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Increasing the Initiation Efficiency of Ruthenium-Based Ring-Opening Metathesis Initiators: Effect of Excess Phosphine

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Ring-opening metathesis polymerization (ROMP) has evolved into a valuable tool for the polymer chemist. The polymerization is generally mild and well controlled, and a large pool of readily available cyclic olefins (monomers) can be polymerized to nearly any size or shape.[1] Employing the Ru-based initiator[2] **1** (or its more active derivative[3] **2**) permits incorporation of high degrees of functionality and affords polymers with novel mechanical, electronic, and more recently biological properties.[4] However, the polydispersity indices (PDIs) of the polymers obtained from initiator **1** are generally broad (between 1.3 and 1.5), which arises from an unfavorable rate of initiation (k_i) relative to propagation (k_p) as well as considerable secondary metathesis ("back-biting"). This creates difficulties when attempting to accurately predict polymer molecular weight a priori or when preparing well-defined block copolymers (where complete initiation is necessary). A recent disclosure from Gibson and co-workers revealed that the initiation efficiency of **1** was enhanced when the PCy_3 ligands were substituted with $Cy_2PCH_2Si(CH_3)_3$.[5] When the resulting complex (**3**) was used to initiate the ROMP of norbornene derivatives (similar to **4**), the k_i/k_p was found to be 4.35 (up from 0.06 when initiated with **1**), and the resulting polymers were nearly monodispersed (PDIs ~ 1.1). The enhanced initiation was attributed to a combination of the lower basicity and smaller size of $Cy_2PCH_2Si(CH_3)_3$ (relative to PCy_3) which respectively helped facilitate phosphine dissociation (a key step in Ru-based ROMP, see below)[6] and increase monomer accessibility.

Herein, we claim that similar results can be obtained without synthesizing new complexes or phosphines. Recent studies in our group have determined that the rate of phosphine exchange is much faster (~10^4) than the rate of reaction with olefin in $X_2(PR_3)_2Ru{=}CHR'$ type catalysts.[6] We have also previously noted that complexes with more labile phosphines (e.g., PPh_3) exhibit high rates of initiation.[2] These concepts were combined to enhance the initiation efficiency of complex **1** by simply including additional phosphine (specifically phosphines more labile than PCy_3) during the polymerization. Since phosphine exchange is relatively fast, formation of a Ru complex with a relatively labile phosphine precedes initiation (eq 1) and thus exhibits better initiation characteristics (higher k_i). In addition, as shown in Scheme 1, the added phosphine effectively competes with monomer for the Ru center and thus helps attenuate the polymerization rate (lower k_p). This concept is similar to controlled free radical polymerizations where various transition metals (e.g., Cu or Ru) or nitroxides (e.g., TEMPO) are added to minimize the concentration of propagating radicals.[7]

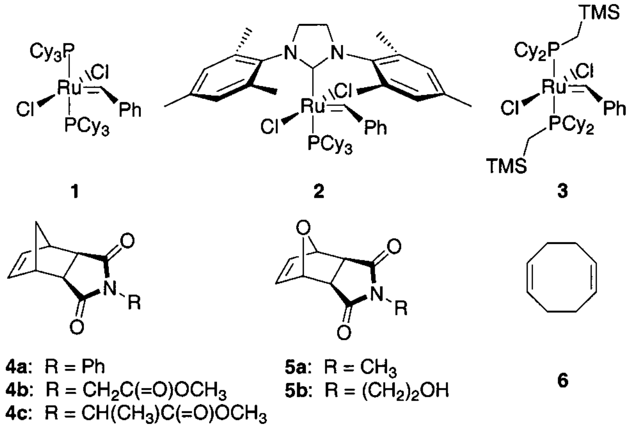
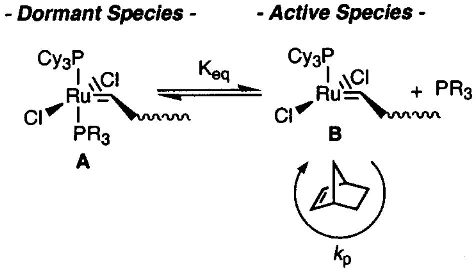
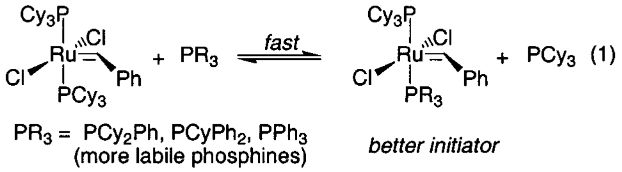


Figure 1. Various ruthenium-based ROMP initiators and monomers.

Scheme 1





The rates of initiation (k_i) and propagation (k_p) were measured in CD_2Cl_2 at 20 °C using ^1H NMR spectroscopy.[8] The polymerizations were initiated with Ru complex **1** and the *exo*-norbornene phenylimide **4a** was chosen as the monomer. To ascertain the inherent initiation efficiency of Ru complex **1** under these conditions, k_i and k_p were initially measured in the absence of any additional phosphine. The k_i/k_p ratio was found to be 0.73, which is significantly higher than the value (0.06) reported by Gibson for the related monomer **4b**.[5] Although **4b** contains a polar ester functional group that may coordinate (inter- or intramolecularly) to the Ru center, such effects were negligible as a similar k_i/k_p ratio (0.96) was found for this monomer. Thus, solvent ($CDCl_3$ vs CD_2Cl_2) appears to be the source of the discrepant k_i/k_p ratios since both studies were performed under otherwise similar conditions (M_0/I_0, temperature, etc.).[9]

As shown in Table 1, inclusion of free phosphines with varying steric and electronic properties (PCy_3, PCy_2Ph, $PCyPh_2$, and PPh_3) during the ROMP had remarkable effects on the k_i/k_p ratio. In general, the k_i/k_p improved

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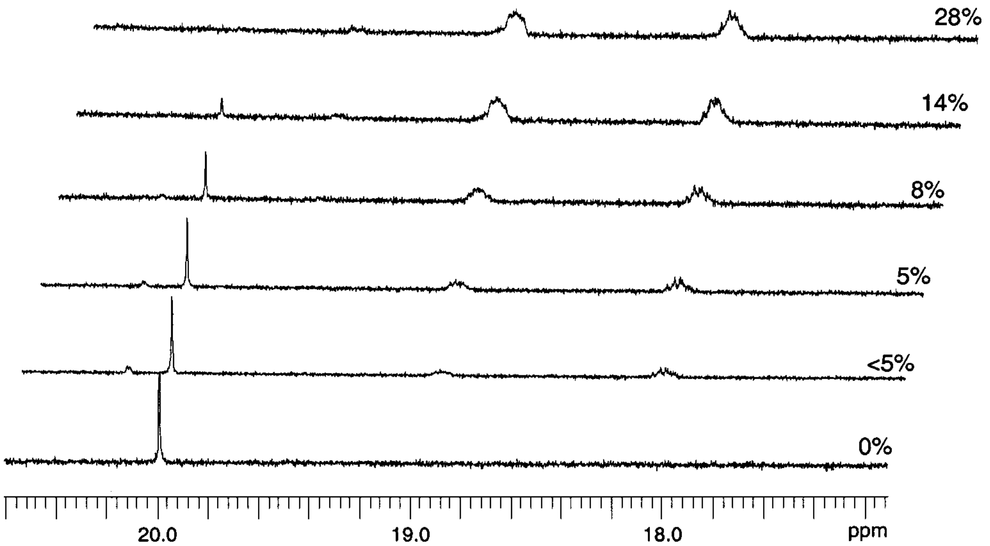

Figure 2. Stacked ^{1}H NMR spectra of the [Ru]=CHR region showing the initiation process of **1** in the presence of PPh_3. See Table 1, entry 9 for conditions. Monomer conversion is indicated on the right.

Table 1. Effect of Added Phosphine on k_i/k_p[a]

entry	PR_3	equiv[b]	k_i[c] ($\times10^{-3}$ min^{-1})	k_p[d] ($\times10^{-3}$ min^{-1})	k_i/k_p
1	(none)		204	278	0.73
2	PCy_3	1	27.6	27.1	1.02
3	PCy_3	5	8.37	8.24	1.02
4	PCy_2Ph	1	47.7	36.9	1.29
5	PCy_2Ph	5	17.3	8.83	1.96
6	$PCyPh_2$	1	22.2	11.0	2.02
7	$PCyPh_2$	5	7.10	1.41	5.04
8	PPh_3	1	44.3	18.2	2.43
9	PPh_3	5	20.5	2.02	10.2

[a] Polymerizations were performed in CD_2Cl_2 at 20 °C and monitored using ^{1}H NMR spectroscopy. $[\mathbf{1}]_0 = 10$ mM. $[\mathbf{4a}]_0/[\mathbf{1}]_0 = 25$. [b] Molar equivalents of added phosphine to initiator. [c] Initiation rate constant. [d] Propagation rate constant.

Table 2. ROMP of Monomers 4–6 in the Presence of Phosphine[a]

monomer	M_0/I_0	PR_3	equiv[b]	yield[c] (%)	$M_{n,calcd}$[d]	$M_{n,GPC}$[e]	PDI[e]
4a	50	(none)		95	12 000	16 000	1.25
4a	50	PCy_3	1	90	12 000	14 900	1.14
4a	50	PCy_2Ph	1	90	12 000	14 600	1.13
4a	50	$PCyPh_2$	1	92	12 000	12 900	1.10
4a	50	PPh_3	5	85	12 000	11 600	1.07
4a	25	PPh_3	1	95	6 000	5 400	1.08
4a	100	PPh_3	1	90	24 000	22 300	1.06
4a	250	PPh_3	1	85	59 800	70 200	1.04
4c	100	PPh_3	2	96	29 500	32 000	1.18
5a	100	PPh_3	2	97	28 000	31 200	1.13
5b	100	PPh_3	2	75	27 300	26 000	1.10
6	100	PPh_3	2	91	10 800	8 000	1.19

[a] Polymerizations were performed in CH_2Cl_2 at 23 °C and were initiated with Ru complex **1**. $[\mathbf{1}]_0 = 10$ mM. [b] Molar equivalents of added phosphine to initiator. [c] Isolated yields after quenching the ROMP with excess ethyl vinyl ether and precipitation from methanol. [d] Calculated from the M_0/I_0. [e] M_n and PDI were determined by GPC and are reported relative to monodispersed polystyrene standards.

as the size and basicity of the phosphine decreased. Additional enhancement was observed by increasing the quantity of added phosphine. However, the best results were obtained with PPh_3 where as little as 1 equiv (relative to initiator) afforded a k_i/k_p of 2.43 (which subsequently increased to 10.2 when 5 equiv were added).

The enhancement appears to stem from a combination of steric and electronic effects. The propagating species contains a bulky polymer chain that may sterically hinder phosphine coordination and thus result in relatively high concentrations of the "active" (phosphine-dissociated) species (**B**) (Scheme 1). (Incidentally, this provides an explanation for the relatively high propagation rates commonly observed with **1**.) Smaller phosphines should coordinate to this bulky species easier and subsequently shift the equilibrium toward the "dormant" (phosphine-associated) species (**A**). In addition, ^{1}H NMR spectroscopy confirmed that the lower limit of phosphine exchange ($\sim10^2$ min^{-1} for all phosphines studied) was several orders of magnitude greater than the rate of propagation (see Table 1). Thus, when PCy_2Ph, $PCyPh_2$, or PPh_3 was employed, equilibrium between initiator **1** and an initiator containing a mixed ligand set, i.e., $(PR_3)(PCy_3)Cl_2Ru{=}CHPh$, was established prior to initiation. Therefore, the enhanced initiation may also be related to the greater ability of PCy_3 to labilize the relatively less basic PCy_2Ph, $PCyPh_2$, or PPh_3, affording relatively increased rates of phosphine dissociation.

Direct observation of this fast exchange and initiation process was observed by ^{1}H NMR spectroscopy. As shown in Figure 2, in the presence of 5 equiv of PPh_3, the mixed ligand initiator, $(PCy_3)(PPh_3)Cl_2Ru{=}CHPh$, was observed (20.2 ppm) at low monomer conversion (<5%) and rapidly converted to growing polymer chains. In addition, signals attributed to the propagating species $(PCy_3)Cl_2Ru{=}CHR$ (18.8 ppm) and $(PPh_3)Cl_2Ru{=}CHR$ (17.8 ppm) (R = polymer) maintained a relatively equal intensity throughout the polymerization (which we believe is a consequence of the rapid phosphine exchange process). As expected, only small amounts (<10%) of the propagating species $(PCy_3)_2Cl_2Ru{=}CHR$ (19.5 ppm) were observed.

As shown in Table 2, the inclusion of phosphine during ROMP had remarkable effects on the molecular weights and polydispersities of the resulting polymers.[8] In accord with increased initiation rates, the resulting polymers were in better agreement with their predicted values and became nearly monodispersed (PDIs as low as 1.04) as increased quantities of smaller phosphines were used. This was observed over various M/C loadings and concentrations. The presence of excess phosphine did not compromise the functional group integrity of **1** as the polymers from highly functionalized monomers, such as the amino esters **4b** and **4c** and a monomer containing a free alcohol (**5b**), exhibited very low polydispersity. Similar results were obtained when a monomer with relatively low ring strain, 1,5-cyclooctadiene (COD) (**6**), was employed.

In summary, we report that polymers with narrow polydispersities can be obtained from ROMP initiator **1** when commercially available phosphines are included. Similar to controlled radical polymerizations, we believe the enhanced control is related to a fast, dynamic equilibrium that exists between dormant and active species and is mediated by the type and quantity of phosphine employed. Efforts toward applying toward these concepts to enhance the initiation efficiency of Ru complex **2** are currently in progress.

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Supporting Information Available: Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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