Increasing The Initiation Efficiency of Ruthenium Based Ring-Opening Metathesis (ROMP) Initiators: The Effect of Excess Phosphine

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Supplementary Material

Determination of Initiation and Propagation Rates

In a nitrogen filled drybox, monomer 4a (150 μmol, 25 equiv), an appropriate amount (6 μmol or 30 μmol) of desired phosphine (PC₅, PC₅Ph, or PPh₃), and ferrocene (3 mg, internal standard) were weighed into a NMR tube and dissolved in CD₂Cl₂ (0.5 mL). The resulting mixture was then treated with a CD₂Cl₂ solution of Ru initiator 1 (0.2 mL, 6 μmol, 1 equiv) and a ¹H NMR routine immediately commenced. The initiation rate constants (k_i) were determined by integrating the Ru=CH resonances of the initiating and propagating species. The propagating rate constants (k_p) were determining by monitoring the conversion of monomer to polymer vs. the internal standard. Representative plots are shown below. Additional results are given in Table 1.
General Procedure for Preparative Scale Polymerizations

All polymerizations were set-up in a nitrogen filled drybox. An appropriate amount of monomer (25-250 equiv) and phosphine (1-5 equiv) were added to a small vial and dissolved in ca. 2 mL of CH₂Cl₂. A CH₂Cl₂ solution of the initiator (0.1 mL, ca. 7 mg, 1 equiv) was then added directly to the rapidly stirring monomer solution. After an adequate amount of time (5 – 24 h), excess ethyl vinyl ether was added to quench the polymerization. After stirring for an additional 1 h, the reaction mixture was added dropwise to an excess of rapidly stirring methanol (30 mL) which caused a white powder to precipitate. The powder was collected by filtration and dried under dynamic high vacuum.
Representative plot of monomer concentration vs time.
(Data is from Table 1, Entry 9)

\[ Y = M_0 + M_1 \times X \]

\begin{tabular}{|c|c|}
\hline
M0 & -0.014401 \\
M1 & 0.0020161 \\
\hline
\end{tabular}

\[ R^2 = 0.998 \]
Representative plot of initiator concentration vs time.
(Data is from Table 1, Entry 9)

\[ Y = M0 + M1 \times X \]

<table>
<thead>
<tr>
<th></th>
<th>M0</th>
<th>M1</th>
<th>R²</th>
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<tbody>
<tr>
<td>M0</td>
<td>0.66698</td>
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<td></td>
</tr>
<tr>
<td>M1</td>
<td>0.020542</td>
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<tr>
<td>R²</td>
<td>0.991</td>
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