

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

Christopher W. Bielawski and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories for Chemical Synthesis, Division of Chemistry
and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

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 (PCy_3 , PCy_2Ph , or PPh_3), and ferrocene (3 mg, internal standard) were weighed into a NMR tube and dissolved in CD_2Cl_2 (0.5 mL). The resulting mixture was then treated with a CD_2Cl_2 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 $\text{Ru}=\text{CH}$ resonances of the initiating and propagating species. The propagating rate constants (k_p) were determined 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 CH_2Cl_2 . A CH_2Cl_2 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.

3

Representative plot of monomer concentration vs time.
(Data is from Table 1, Entry 9)



