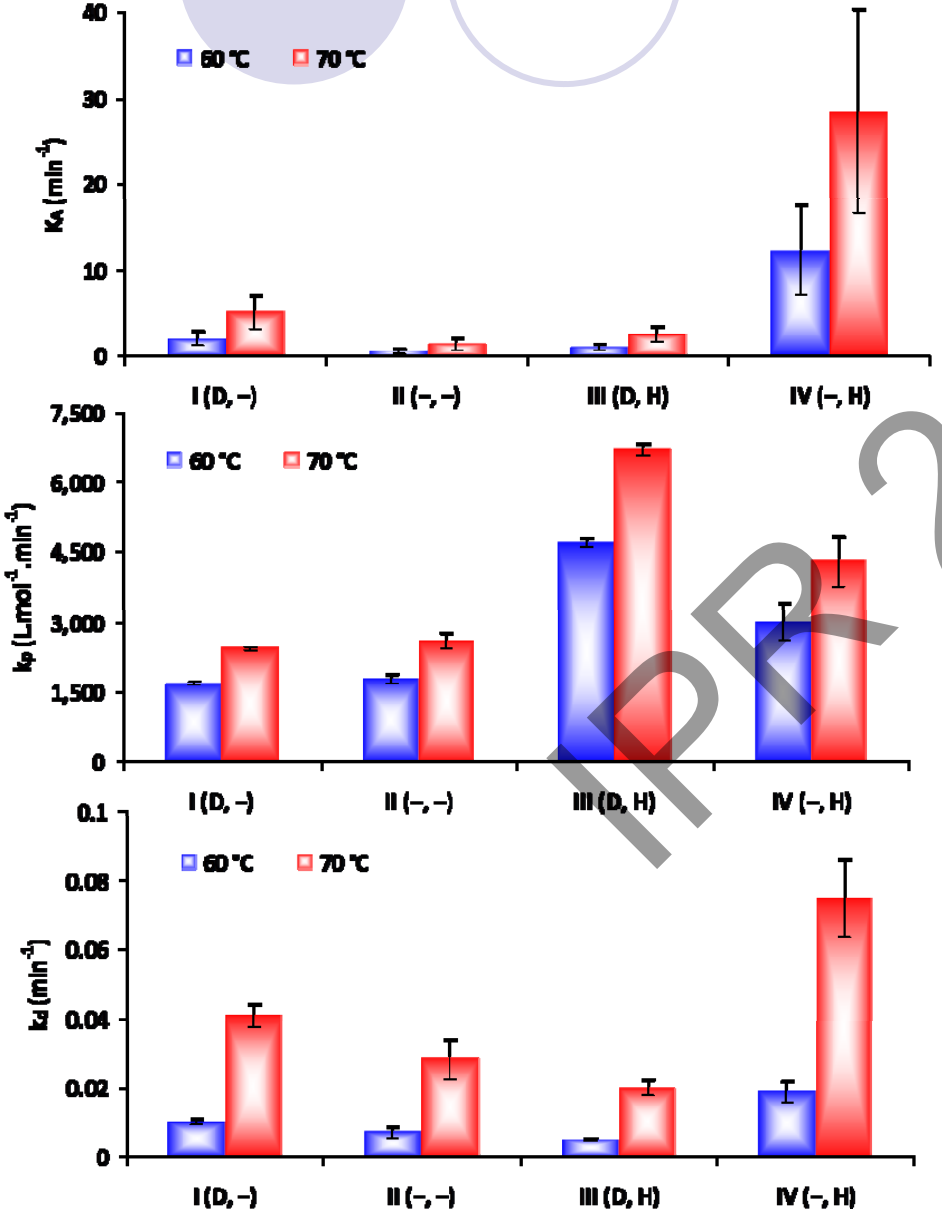


	60 °C	70 °C	E kcal/mol
K_a (min)$^{-1}$	0.33	0.89	22.8
k_p (L·mol^{-1}· min^{-1})	1.7x10^3	2.5x10^3	8.6
k_d (min)$^{-1}$	0.010	0.041	31.8

Polymerization Experiments



Summary of the Estimated Kinetic Constants



- K_a increases as T increases.
- K_a increases by adding H_2 in absence of Do.
- K_a get's the highest value at the presence of H_2 only (IV).

- K_p increases as T increases.
- k_p get's the highest value at the presence of Do & H_2 (III).
- k_p increases by adding H_2 (III) & (IV).

- k_d increases as T increases.
- k_d increases by adding H_2 in absence of Do (IV).

Conclusion

- Developed a detailed mathematical model that describes propylene polymerization kinetics and polypropylene microstructure, taking in consideration the effect of external electron donors.(*)

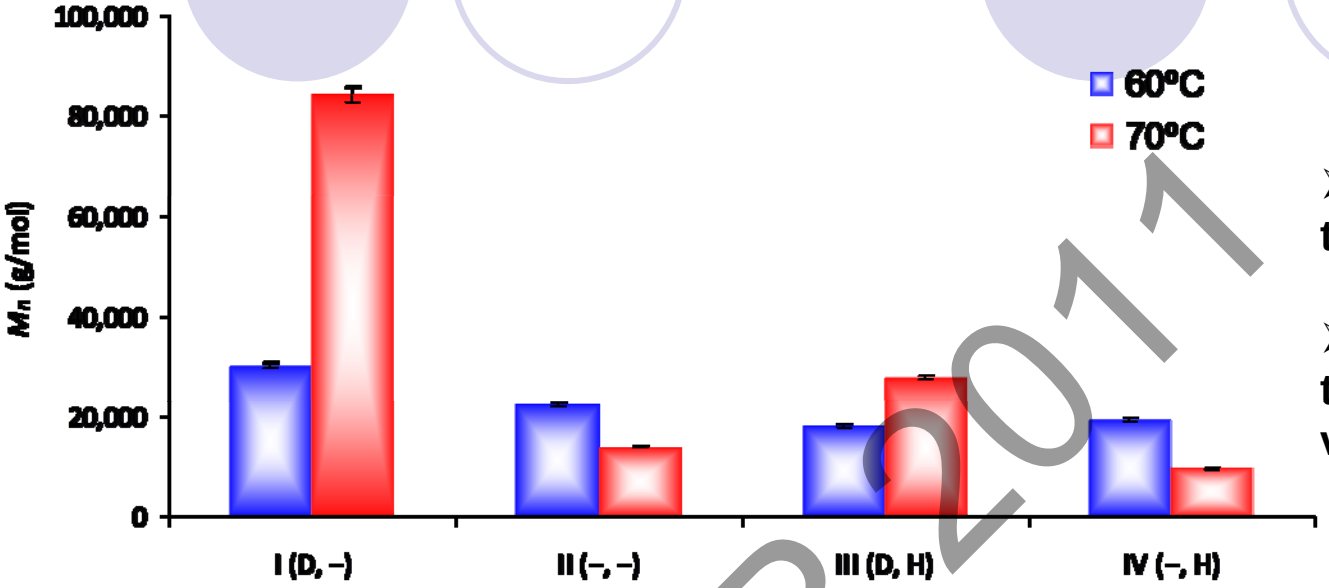
- Estimated the activation energies of activation, propagation, and deactivation of a commercial heterogeneous Ziegler Natta catalyst for propylene polymerization in order to be integrated with the commercial process simulator.

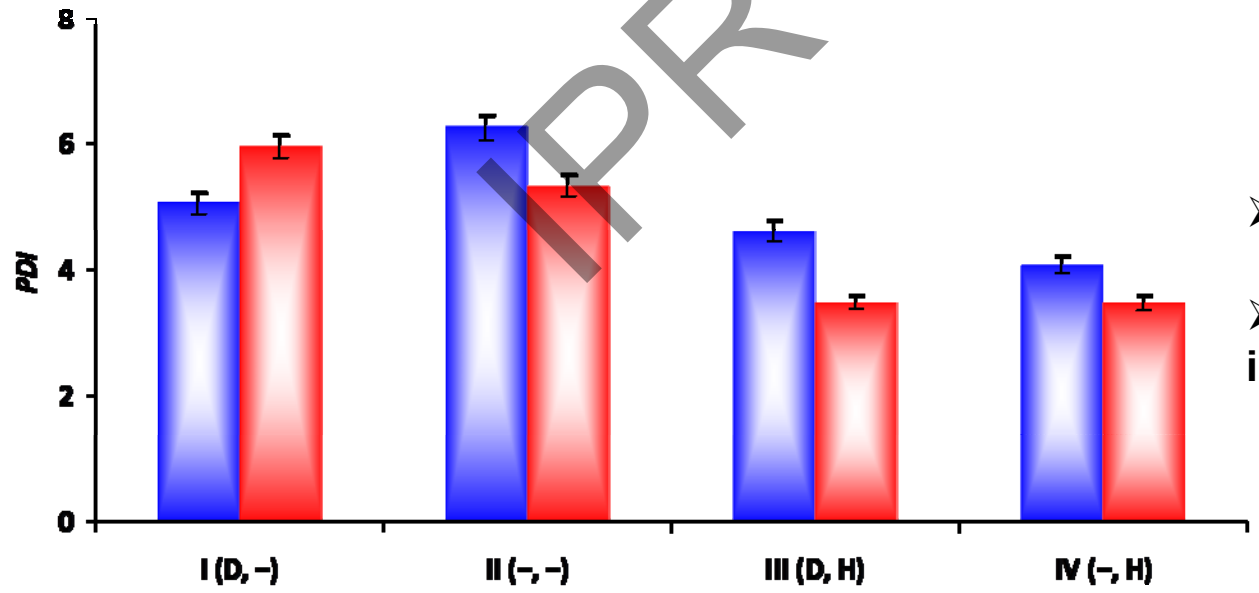
(*) A. Alshaiban and J. B. P. Soares, *Macromol. Symp.*, **285**, 8 (2009)

A. Alshaiban and J.B.P. Soares, *Macromol. React. Eng.*, **5**, 96 (2011)

GPC Analysis

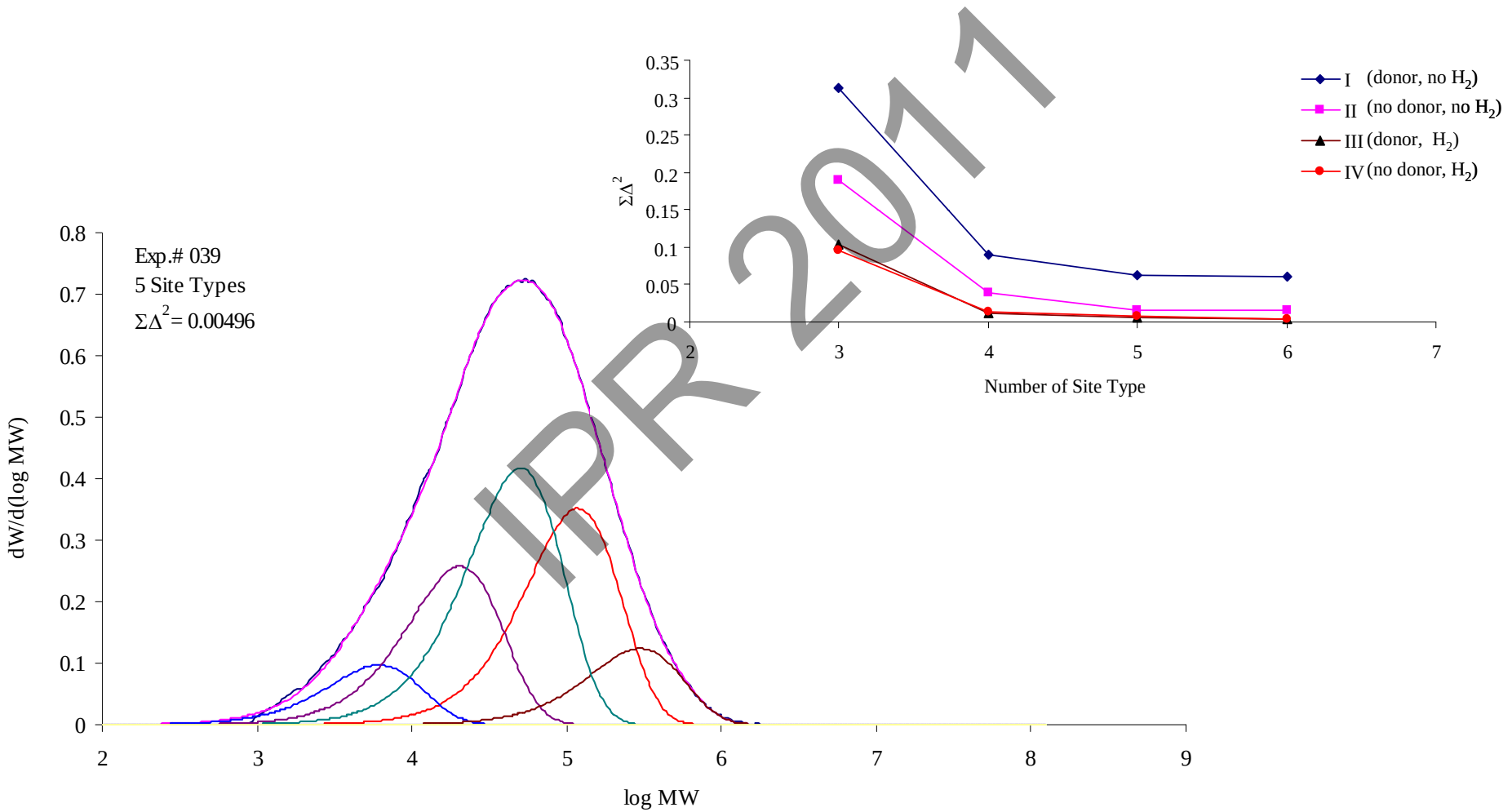
GPC Analysis





- M_n decreases with H_2 at the same T.
- M_n increases with T in the presence of Do and vice versa.
- PDI decreases with H_2.
- PDI decreases with increasing T.

GPC Analysis



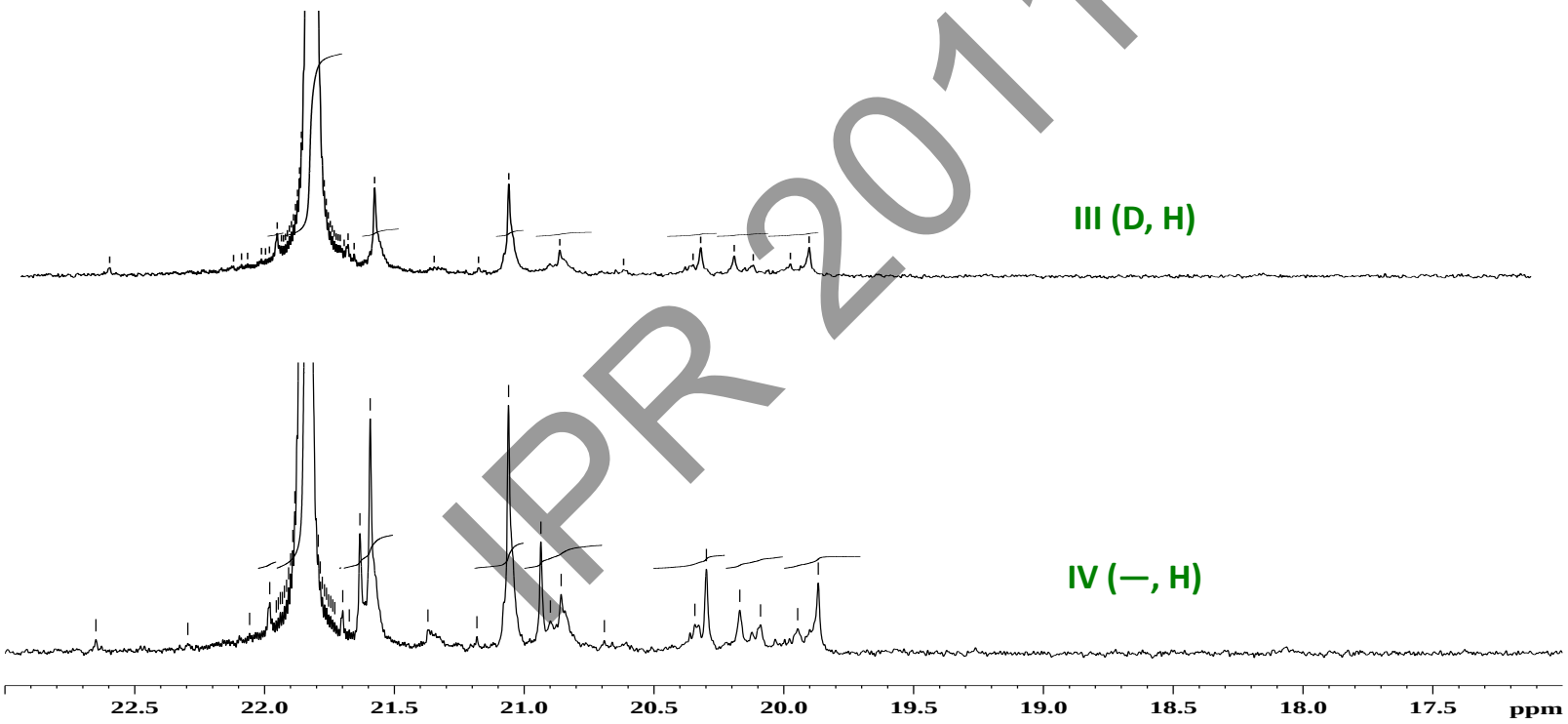
GPC Analysis

Parameter	60°C I (D, —)	II (—, —)	III (D, H)	IV (—, H)
M_n (g·mol^{-1})	30.1 x 10^3	22.5 x 10^3	18 x 10^3	19 x 10^3
M_w (g·mol^{-1})	151.6 x 10^3	140.3 x 10^3	82.9 x 10^3	77.3 x 10^3
PDI	5.0	6.2	4.6	4.1
Number of site types (n)	5	5	5	5

Parameter	70°C I (D, —)	II (—, —)	III (D, H)	IV (—, H)
M_n (g·mol^{-1})	84.1 x 10^3	13.7 x 10^3	27.5 x 10^3	9.4 x 10^3
M_w (g·mol^{-1})	499.4 x 10^3	72.5 x 10^3	95.5 x 10^3	32.6 x 10^3
PDI	5.9	5.3	3.5	3.5
Number of site types (n)	5	5	4	4

^{13}C NMR Analysis

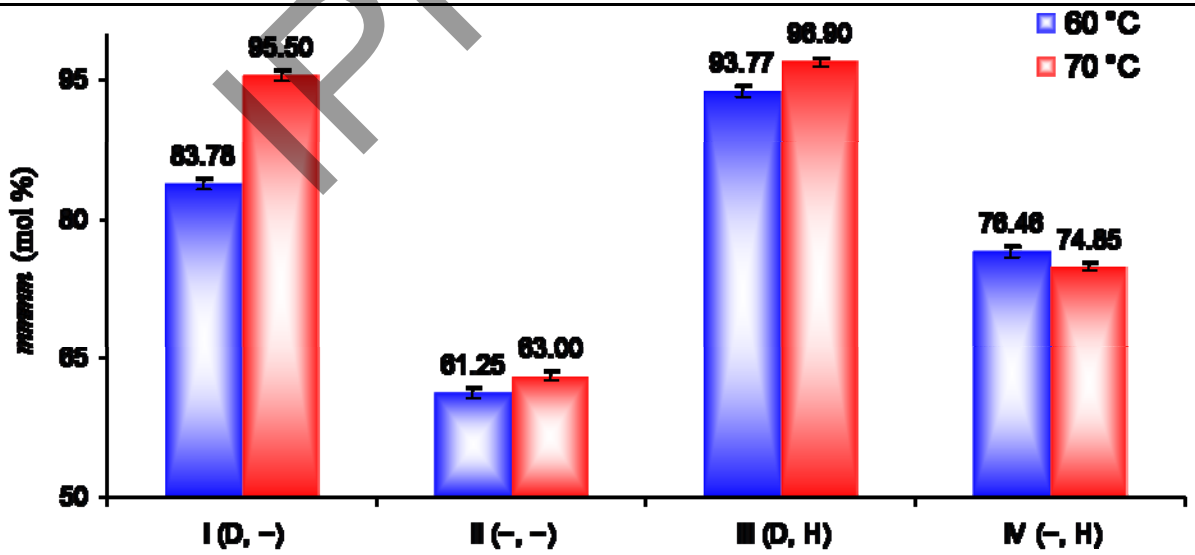
^{13}C NMR Analysis



^{13}C NMR Analysis

Seq.#		Range (d)*	I (D, —)	II (—, —)	III (D, H)	IV (—, H)
1	*mmmm*	22.0 – 21.7	83.78	61.25	93.77	76.46
2	*mmmr*	21.7 – 21.4	3.73	9.51	3.06	6.73
3	*rmmr*	21.4 – 21.2	0.53	1.87	0.00	0.00
4	*mmrr*	21.2 – 21.0	4.17	7.76	2.48	4.96
5	*mmrm + rmrr*	21.0 – 20-7	2.01	6.38	0.00	4.60
6	*rmrm*	20.7 – 20.5	0.00	1.67	0.00	0.00
7	*rrrr*	20.5 – 20.25	2.90	3.55	0.00	2.61
8	*rrrm*	20.25 – 20.0	1.67	5.18	0.00	2.29
9	*mrrm*	20.0 – 19.7	1.21	2.82	0.69	2.35

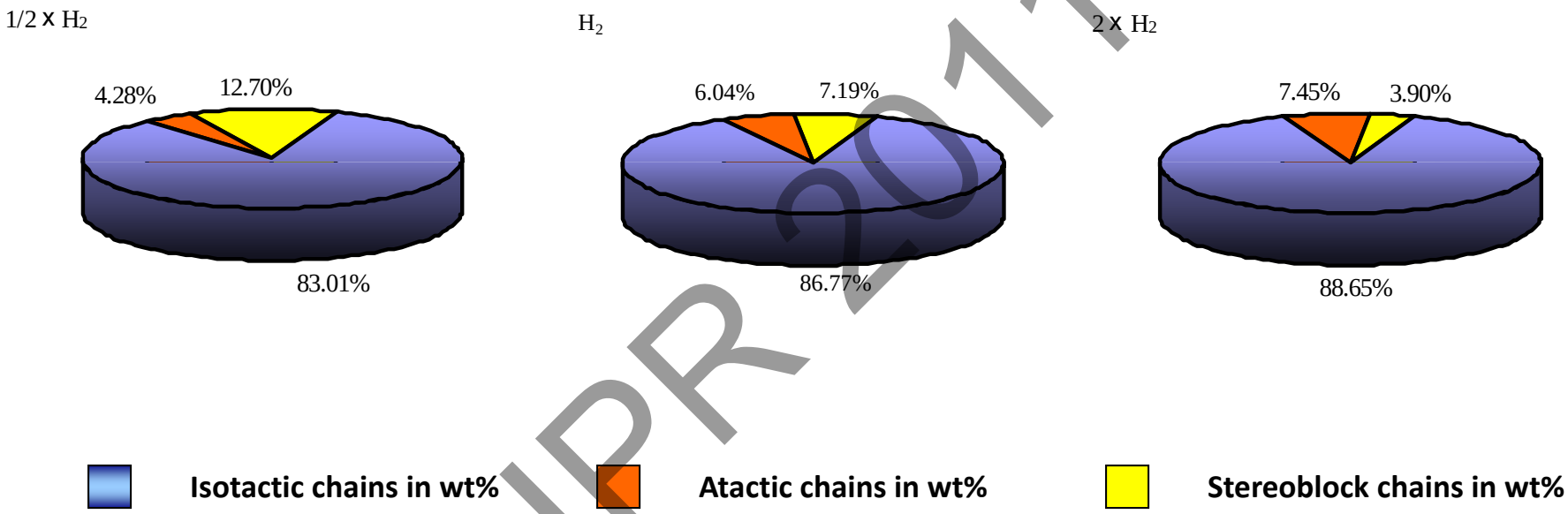
•Range of d reported by Busico *et al.*(2001)



^{13}C NMR Analysis: Simulated H_2 effect on polypropylene tacticity

Polymerization Experiments

Characterization



A. Alshaiban, **2008**, MASc. Thesis, University of Waterloo

A. Alshaiban and J. B. P. Soares, *Macromol. Symp.*, **285**, 8 (2009)

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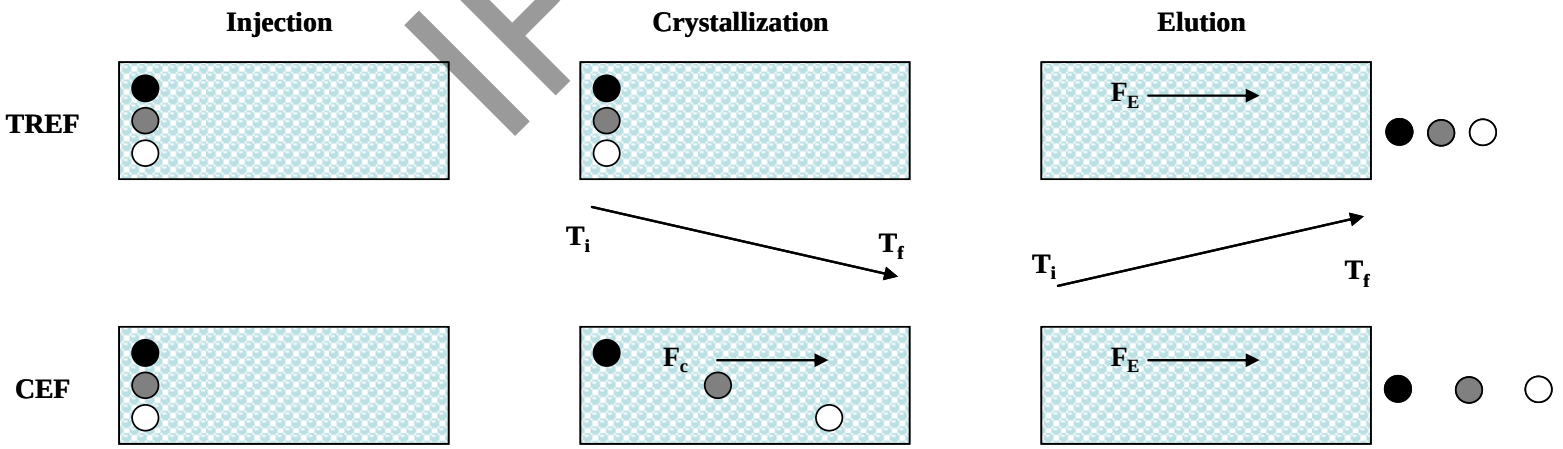
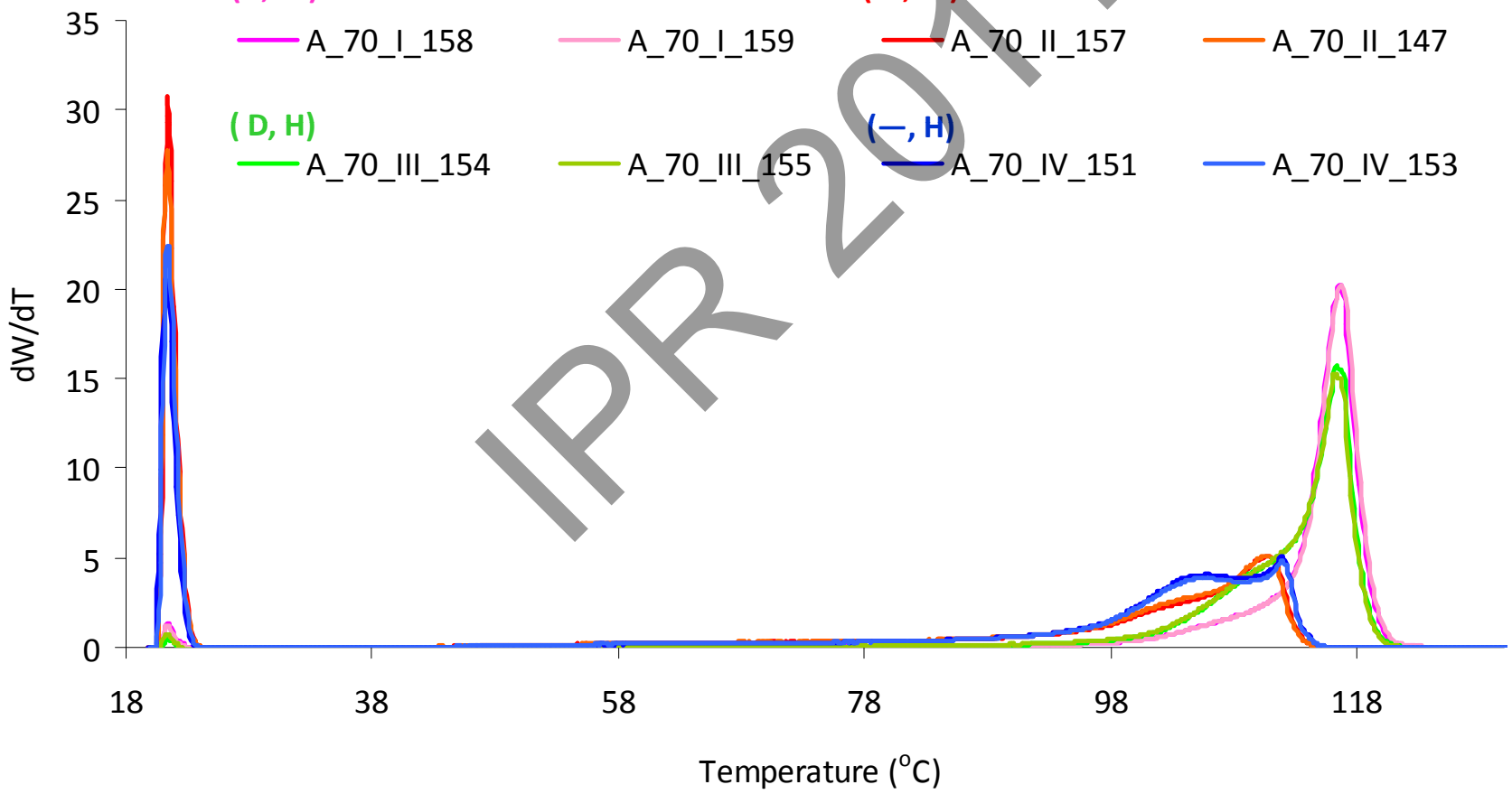
CEF Analysis



CEF Analysis

Polymerization Experiments

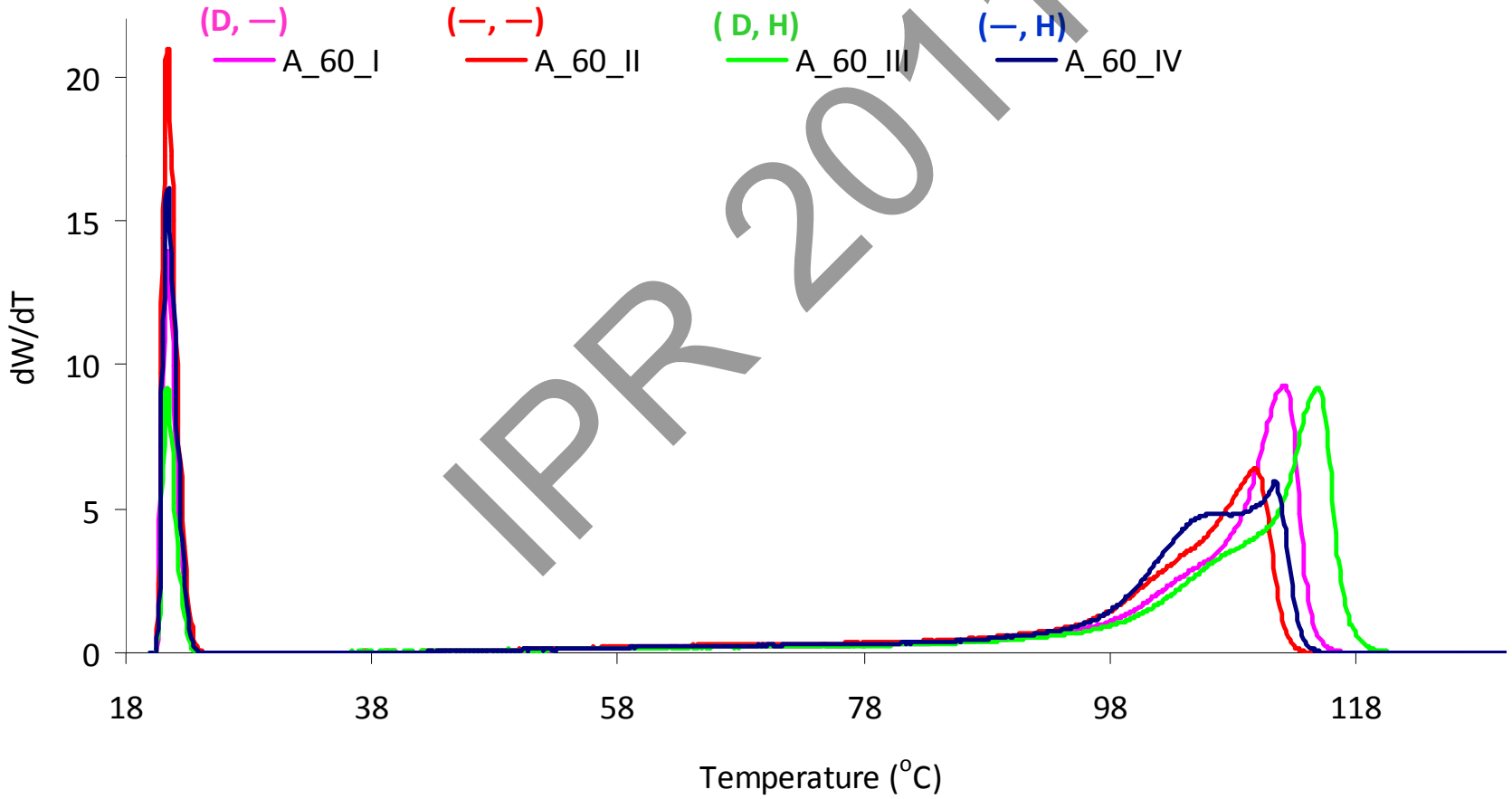
Characterization



CEF Analysis

Polymerization Experiments

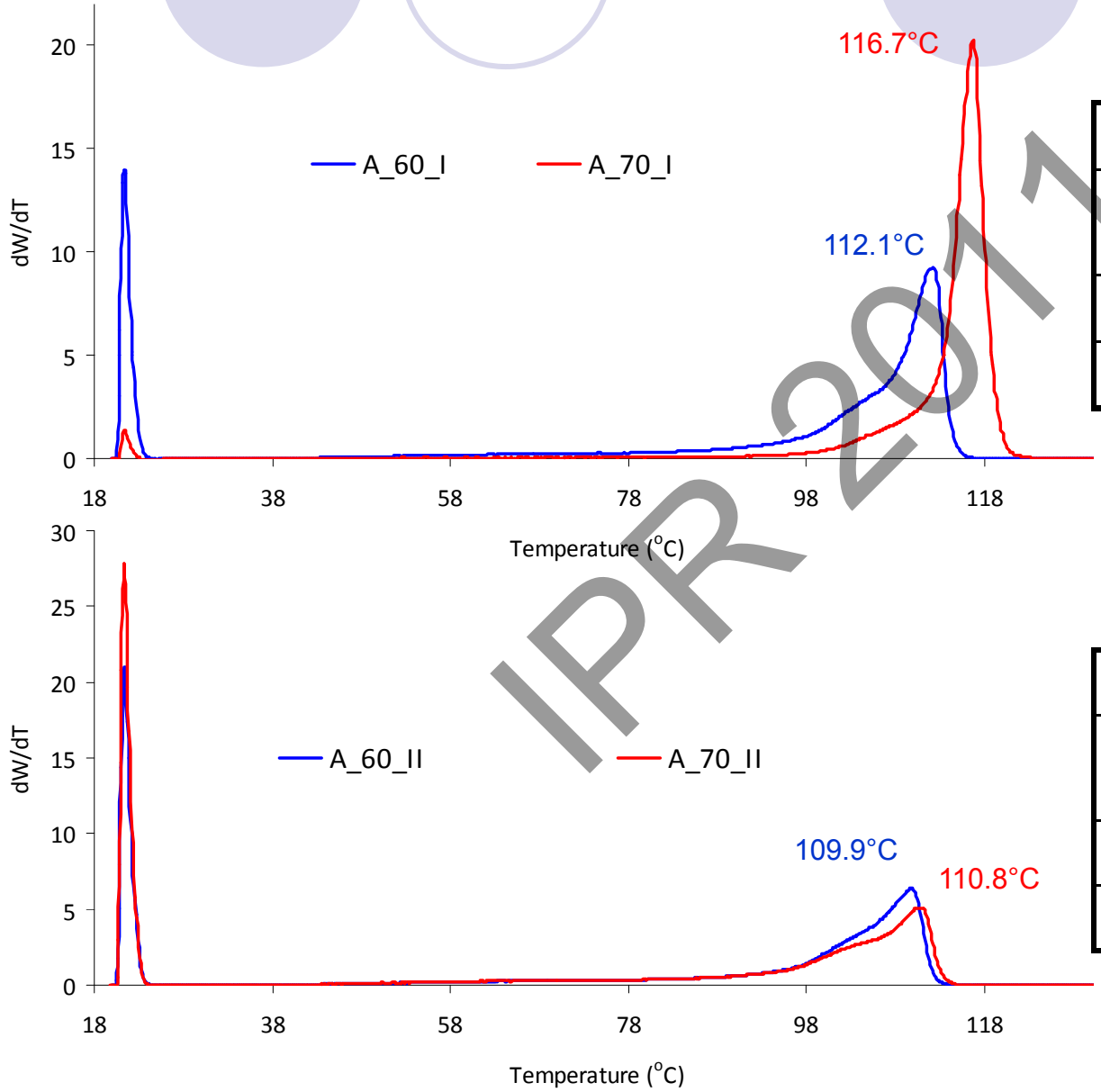
Characterization



CEF Analysis

Polymerization Experiments

Characterization



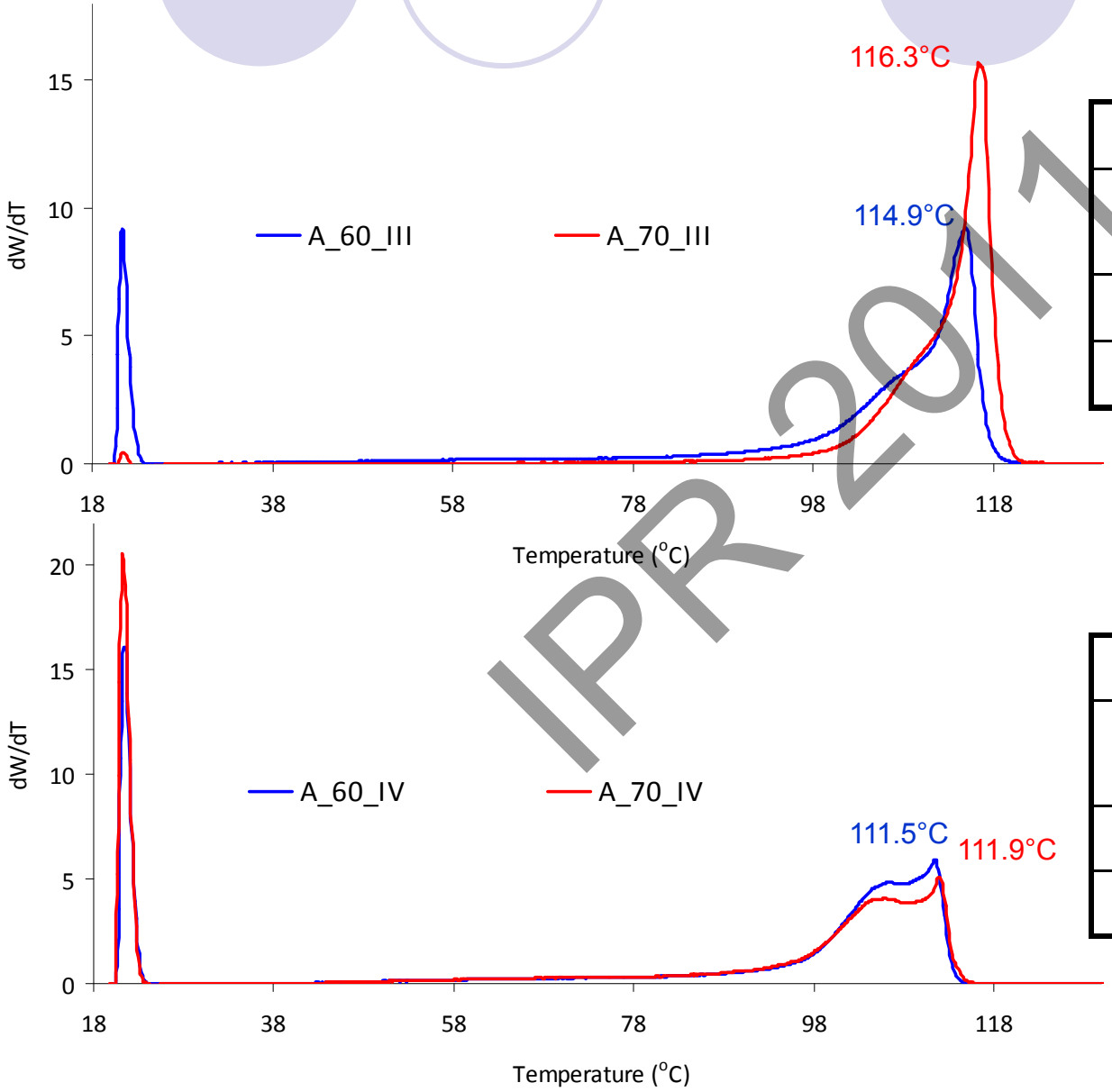
Group I (D, —)		
M_n g/mol	PDI	*mmmm* %
30.1 x 10^3	5.0	83.78
84.1 x 10^3	5.9	95.5

Group II (—, —)		
M_n g/mol	PDI	*mmmm* %
22.5 x 10^3	6.2	61.25
13.7 x 10^3	5.3	63.00

CEF Analysis

Polymerization Experiments

Characterization



Group III (D, H)		
M_n g/mol	PDI	*mmmm* %
18 x 10^3	4.6	93.77
27.5 x 10^3	3.5	96.90

Group IV (—, H)		
M_n g/mol	PDI	*mmmm* %
19 x 10^3	4.1	76.46
9.4 x 10^3	3.5	74.85

Conclusion

- **Conducted a systematic polymerization kinetics and microstructural studies for polypropylene produced using 4th generation ZN catalyst and compared the hydrogen effect with the simulation results obtained from the developed mathematical model.**
- **Adding Do increases M_n; and at Do presence, M_n increases with T as in groups I (D,—) & III (D,H).**
- **M_n decreases with H_2 at the same T as we go from II (—, —) to IV(—, H) and from I (D,—) to III (D,H)**
- **Number of site types decreased by one at high T in the presence of H_2.**
- **No significant change in pentad assignments with T except for group I (Do, —)**
- **Introducing H_2 tends to increase the tacticity [I (D,—) → III (D,H)] and [II (—, —) → IV (—, H)] which is in agreement with our simulation of the developed mathematical model.**
- **Group III (D, H) shows the highest crystallization peak temperature.**
- **Crystallinity increases with T in the presence of Do, I (D,—) & III (D,H).**

A. Alshaiban and J. B. P. Soares, *Macromol. Symp.*, **285**, 8 (2009)

A. Alshaiban and J. B. P. Soares, *Macromol. Symp.*, **Accepted**

A. Alshaiban and J. B. P. Soares, *Macromol. React. Eng.*, **5**, 96 (2011**)**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Thank You