National Chung Hsing University / Polymer Synthesis / Spring 2013
Homework 4

Name______________________

1. A gas-phase Ziegler-Natta polymerization is carried out in a constant-volume, isothermal batch reactor. Assume that surface monomer concentration is always proportional to bulk monomer concentration, $[M_s] = k\ M$. Obtain expressions for conversion as a function of time for two cases:

a. With a constant-activity catalyst.

b. With a catalyst that deactivates according to a second-order mechanism.

(4 point)

a. $r_p = k_p C^* [M_s] = k_p C^* k M = -\frac{1}{m_{cat}} \frac{dM}{dt}$

$\Rightarrow \frac{dM}{M} = -m_{cat} k_p C^* k\, dt$

$\Rightarrow \ln M = -m_{cat} k_p C^* k t + \text{Constant}$

at $t=0$, $M=M_0$

$\Rightarrow \ln M_0 = 0 + \text{constant} \Rightarrow \text{constant} = \ln M_0$

$\Rightarrow \ln \frac{M}{M_0} = -m_{cat} k_p C^* k t \Rightarrow \frac{M}{M_0} = \exp(-m_{cat} k_p C^* k t)$

$X = \frac{M_0 - M}{M_0} = 1 - \frac{M}{M_0} = 1 - \exp(-m_{cat} \cdot k_p C^* k t)$

b. $\frac{dC^*}{dt} = -k^* C^{*2}$ at $t=0$, $C^* = C_0^*$ $\Rightarrow C^* = \frac{C_0^*}{C_0^* k^* t + 1}$ (derived in class)

$\Rightarrow r_p = -\frac{1}{m_{cat}} \frac{dM}{dt} = k_p C^* [M_s] = k_p C^* k M = \frac{k_p C^* k M}{C_0^* k^* t + 1}$

$\Rightarrow \frac{dM}{M} = -m_{cat} \frac{k_p C^* k}{C_0^* k^* t + 1} dt$

$\Rightarrow \ln M = -\frac{m_{cat} k_p C^* k}{C_0^* k^*} \ln(C_0^* k^* t + 1) + \text{constant}$ at $t=0$. $M = M_0 \Rightarrow \text{constant} = \ln M_0$

$\Rightarrow \frac{M}{M_0} = \exp\left[\frac{-m_{cat} k_p C^* k}{C_0^* k^*} \ln(C_0^* k^* t + 1)\right]$