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

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Outline

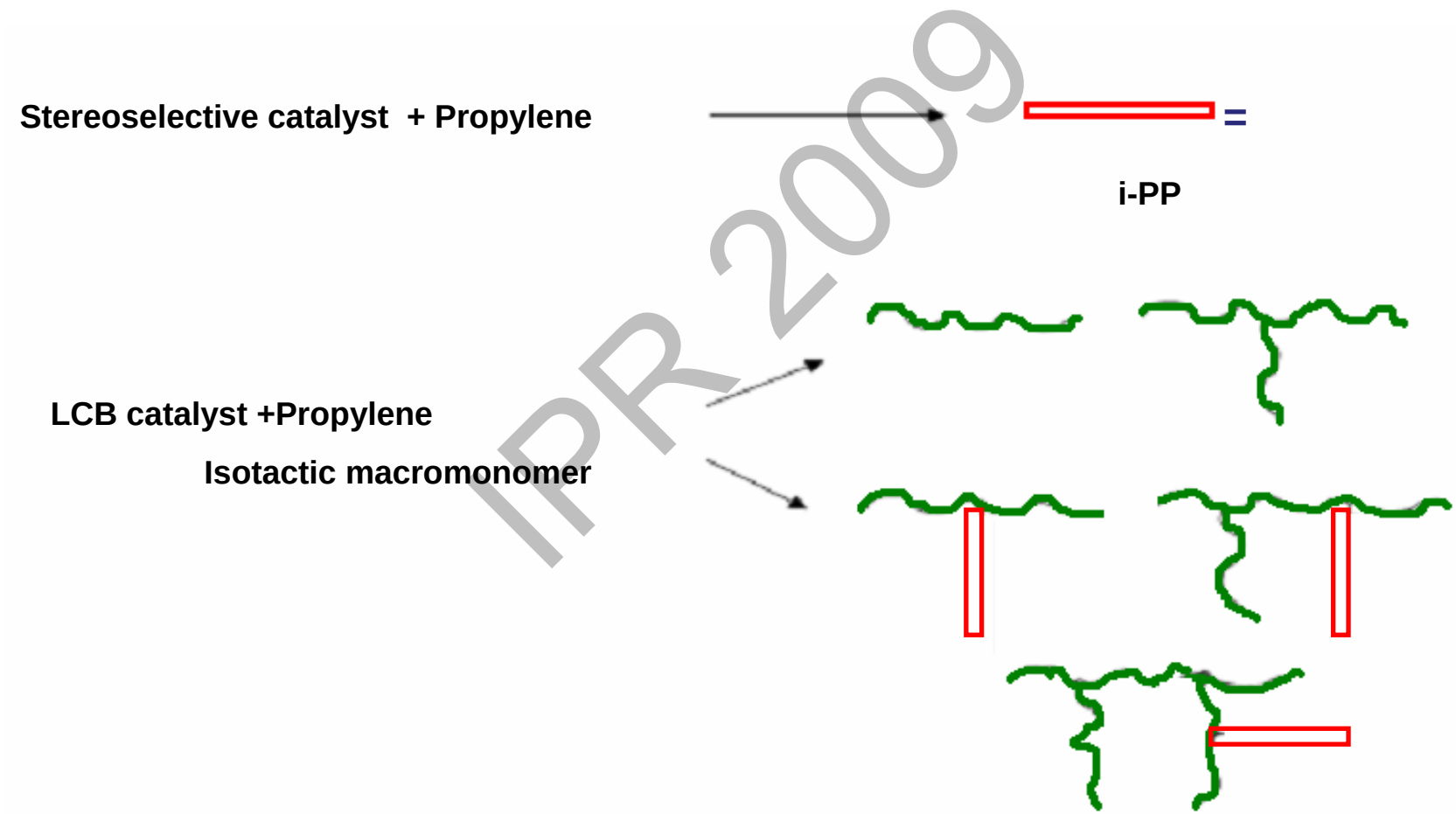
1. Introduction
2. Experimental results and Conclusions

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**

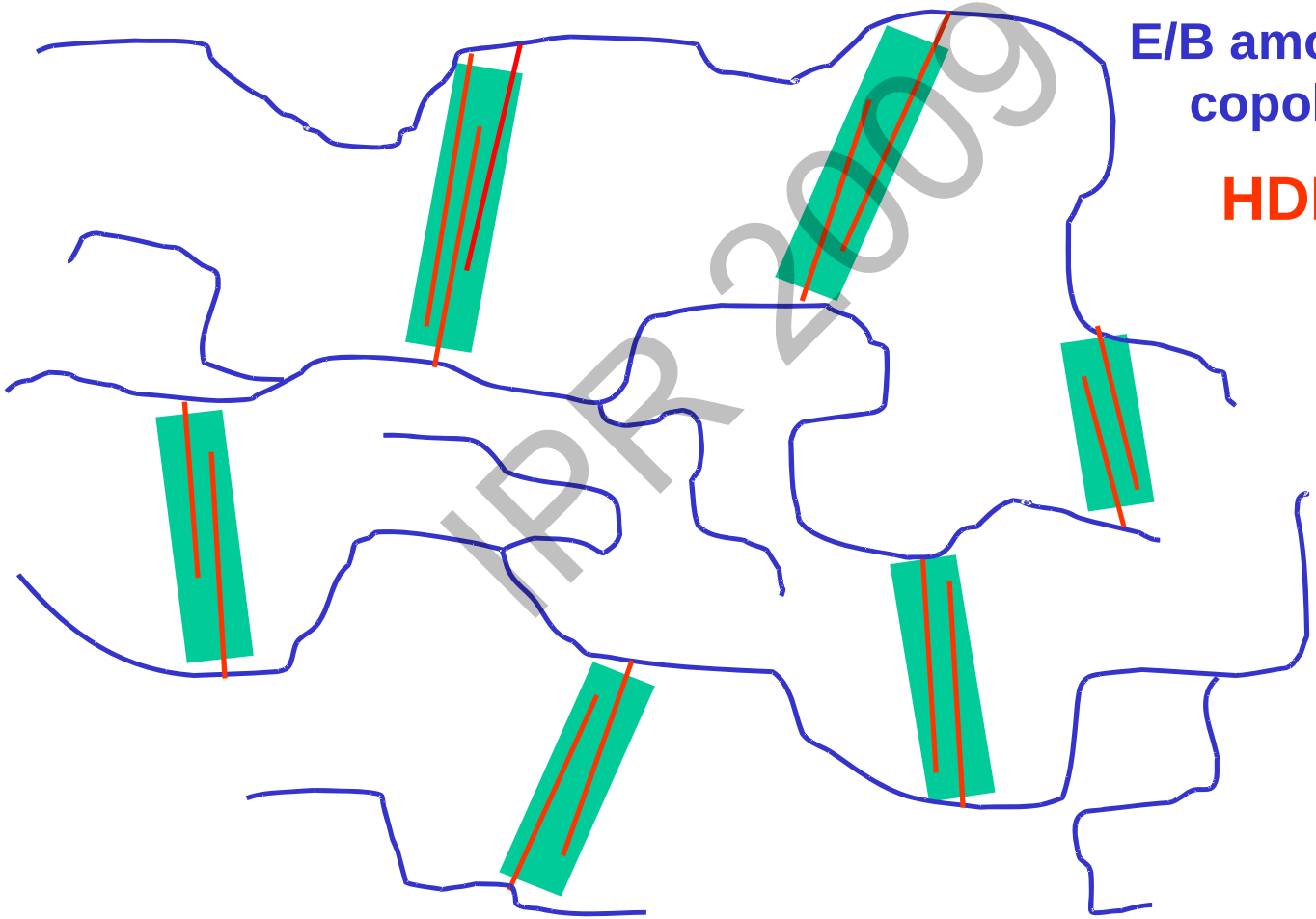
Graft copolymer (Branch-block)

iPP-g-aPP

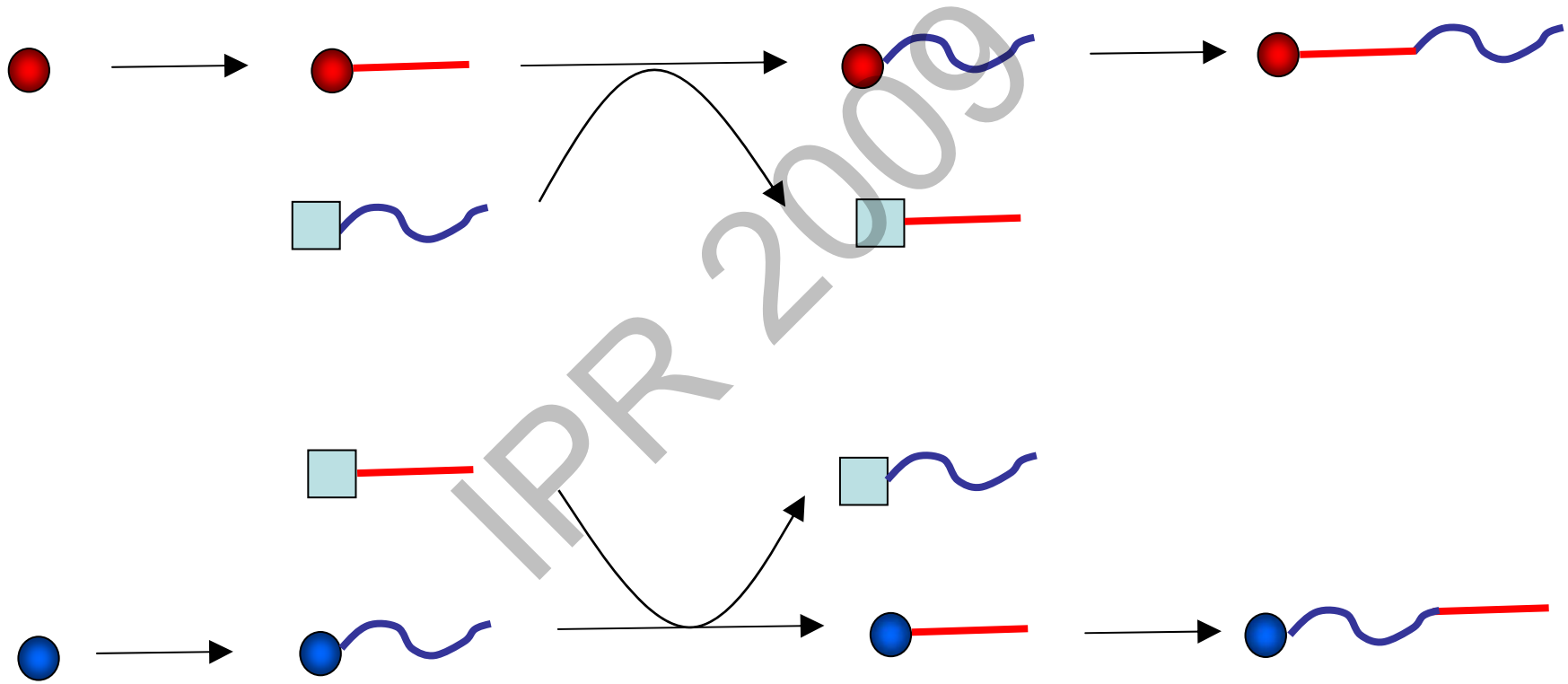


Graft Block Copolymers

Amorphous Backbones + Crystalline LCBs



Block copolymers via chain shuttling



Experimental part

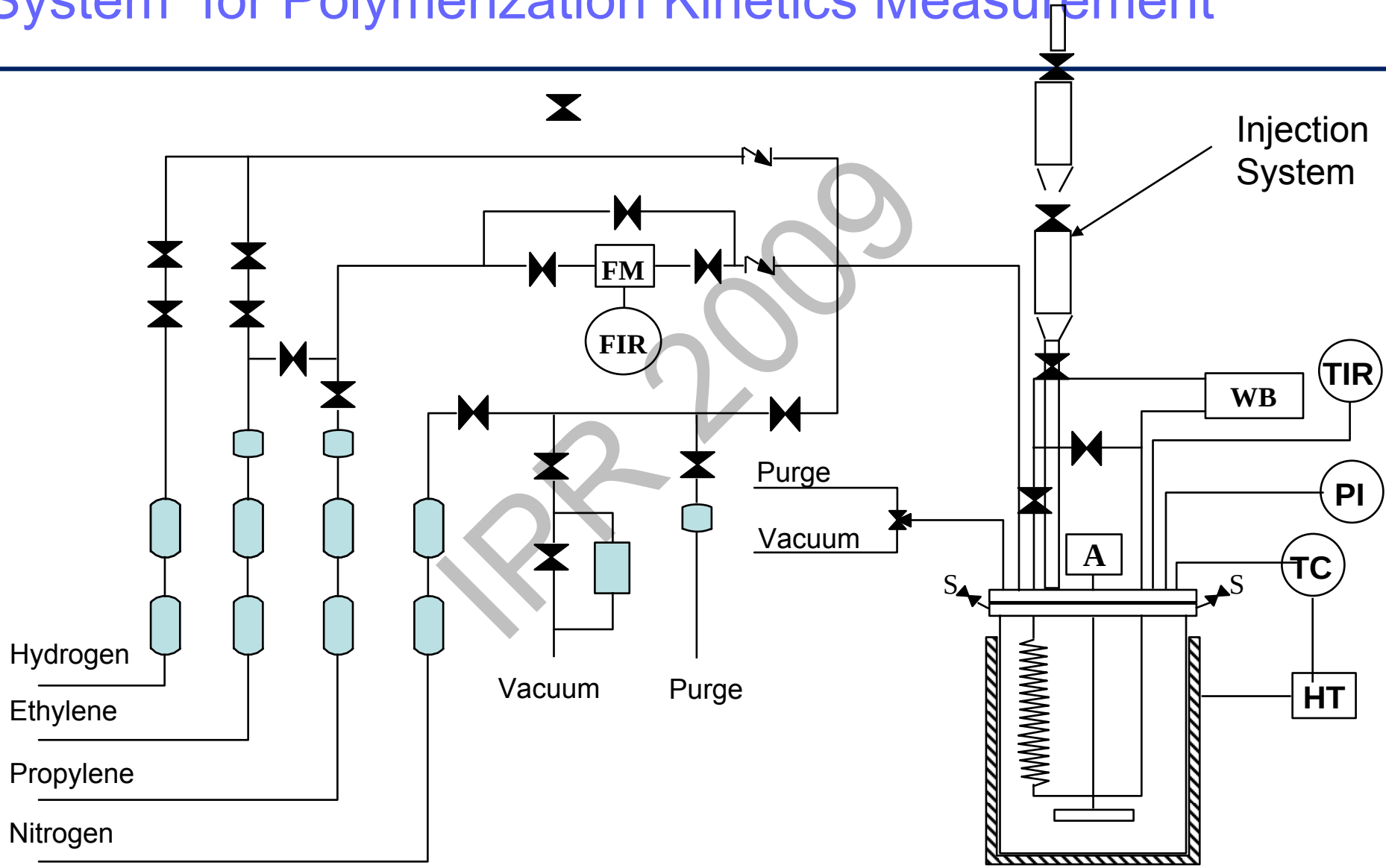
Case Study 1

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

Case Study 2

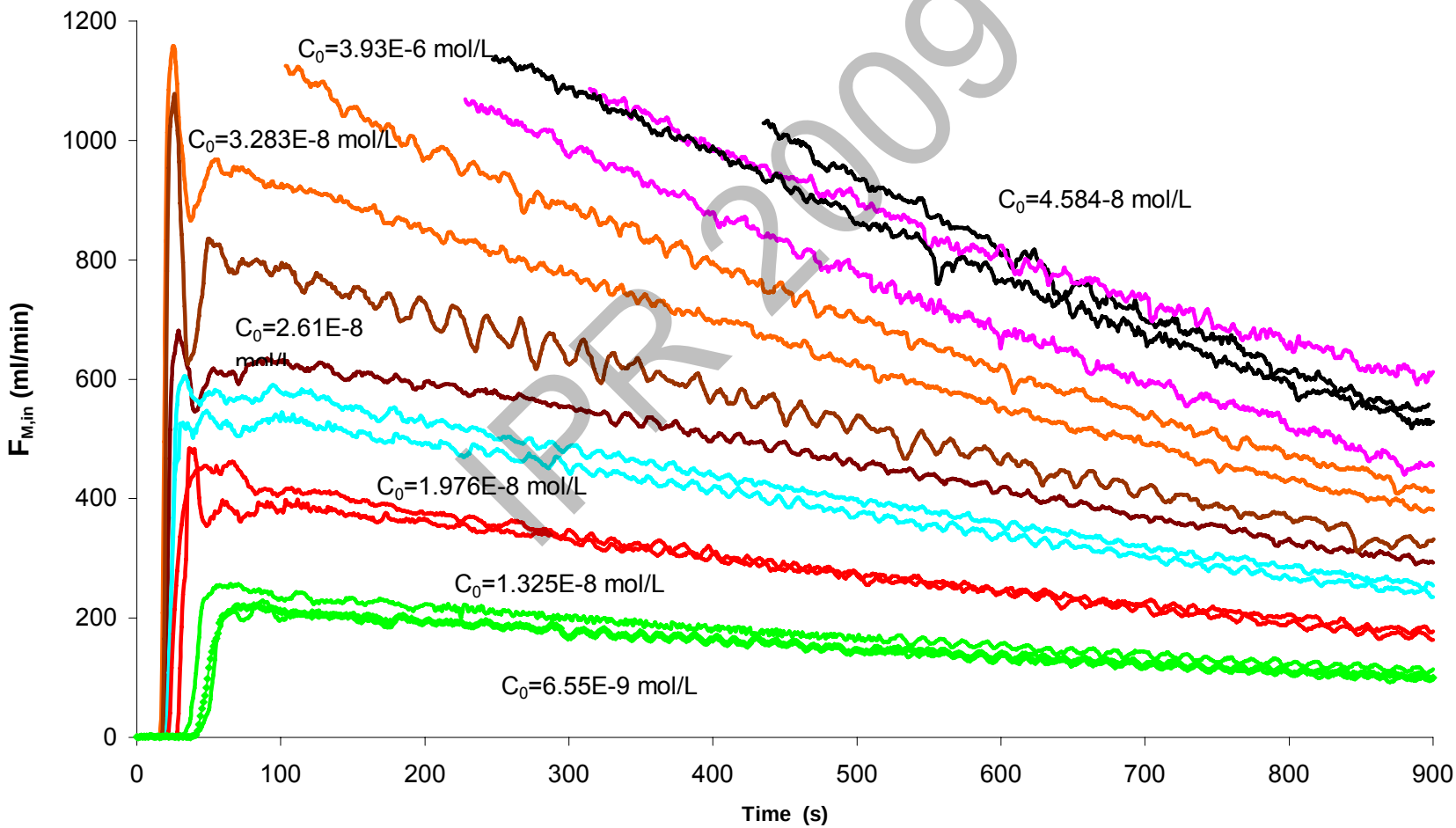
Solution homo- and co-Polymerization of ethylene using CGC-Ti catalyst

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

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

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

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

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

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

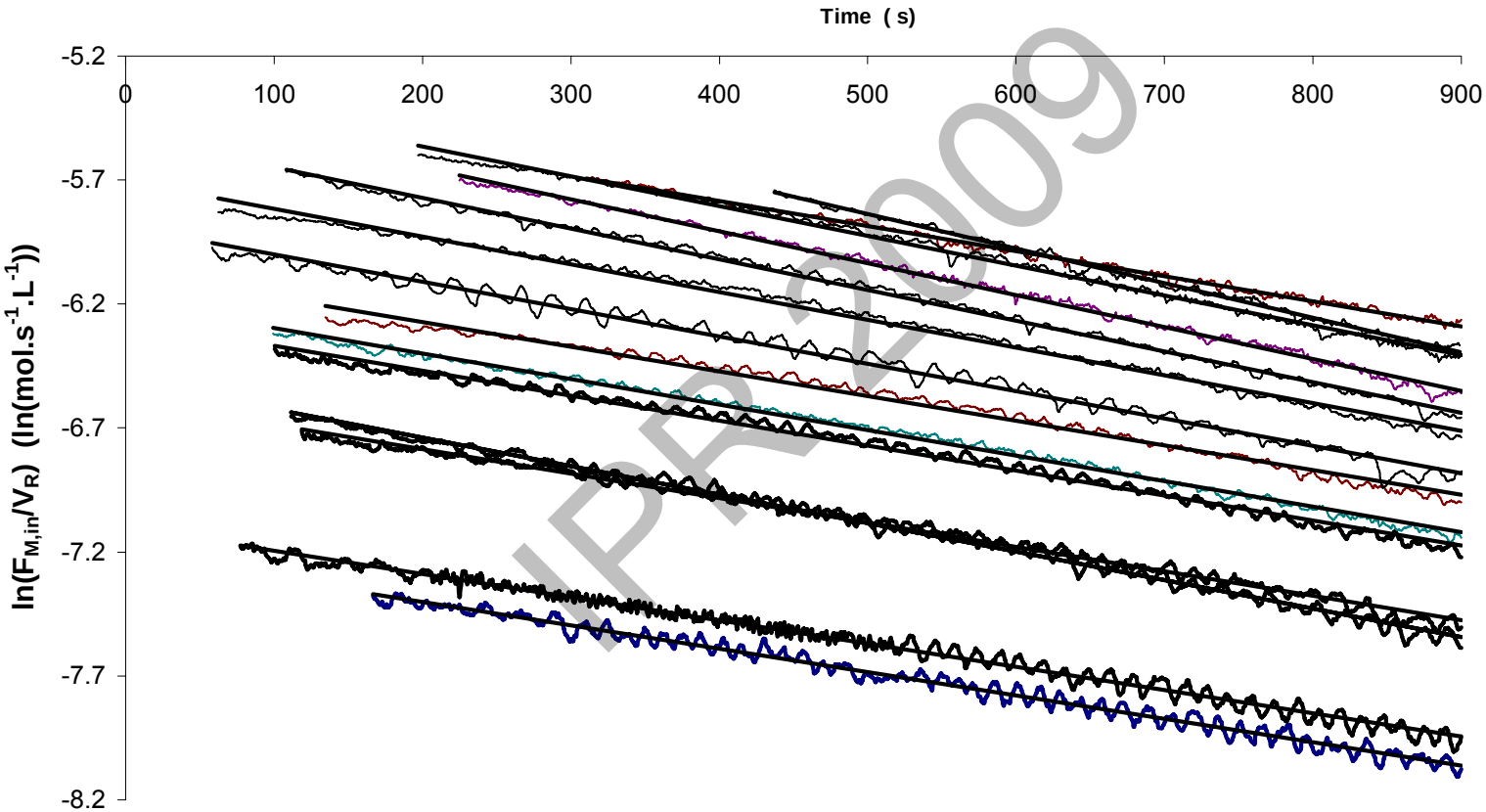
Initial conditions

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

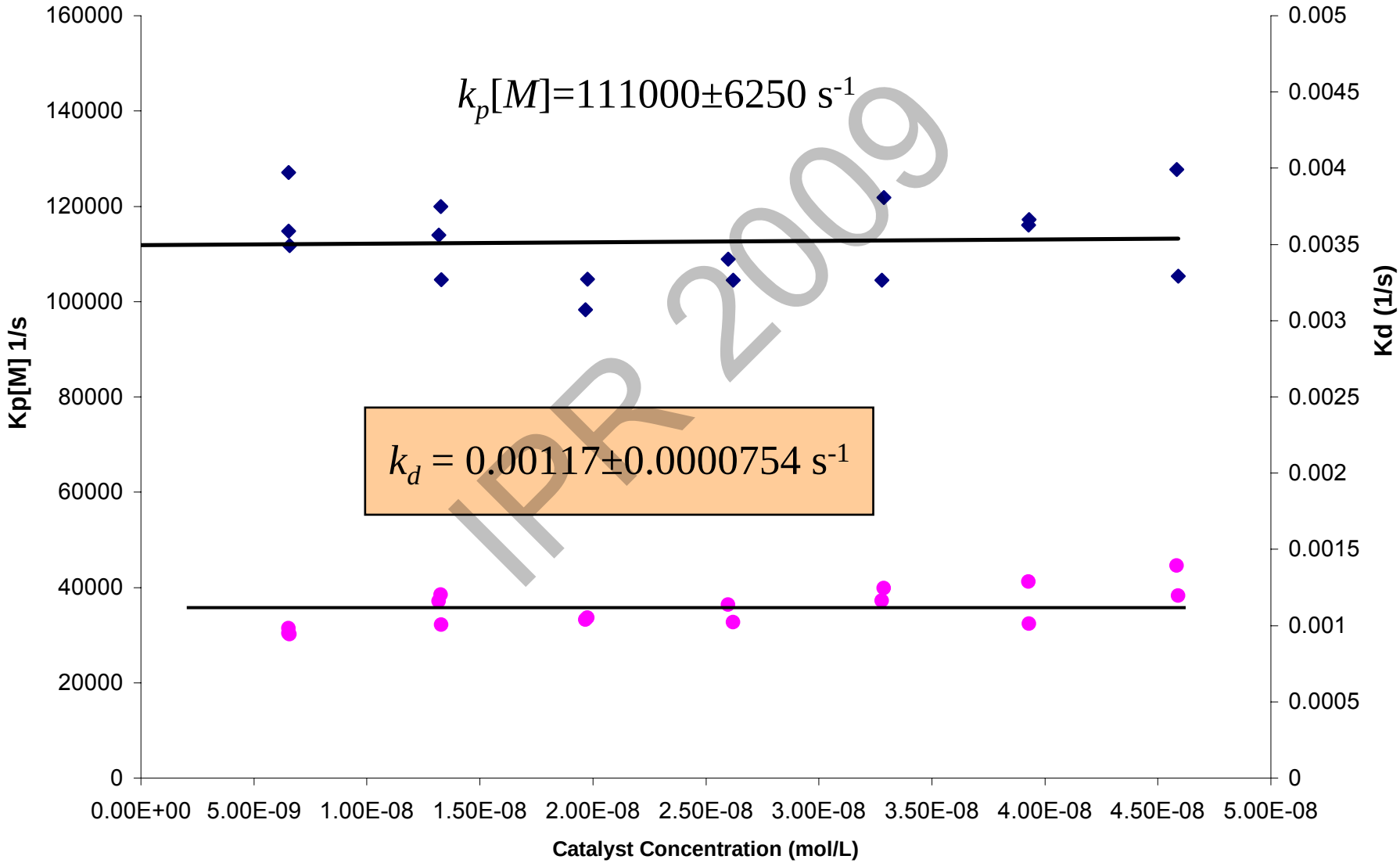
$$[M] = cons.$$

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

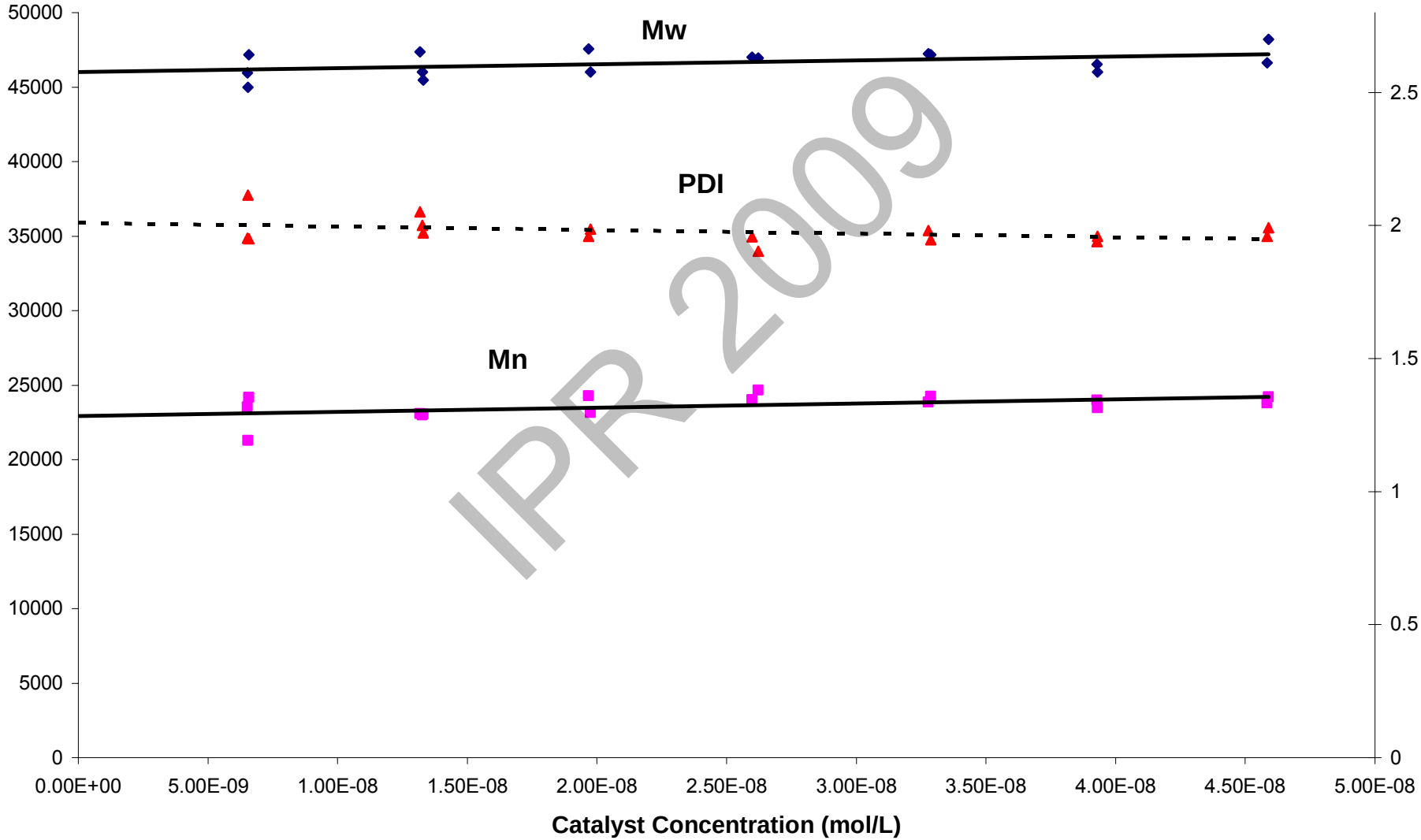
Plot of $\ln\left(\frac{F_{M,in}}{V_R}\right)$ versus time catalyst: rac-Et(Ind)$_2$ZrCl$_2$



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



Effect of Catalyst Concentration on Molecular weight

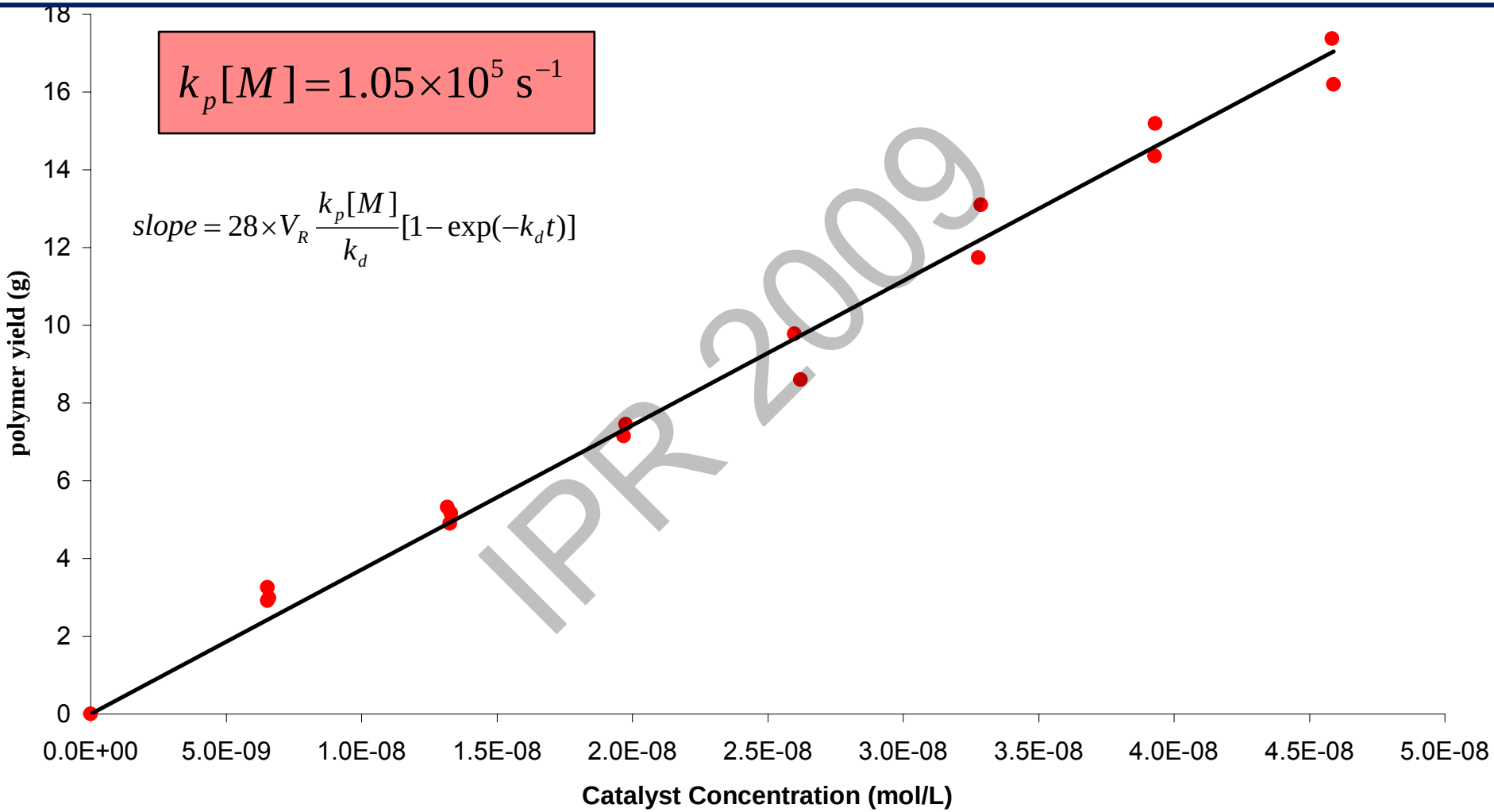


Experimental Data Fit – 1st Order Model

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

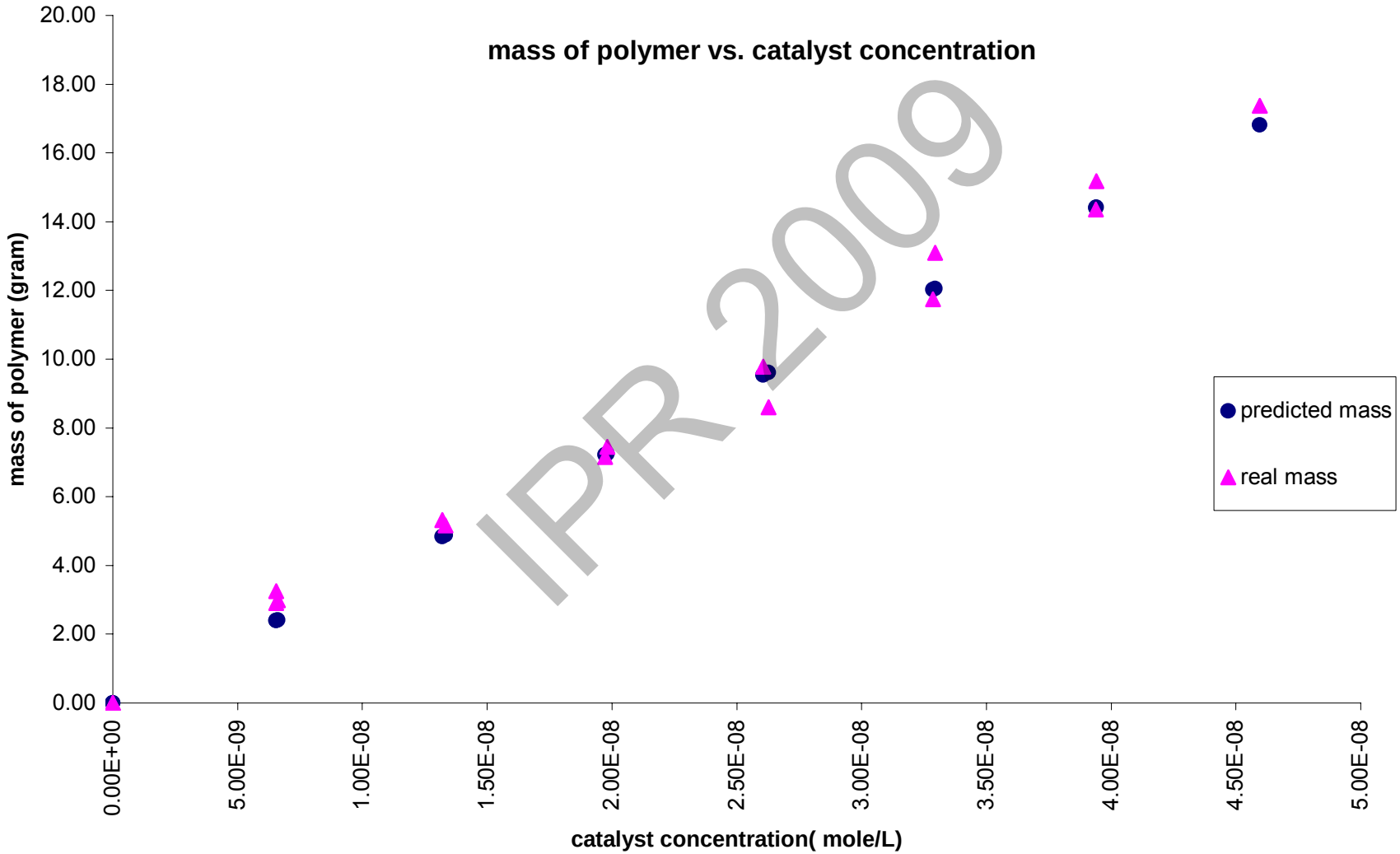
$$k_p[M] = 1.05 \times 10^5 \ s^{-1}$$

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



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$_2$