Supporting Information

Titanium and Zirconium Complexes for Polymerization of Propylene and Cyclic Esters

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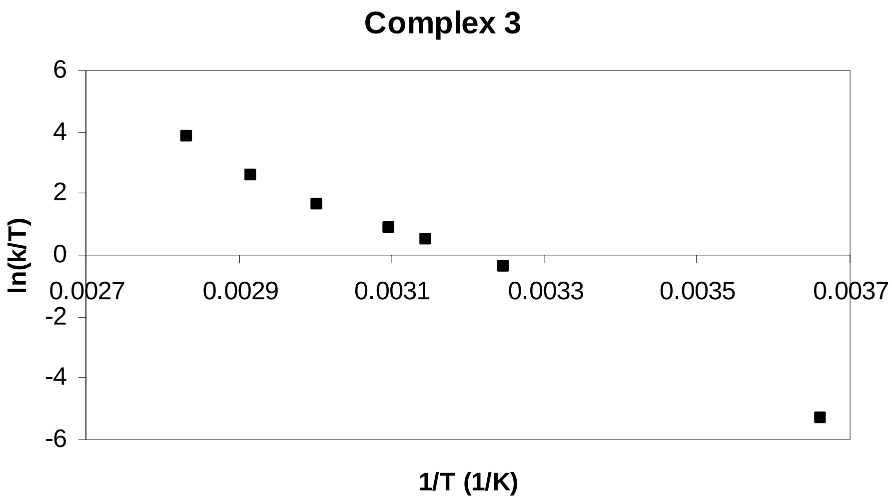
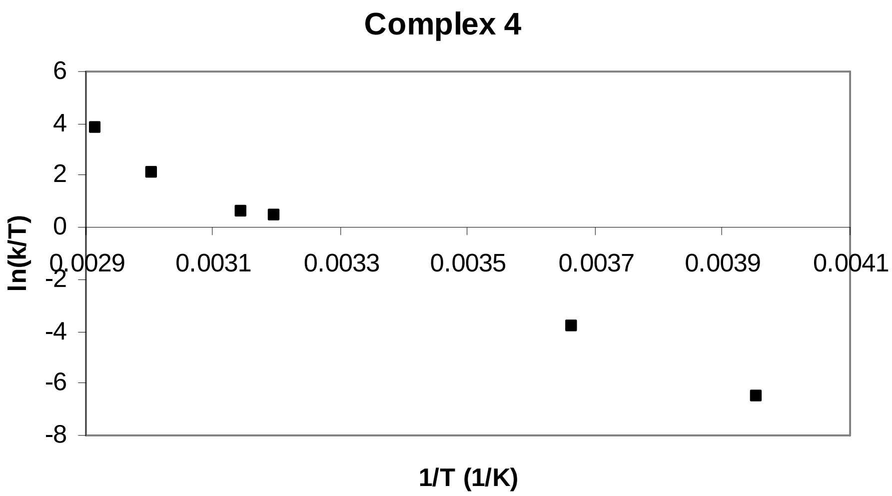
Eyring plots





Eyring equation: $k = (k_B T/h) \cdot e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S^{\ddagger}/R}$

k values were calculated using line shape analysis

Derivation of Equation 5 – Calculative method for finding the number of the moles of living species in a mixture of living and non-living species:

<u>Definitions:</u>

M_n - number-average molecular weight

m_{pp} - polymer's mass

n_{pp} - moles of polymer chains

R_i - rate of monomer insertion

R_t - rate of termination

t - polymerization time

n_{cat} - moles of catalyst

D.P - degree of polymerization

1. $M_n = m_{pp}/n_{pp}$
2. $R_i = n_{propylene}/t$
3. $R_t = n_{pp}/t$

<u>Living polymerization - time dependencies:</u>

R_i = constant	$m_{pp} \propto t$
$R_t = 0$	$M_n \propto t$
$n_{pp} = n_{cat}$	$D.P \propto t$

Non-living polymerization - time dependencies:

R_i = constant $m_{pp} \propto t$

R_t = constant $\neq 0$ M_n = constant

$n_{pp} = m_{pp}/M_n \propto t$ D.P = constant

In a mixture containing both living (l) and non-living (n) species the following relationships can be written:

4. $n_{pp}(mix) = n_l + n_n$
5. $m_{pp}(mix) = MW_{monomer}t(R_{il} + R_{in}) = MW_{monomer}tR_{itot}$
6. $M_n(mix) = m_{pp}(mix)/n_{pp}(mix)$

Substitution of Eq. 6 with Eq. 4 and Eq. 5 yields:

7. $M_n(mix) = MW_{monomer}tR_{itot}/(n_l + n_n)$

Expressing n_n in terms of M_{nn} and R_{in} (Eq. 1 and Eq. 2, respectively) gives:

8. $M_n(mix) = MW_{monomer}tR_{itot}/(n_l + (MW_{monomer}tR_{in})/M_{nn})$

If $t \rightarrow \infty$ then n_l is negligible and Eq. 8 can be written as:

9. $R_{in}/M_{nn} = R_{itot}/M_{n(t\rightarrow\infty)}$

Substitution of the R_{in}/M_{nn} ratio in Eq. 8 with that found in Eq. 9 gives the expression from which n_l (moles of living species) can be isolated:

10. $\mathbf{M_n = MW_{monomer}tR_i/(n_l + (MW_{monomer}tR_i)/M_{n(t\rightarrow\infty)})}$