

Simulation of polymerization and long chain branch formation in a semi batch reactor using two single-site metallocene catalysts

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Outline

1. Introduction (Thermoplastic elastomers)
2. Simulation results

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Thermoplastic Elastomers (TPEs)

Thermoplastic elastomers (TPEs) are materials with functional properties of conventional thermoset rubbers and processing characteristic of thermoplastics

The idea behind TPEs is the notion of reversible crosslink

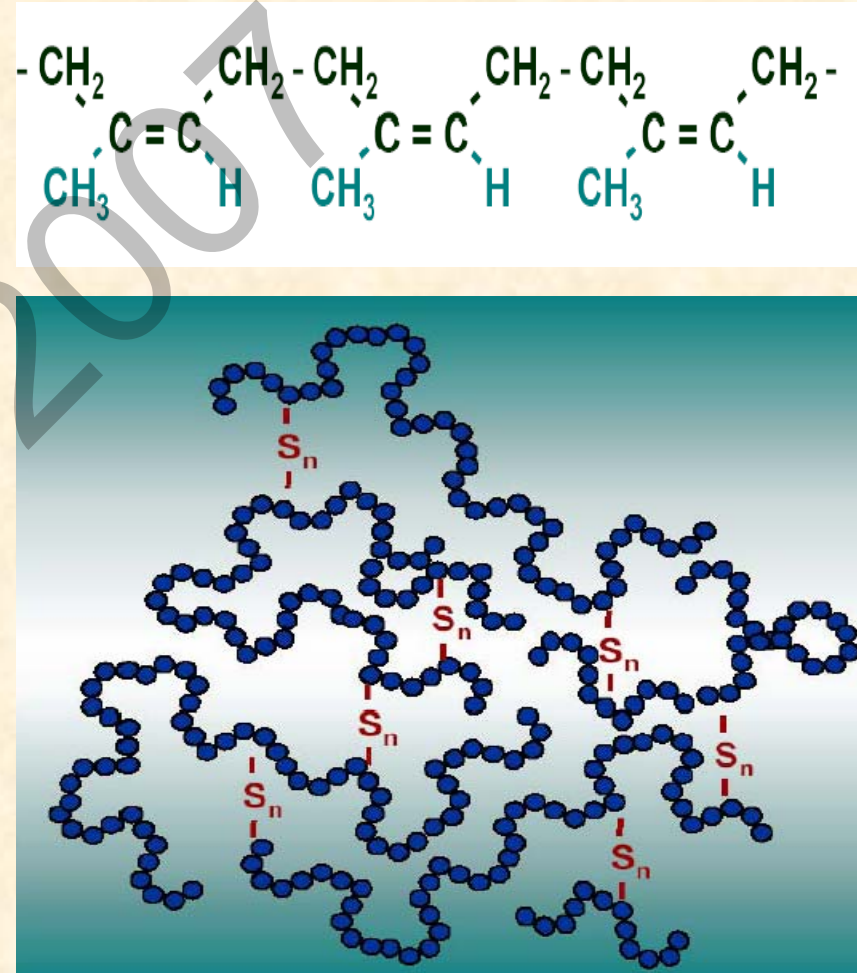
There are two types of crosslinks

Chemical cross-link (Cross linking by covalent bond)

Physical crosslink

Cross linking by covalent bond

- An example of cross-linking is the reaction of natural rubber or poly(isoprene)
- By a process called **vulcanization**, sulfur interconnects the chains by reacting with the **double bonds**



Physical Crosslinking

A simple structure is **ABA** block copolymer

A: Short, rigid polystyrene

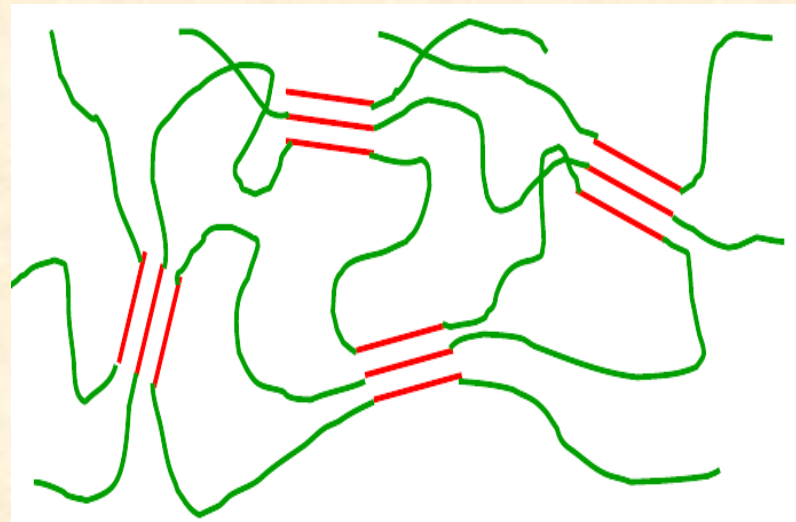
B: long, flexible polybutadiene

Other possibilities include

Multiblock **A-B-A-B-A-.....**

Graft copolymer

Immiscible (incompatible) microdomains within polymer matrix



Copolymers

-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-B-A-A-A-A-A-

Block Copolymers

-B-

A-A-A-A-A-A-A-

A-A-A-A-A-

A-A-A-A-A-A-A-

Hard
segments

graft copolymers

Graft copolymer (Branch-block)

iPP-g-aPP

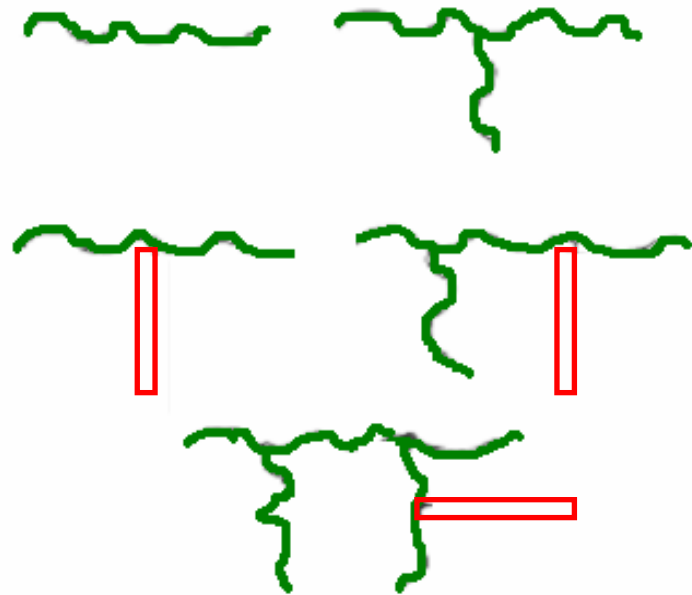
Stereoselective catalyst + Propylene



i-PP

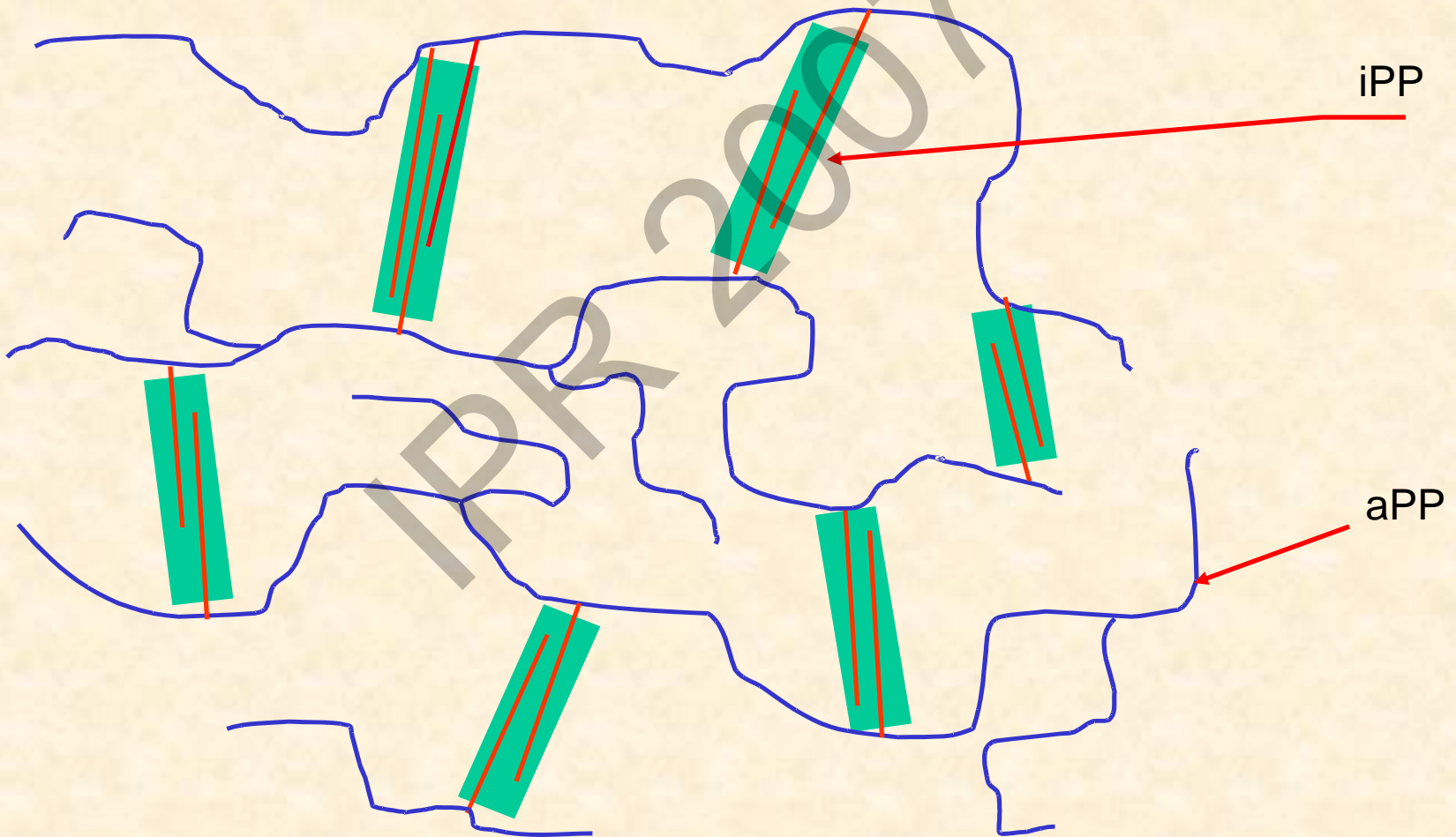
LCB catalyst + Propylene

Isotactic macromonomer



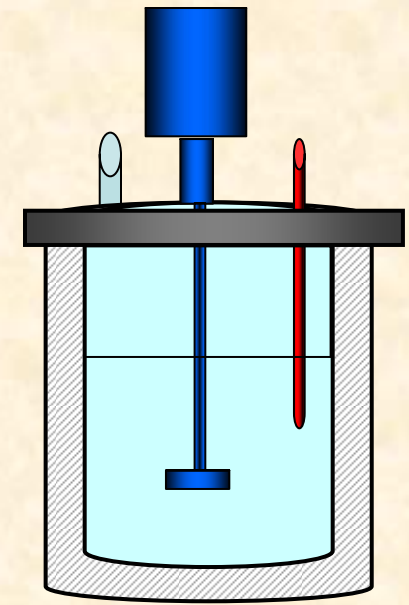
Graft Block Copolymers

Amorphous Backbones + Crystalline LCBs



Simulation in a **Semi batch** Reactor

- **Assumptions:**
- Constant monomer concentration
- No mass transfer limitations
- **Model Predictions**
- Molar (n %) and weight (w %) percentages vs. time
- Number (r_n) and weight (r_w) average chain lengths vs. time
- Average LCB per 1000 C atoms ($LCBD$) and per chain ($LCBF$) vs. time

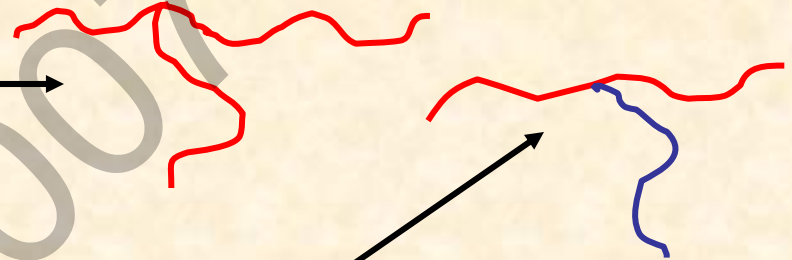


M1

+ Monomer



LCB 1



Cross-product

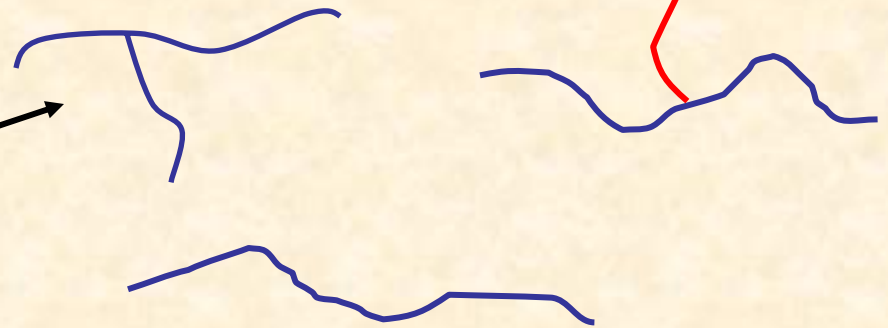


M2

+ Monomer



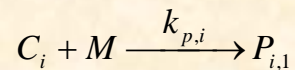
LCB 2



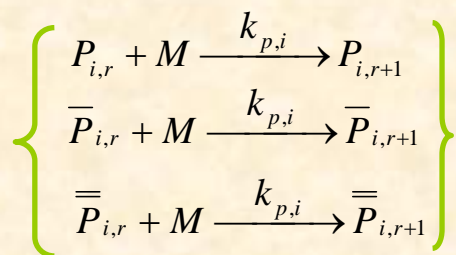
Kinetic Mechanism

Long chain branches are formed by incorporation of macromonomers of different types:

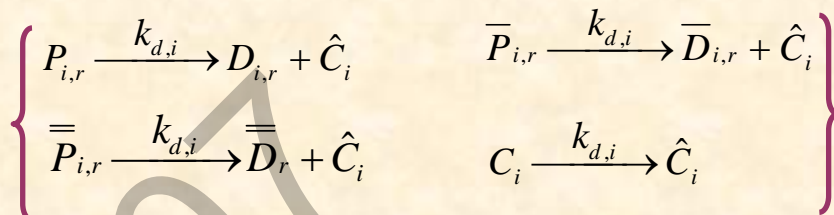
Initiation



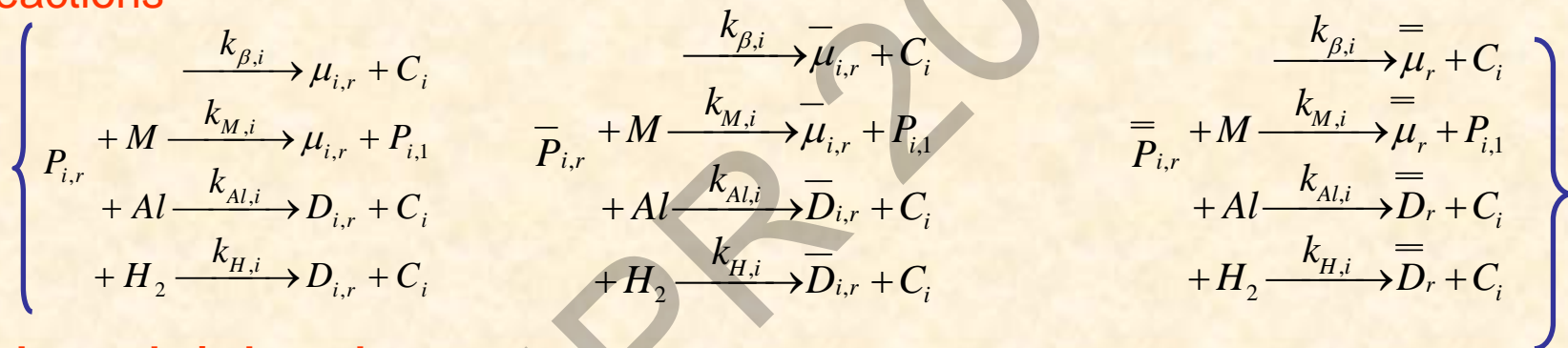
Propagation



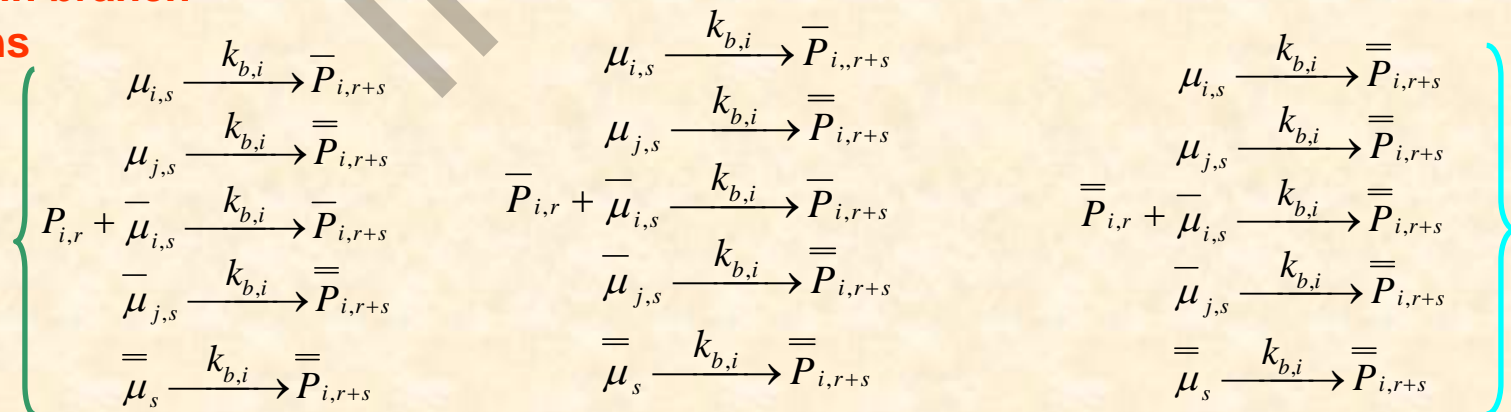
Deactivations



Chain transfer reactions



Long chain branch formations

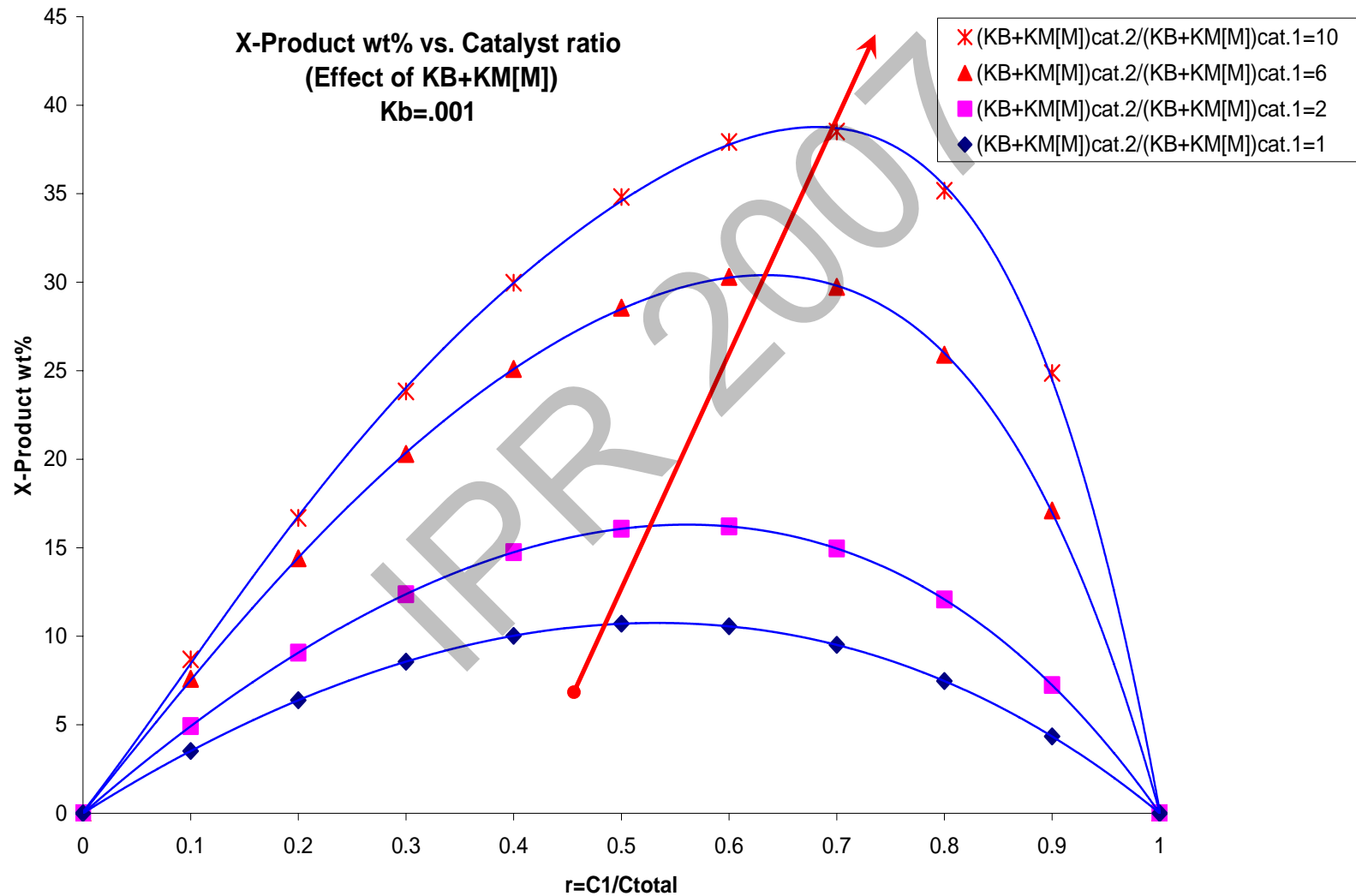


Case study 1: *Effect of $k_{\beta}+k_M[M]$*

				C1 LCB Cat.	C2 Linear	
C1 LCB CAT.		Initial conc. of catalyst 1	k_p	5000	5000	Propagation rate constant
C2		Initial conc. of catalyst 2	k_b	400	0.001	Long chain formation Rate constant
M	0.5	Monomer conc.	K_d	0.005 1/s	0.005 1/s	Deactivation rate constant
H2	0.0		k_{β}	0.4	0.4	B-hydride elimination
Al	0.0		K_M	1	1	Transfer to monomer
tr	600		K_{Al}	0	0	Transfer to Al
			K_{H2}	0	0	Transfer to Hydrogen
Ctotal	4 μ mole/L		$K_{\beta}+K_M[M]$	0.9	0.9	

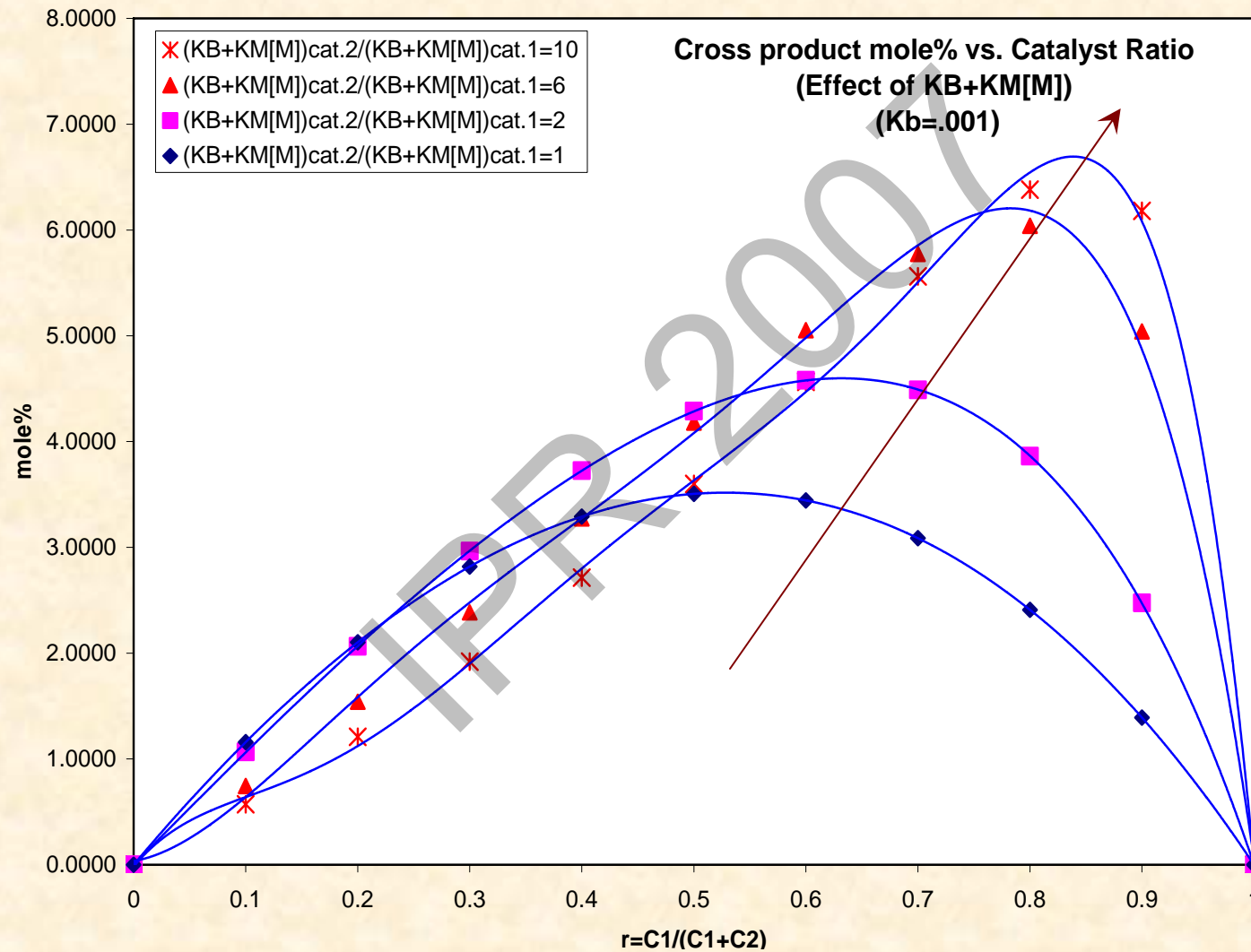
Cross-product weight percent at different values of $k_{\beta}+K_M[M]$.

Case 1

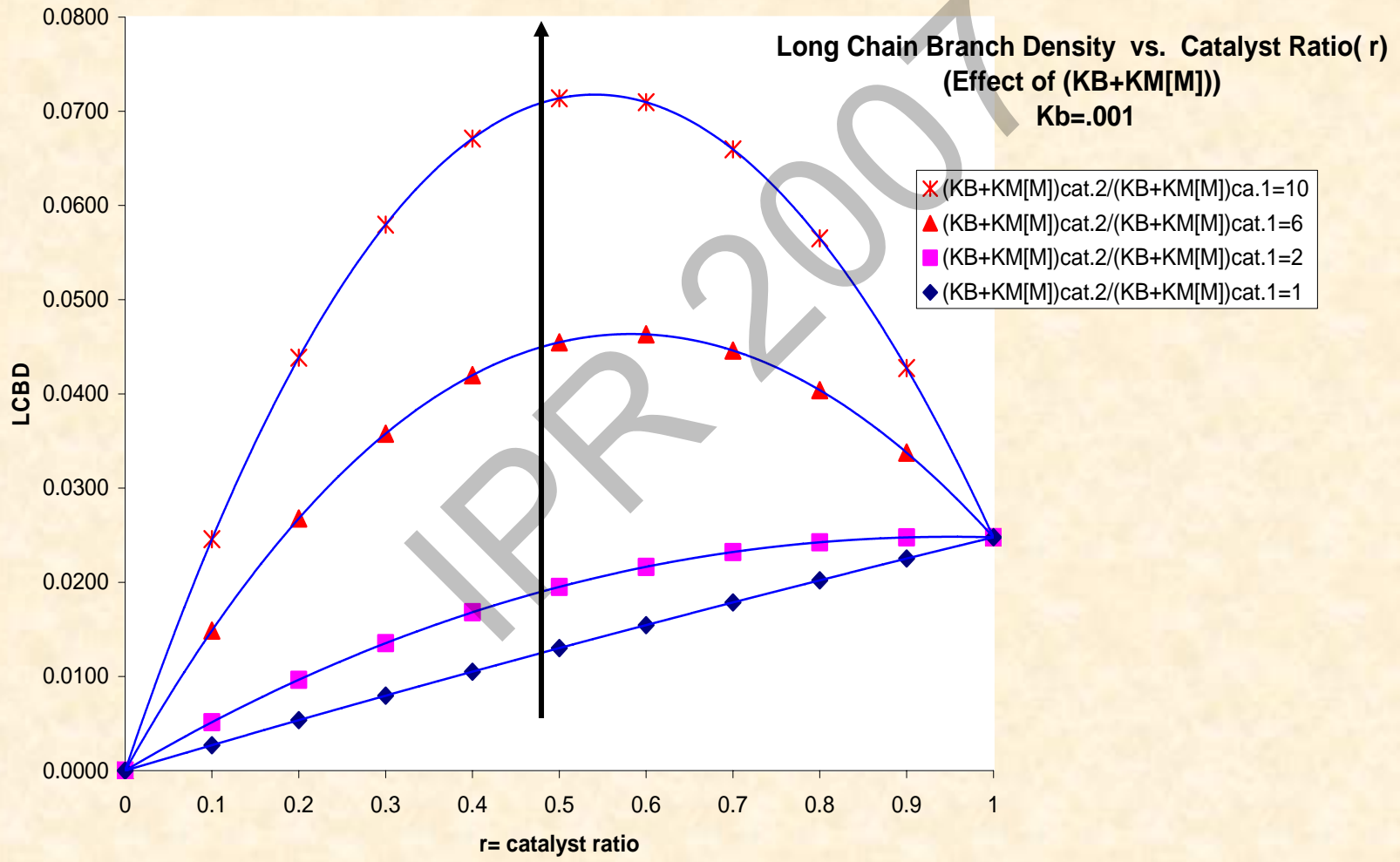


Cross-product mole percent at different values of $k_{\beta}+K_M[M]$.

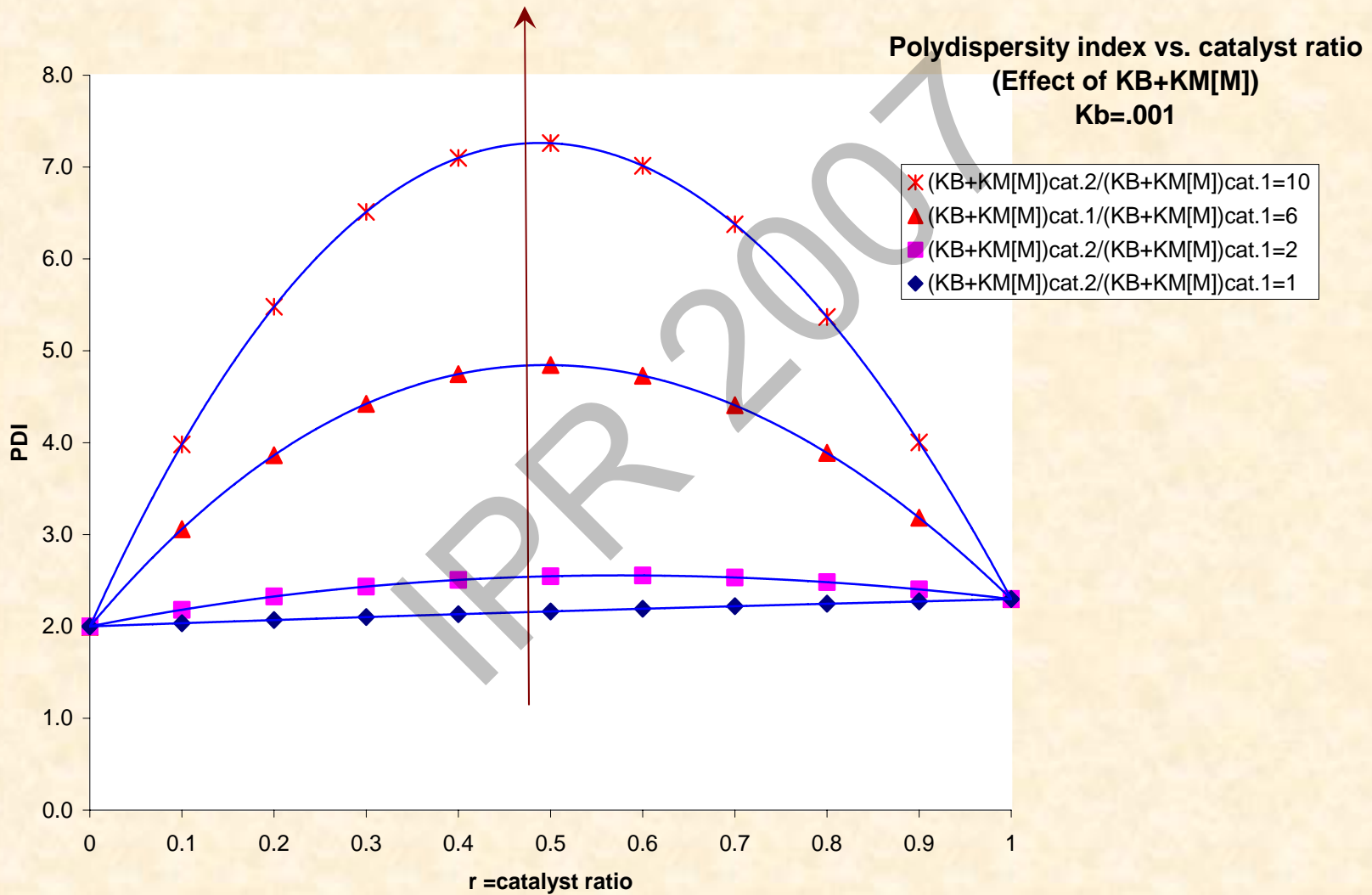
Case 1



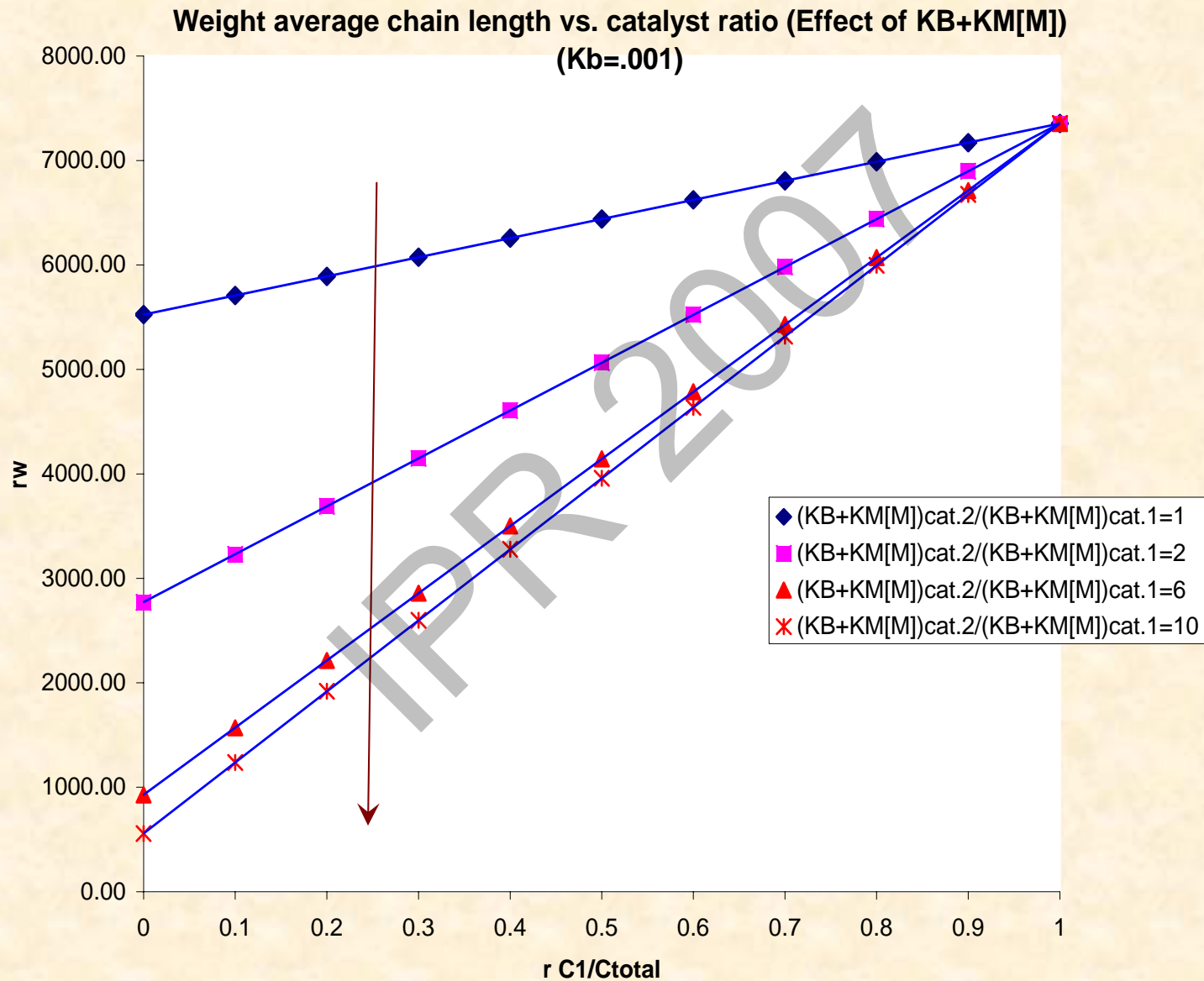
Effect of $k_{\beta}+K_M[M]$ on long chain branch density(LCBD)



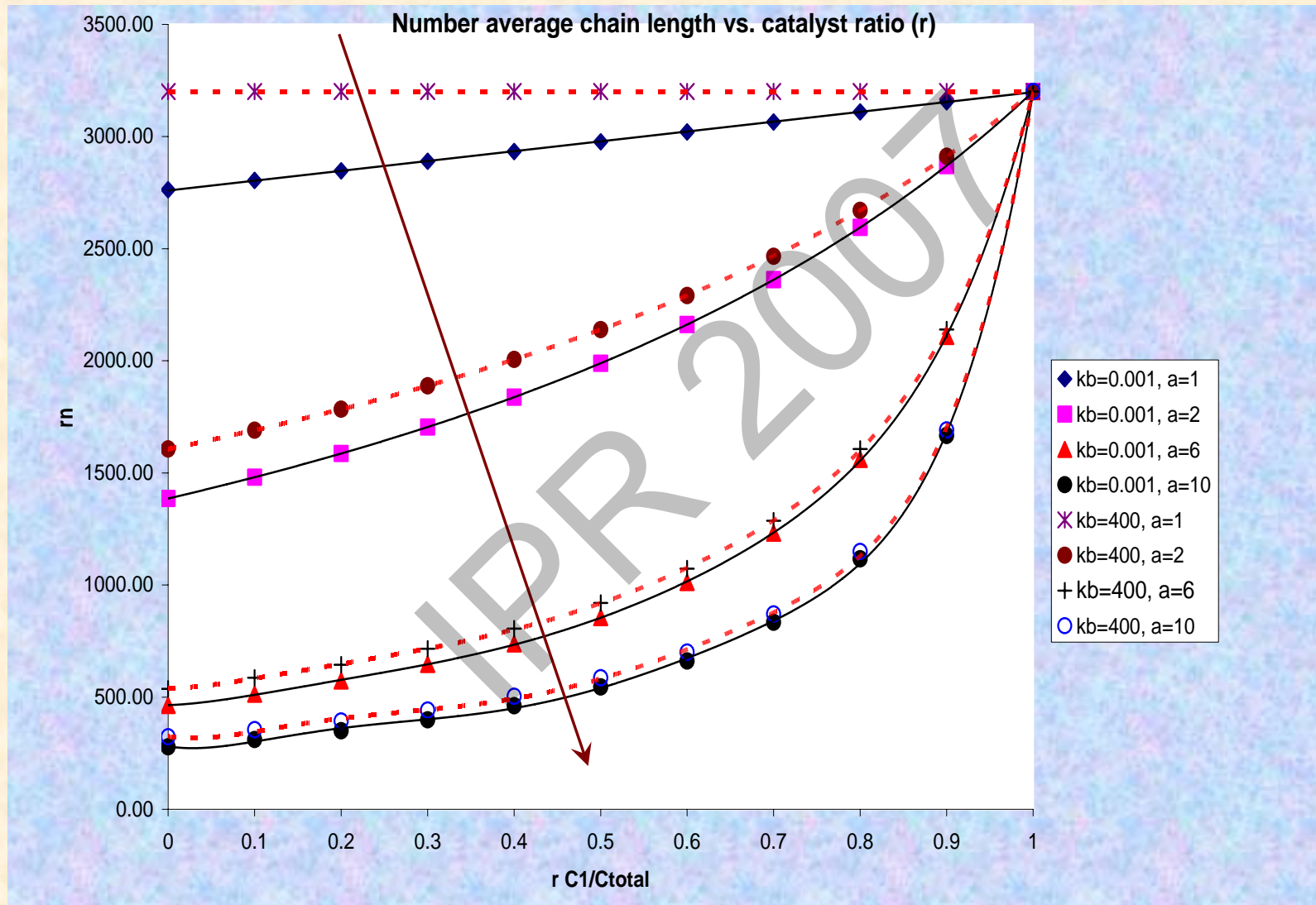
Effect of $k_{\beta}+K_M[M]$ on Polydispersity index (PDI)



Effect of $k_{\beta}+K_M[M]$ on weight average molecular weight (r_w)



Effect of $k_{\beta} + K_M[M]$ on number average molecular weight (r_w)

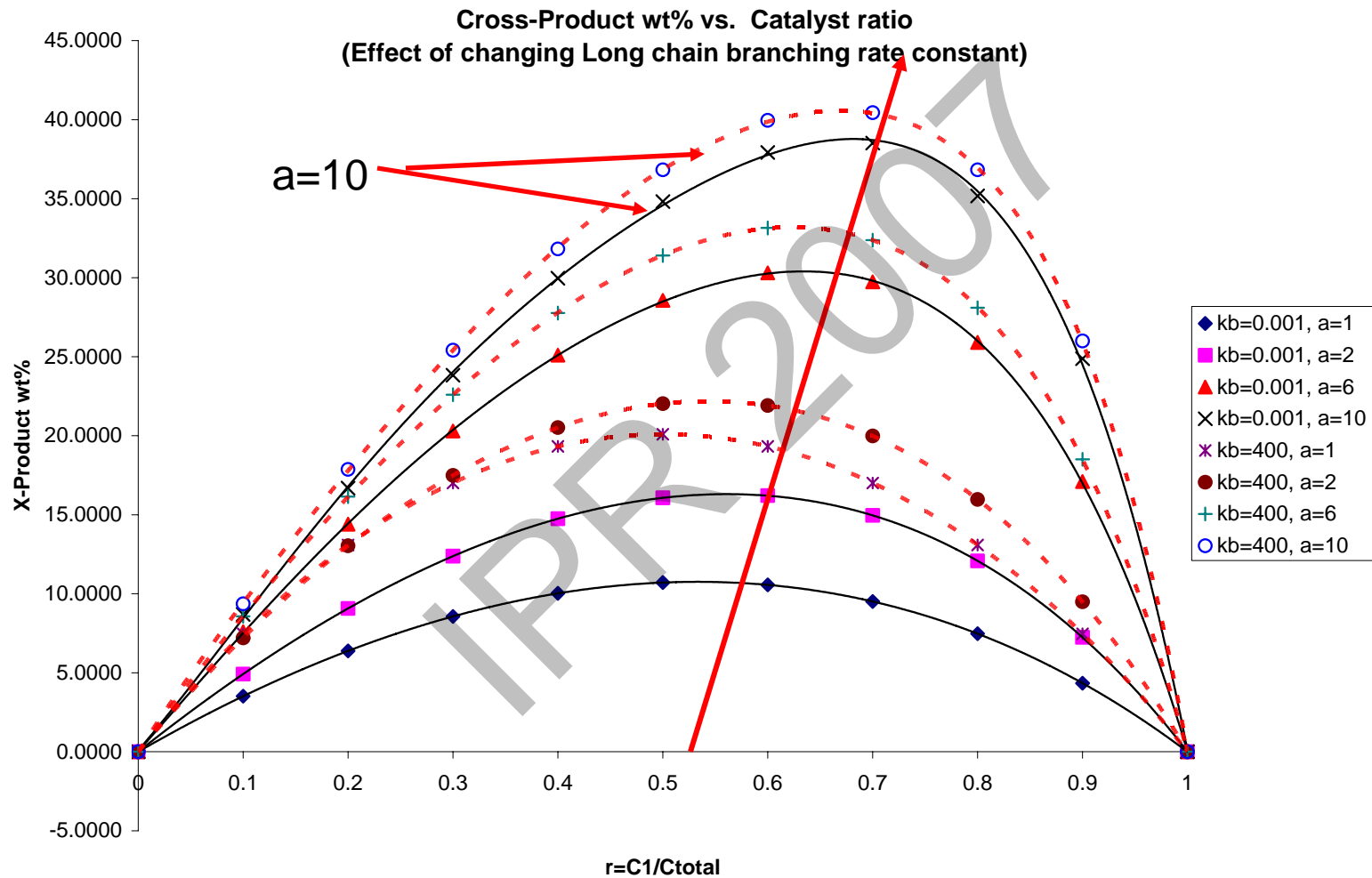


Results: Effect of parameter $k_{\beta}+K_M[M]$ of linear catalyst

- Increase in $k_{\beta}+K_M[M]$:
- will increase **cross-product wt%** and mole %
- Will increase **LCBD**
- Will increase **PDI**
- Will decrease **weight average** and number average chain lengths
- **Weight average chain length is a linear function of catalyst ratio**

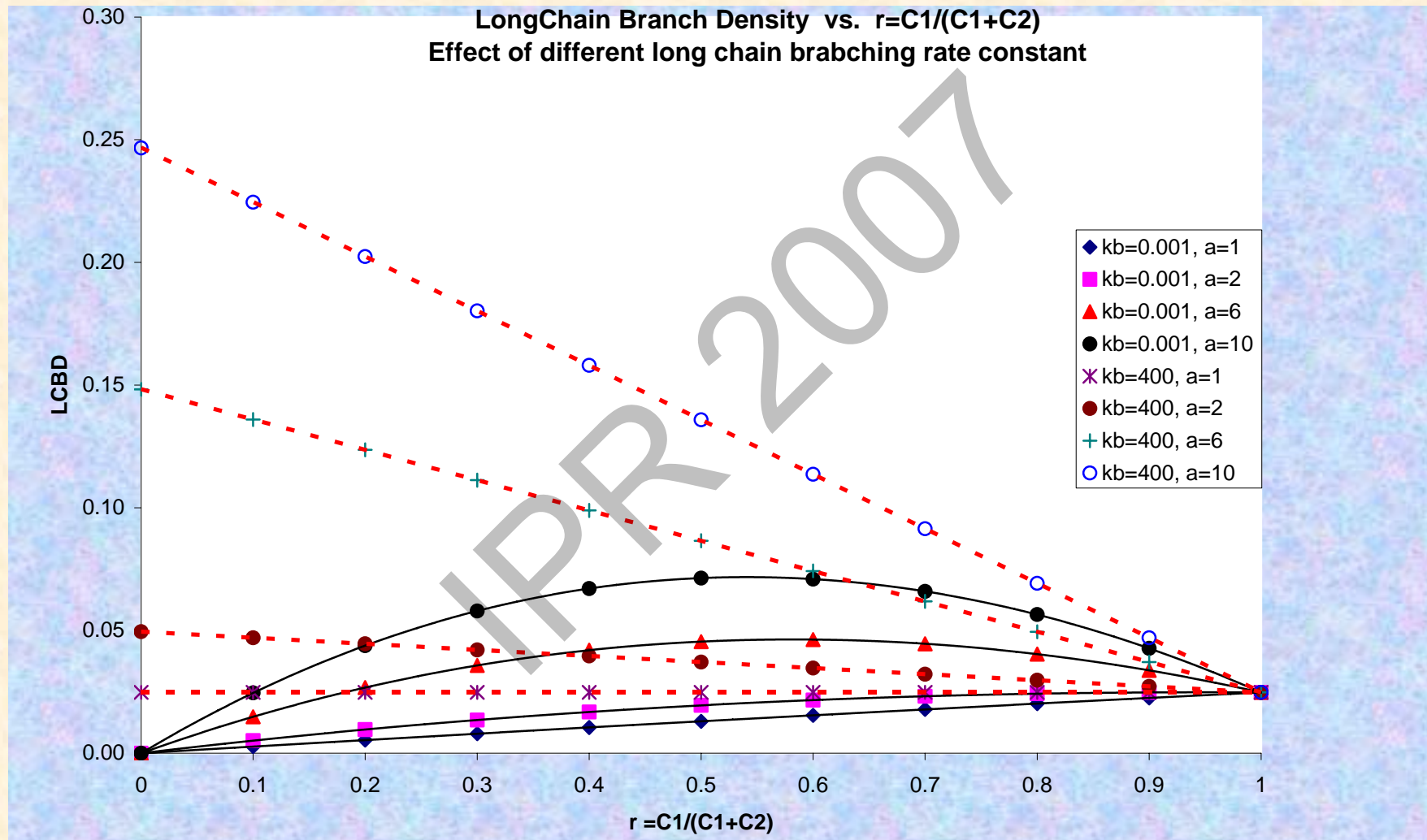
Case study 2: *Effect of $k_{b,2}$*

X-product wt% vs. catalyst ratio



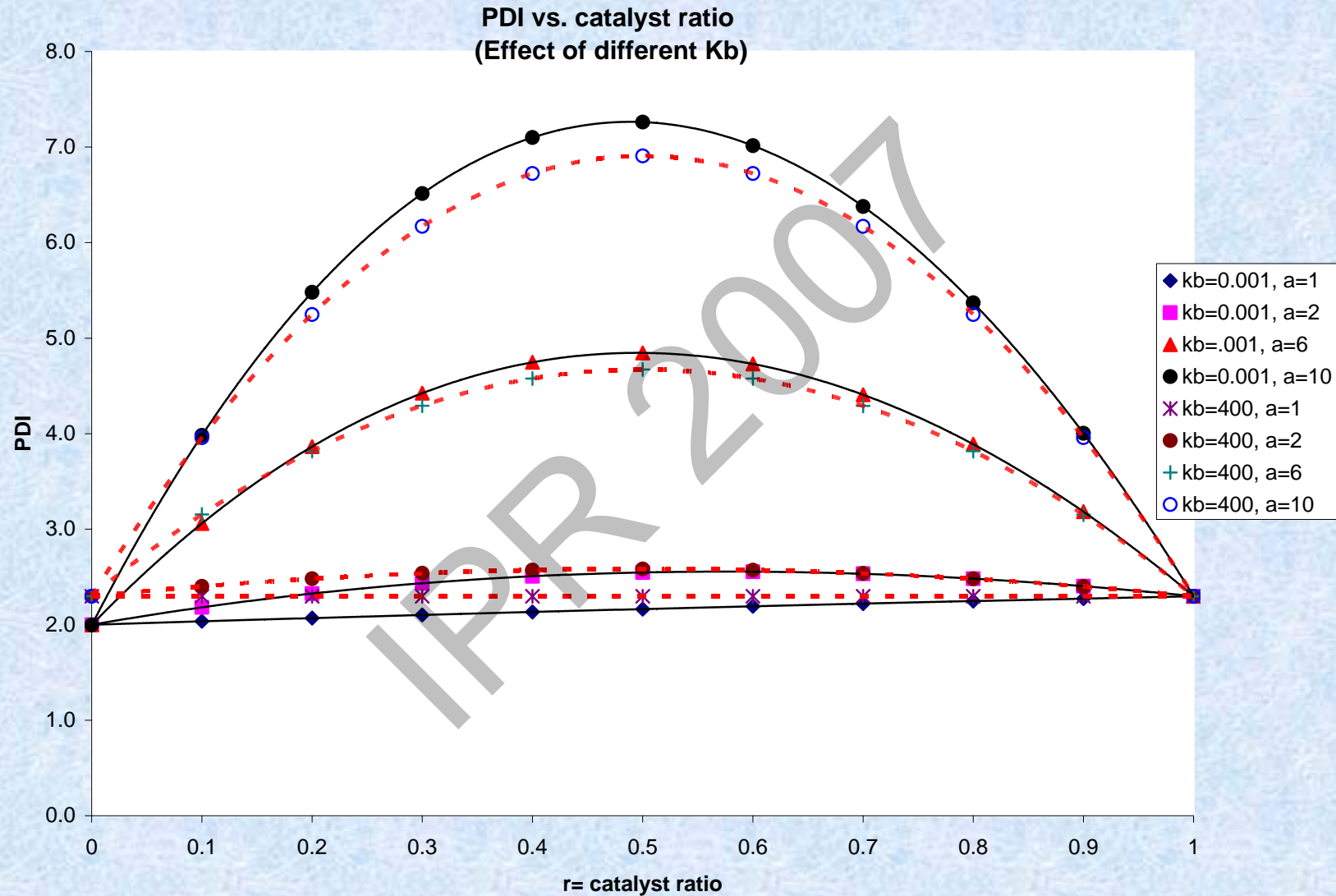
Case study 2 *Effect of $k_{b,2}$*

LCBD vs. catalyst ratio

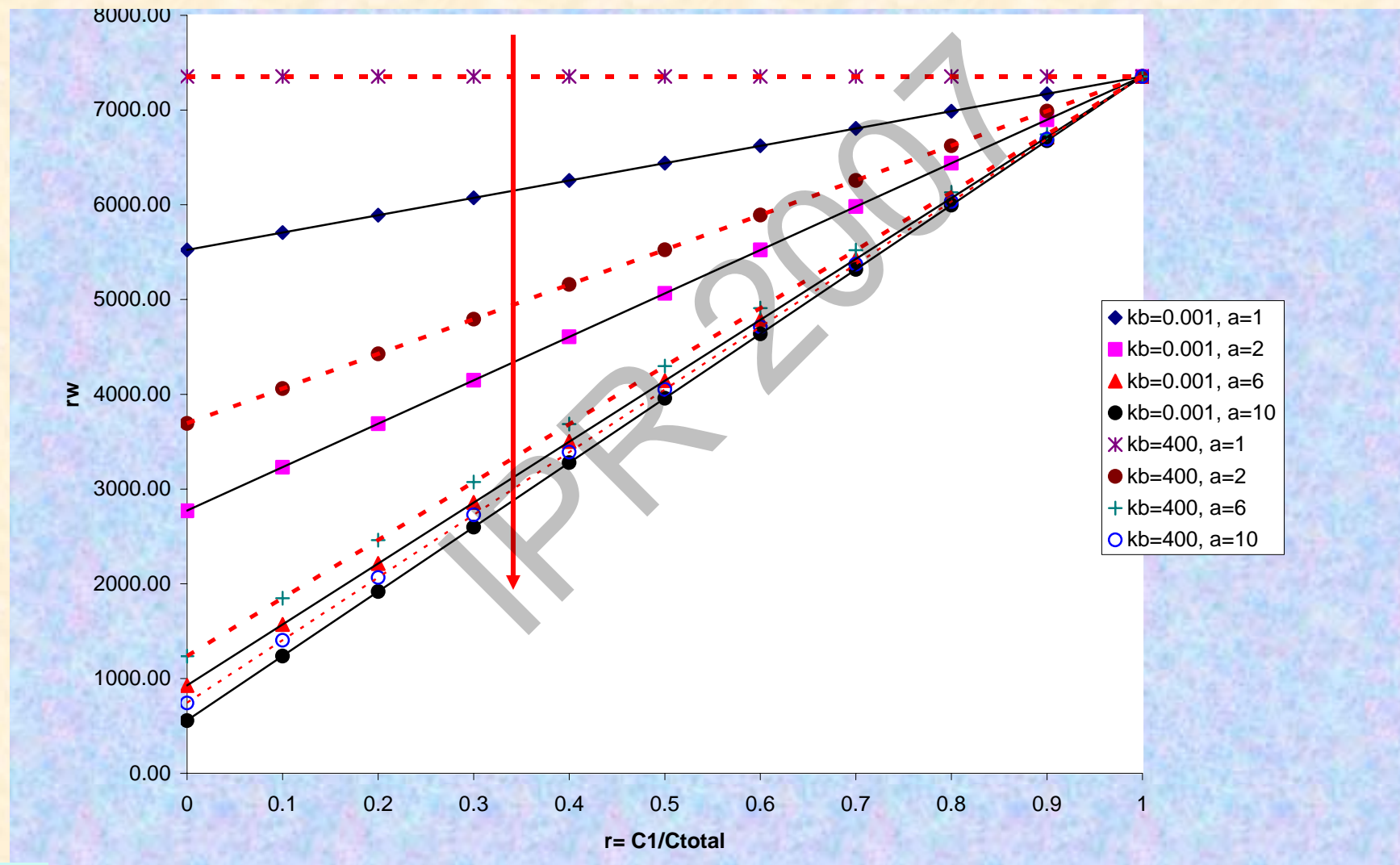


Case study 2 *Effect of $k_{b,2}$*

PDI vs. Catalyst ratio



Case study 2 *Effect of $k_{b,2}$*

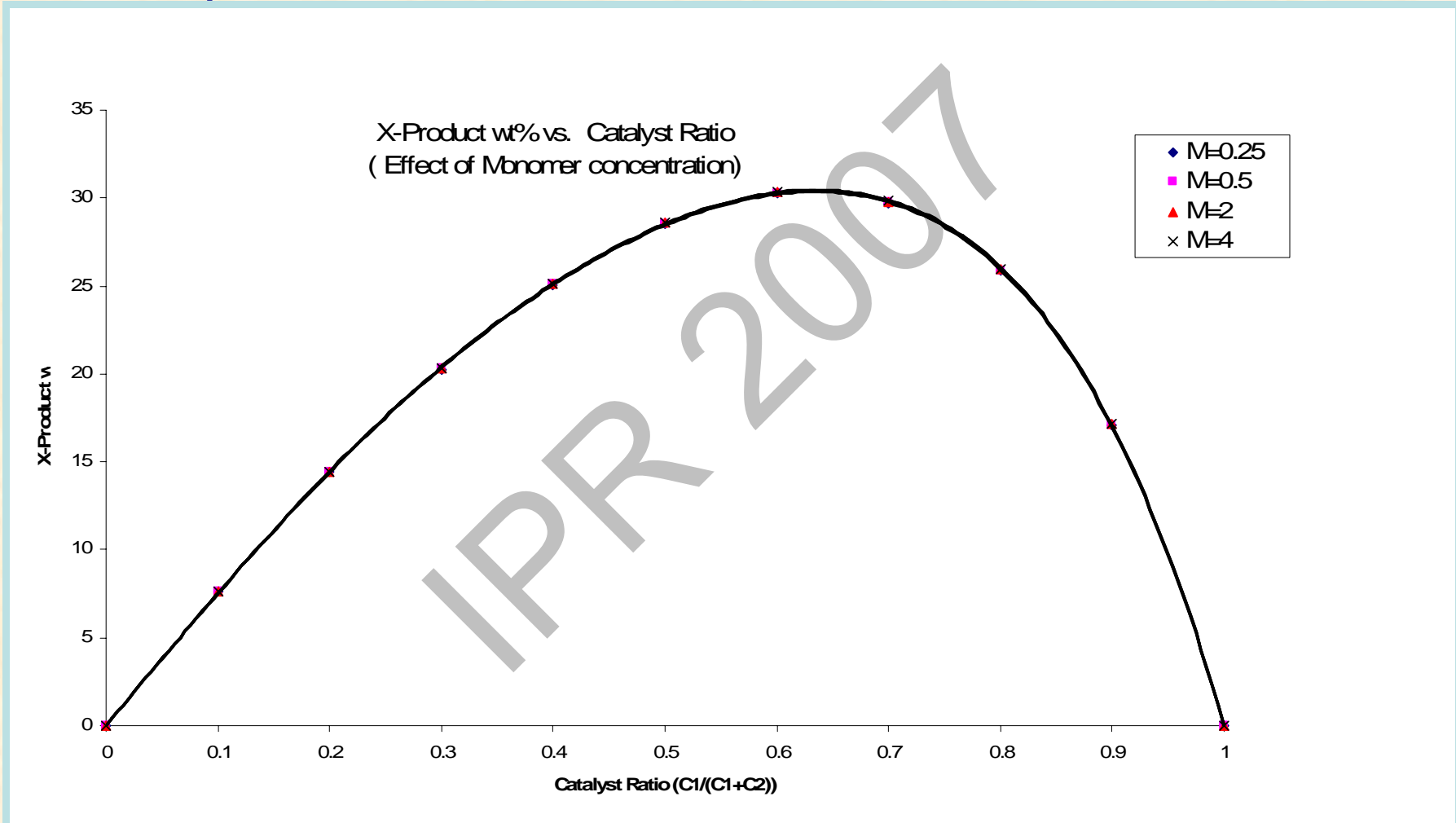


Case 2: Results

When $Kb_2=kb_1$

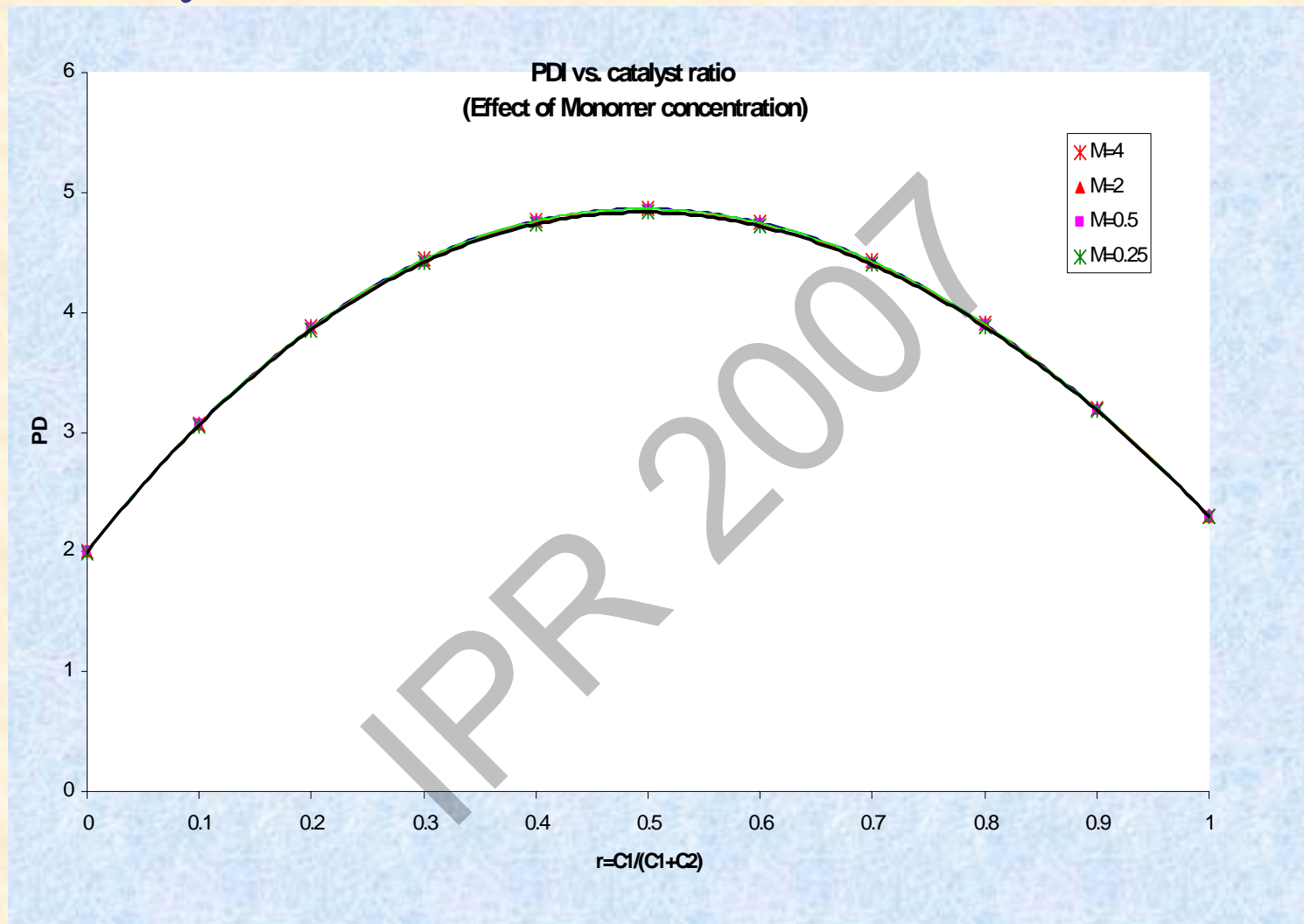
1. A **linear relationship** between LCBD and catalyst ratio is observed
2. If our only objective is to **maximize LCBD** there is no need for adding catalyst 1. Using only one catalyst with high macromonomer formation rate and high long chain branch incorporating ability is preferred than using combination of two catalysts.

Case study 3: Effect of monomer concentration on cross-product wt %



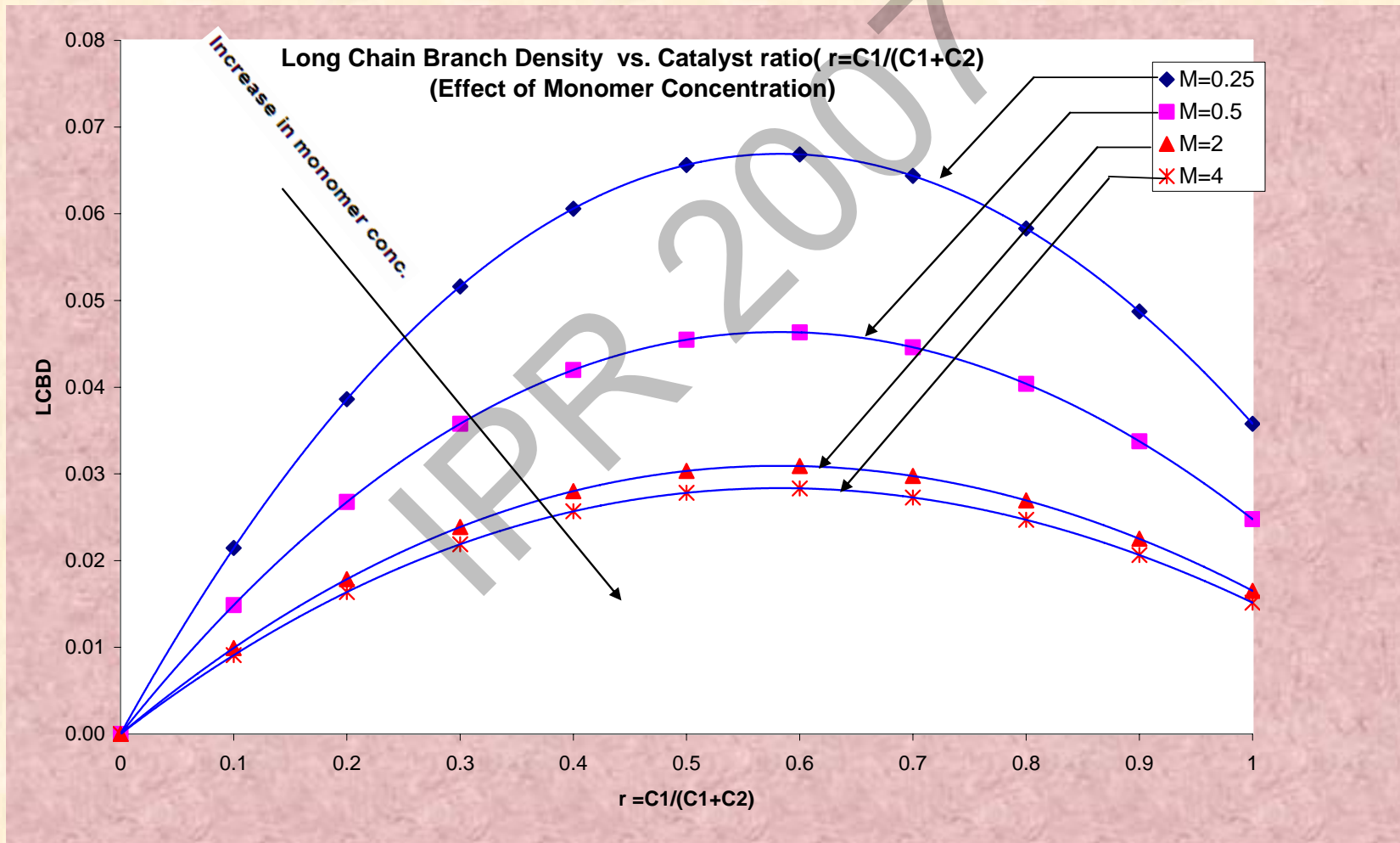
Weight % of Cross product vs. catalyst ratio at different monomer concentrations

Case study 3: Effect of monomer concentration on PDI

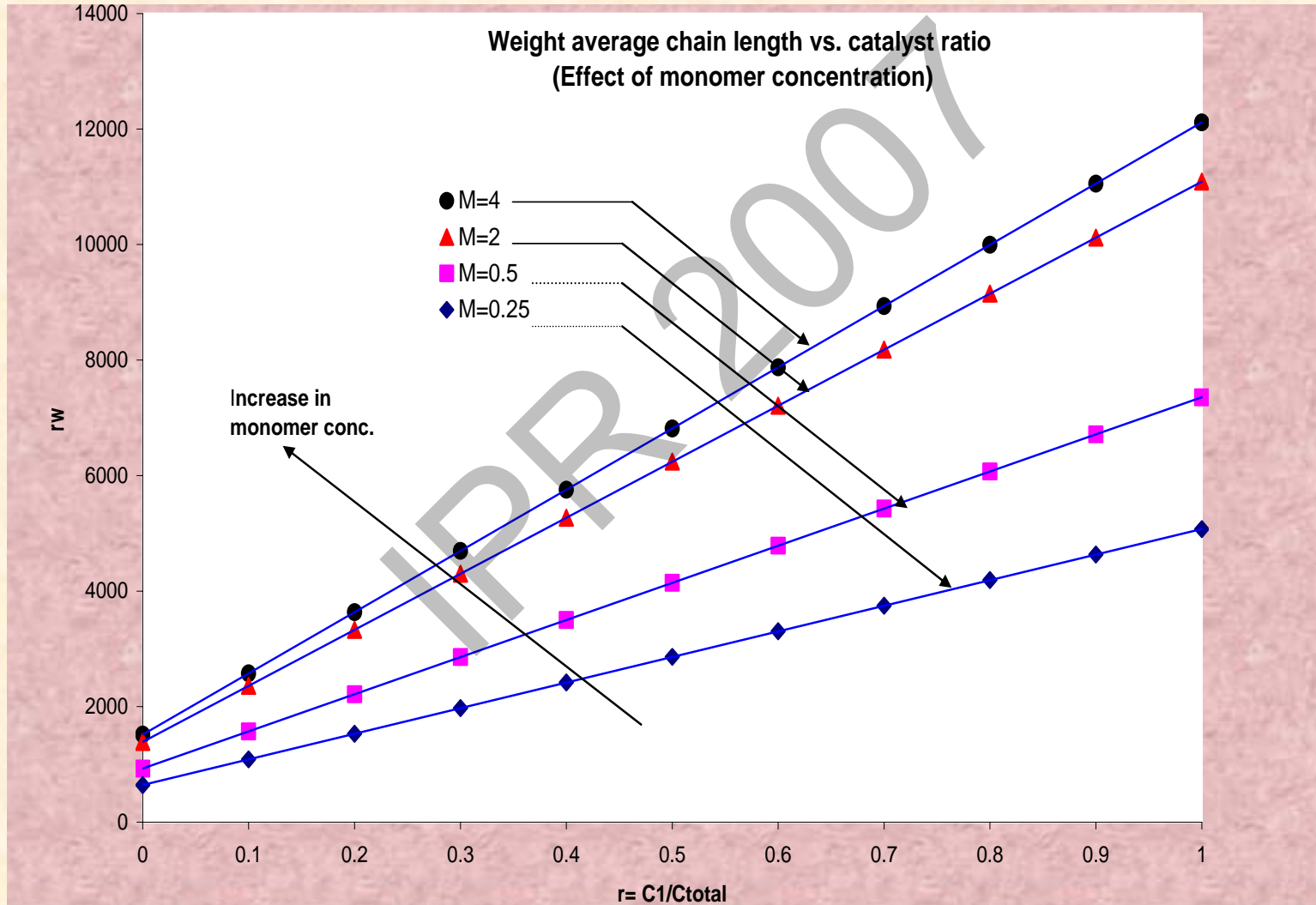


Polydispersity index vs. catalyst ratio at different monomer concentrations

Case study 3: Effect of monomer concentration on LCBD



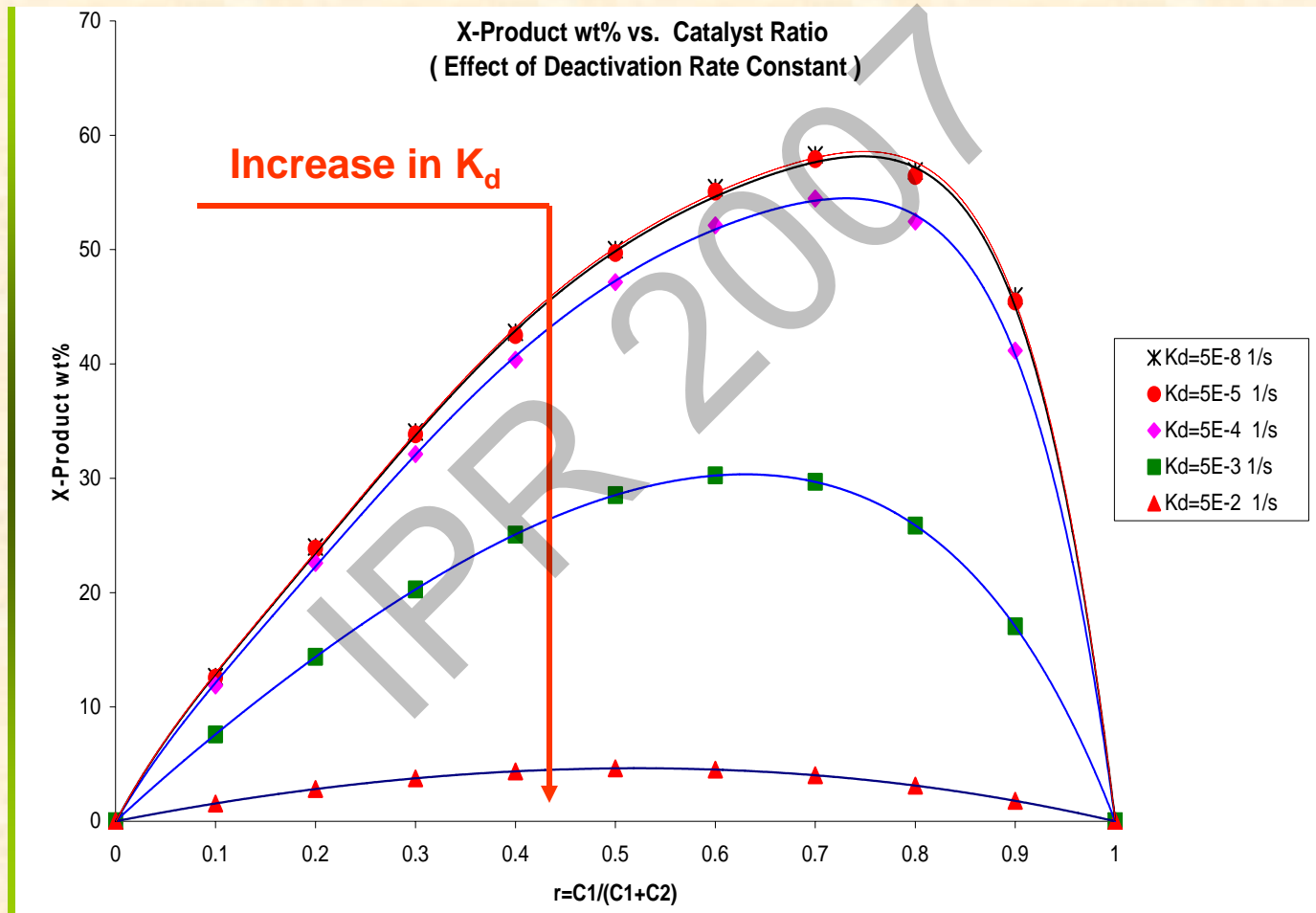
Case study 3: Effect of monomer concentration on weight average molecular weight



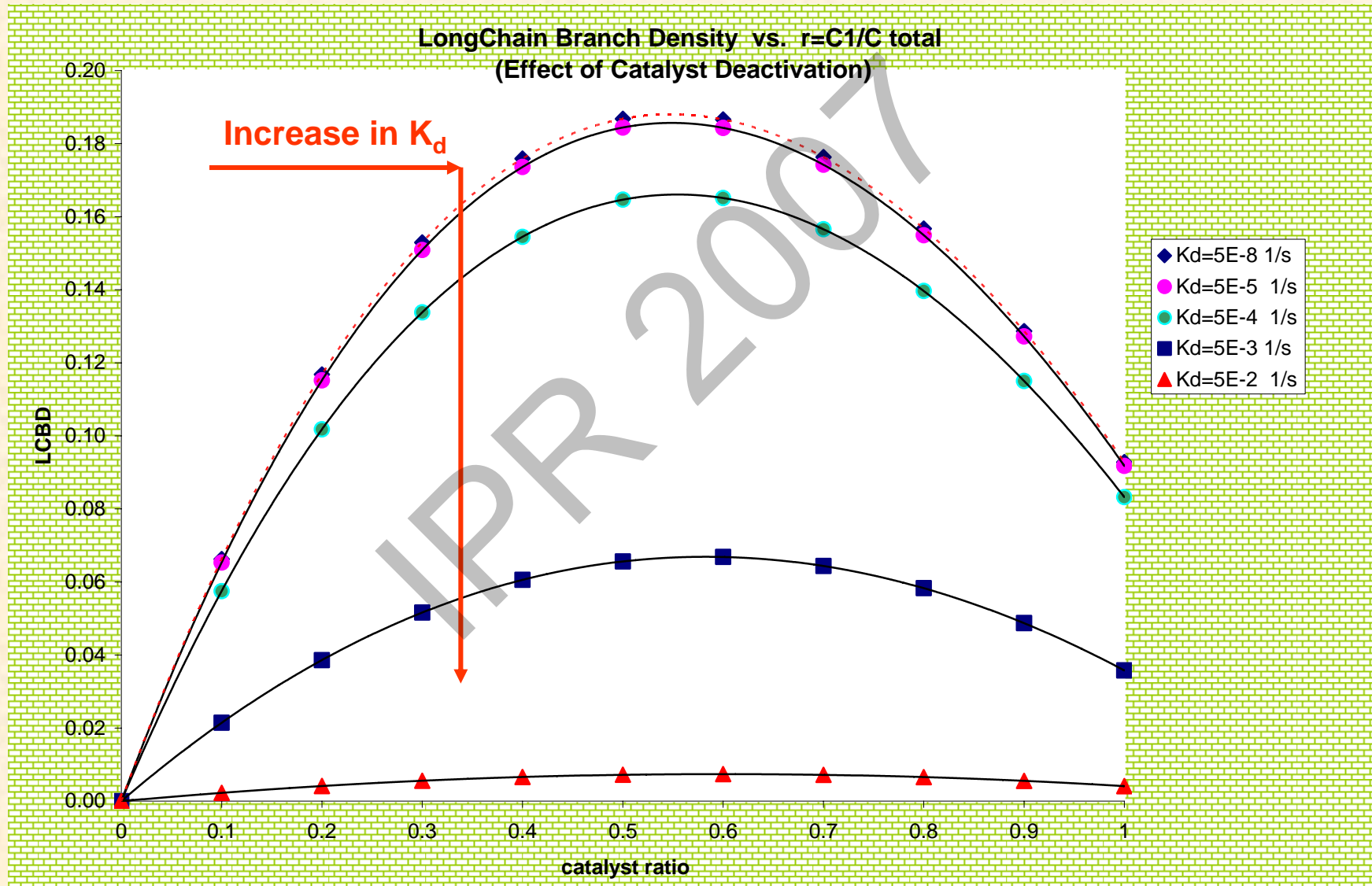
Result: Effect of monomer concentration

- **Increase in monomer Concentration Has no effect on PDI**
- **Cross-product wt % is independent on monomer concentration**
- **LCBD decreases with increasing monomer concentration**
- **Increase in monomer concentration increase both number and weight average chain lengths**

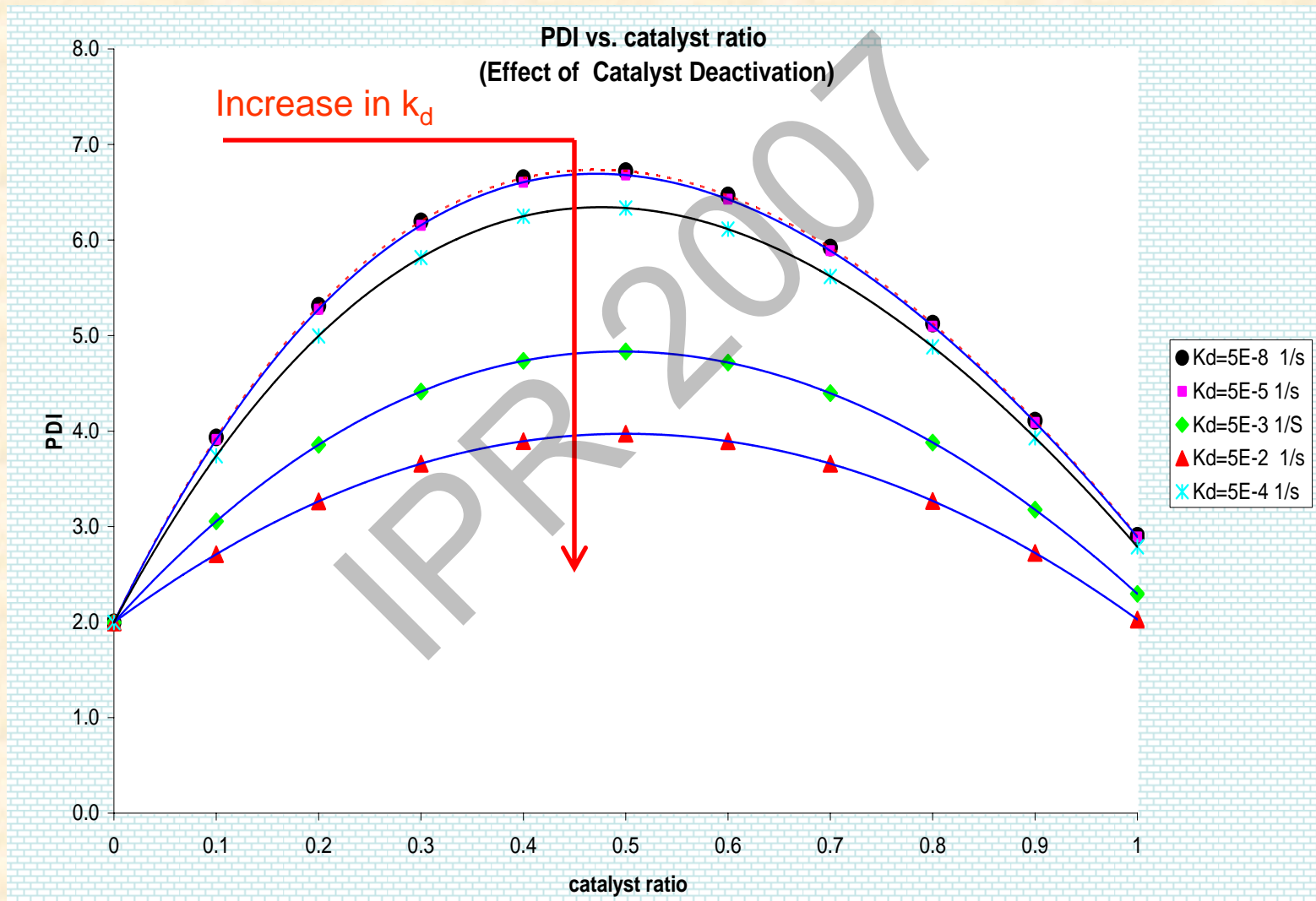
Case study 4: Effect of catalyst deactivation on cross-product wt%



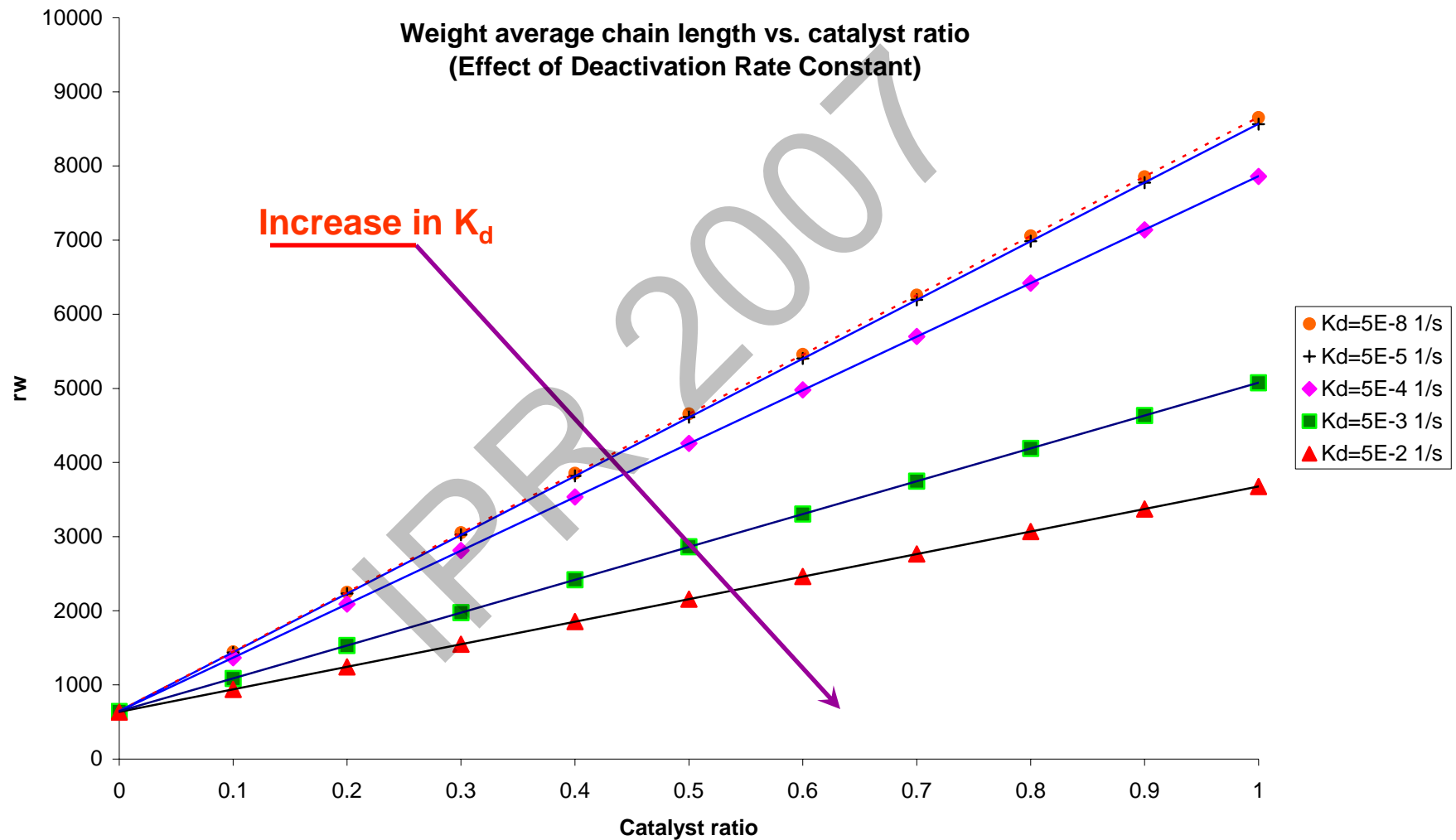
Case study 4: Effect of catalyst deactivation on LCBD



Case study 4: Effect of catalyst deactivation on PDI



Case study 4: Effect of catalyst deactivation on weight average chain length



Case study 4

Results:

Increase in catalyst deactivation

1- Decrease in cross-product wt %

2- Decrease in LCBD

3- Decrease in PDI

Thank you

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