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

Thermoplastic Elastomers (TPEs)

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

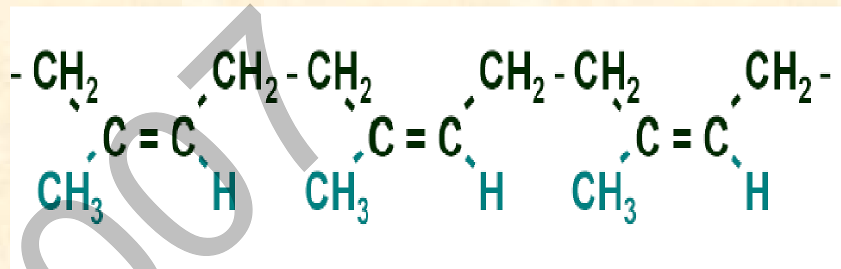
The idea behind TPEs is the notion of reversible crosslink

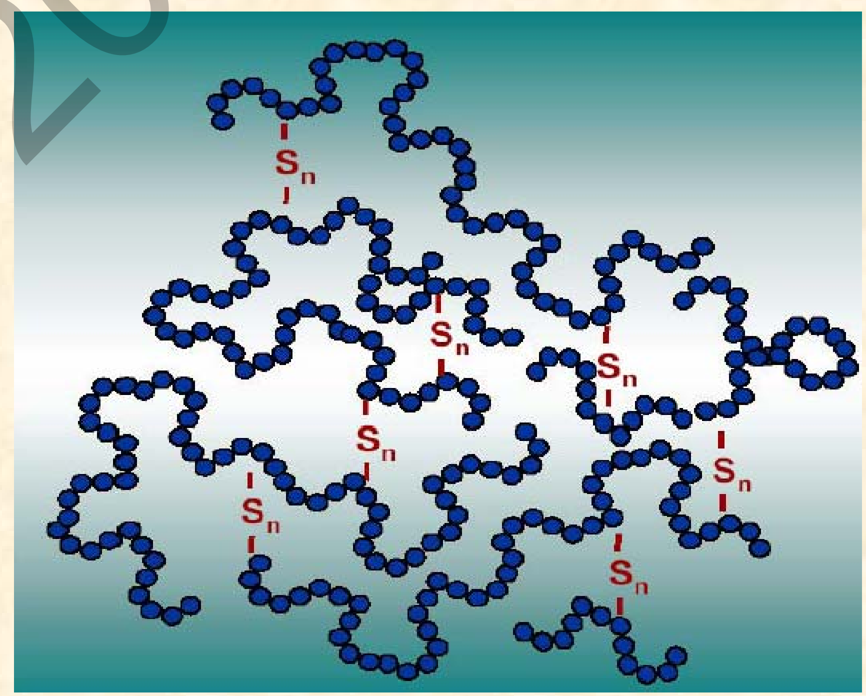
There are two types of crosslinks

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

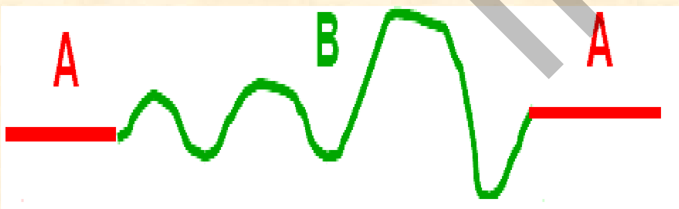
B: long, flexible polybutadiene

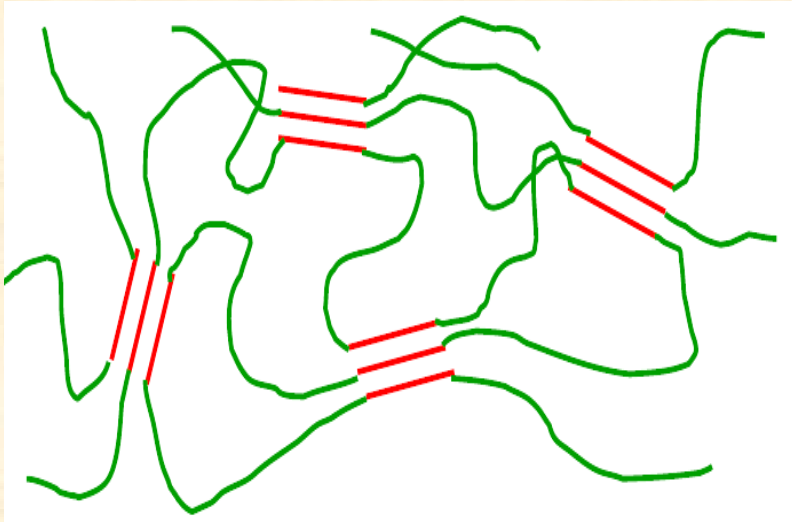
Other possibilities include

Multiblock A-B-A-B-A-……..

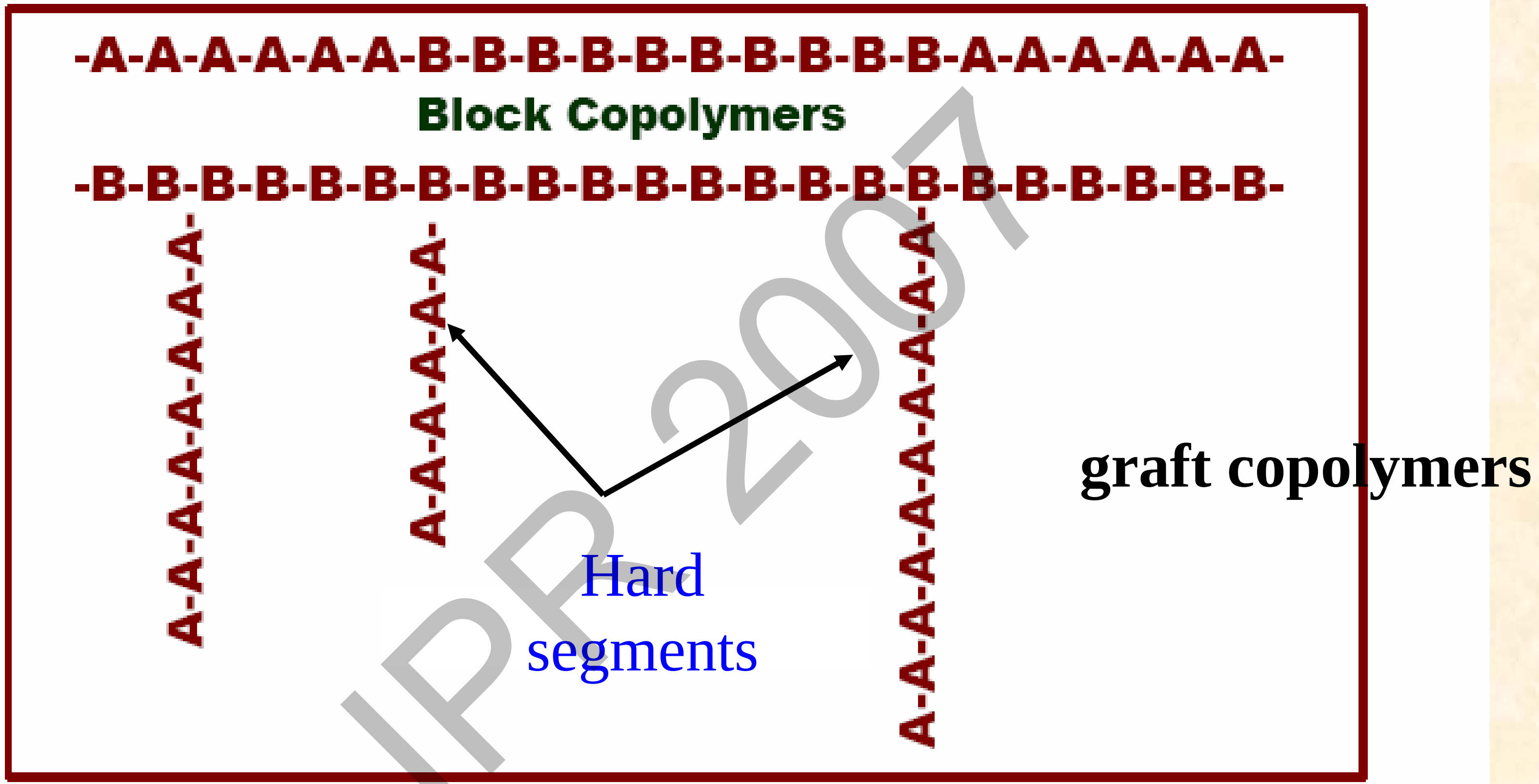
Graft copolymer

Immiscible (incompatible) microdomains within polymer matrix





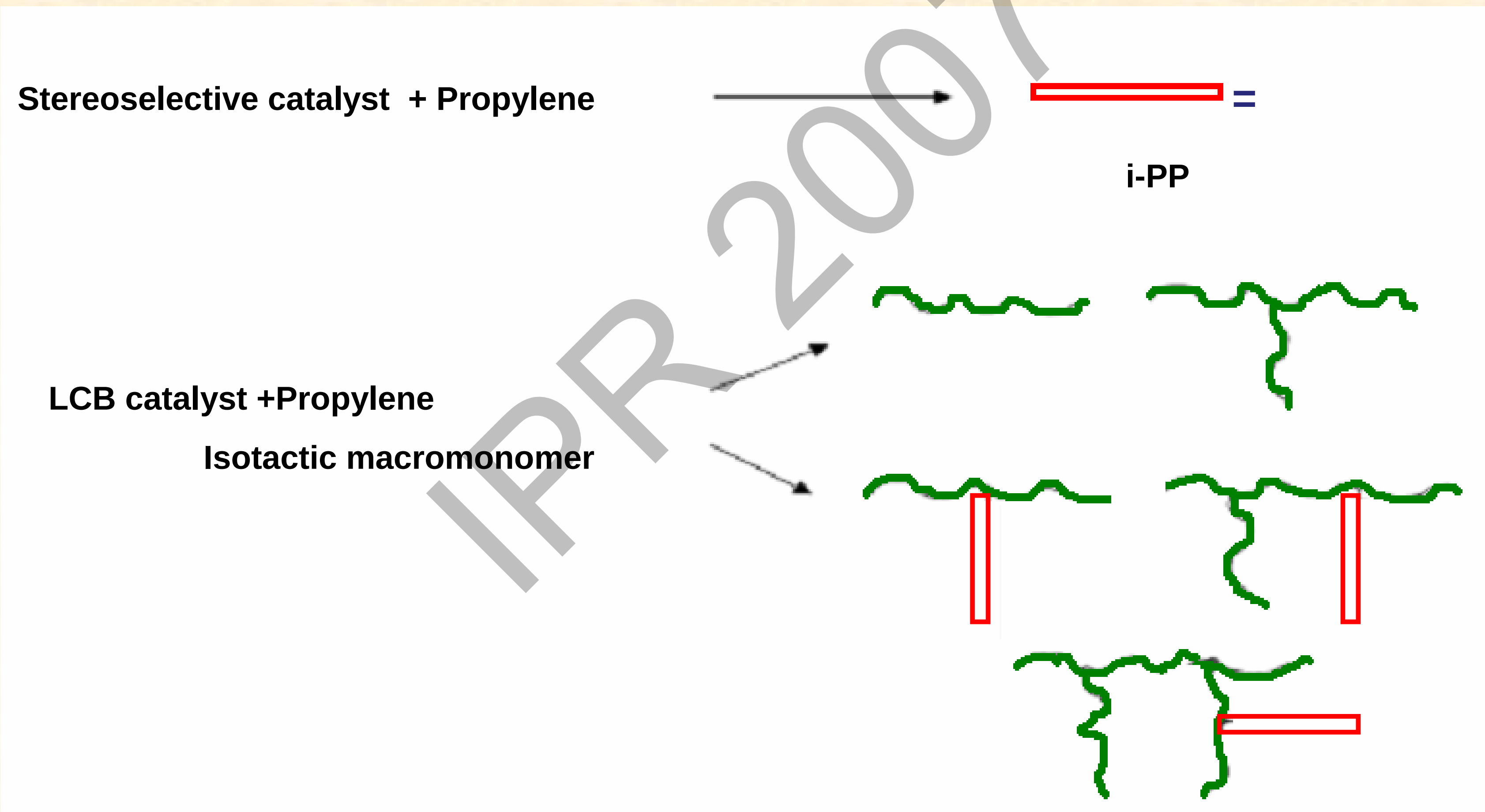
Copolymers



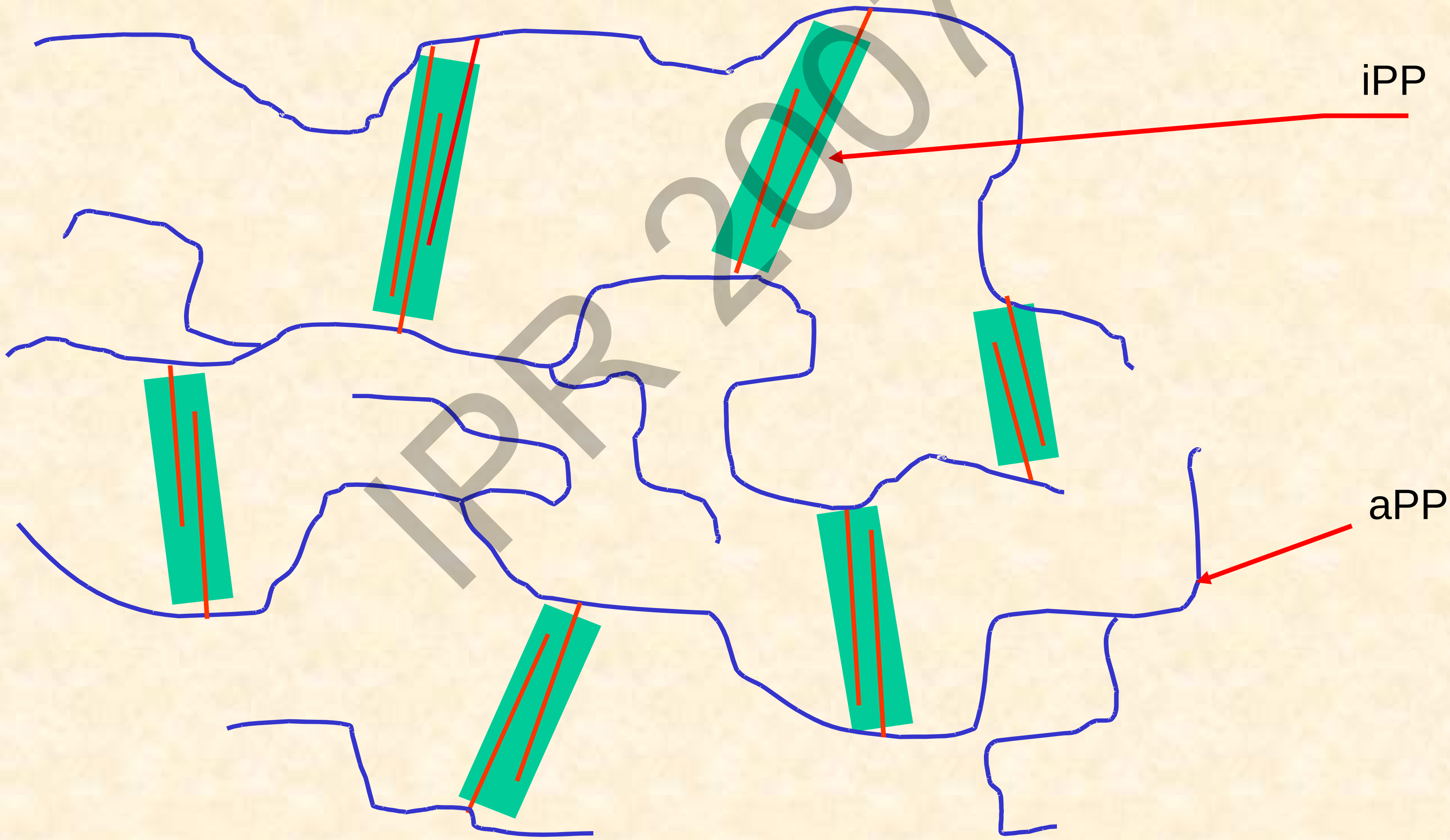
-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-A-A-A-A-A-A-
Block Copolymers
-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-
A-A-A-A-A-A-A-A-A-
A-A-A-A-A-A-
A-A-A-A-A-A-A-A-A-A-A-
Hard segments
graft copolymers

Graft copolymer (Branch-block)

iPP-g-aPP



Graft Block Copolymers
Amorphous Backbones + Crystalline LCBs

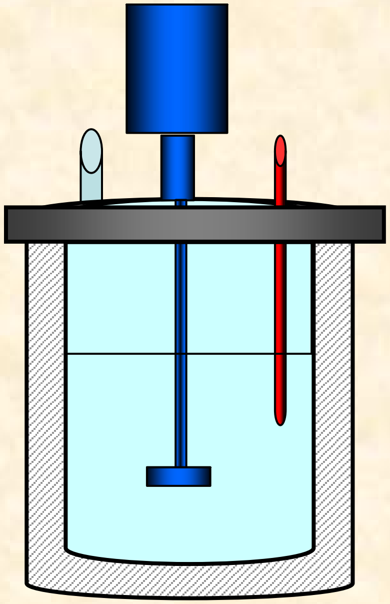


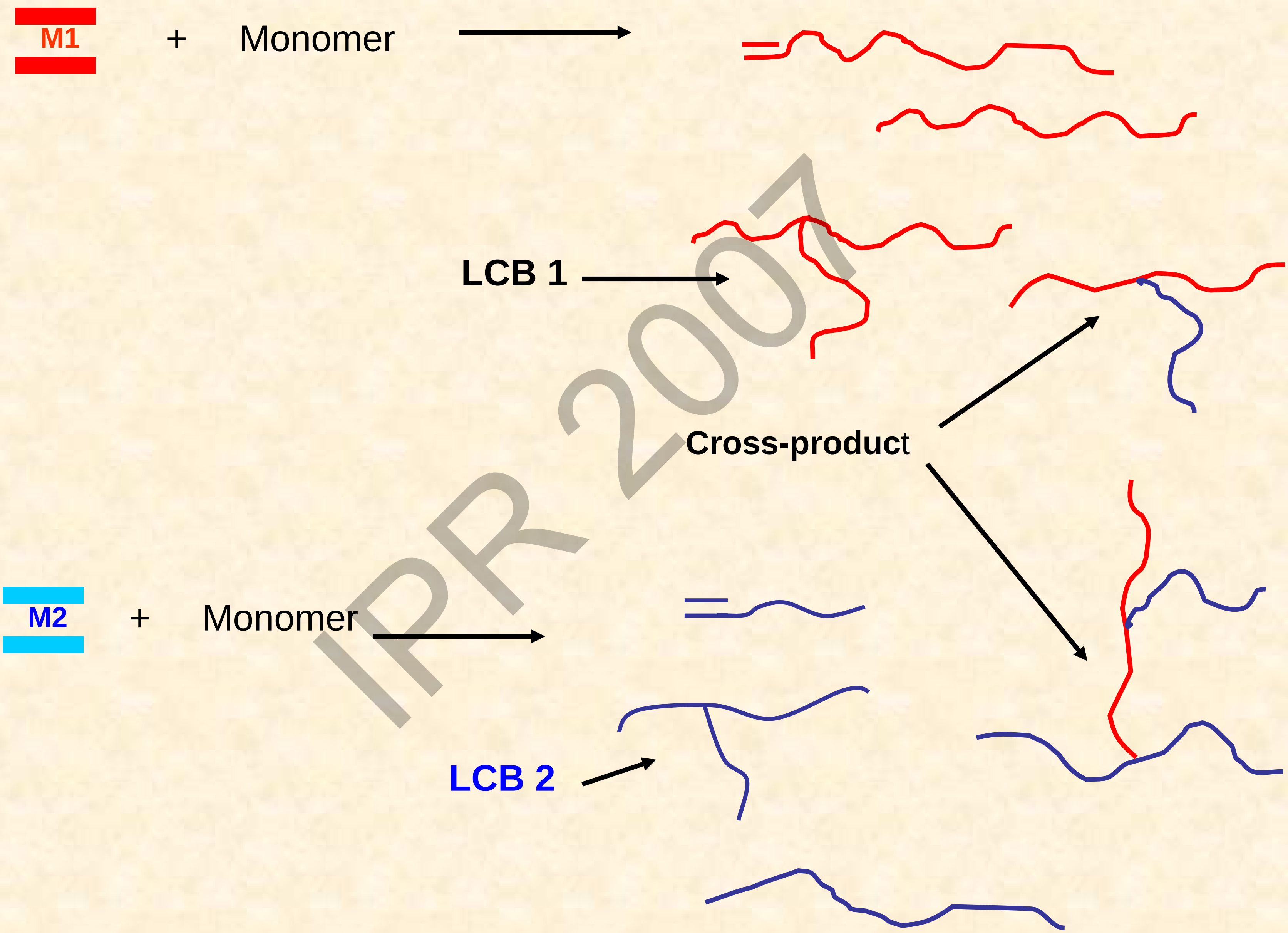
Simulation in a Semi batch Reactor

- 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

$$C_i + M \xrightarrow{k_{p,i}} P_{i,1}$$

Propagation

$$\left\{\begin{array}{l} P_{i,r} + M \xrightarrow{k_{p,i}} P_{i,r+1} \\ \bar{P}_{i,r} + M \xrightarrow{k_{p,i}} \bar{P}_{i,r+1} \\ \bar{\bar{P}}_{i,r} + M \xrightarrow{k_{p,i}} \bar{\bar{P}}_{i,r+1} \end{array}\right\}$$

Deactivations

$$\left\{\begin{array}{ll} P_{i,r} \xrightarrow{k_{d,i}} D_{i,r} + \hat{C}_i & \bar{P}_{i,r} \xrightarrow{k_{d,i}} \bar{D}_{i,r} + \hat{C}_i \\ \bar{\bar{P}}_{i,r} \xrightarrow{k_{d,i}} \bar{\bar{D}}_r + \hat{C}_i & C_i \xrightarrow{k_{d,i}} \hat{C}_i \end{array}\right\}$$

Chain transfer reactions

$$\left\{ P_{i,r} \begin{array}{l} \xrightarrow{k_{\beta,i}} \mu_{i,r} + C_i \\ + M \xrightarrow{k_{M,i}} \mu_{i,r} + P_{i,1} \\ + Al \xrightarrow{k_{Al,i}} D_{i,r} + C_i \\ + H_2 \xrightarrow{k_{H,i}} D_{i,r} + C_i \end{array} \quad \bar{P}_{i,r} \begin{array}{l} \xrightarrow{k_{\beta,i}} \bar{\mu}_{i,r} + C_i \\ + M \xrightarrow{k_{M,i}} \bar{\mu}_{i,r} + P_{i,1} \\ + Al \xrightarrow{k_{Al,i}} \bar{D}_{i,r} + C_i \\ + H_2 \xrightarrow{k_{H,i}} \bar{D}_{i,r} + C_i \end{array} \quad \bar{\bar{P}}_{i,r} \begin{array}{l} \xrightarrow{k_{\beta,i}} \bar{\bar{\mu}}_r + C_i \\ + M \xrightarrow{k_{M,i}} \bar{\bar{\mu}}_r + P_{i,1} \\ + Al \xrightarrow{k_{Al,i}} \bar{\bar{D}}_r + C_i \\ + H_2 \xrightarrow{k_{H,i}} \bar{\bar{D}}_r + C_i \end{array} \right\}$$

Long chain branch formations

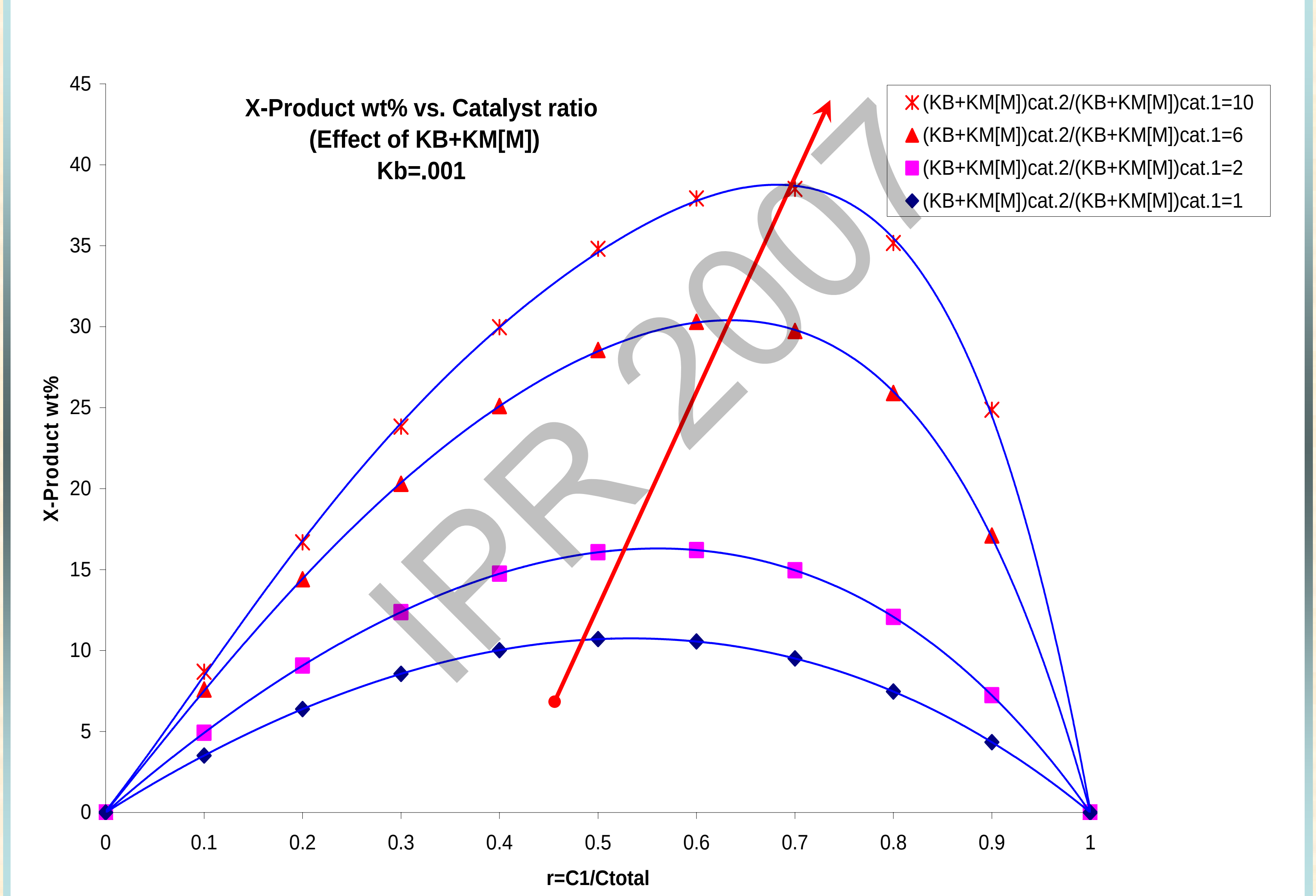
$$\left\{ P_{i,r} + \begin{array}{l} \mu_{i,s} \xrightarrow{k_{b,i}} \bar{P}_{i,r+s} \\ \mu_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\mu}_{i,s} \xrightarrow{k_{b,i}} \bar{P}_{i,r+s} \\ \bar{\mu}_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\bar{\mu}}_s \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \end{array} \quad \bar{P}_{i,r} + \begin{array}{l} \mu_{i,s} \xrightarrow{k_{b,i}} \bar{P}_{i,,r+s} \\ \mu_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\mu}_{i,s} \xrightarrow{k_{b,i}} \bar{P}_{i,r+s} \\ \bar{\mu}_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\bar{\mu}}_s \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \end{array} \quad \bar{\bar{P}}_{i,r} + \begin{array}{l} \mu_{i,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \mu_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\mu}_{i,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\mu}_{j,s} \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \\ \bar{\bar{\mu}}_s \xrightarrow{k_{b,i}} \bar{\bar{P}}_{i,r+s} \end{array} \right\}$$

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	

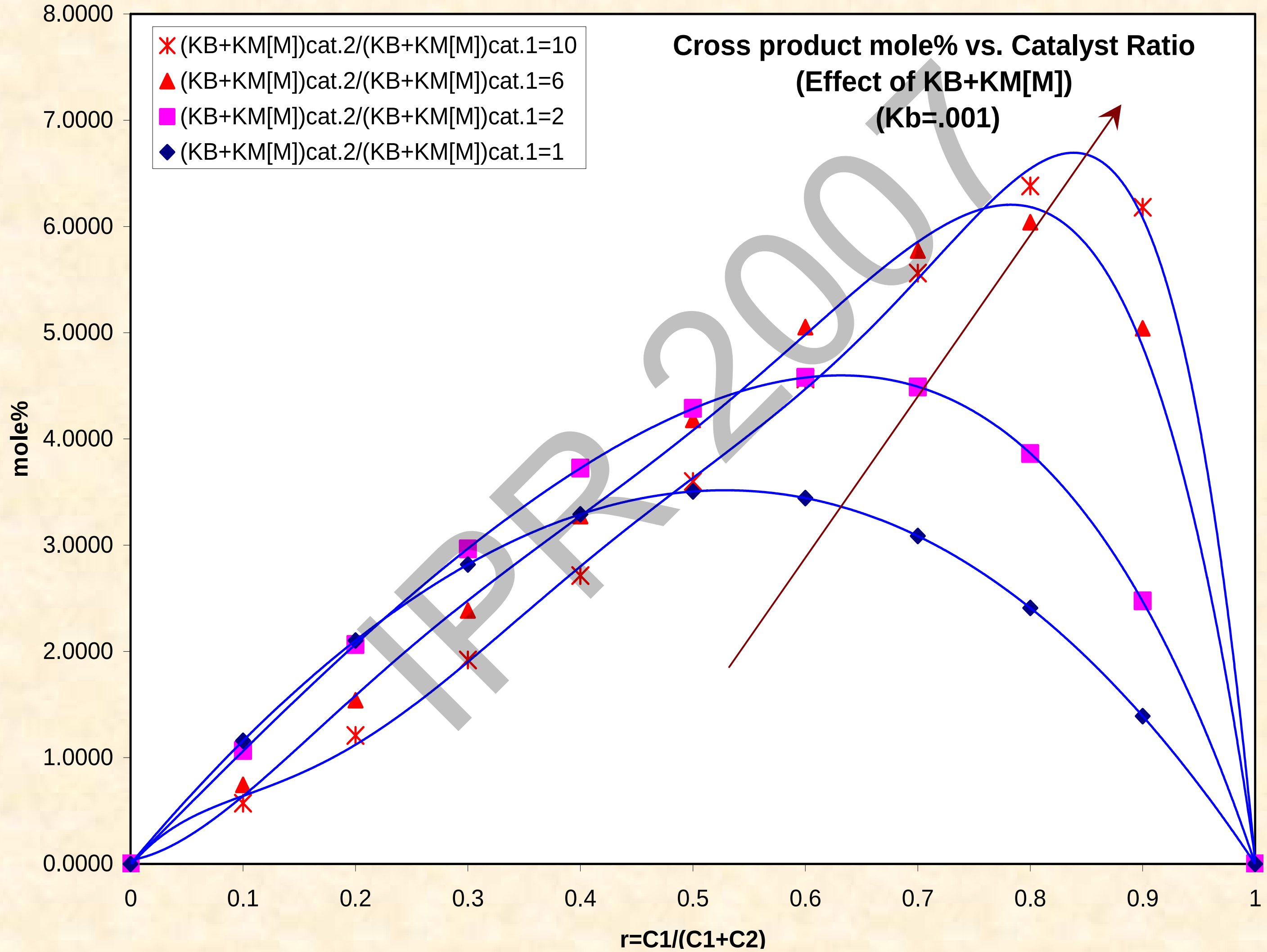
Cross-product weight percent at different values of $k_\beta + K_M[M]$.

Case 1

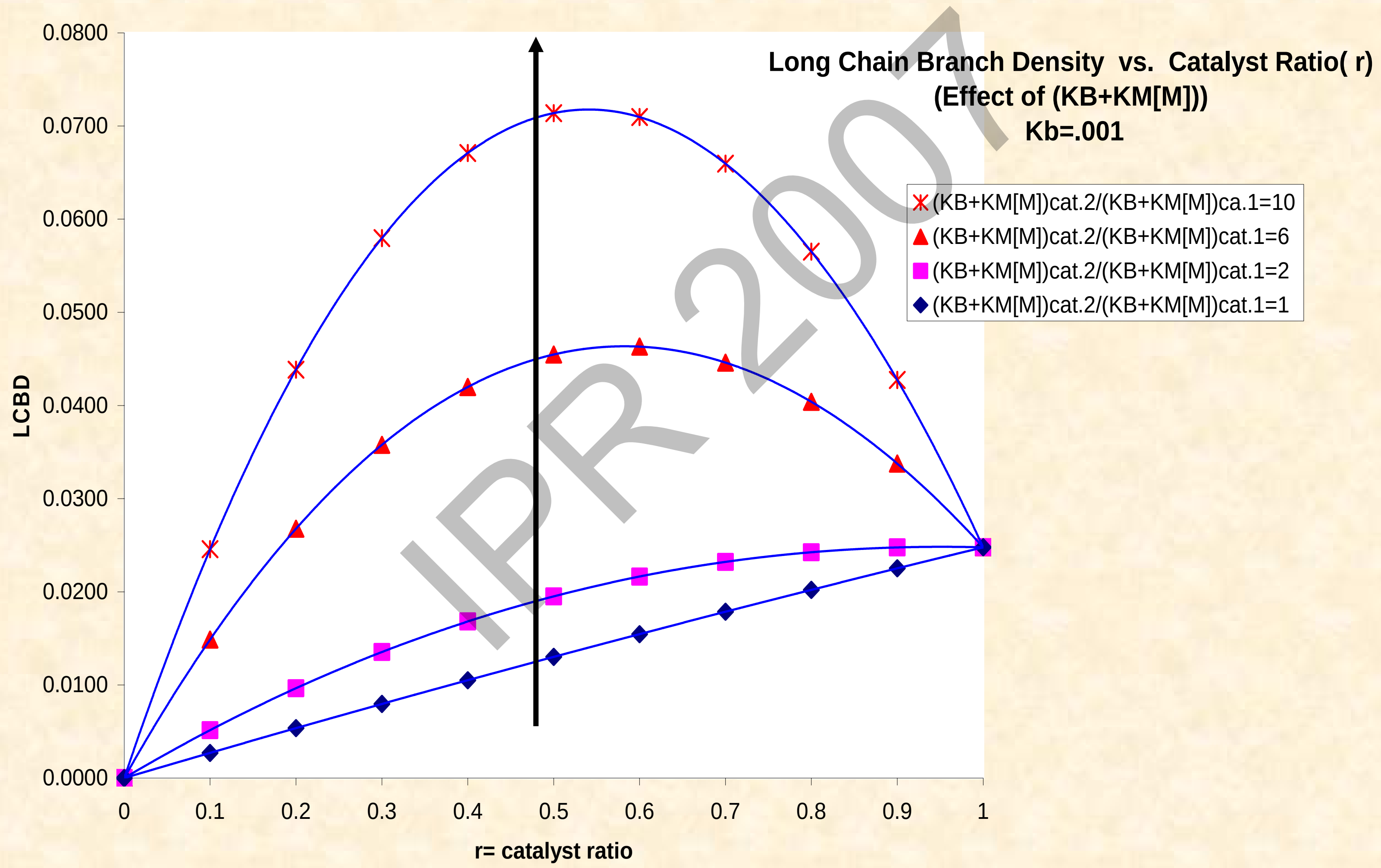


Cross-product mole percent at different values of $k_\beta + K_M[M]$.

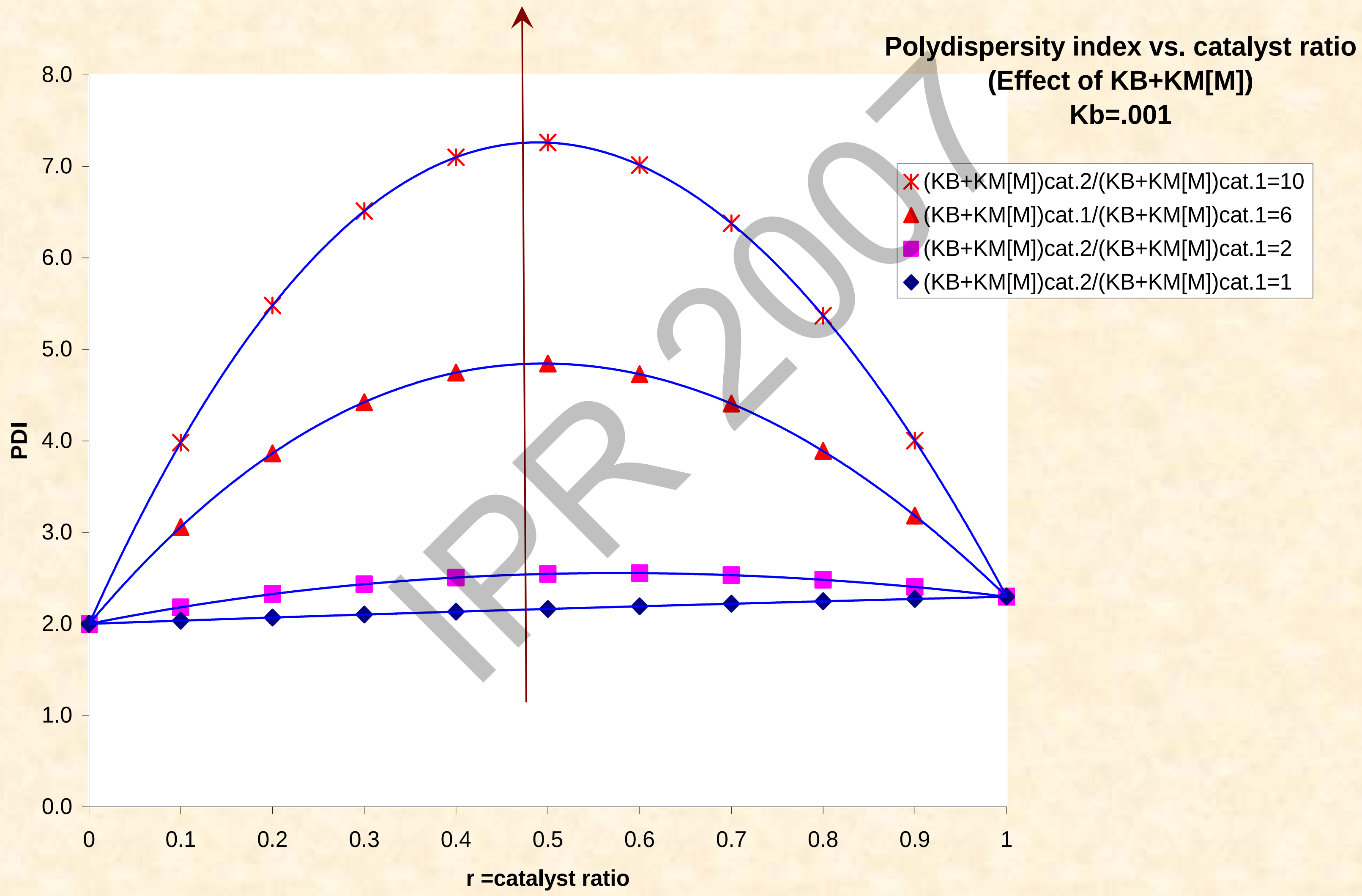
Case 1



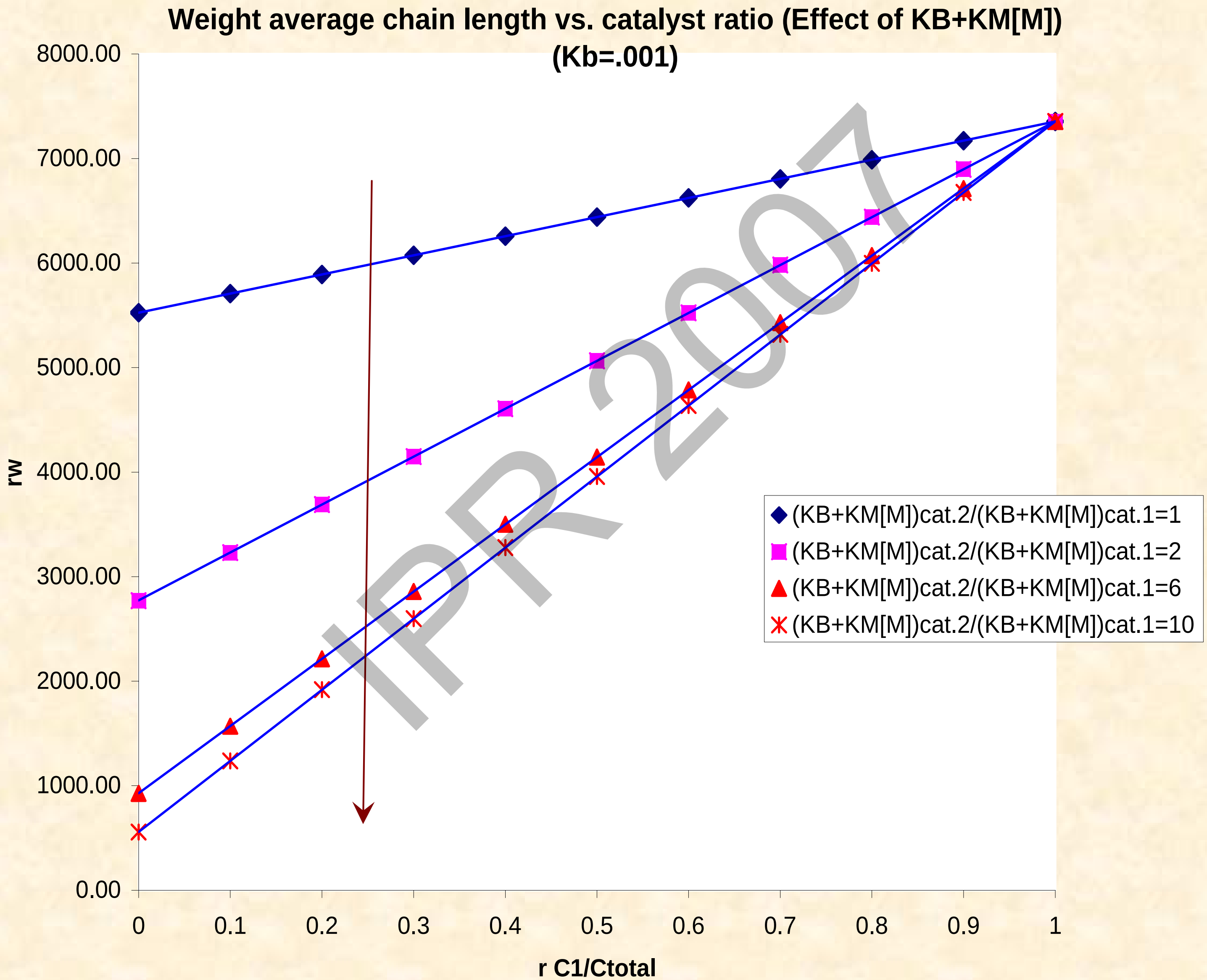
Effect of $k_\beta + K_M[M]$ on long chain branch density(LCBD)



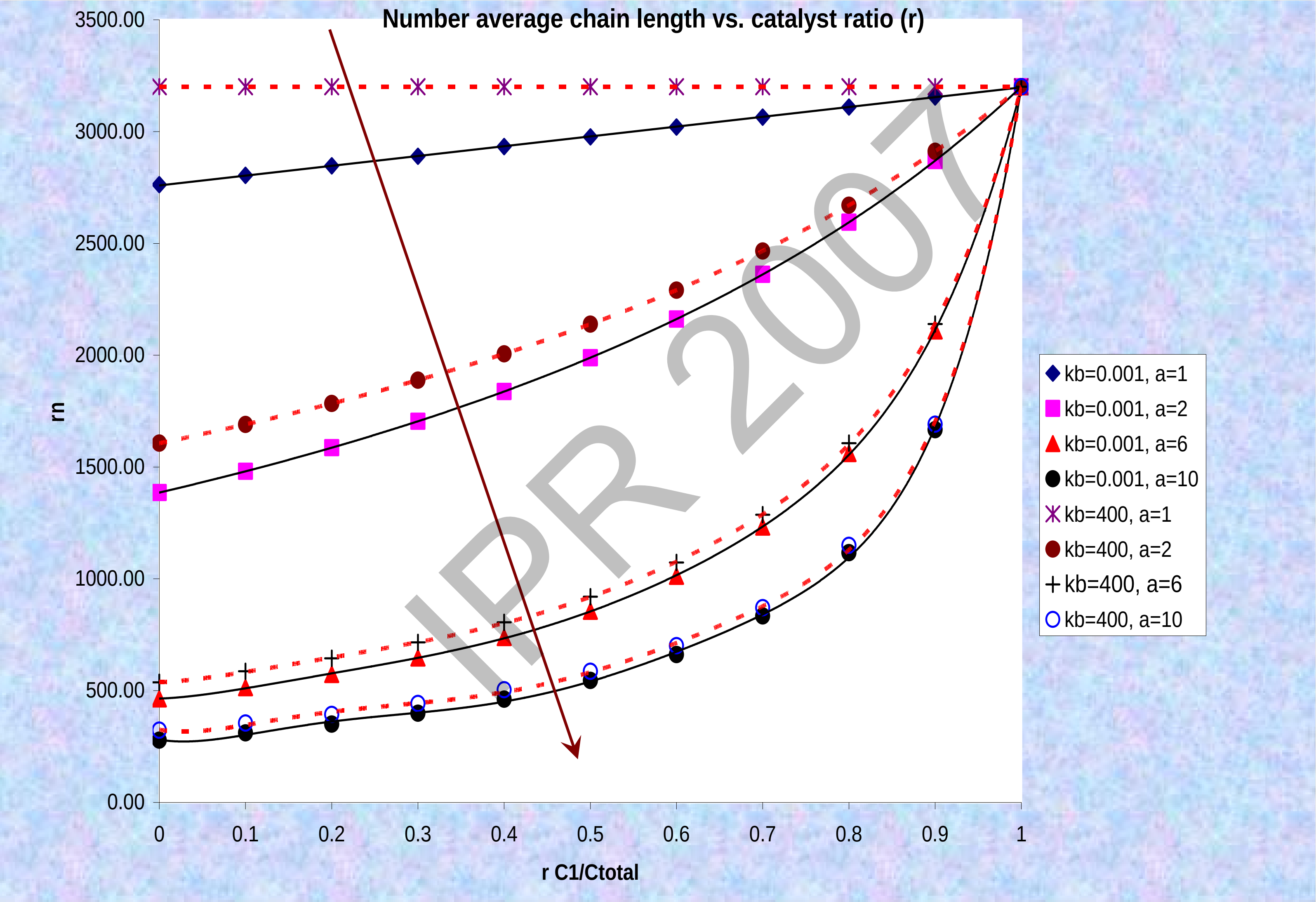
Effect of $k_\beta+K_M[M]$ on Polydispersity index (PDI)



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



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



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