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Tandem Catalysis: Three Mechanistically Distinct Reactions from a Single Ruthenium Complex

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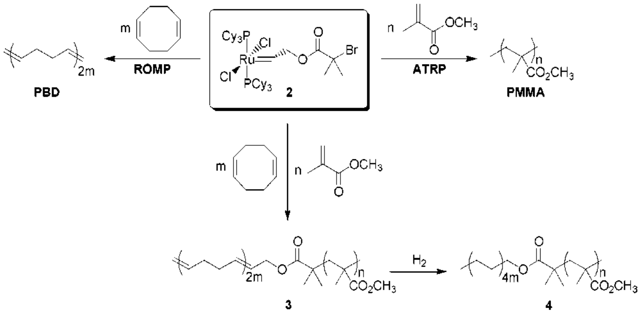
Organometallic catalysts are traditionally designed and optimized to mediate a single reaction.[1] As the number of applications that require combinatorial and other high-speed synthetic protocols increases,[2] it will become desirable for catalysts to mediate multiple, mechanistically distinct transformations directly or upon simple modification. As an example of such a system, we demonstrate the ability of a single component precatalyst to mediate three different reactions to form well-defined block copolymers.

The preparation of block copolymers composed of segments that cannot be prepared by the same polymerization mechanism remains a challenge in synthetic polymer chemistry.[3] Thus, many new strategies have emerged which are based on using substrates that are capable of initiating more than one type of polymerization. In general, various "controlled"/living radical polymerization methods[4] have been combined with ionic or ring-opening polymerization.[5] However, while a few of these protocols permit the combination of all the desired monomers at the beginning of the polymerization, the majority require timed additions (i.e., one polymerization must finish before another can begin).[6] Furthermore, in addition to the initiator, a number of organometallic complexes and cocatalysts must be included to control the polymerizations. Ultimately, it would be desirable to have the necessary catalyst(s) and initiator(s) in a single component system, therefore requiring only the addition of desired monomers (preferably at the same time) to form block copolymers.[7]

Scheme 1



The ruthenium-based catalyst, $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**), is effective for initiating the ring-opening metathesis polymerization (ROMP) of a variety of cyclic olefins.[8] Recently, Noels and coworkers demonstrated that **1** is also an effective catalyst for the atom-transfer radical polymerization (ATRP) of methyl methacrylate.[9] We proposed that a difunctional complex that incorporates both a ROMP and an ATRP initiator could mediate both polymerizations simultaneously.[10] A complex that meets these requirements (**2**) was conveniently prepared from commercially available allyl 2-bromo-2-methylpropionate[11] and **1** in 75% isolated yield using previously reported methods.[8a] Furthermore, at the conclusion of the aforementioned polymerizations, we reasoned that the residual ruthenium species could be transformed into a catalyst capable of hydrogenating the unsaturation in the polymer backbone (formed during the ROMP of the cyclic olefin).[12]

As shown in Scheme 1, initial investigations confirmed that **2** initiated both ROMP and ATRP independently. For example, the ROMP of 1,5-cyclooctadiene (COD) in solution or bulk afforded poly(cyclooctadiene), equivalent to poly(butadiene) (PBD), in yields ranging from 85 to 95% and with polydispersity indices (PDIs) near two (Table 1). As expected, these results were similar to those obtained when $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) was used as the ROMP initiator.[8] Similarly, addition of MMA to a solution of **2** in toluene afforded poly(methyl methacrylate) (PMMA) after 18 h at 65 °C (75% yield, Table 1). In addition, a linear relationship between monomer conversion and polymer molecular weight was observed which suggested **2** effectively controlled the polymerization. However, as observed in other ruthenium-based ATRP systems, the molecular weights were higher than expected which may be related to the initiation efficiency.[9,12] Nevertheless, nearly monodispersed polymers (PDI < 1.2) were obtained. To the best of our knowledge, **2** is the first example of a complete ATRP system containing both the transition metal mediator and the radical initiator, all in a single complex.

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Table 1. Synthesis of Homopolymers and Block Copolymers[a]

polymer	t[b]	F_{MMA}[c]	Y[d]	$M_{n,th}$[e]	$M_{n,gpc}$[f]	PDI
PMMA	18	100 (100)	75	9100	12600	1.2
PBD	18	0 (0)	91	5000	6200[g]	2.1
3a	18	43 (42)	65	9400	9700	1.5
3b	24	42 (42)	71	7500	8500	1.6
3c[h]	30	37 (38)	58	6300	7700	1.6
3d	18	73 (77)	68	15440	14500	1.5
3e	18	16 (18)	82	20480	17300	1.6

[a] General polymerization conditions: 65 °C, nitrogen atmosphere, toluene as solvent, $[\mathbf{2}]_0 = 20-40$ mM, $[MMA]_0 = 0.9-3.9$ M, $[COD]_0 = 1.0-3.8$ M. [b] Reaction time (hours). [c] Molar percent of MMA in the total monomer feed. The value in parentheses is the molar percent of MMA found in the polymer as determined by ^1H NMR spectroscopy. [d] Isolated yield (%). [e] Theoretical molecular weight based on percent conversion as determined using gas chromatography. [f] Molecular weight relative to monodispersed PMMA standards in CH_2Cl_2 [g] Molecular weight relative to monodispersed PBD standards in CH_2Cl_2. [h] THF was used as solvent.

As summarized in Table 1, **2** was employed in the "one pot" copolymerization of COD and MMA under a variety of conditions. After 18−30 h, the reaction mixtures were poured into excess methanol to afford polymer in yields of 58−82%. Analysis of the resulting polymers by ^1H NMR spectroscopy indicated the presence of both PBD and PMMA in the expected ratios based on percent conversion. Gel permeation chromatography (GPC) suggested that PBD-PMMA diblock copolymers (**3**) were formed as monomodal polymer distributions were observed (PDI 1.5−1.6) with apparent molecular weights in qualitative agreement with their theoretical values.[13] To verify that the copolymers were structurally diblock, isolated copolymer **3d** (Table 1) was treated with OsO_4/H_2O_2 to completely degrade the PBD segment.[14] The molecular weight of the remaining PMMA ($M_n = 15800$, PDI = 1.2) was found to be in agreement with the value expected[15] ($M_n = 16100$) based on the amount of monomer consumed during the polymerization.[16]

The ability of a single metal complex to mediate two different types of polymerizations was further explored. The large differential rate between the ROMP of COD ($k_{obs} = 3.5 \times 10^{-3}$ s^{-1}) and the ATRP of MMA ($k_{obs} = 1.2 \times 10^{-5}$ s^{-1}) indicated that the polymerizations occurred in tandem.[17] However, the rates were nearly identical (ROMP $k_{obs} = 3.6 \times 10^{-5}$ s^{-1} vs ATRP $k_{obs} = 3.7 \times 10^{-5}$ s^{-1}) when excess PCy_3 (10 equiv) was added to the reaction mixture (Figure 1).[18] Furthermore, these copolymerization rates were comparable to the individual homopolymerization rates performed separately in the presence of PCy_3.[19] This suggested that a single ruthenium alkylidene complex successfully mediated two mechanistically distinct polymerizations, *simultaneously*.[20]

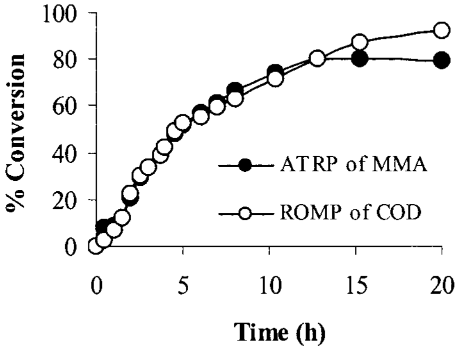

Figure 1. ROMP of COD and ATRP of MMA monitored using ^1H NMR spectroscopy. Conditions: $[\mathbf{2}]_0 = 0.03$ M, $[PCy_3] = 0.30$ M, $[COD]_0 = [MMA]_0 = 0.75$ M, in toluene-d_8, 65 °C.

At the conclusion of a COD/MMA copolymerization using **2**, the reaction vessel was exposed to a constant hydrogen pressure (150 psi, 65 °C) for 8 h. We propose that under an atmosphere of hydrogen the residual ruthenium species were transformed[21] into $Ru(H_2)(H)Cl(PCy_3)_2$, a known[22] hydrogenation catalyst.[11] The extent of the hydrogenation was determined to be approximately 75% by ^1H NMR spectroscopy. The degree of hydrogenation increased to greater than 95% when THF was included, which may help attenuate bimolecular decomposition pathways through coordination.[23] This provides an extremely efficient route to copolymers composed of poly(ethylene) and PMMA (**4**).[24]

In summary, we have demonstrated the ability of a single multifunctional complex (**2**) to mediate three mechanistically distinct reactions. Under appropriate conditions, two of the reactions were catalyzed simultaneously. Future studies will focus on the rapid preparation of other polymers and small molecules using multifunctional catalysts.

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Supporting Information Available: Experimental details on the synthesis and characterization of complex **2** and a representative polymerization procedure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The copolymers (**3**) exhibited glass transition temperatures (T_g) near −103 °C (PBD) and 104 °C (PMMA).

(14) Yu, Y. S.; Jérôme, R.; Fayt, R.; Teyssie, P. *Macromolecules* **1994**, *27*, 5957.

(15) The expected value was based on the initiation efficiency determined from the homopolymerization of MMA under identical conditions.

(16) While secondary metathesis reactions could theoretically lead to the formation of PBD homopolymer and PMMA-PBD-PMMA triblock copolymers, we found no evidence for their existence by GPC or chromatographic analysis.

(17) The polymerization rates were determined using ^1H NMR spectroscopy. Conditions: $[\mathbf{2}]_0 = 0.03$ M, $[COD]_0 = [MMA]_0 = 0.75$ M, in toluene-d_8, 65 °C.

(18) The mechanism of ruthenium-based ROMP appears to be predominately dissociative in phosphine, see: Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.

(19) Homopolymerization rates in the presence of 10 equiv of PCy_3 (see Figure 1 for conditions): k_{obs}(ROMP of COD) = 3.4×10^{-5} s^{-1}, k_{obs}(ATRP of MMA) = 3.2×10^{-5} s^{-1}.

(20) No catalyst decomposition was observed over the course of the polymerizations.

(21) The addition of H_2 to complex **1** (or **2**) afforded $Ru(H)_2Cl_2(PCy_3)_2$ or $Ru(H_2)(H)Cl(PCy_3)_2$ depending on reaction conditions. Both complexes are effective hydrogenation precatalysts.[22] See also: Montserrat, O.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 566.

(22) Beatty, R. P.; Paciello, R. A. U.S. Patent 5,554,778, 1996.

(23) Similar conclusions have been drawn using **1** immobilized on a silica support for the heterogeneous hydrogenation of olefins.[11b]

(24) Optically clear films were obtained by casting toluene solutions of the isolated PMMA-PE copolymers. This provides further support for efficient diblock formation.