Kinetic study of Ethylene homo- and co-polymerization using metallocene catalysts in a solution reactor

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Outline

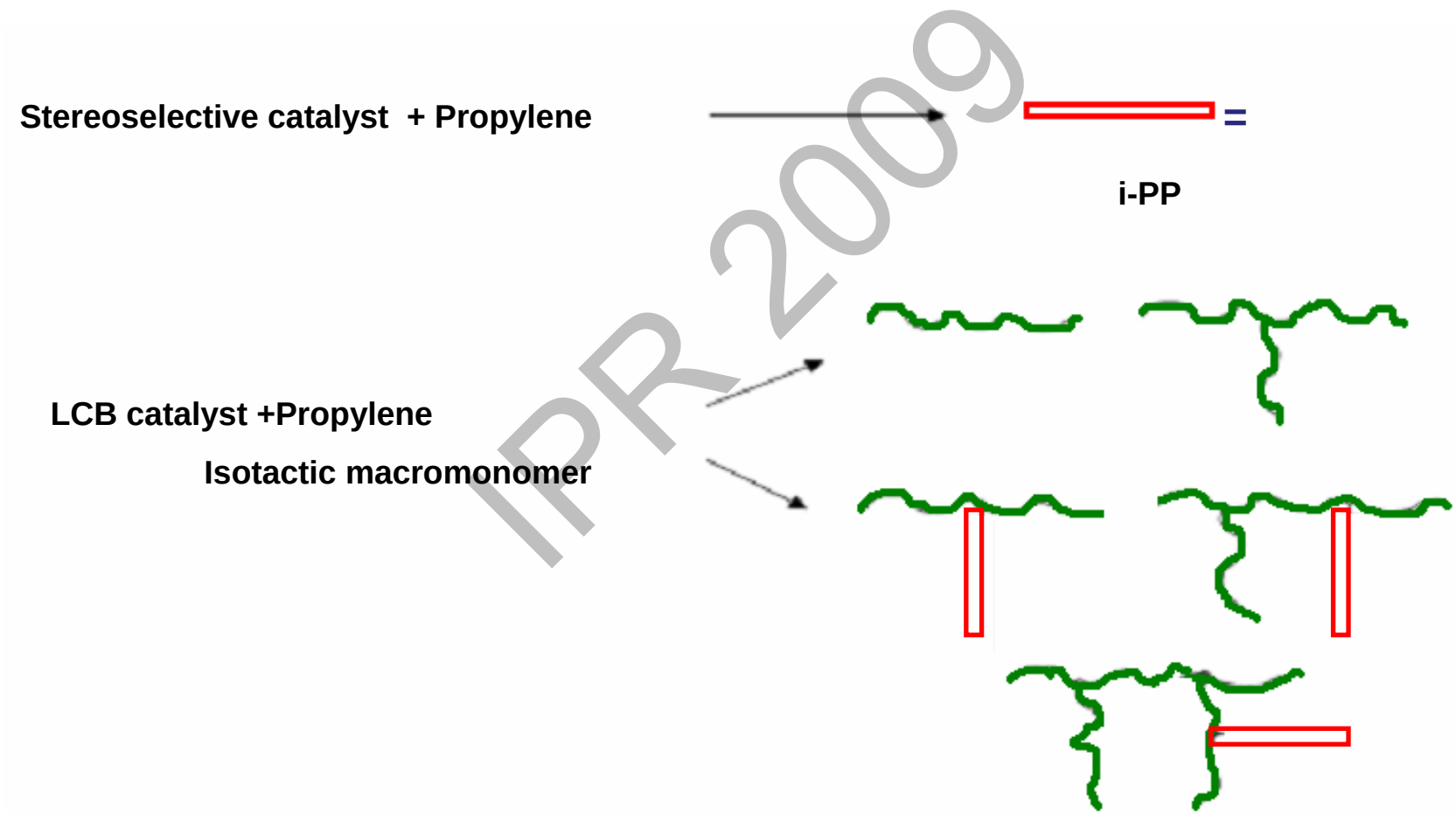
1. Introduction
2. Experimental results and Conclusions

Introduction

- **The use of two single-site catalysts to synthesize polymers with complex microstructures is a very promising way to create novel polyolefins**
- **Dual metallocene systems have been used to produce polyolefins with**
- **Bimodal distributions of molecular weight and chemical composition**
- **Maximize the formation of long chain branches in polyethylene**
- **produce branched and linear olefin block copolymers**

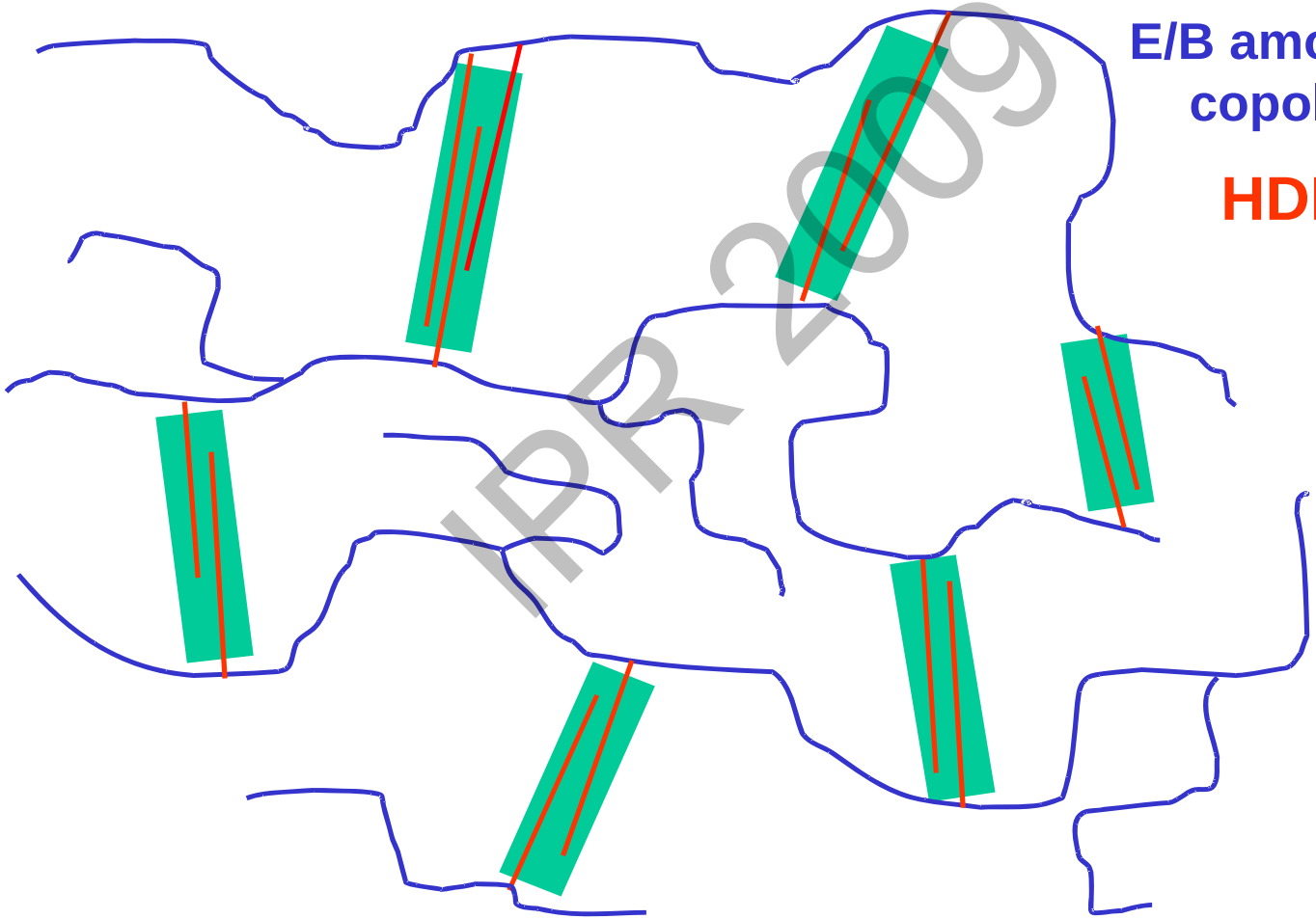
Graft copolymer (Branch-block)

iPP-g-aPP

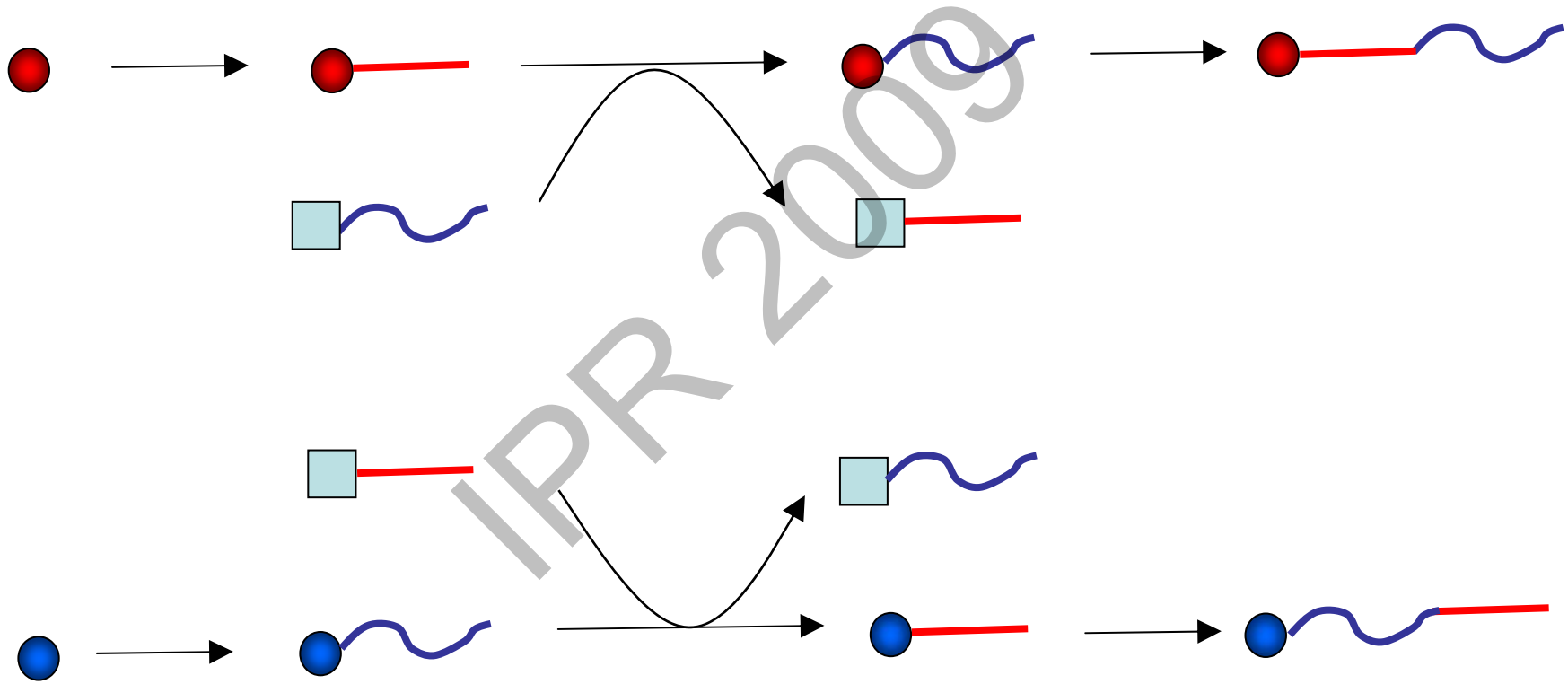


Graft Block Copolymers

Amorphous Backbones + Crystalline LCBs



Block copolymers via chain shuttling



Experimental part

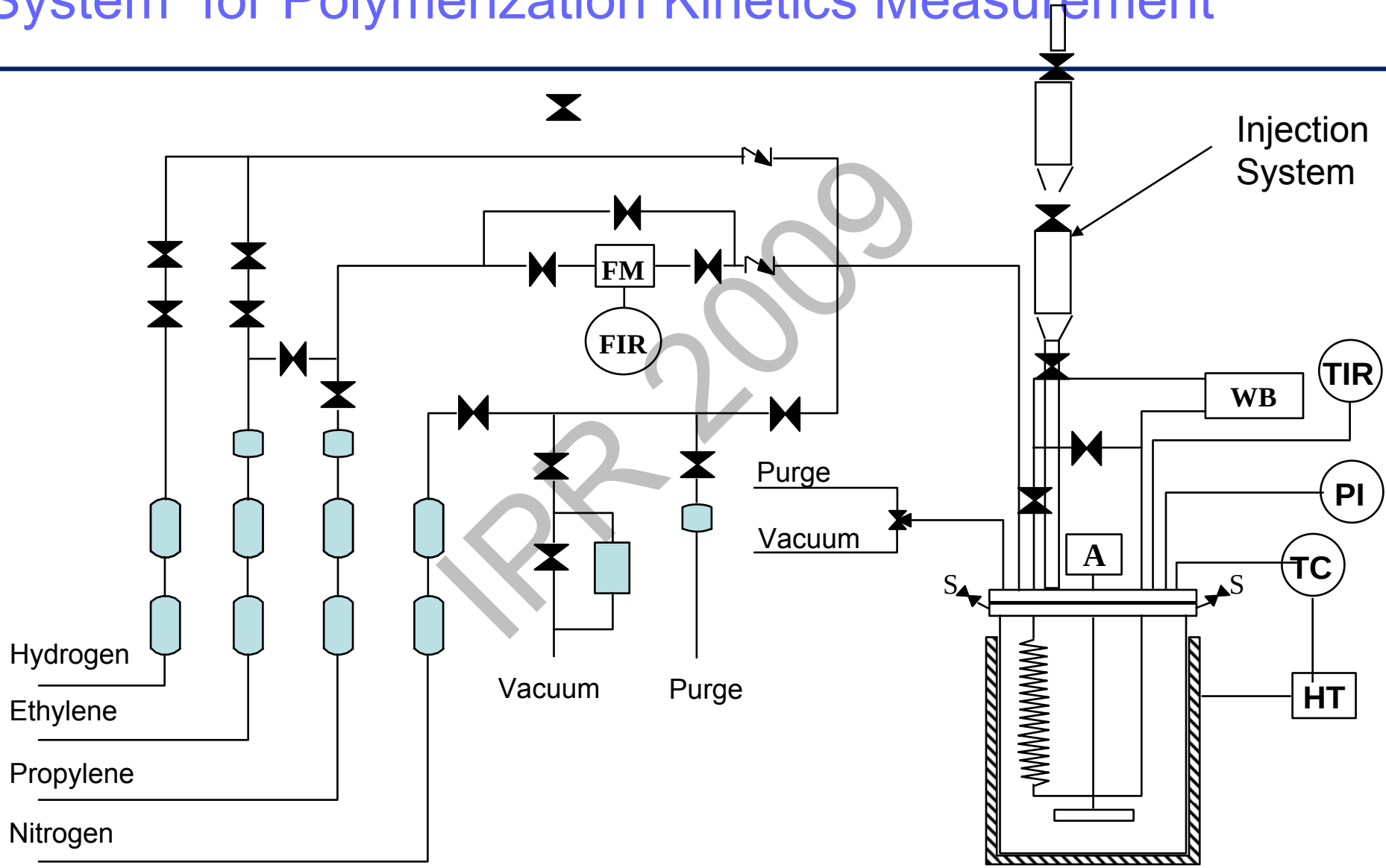
Case Study 1

Solution homo- and co-Polymerization of ethylene using *rac*-Et(Ind)$_2$ZrCl$_2$ catalyst

Case Study 2

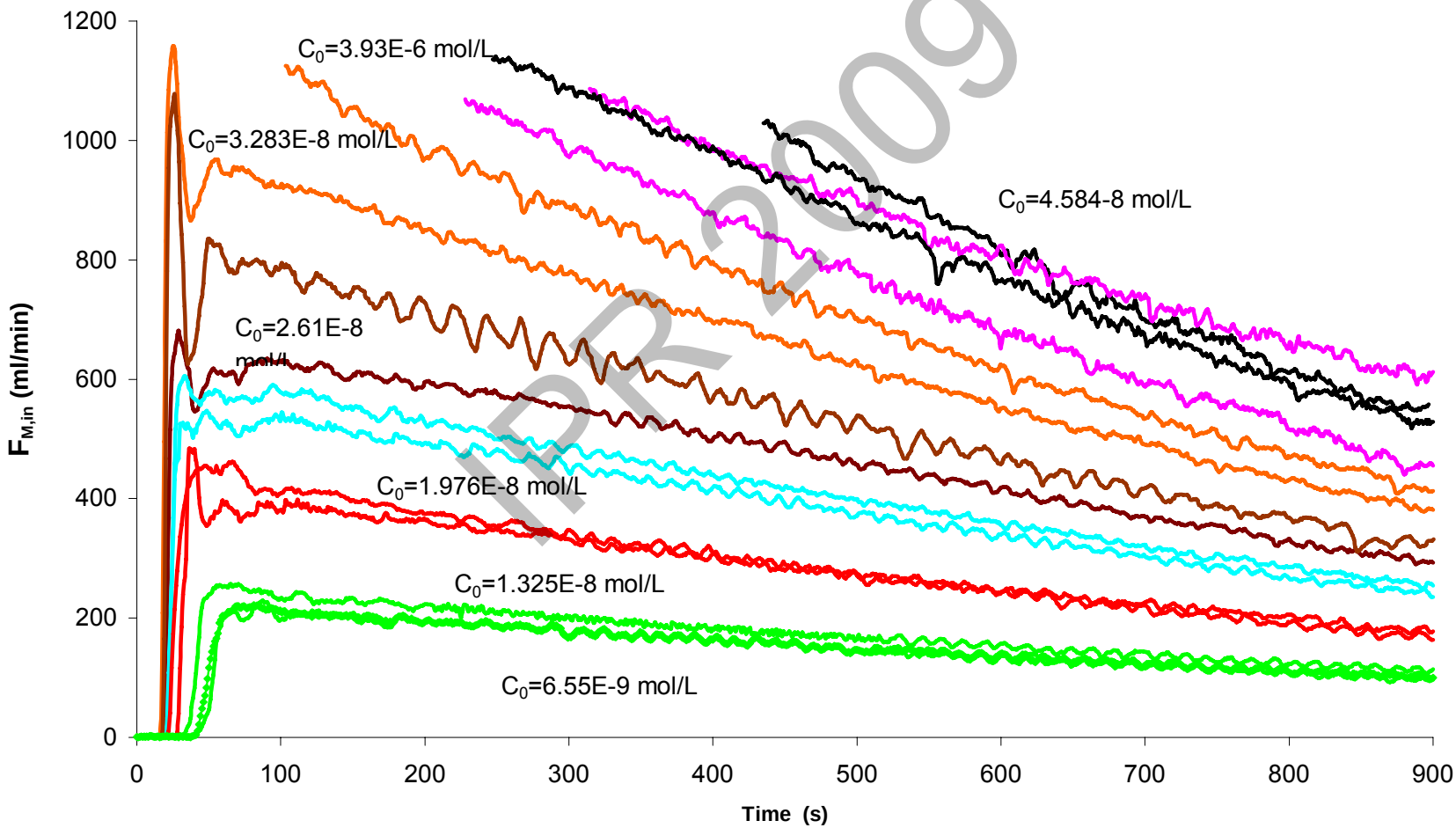
Solution homo- and co-Polymerization of ethylene using CGC-Ti catalyst

Simplified Schematic Representation of the Reactor System for Polymerization Kinetics Measurement



Effect of Catalyst Concentration

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$



Several elementary reactions take place during coordination polymerization: initiation, propagation, long chain branch formation, transfer reactions, and deactivation. For catalyst deactivation studies, however, just the initiation, propagation and deactivation steps need to be considered.

Initiation

$$C_i + M \xrightarrow{k_p} P^*$$

Propagation

$$P^* + M \xrightarrow{k_p} P^*$$

Deactivation

$$P^* \xrightarrow{k_d} D + \hat{C}_i$$

$$C_i \xrightarrow{k_d} \hat{C}_i$$

$$\frac{\mathrm{d}[C_i]}{\mathrm{d}t} = -k_p[C_i][M] - k_d[C_i] \qquad \textbf{(1)}$$

$$\frac{\mathrm{d}[P^*]}{\mathrm{d}t} = k_p[C_i][M] - k_d[P^*] \qquad \textbf{(2)}$$

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = \frac{F_{M,in}}{V_R} - k_p[P^*][M] \qquad \textbf{(3)}$$

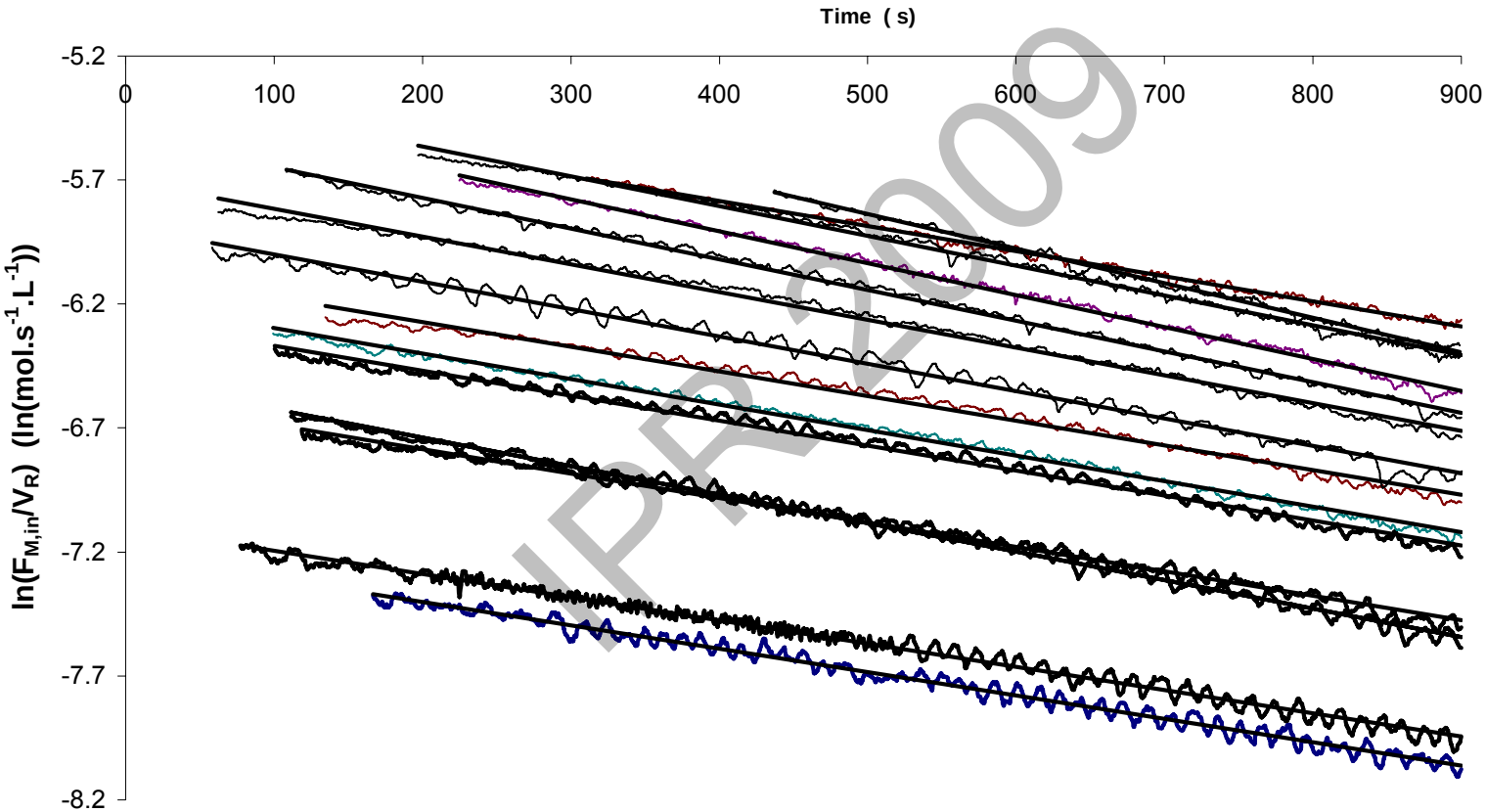
Initial conditions

$$\text{at } t = 0 \begin{cases} [C_i] = [C_i]_0 \\ [P^*] = 0 \end{cases}$$

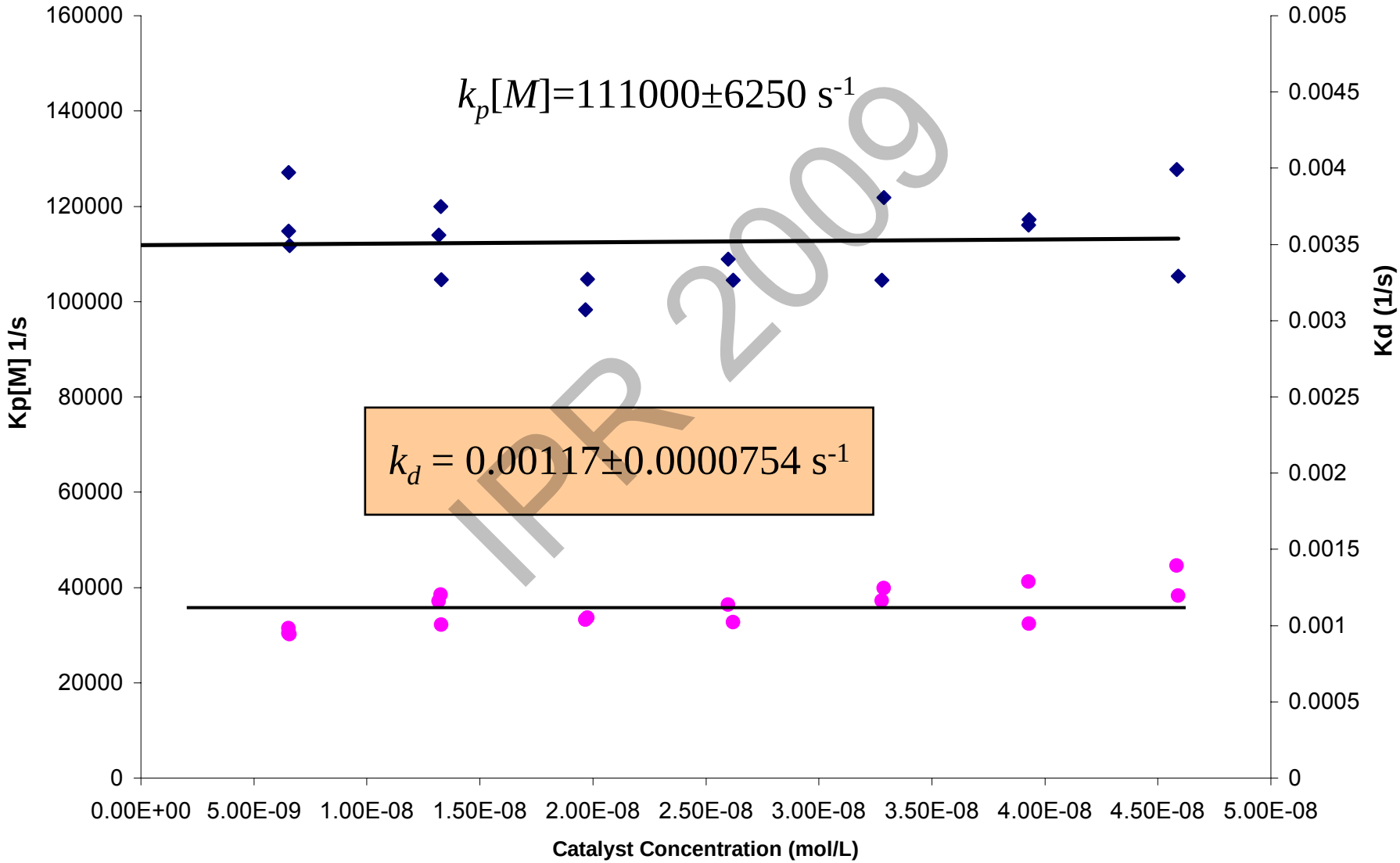
$$[M] = cons.$$

$$\ln\left(\frac{F_{M,in}}{V_R}\right) = \ln(k_p[C_i]_0[M]) - k_d t \qquad \textbf{(4)}$$

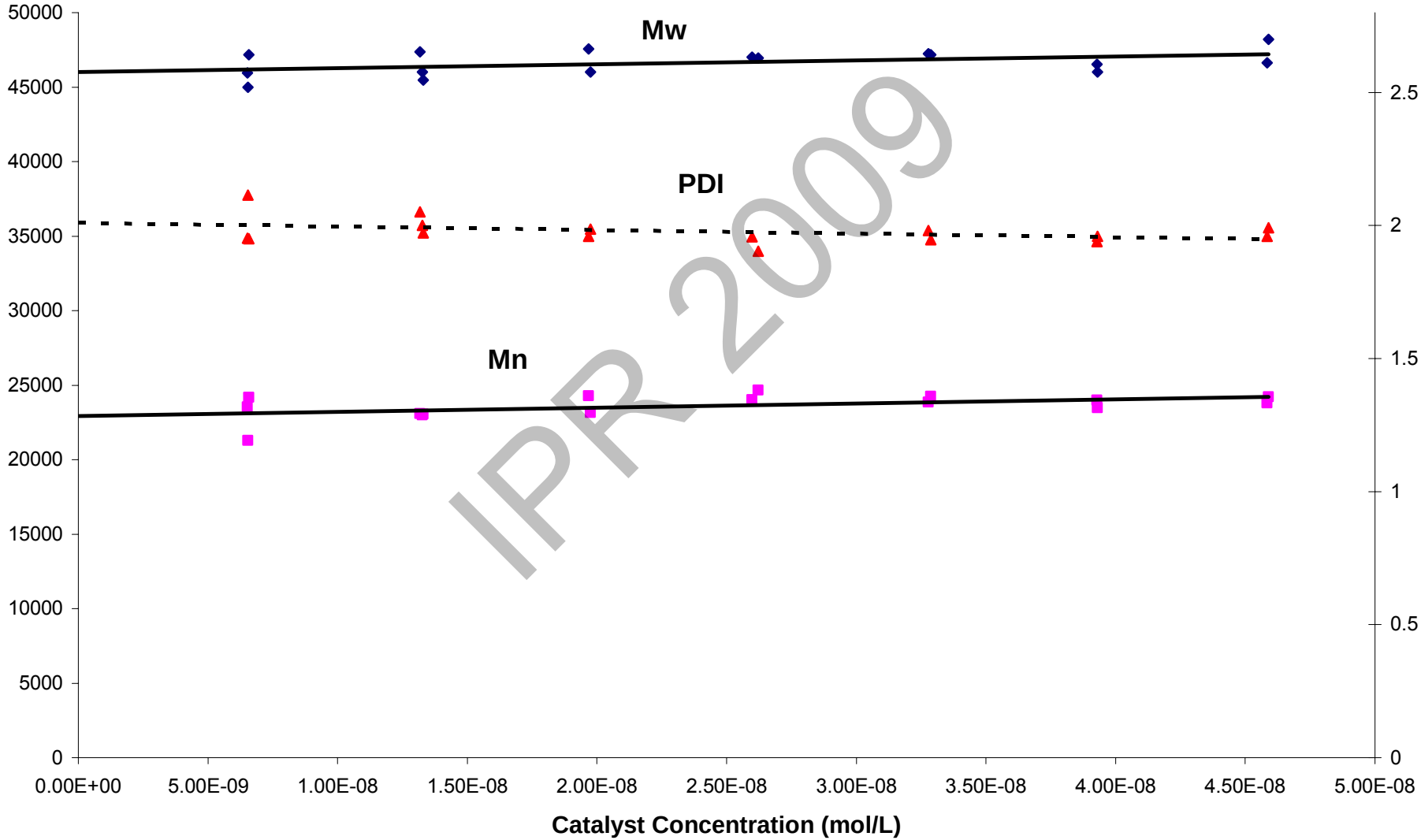
Plot of $\ln\left(\frac{F_{M,in}}{V_R}\right)$ versus time catalyst: rac-Et(Ind)$_2$ZrCl$_2$



Plot of $K_p[M]$ and K_d vs. catalyst concentration



Effect of Catalyst Concentration on Molecular weight

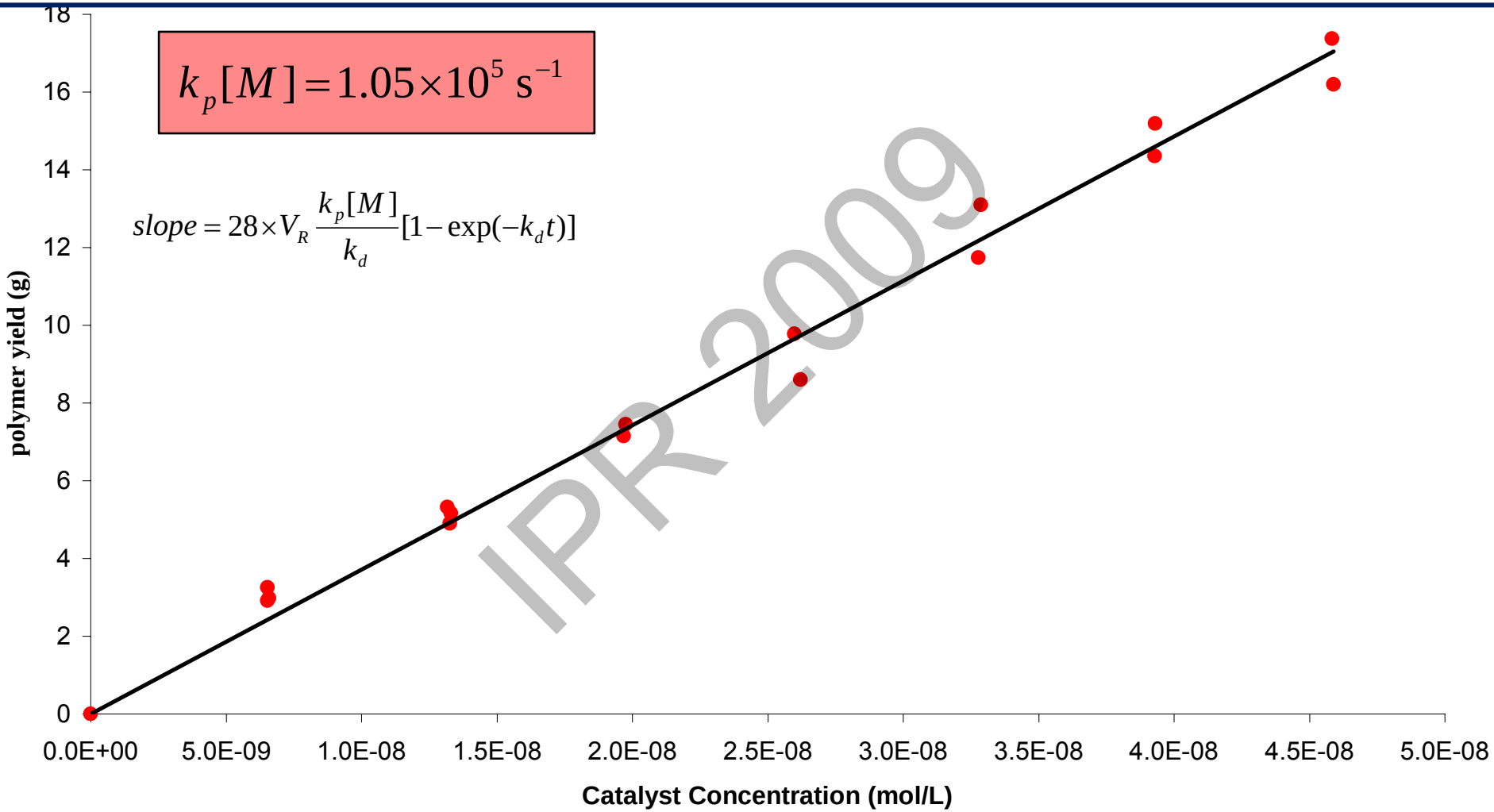


Experimental Data Fit – 1st Order Model

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$

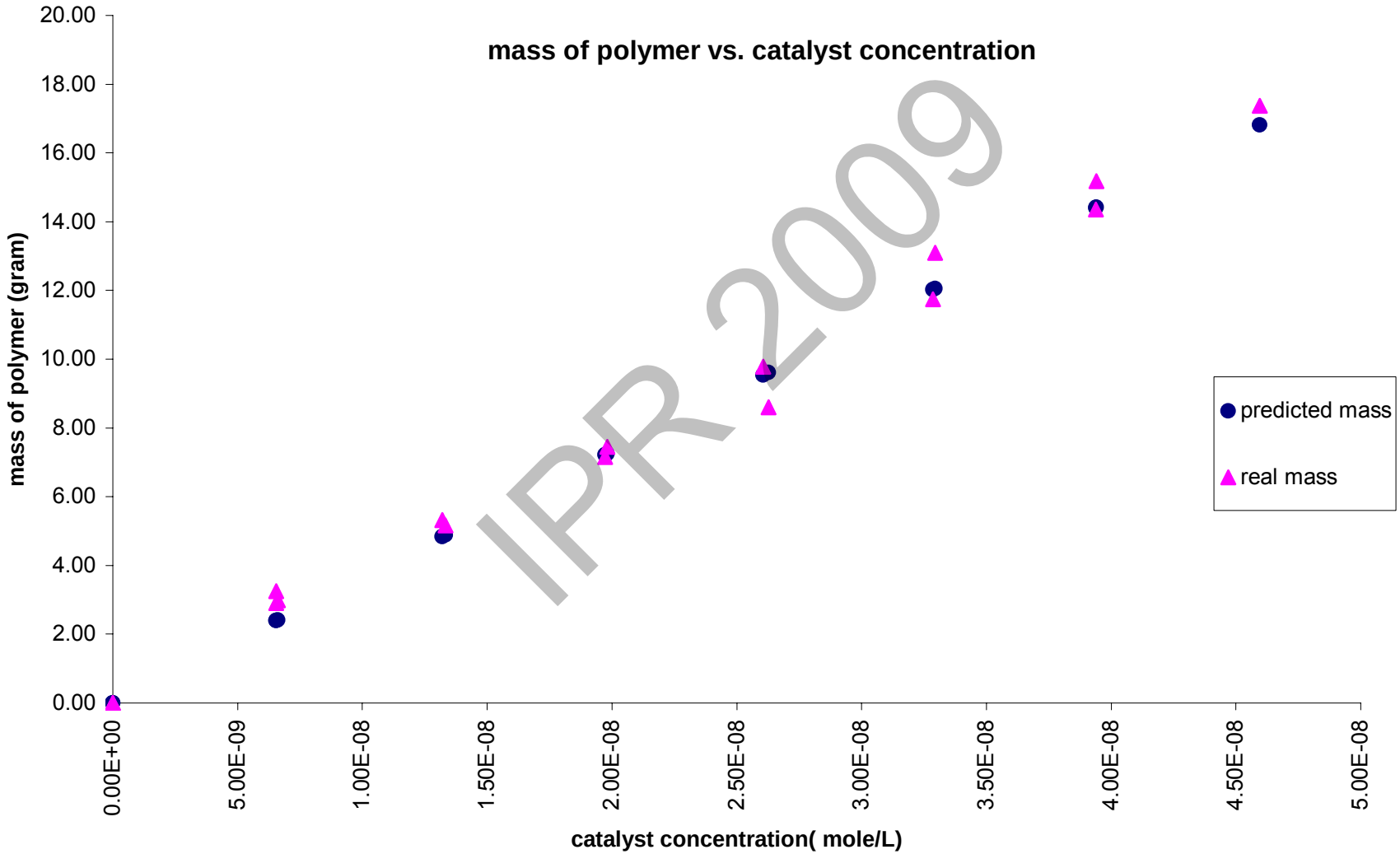
$$k_p[M] = 1.05 \times 10^5 \ s^{-1}$$

$$slope = 28 \times V_R \frac{k_p[M]}{k_d}[1 - \exp(-k_d t)]$$



1st Order Model – Polymer Yield Predictions

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$Cp$_2$ZrCl$_2$



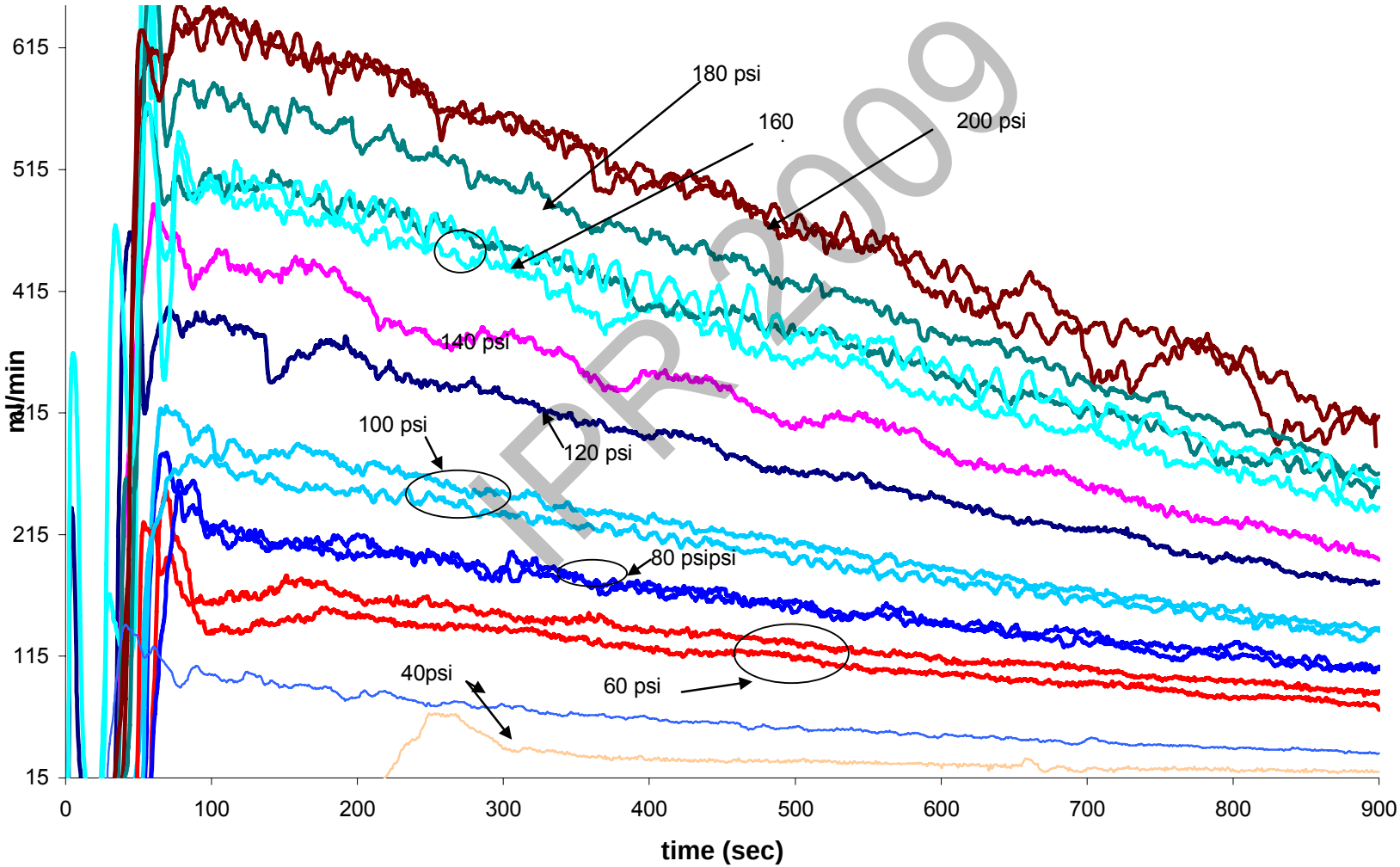
Effect of pressure (monomer concentration)

Experimental Conditions

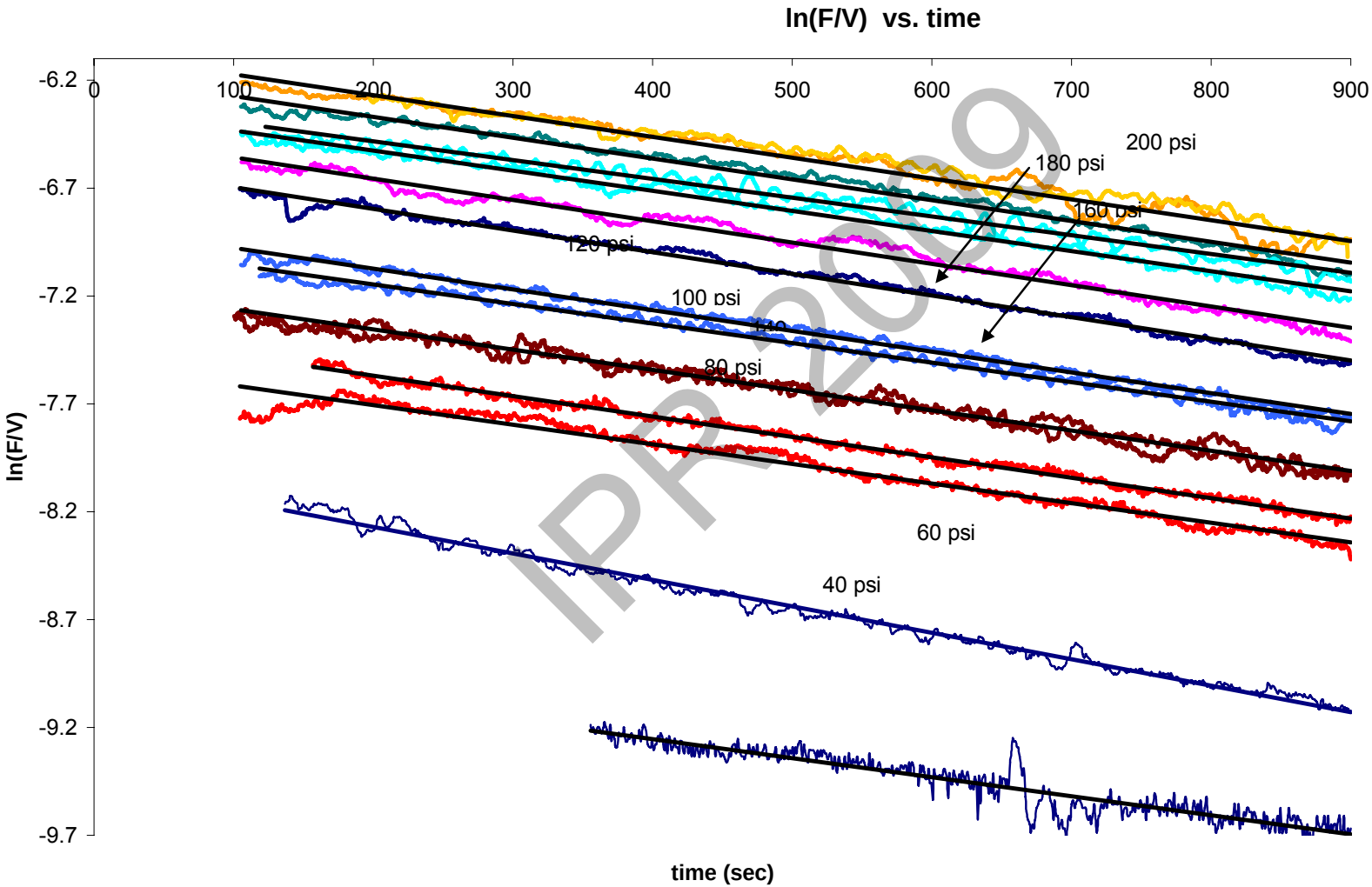
P	40-200	psig
T	120	°C
Solvent	Toluene	
Volume	222.8 ml	

Effect of Monomer Concentration

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$Cp$_2$ZrCl$_2$

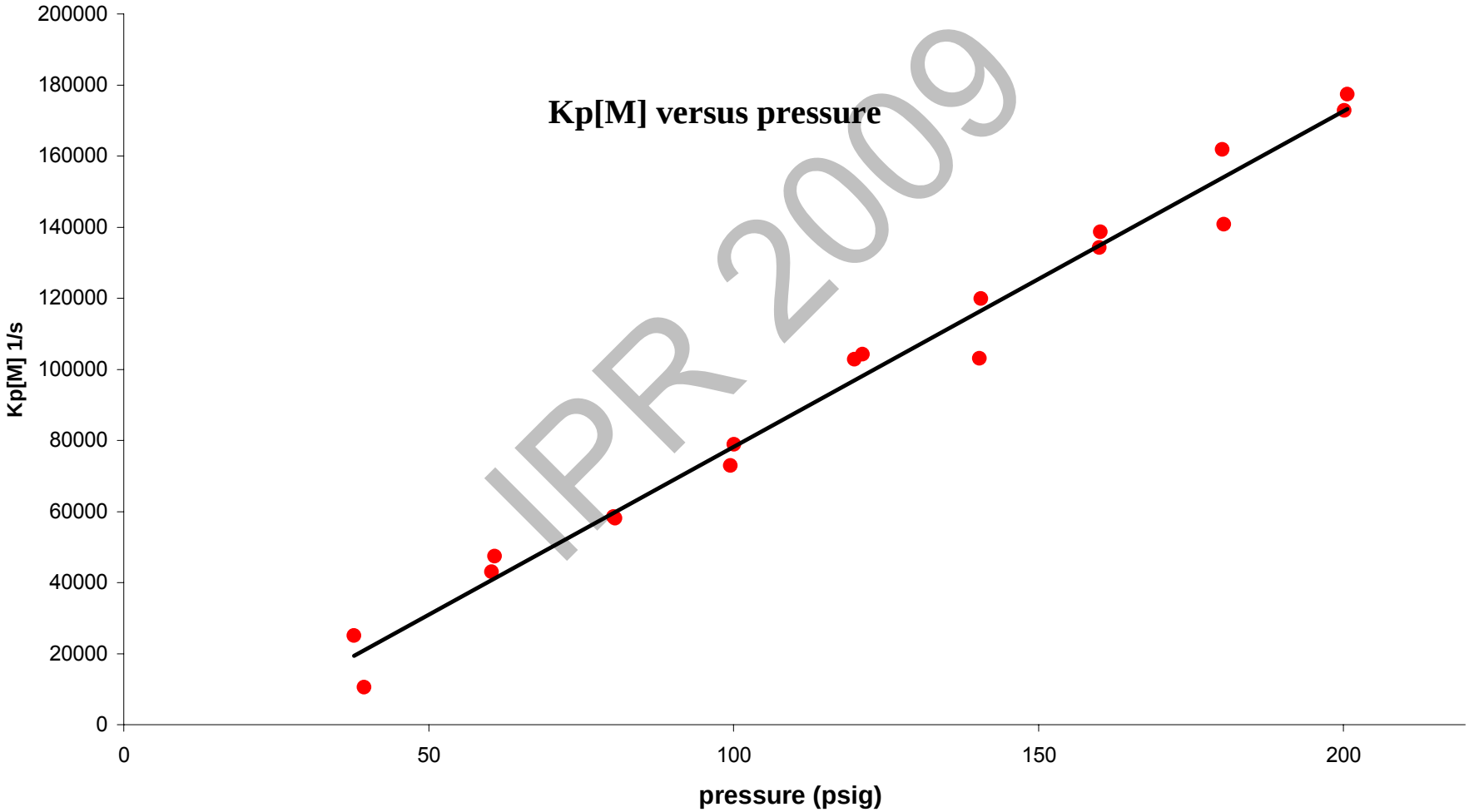


Experimental Data Fit – 1st Order Model
Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$



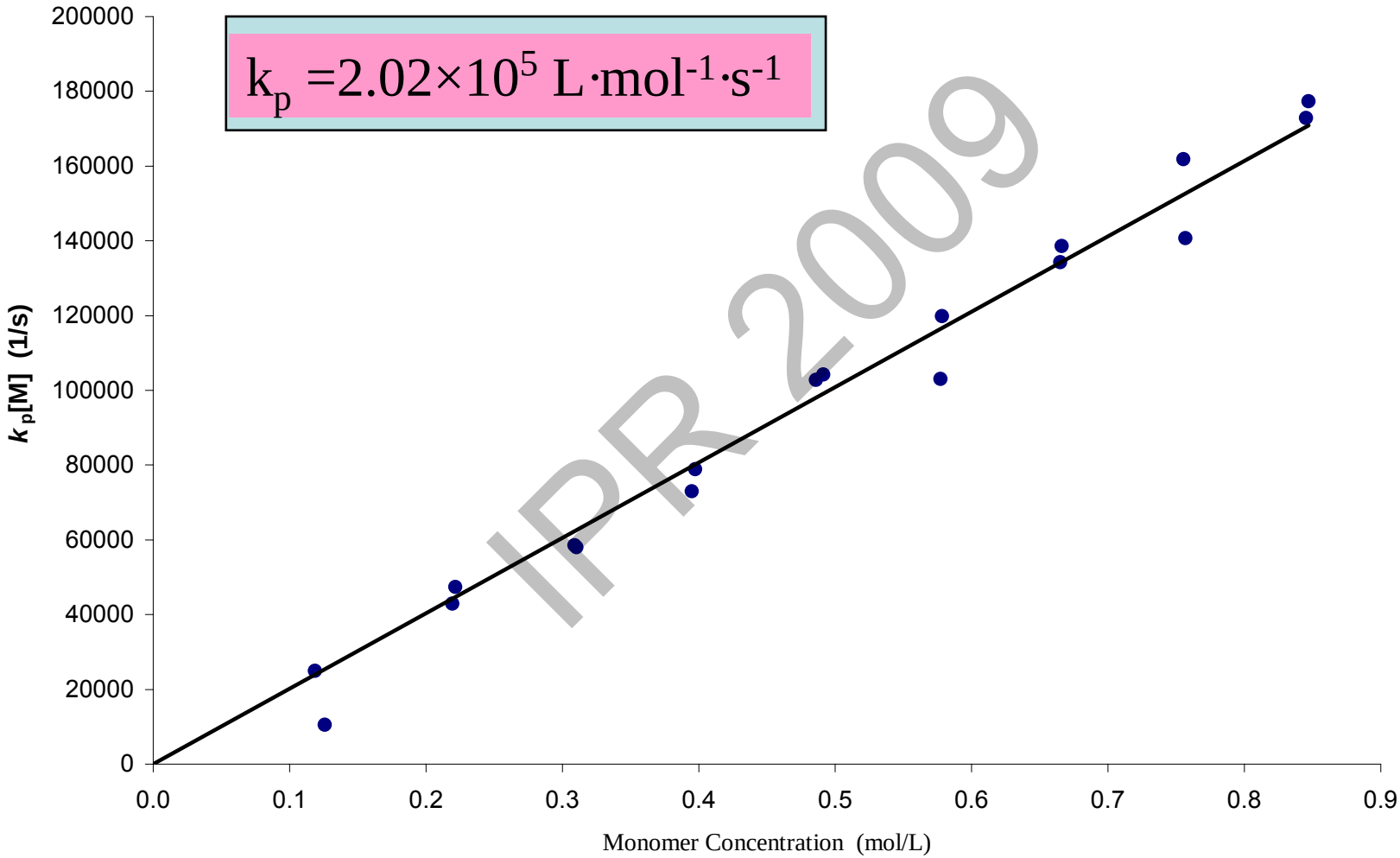
1st Order Model – Propagation Rate Constant

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$



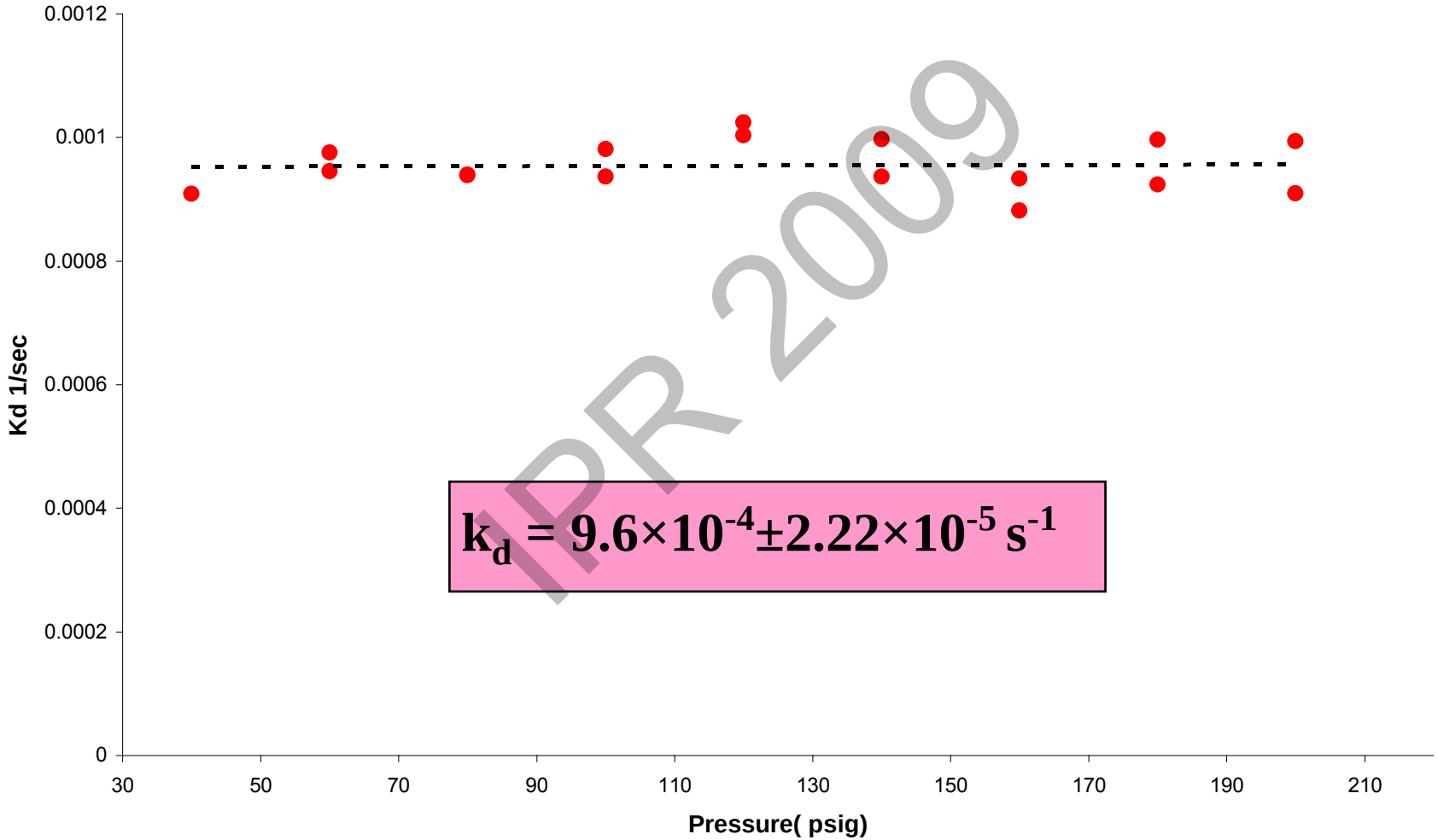
Propagation Rate Constant vs. Monomer Concentration

Ethylene Solution Polymerization with *rac*-Et(Ind)2ZrCl2



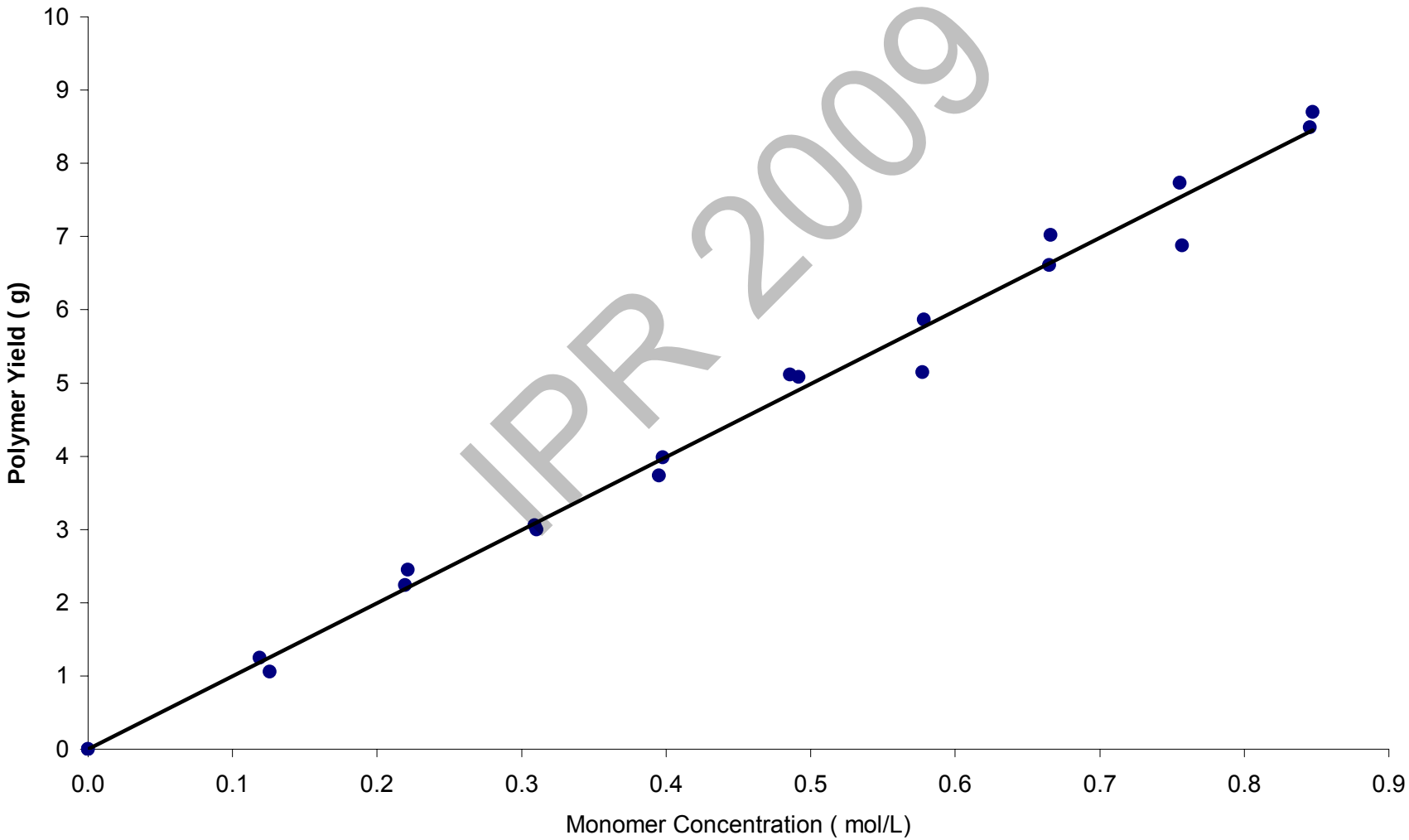
Deactivation Rate Constant vs. pressure

Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$

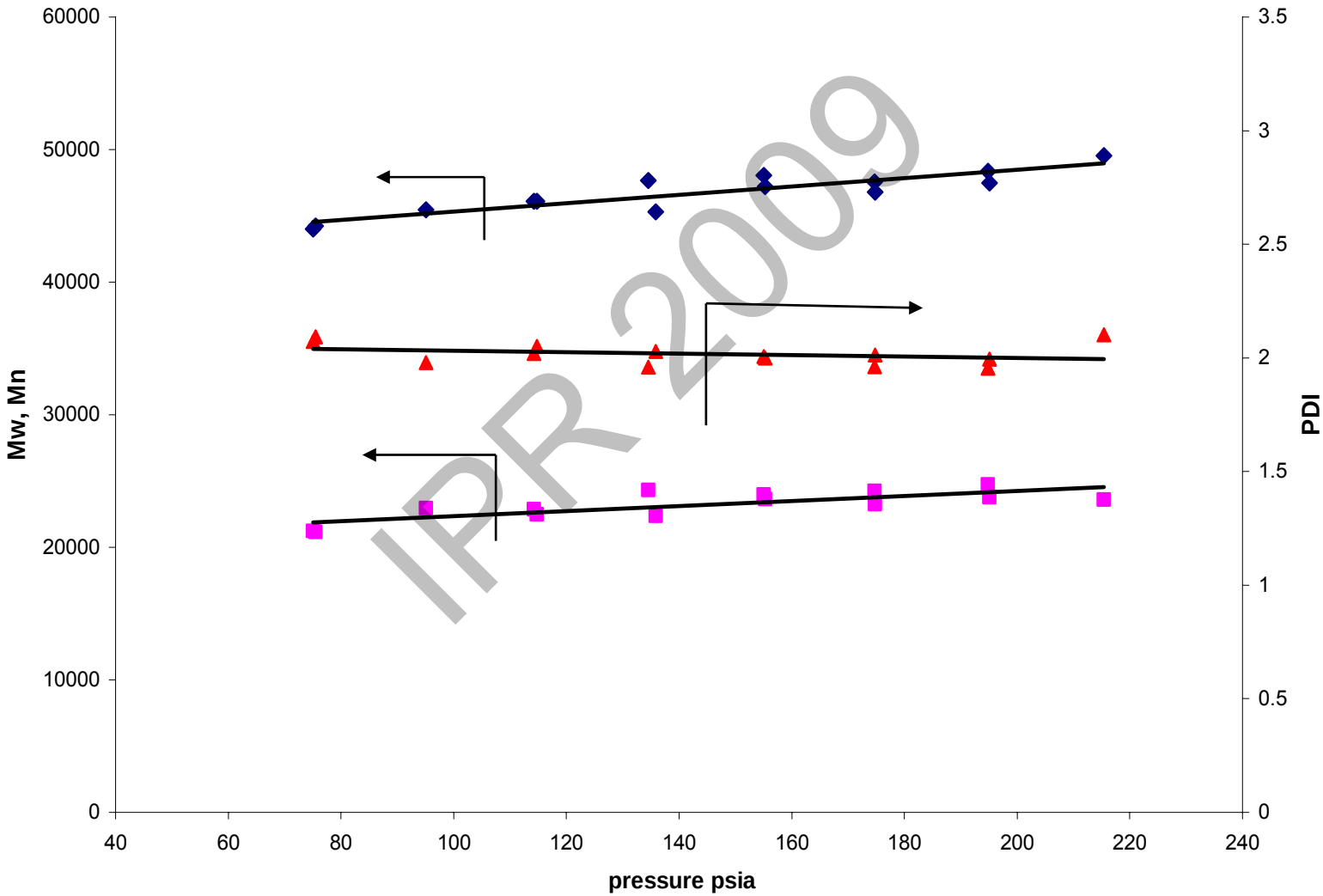


Polymer Yield vs. Monomer Concentration

rac-Et(Ind)$_2$ZrCl$_2$



Effect of Monomer Concentration on M_n and M_w Ethylene Solution Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$

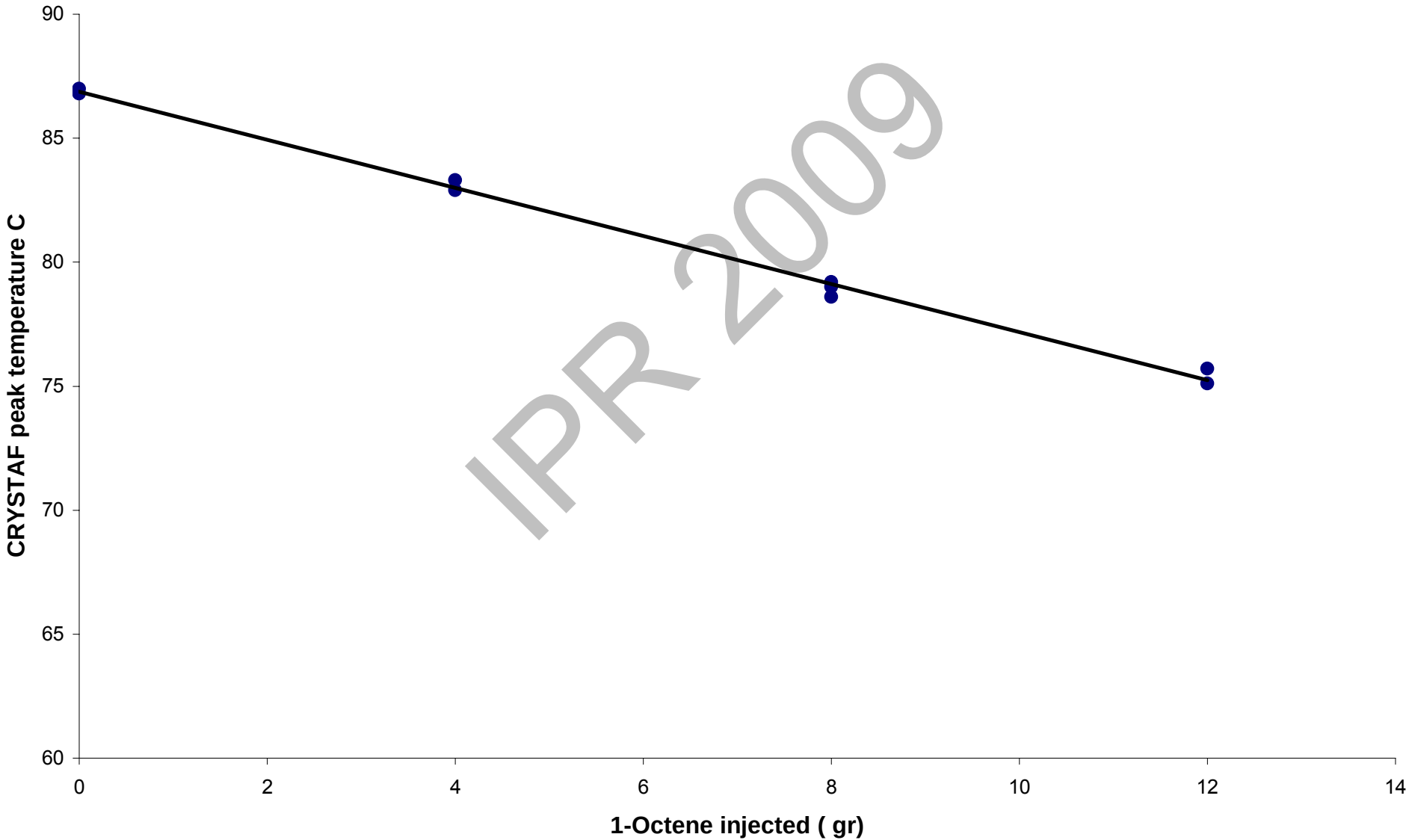


Solution co-polymerization of ethylene and 1-octene using *rac*-Et(Ind)$_2$ZrCl$_2$

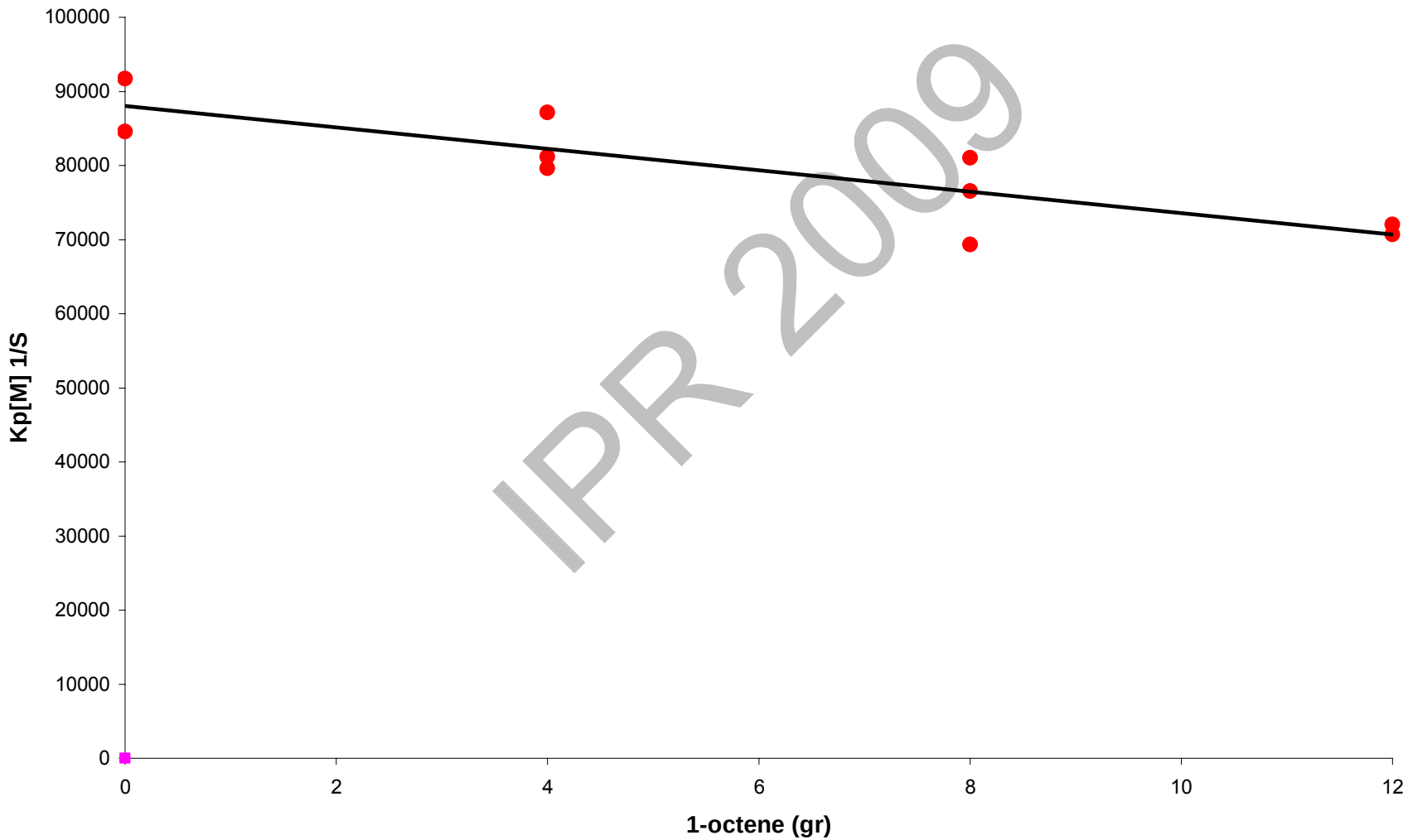
Experimental Conditions

P	120	psig
T	120	^{o}C
Solvent		Toluene
Volume		222.8 ml

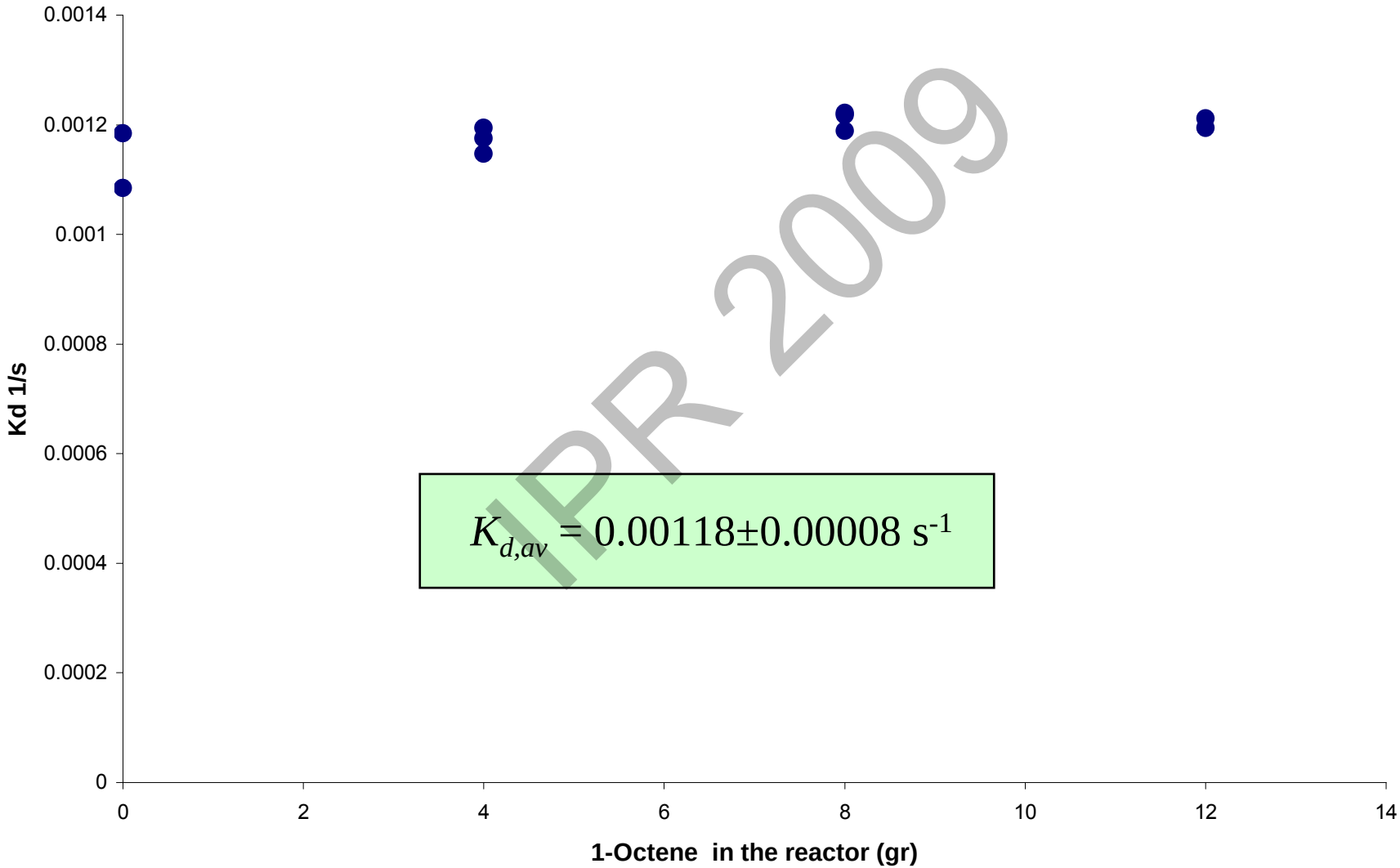
CRYSTAF Peak Temperature vs. 1-octene injected



Solution co-polymerization of ethylene and 1-Octene using *rac*-Et(Ind)$_2$ZrCl$_2$ (plot of k_p[M] vs. 1-octene)



Solution co-polymerization of ethylene and 1-Octene using *rac*-Et(Ind)$_2$ZrCl$_2$ (plot of k_d vs. 1-octene)



Case Study 1 – Conclusions

Ethylene Solution homo- and co- Polymerization with *rac*-Et(Ind)$_2$ZrCl$_2$

- 1st order polymerization rate with respect to monomer concentration
- 1st order polymerization order with respect to catalyst concentration
- 1st order deactivation rate
- Single (or near single) site nature: PDI ≈ 2.0

•Transfer to ethylene is dominant: M_n and M_w do not depend strongly on ethylene pressure

Case Study 2

Ethylene Solution Polymerization with CGC-Ti

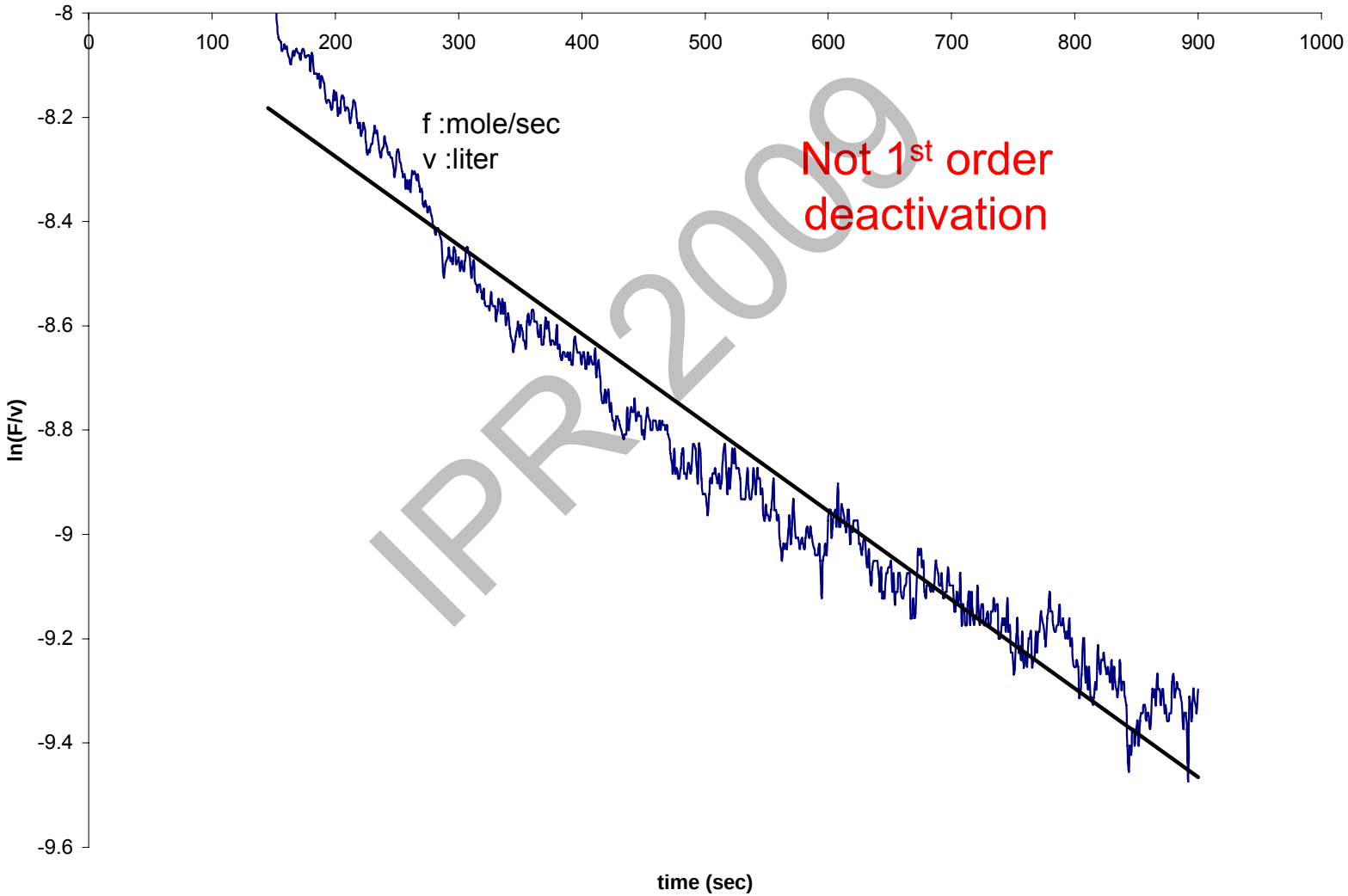
Monomer Concentration Study

Experimental Conditions

P	25 to 220 psi
T	120 °C
Solvent	Toluene
Volume	223 ml

Experimental Data Fit – Deactivation Kinetics

Ethylene Solution Polymerization with CGC-Ti



Model for 2nd Order Deactivation

Ethylene Solution Polymerization with CGC-Ti

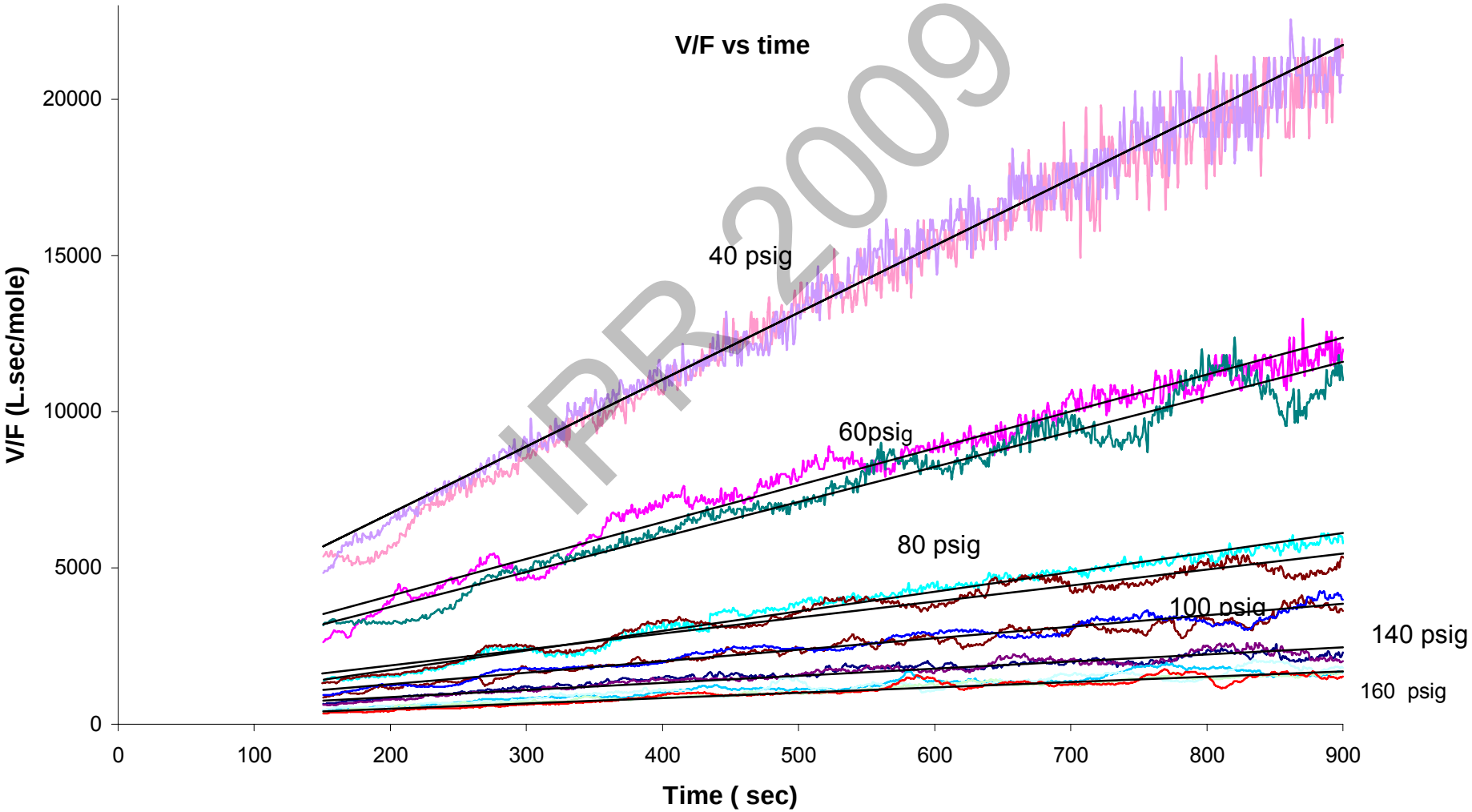
Assuming a second order Catalyst Decay
With Fast initiation step

$$\frac{\mathrm{d}[C_i]}{\mathrm{d}t} = -k_d[C_i]^2 \qquad \textbf{(6)}$$

$$\left(\frac{V_R}{F_{M,in}}\right) = \frac{k_d}{k_p[M]}t + \frac{1}{k_p[M][C_0]} \qquad \textbf{(7)}$$

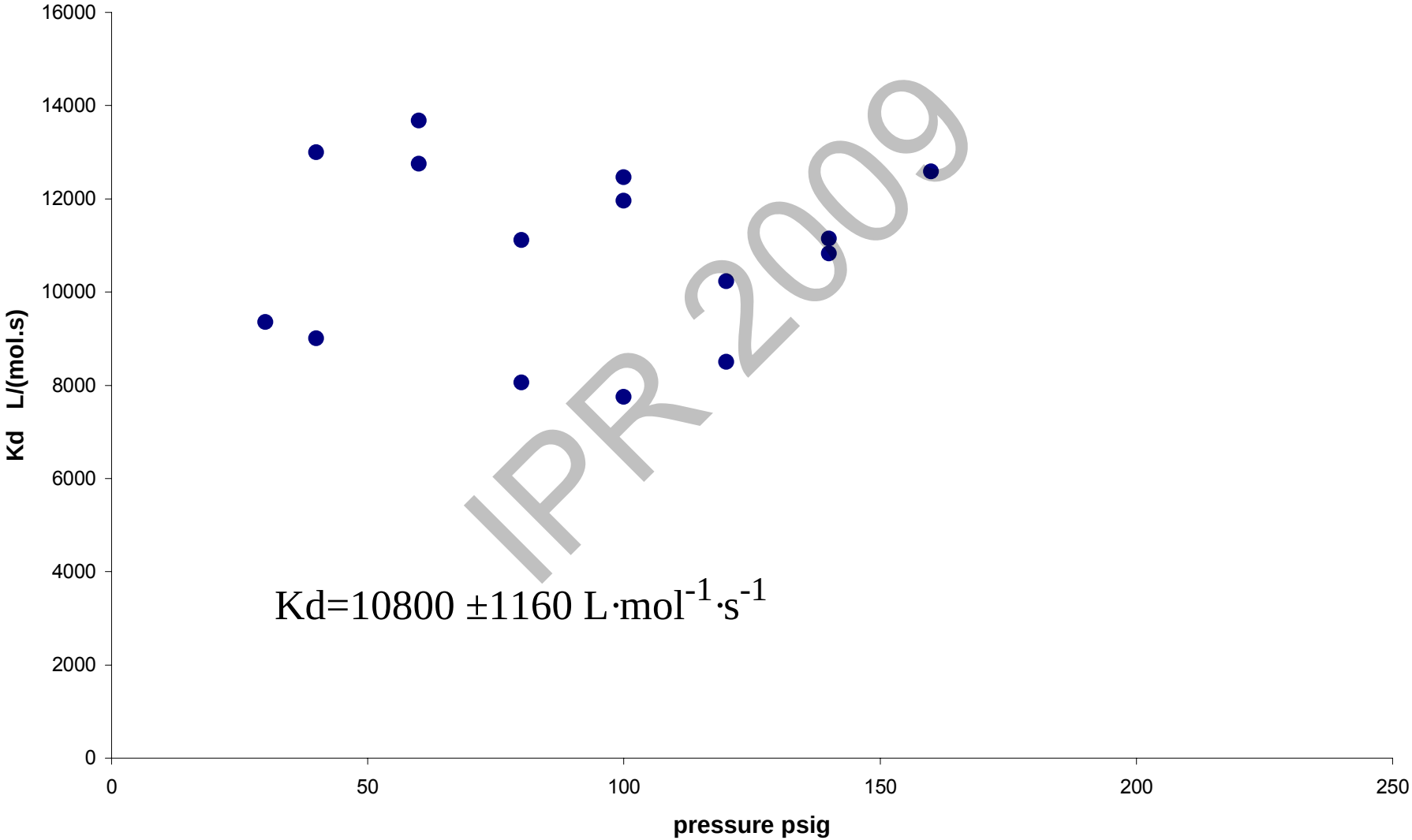
Experimental Data Fit – 2nd Order Deactivation

Ethylene Solution Polymerization with CGC-Ti



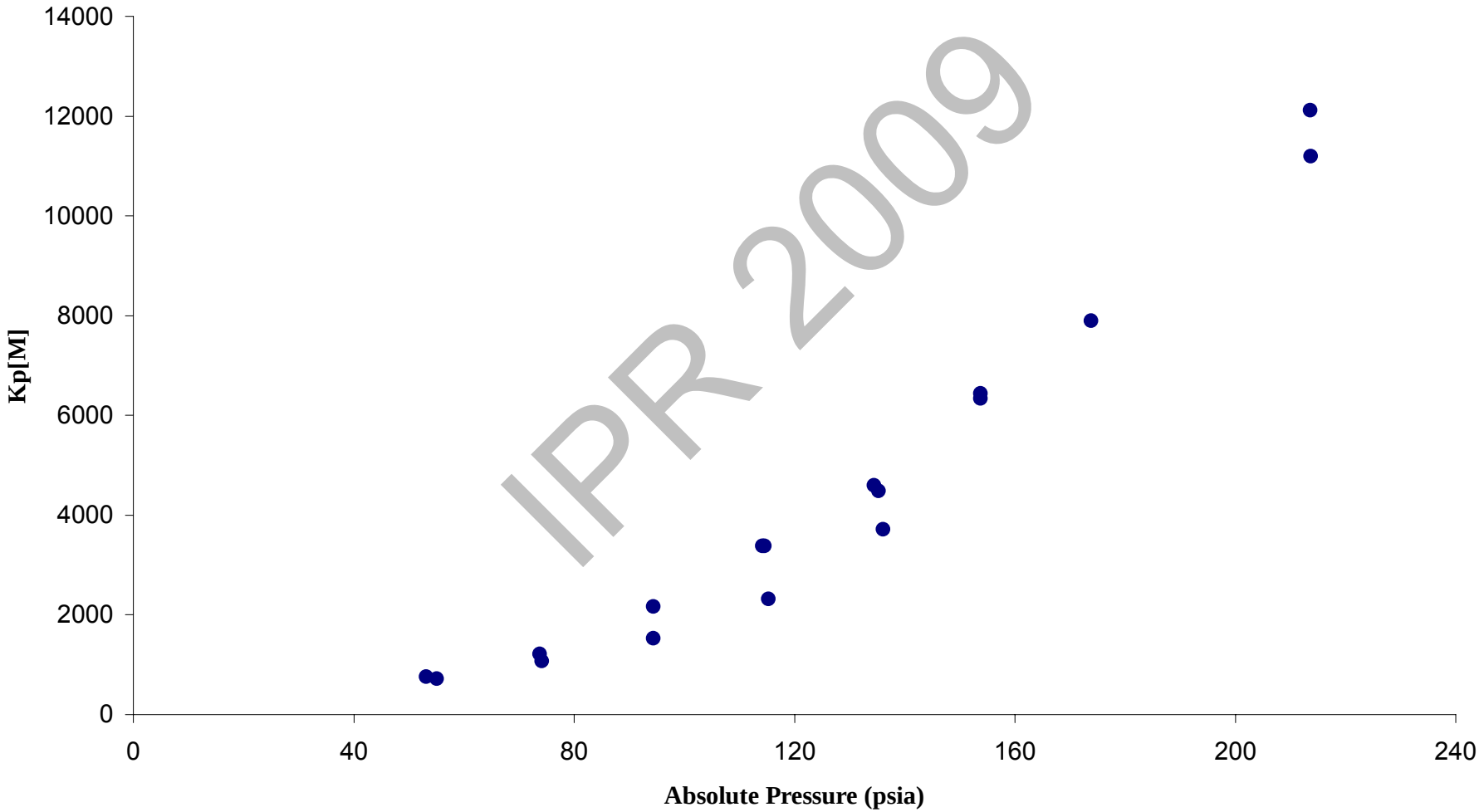
Deactivation Rate Constant

Ethylene Solution Polymerization with CGC-Ti



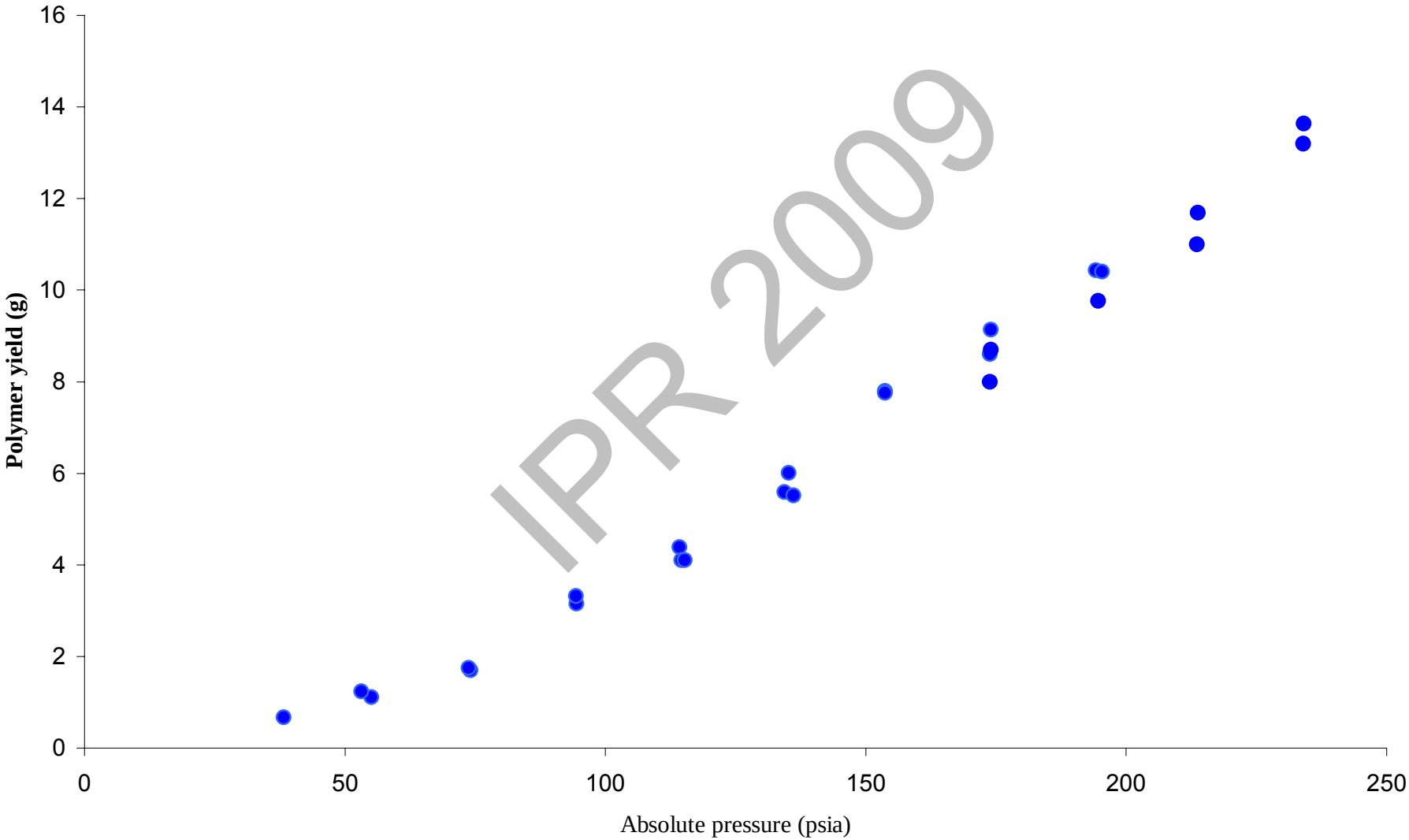
K_p[M] vs. Pressure

Ethylene Solution Polymerization with CGC-Ti



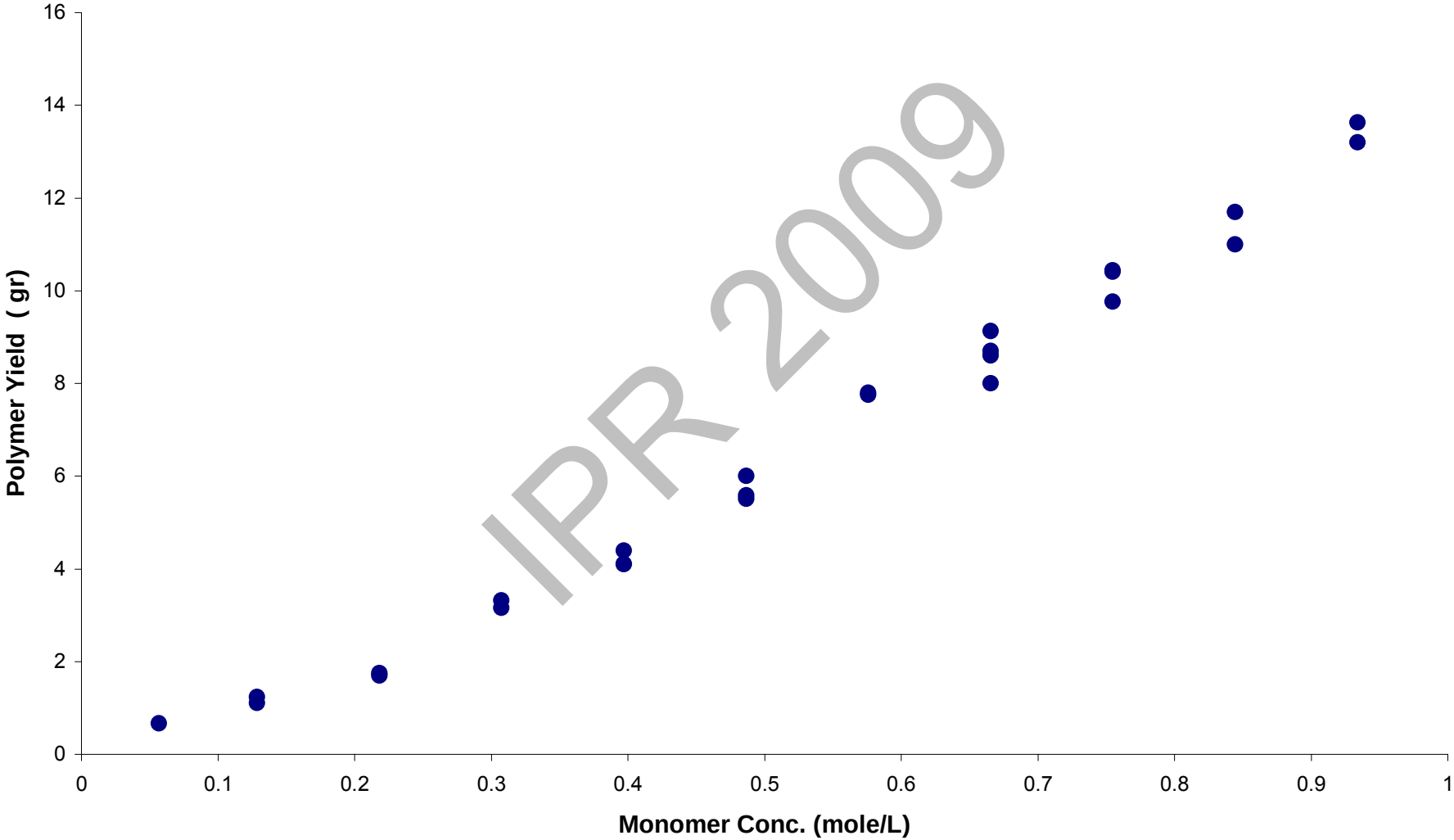
Polymer Yield versus Polymerization Pressure

Ethylene Solution Polymerization with CGC-Ti



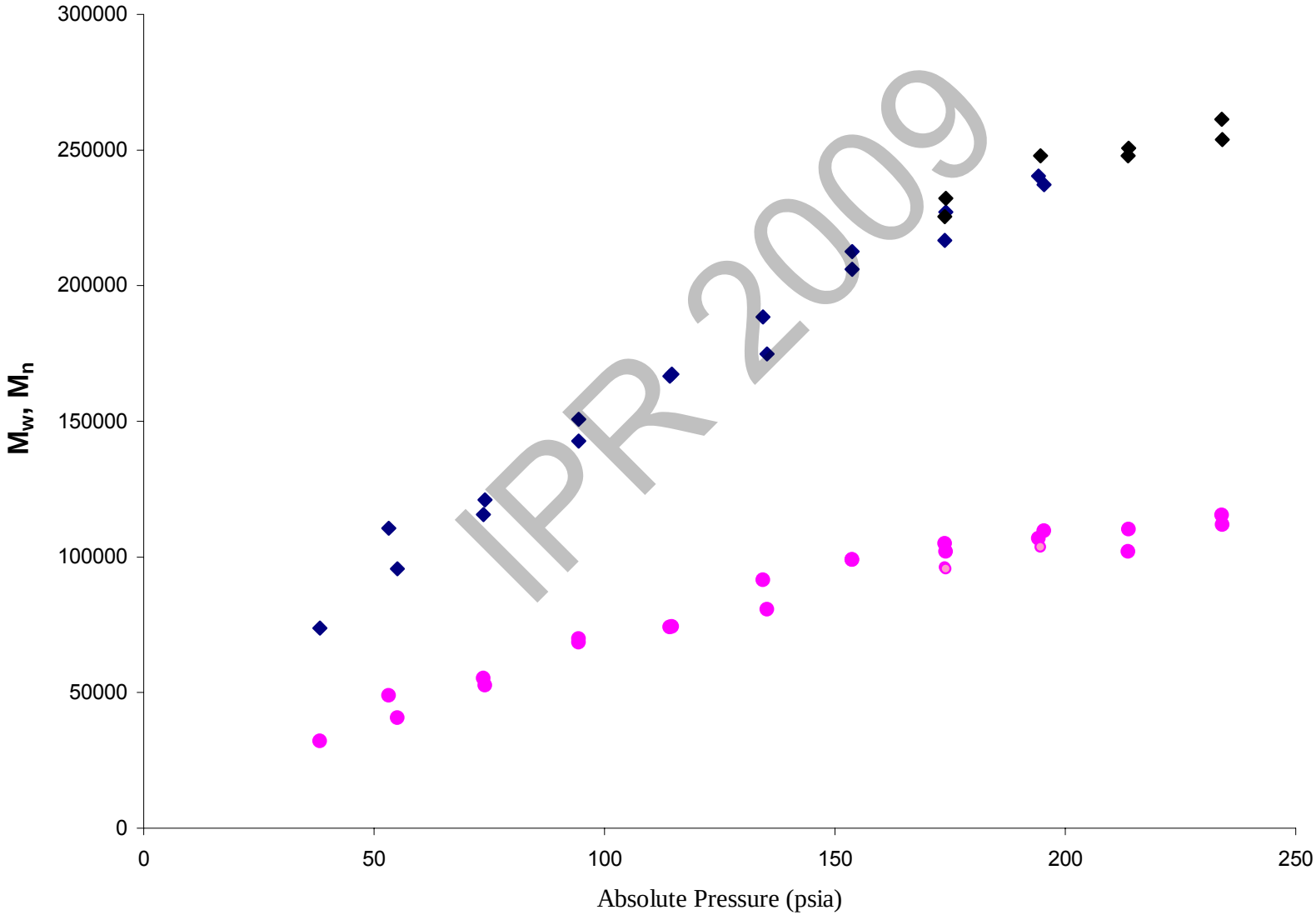
Polymer Yield versus Monomer Concentration

Ethylene Solution Polymerization with CGC-Ti



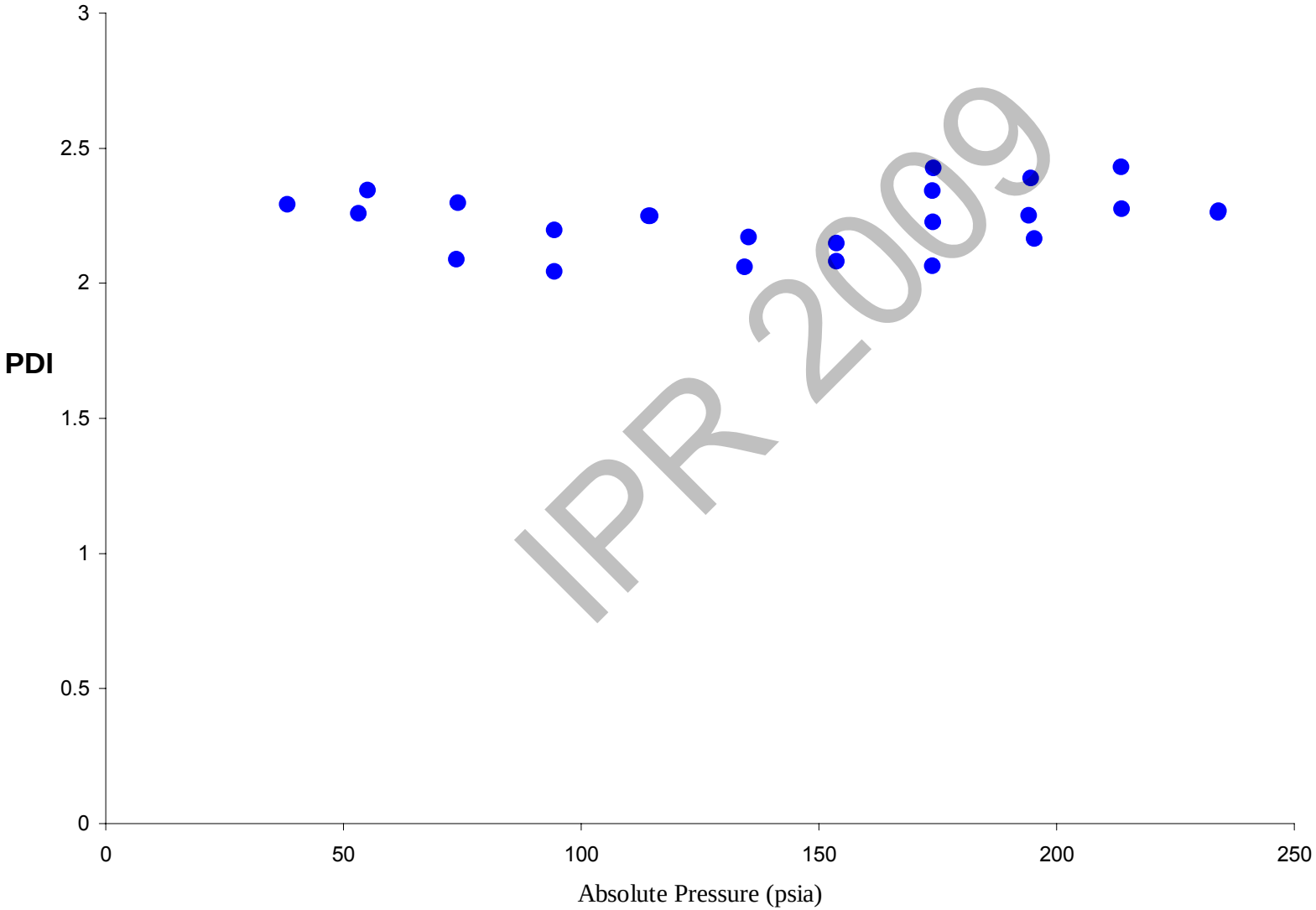
Molecular weight versus abs. pressure

Ethylene Solution Polymerization with CGC-Ti



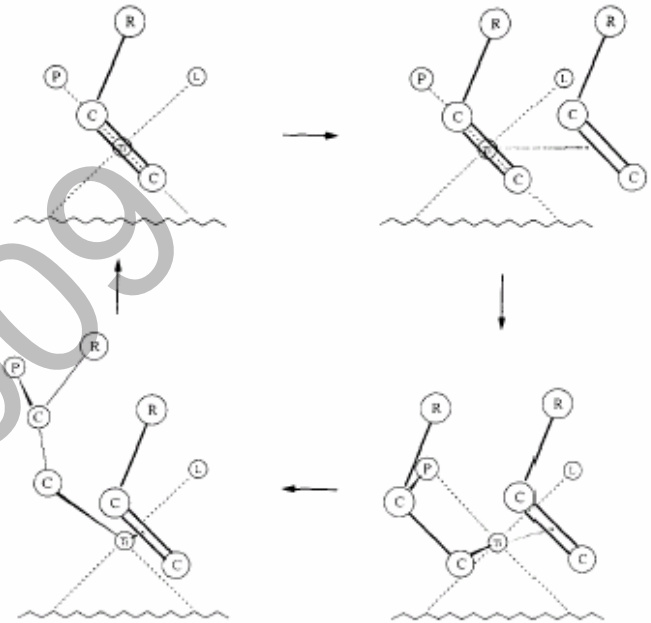
PDI vs. abs. pressure

Ethylene Solution Polymerization with CGC-Ti



The Trigger Mechanism

- The monomer site is never a free site during the propagation, as a new monomer will enter the monomer site at the same time that the first monomer is inserted.
- The insertion of the first monomer will not proceed if no new monomer is available. That is , the new monomer triggers the insertion of the first monomer.
- The transition state is a pseudo-seven-coordinated complex with two monomers interacting with each other and with the central titanium atom.



$$P^* + M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P^* \cdot M \qquad \textbf{(8)}$$

$$P^* \cdot M + M \xrightarrow{k_p} P^* + M \qquad \textbf{(9)}$$

Martin Ystenes. *J Cat* **1991**, *129*, 383.

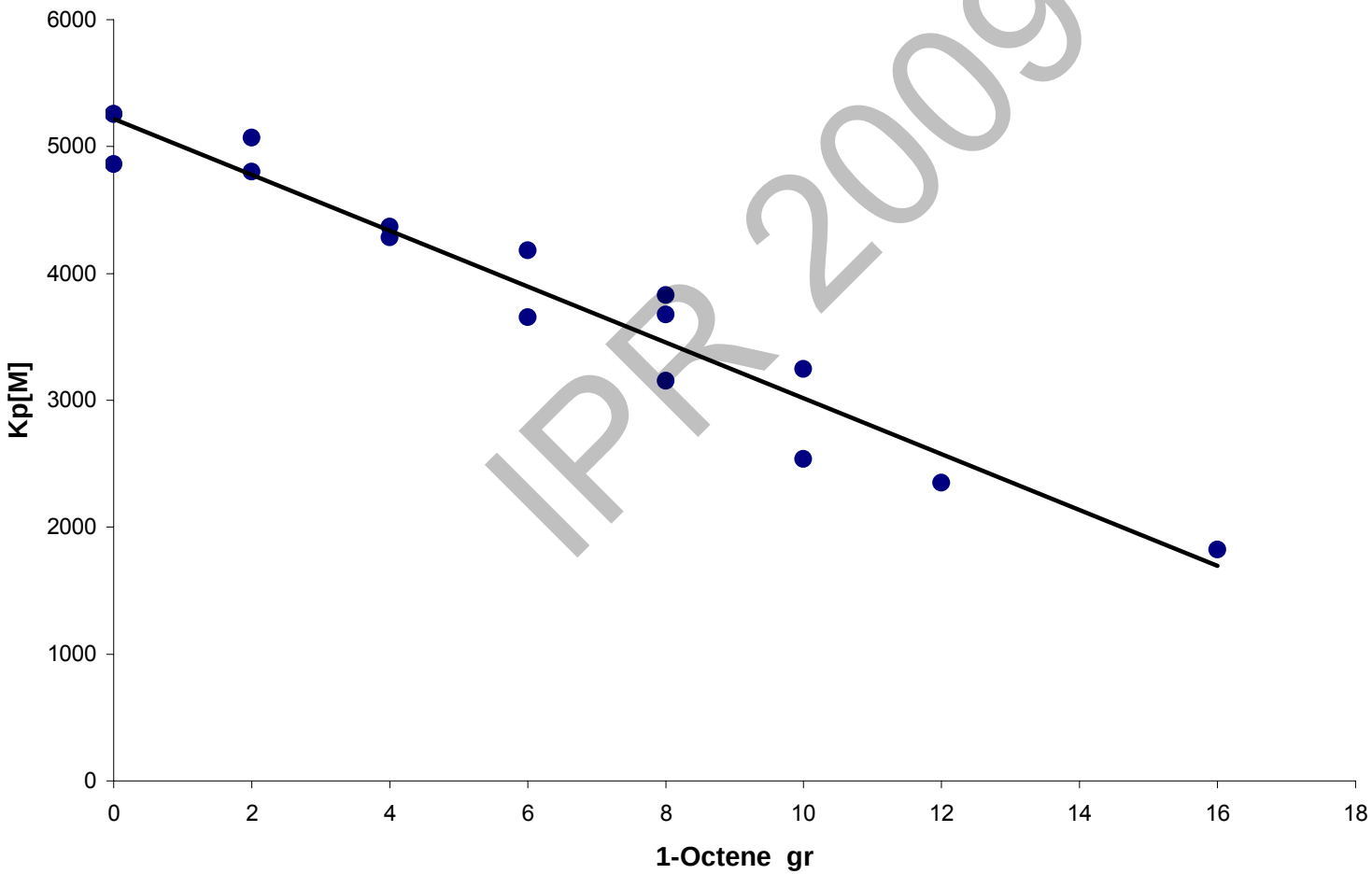
Catalytic active center has two sites for monomer ➔ ligand-assisted insertion mechanism

Solution co-polymerization of ethylene and 1-Octene using CGC-Ti

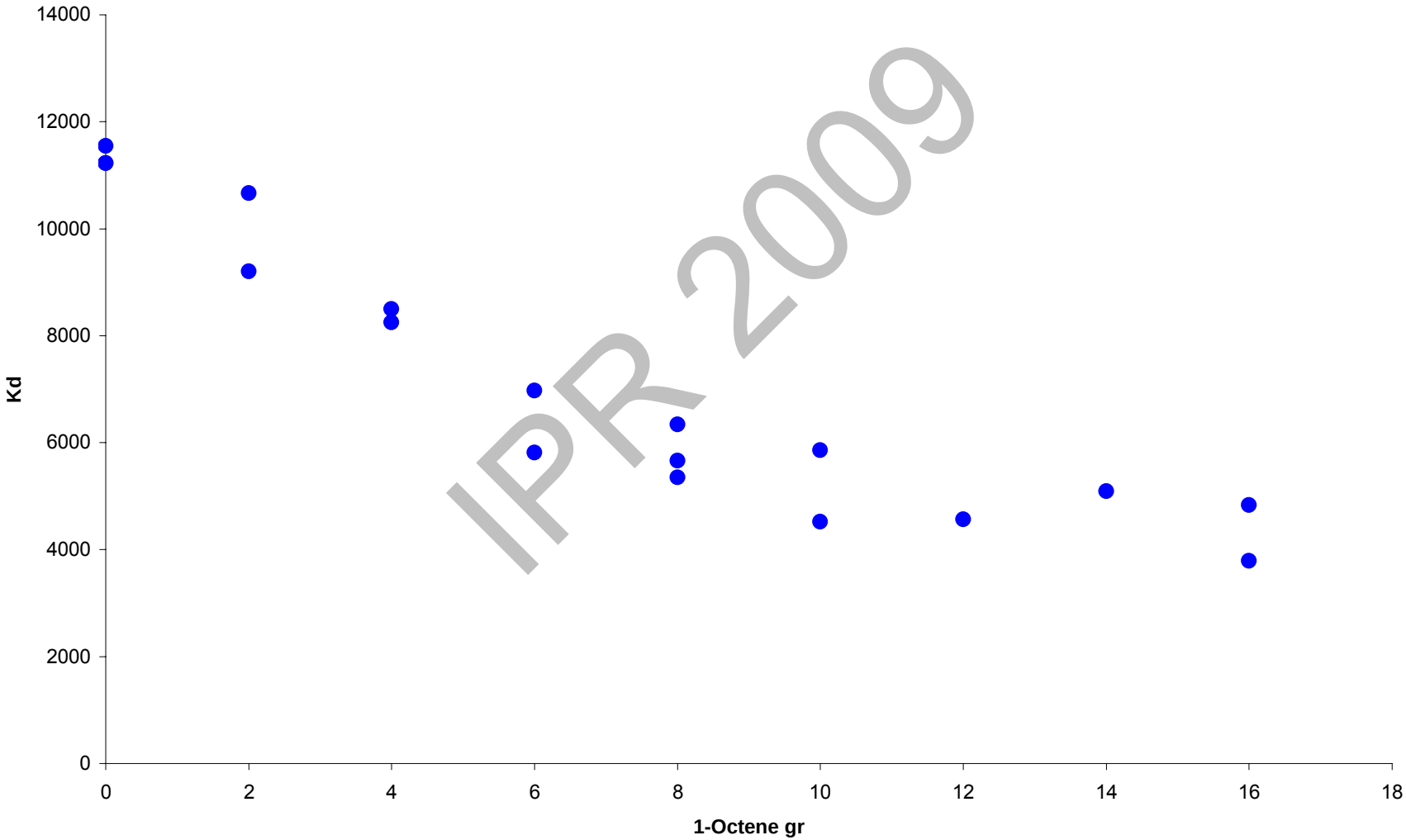
Experimental Conditions

P	120	psig
T	120	°C
Solvent		Toluene
Volume		222.8 ml

Solution co-polymerization of ethylene and 1-Octene using CGC-Ti (plot of k_p[M] vs. 1-octene) p=120 psig T=120 ^{0}C



Solution co-polymerization of ethylene and 1-Octene using CGC-Ti (plot of k_d vs. 1-octene injected)



Case Study 2 – Conclusions

Ethylene Solution homo- and co-Polymerization of ethylene using CGC-Ti catalyst

- Changing order of the polymerization with respect to Monomer concentration
- 2nd order deactivation rate

Thank you for your kind attention