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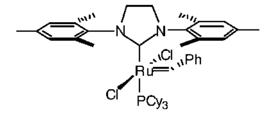
Ultrafast-Initiating ROMP Catalyst

Controlled Living Ring-Opening-Metathesis Polymerization by a Fast-Initiating Ruthenium Catalyst**

*Tae-Lim Choi and Robert H. Grubbs**

Ring-opening-metathesis polymerization (ROMP) has expanded the realm of polymer synthesis, and has provided access to many structurally unique polymers.[1] With the developments of well-defined olefin-metathesis catalysts, such as $[(t\mathrm{BuO})_2(\mathrm{ArN})\mathrm{Mo{=}CH}(t\mathrm{Bu})]$ (**1**)[2] and $[(\mathrm{PCy}_3)_2(\mathrm{Cl})_2\mathrm{Ru{=}CHPh}]$ (**2**; Cy = cyclohexyl),[3] controlled living polymerization became possible, making ROMP a novel method to synthesize polymers with various architectures. However, these catalysts suffer from either a lack of functional-group tolerance (**1**) or decreased activity and produces polymer with a moderate polydispersity index (PDI) around 1.2 (**2**). The recent development of N-heterocyclic carbene ruthenium catalysts[4] led to catalyst **3**, which exhibited activity comparable to or higher than **1**, while retaining the functional group tolerance of **2**.[5] Catalyst **3** was found to be extremely useful in organic transformations such as cross and ring-closing metathesis.[6] Nevertheless, **3** generally gives polymers with uncontrolled molecular weights and broad PDIs, owing to high propagation rates and slow initiation rates (low k_i/k_p; k_i = the rate constant for initiation, k_p = the rate constant for propagation)[7] and competing chain-transfer reactions.[8]



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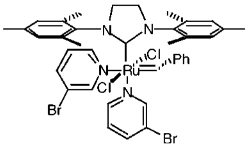

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From the previous study on ring-opening-insertion-metathesis polymerization,[9] we found that norbornene derivatives were not viable comonomers as the steric hindrance around the olefin in the polymers prevented the required insertion into catalyst **3**. This observation suggested that chain transfer or "back-biting" was minimal even with the active catalyst **3** at 40 °C.[10] Previously, a new member of the family of catalysts, **4**, was found to initiate more rapidly than **3**.[11,12] Therefore an increased k_i/k_p ratio should promote the

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[*] Prof. R. H. Grubbs, T.-L. Choi
Arnold and Mabel Laboratories of Chemical Synthesis
California Institute of Technology
Division of Chemistry and Chemical Engineering
MC 164-30 Pasadena, CA 91125 (USA)
Fax: (+1) 626-564-9297
E-mail: rhg@its.caltech.edu

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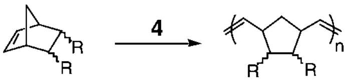
controlled living polymerization if chain transfer and chain termination are absent. Herein, we report the controlled living ROMP of norbornene and 7-oxonorbornene derivatives by the highly active and rapidly initiating Ru-based catalyst **4** to make monodisperse homopolymers and block copolymers.

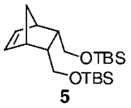
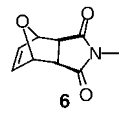
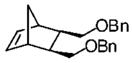
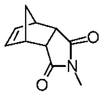
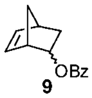
When a solution of monomer was added to a solution of catalyst **4** in dichloromethane (to give a monomer concentration 0.2–0.4 M), the color instantaneously changed from green to yellow, which implies the immediate initiation of catalyst **4**. After 30 minutes, the reactions were complete (monitored by TLC and ^{1}H NMR) and were quenched by adding ethyl vinyl ether, and the polymers were precipitated by pouring the reaction mixture into methanol. The polymers were obtained in high yields with very narrow PDIs, as low as 1.04 (Table 1), which is indicative of controlled living polymerization. All the PDI values are much lower than typical controlled living ROMP products obtained from catalyst **2** (PDI ≈ 1.2).[13] Additionally, *endo*-monomers **5** and **8** (Table 1), which are polymerized slowly if at all with catalyst **2**, undergo ROMP readily with the highly active catalyst, **4**.[3a,13]

Norbornene (**10**) is a unique monomer, since only catalyst **1** and [$(PPh_3)_2(Cl)_2Ru{=}CHPh$] (**11**),[3b] promote its controlled living polymerization. Catalysts **2**, and **3** give poor PDIs because of chain-transfer reactions.[3b,8b] Not surprisingly, **4** also produced polynorbornene (PNB) with a broad PDI (1.65) at room temperature. However, PNB with a narrower PDI (1.28) was obtained when the polymerization was carried out at 0 °C, and furthermore, the PDI was lowered to 1.08 at −20 °C (Table 1), which demonstrates that **4** initiates rapidly even at −20 °C and chain-transfer reactions on PNB are suppressed at low temperatures.[14]

The effects of changing the polymerization conditions were studied using 100 equivalents of monomer **6** to catalyst **4**. When the monomer concentration was lowered to 0.05 M in dichloromethane or the temperature was lowered to 0 °C, there were no effects on the product yields, molecular weights, or PDI values. Furthermore, the reaction of the isolated polymer with 20 mol% of a chain-transfer agent, 1,4-bis(acetoxy)-*cis*-2-butene, and 1 mol% of **4** for 10 hours at room temperature resulted in no change of the polymer structure. A change in the solvent of the reaction had no marked effects, but increasing the starting temperature from 23 °C to 55 °C in 1,2-dichloroethane gave a polymer with a similar $\bar{M}_n$ but a much broader PDI of 1.25. These results suggest that chain transfer or back-biting does occur at higher temperatures.[8a]

Table 1: ROMP of various monomers with catalyst **4**.[a]



Monomer	M/C	Yield[b] [%]	Obs. $\bar{M}_n$ [c] [×10³]	Theo. $\bar{M}_n$ [×10³][d]	PDI[c]
 **5**	50	–[e]	14.0	19.2	1.08
	100	84	24.5	38.3	1.06
	200	84	50.0	76.6	1.05
	400	83	114.0	153.1	1.04
 **6**	100	84	29.1	18.0	1.05
	150	–[e]	41.7	26.8	1.05
	200	86	53.1	35.9	1.06
	400	97	106.0	71.7	1.04
 **7**	100	–[e]	30.4	33.5	1.05
	200	92	60.9	67.0	1.04
	400	90	131.5	133.9	1.06
 **8**	50	–[e]	11.5	8.9	1.08
	100	87	22.9	17.8	1.08
	200	73	40.2	35.5	1.09
 **9**	100	–[e]	28.7	19.9	1.10
	200	81	50.6	39.7	1.09
	400	87	91.1	79.4	1.10
 **10**	100	87	9.0[f]	9.5	1.09
	150	–[e]	15.1[f]	14.2	1.06
	200	93	22.0[f]	18.9	1.10

[a] 0.2 M in CH_2Cl_2 at 23 °C (or −20 °C for **10**) for 30 min. [b] Isolated by precipating into methanol. [c] Determined by CH_2Cl_2 GPC relative to polystyrene standards. [d] Assuming quantitative conversion. [e] Samples prepared by quenching and removing the solvent without precipitation. [f] The correction factor of 0.5 applied to PNB.[8a] GPC = gel-permeation chromatography, TBS = *tert*-butyldimethylsilyl, Bn = Benzyl, Bz = Benzoyl, M/C = monomer to catalyst ratio, $\bar{M}_n$ = number-average molar mass.

Encouraged by the narrow PDI, we examined the relationship between the molecular weight and M/C. Representative graphs of $\bar{M}_n$ versus M/C for monomers **6** and **7** are in Figure 1, which clearly shows a linear relationship between $\bar{M}_n$ and M/C. Importantly, the linear relationship holds for both low- (as low as DP = 10; DP = degree of polymerization) and high-molecular-weight polymers with narrow PDIs (< 1.1). Other monomers give similar linear relationships. The control of the molecular weight through the M/C ratio, and the low PDI values suggest that for **4**, k_i/k_p is high enough that all the chains initiate and grow at a similar rate.[15] The high k_i/k_p ratio is attributed to the fact that although the k_p value of catalyst **4** is much larger than that of catalyst **2**, the extremely high k_i value (more than ten thousands times higher that that of **2**)[7,11] overrides the effect of the increase in k_p relative to that of catalyst **2**, which results in a narrower PDI and good molecular-weight

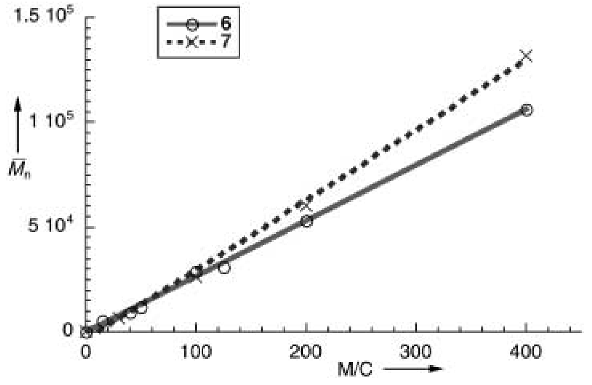


Figure 1. $\bar{M}_n$ versus M/C for the polymers produced from momomers **6** and **7** by using catalyst **4**.

control. Thus, catalyst **4** promotes living ROMP with both higher activity and better control.

If **4** indeed promotes the controlled living polymerization for norbornenes and 7-oxonorbornene derivatives, it should produce block copolymers from sequential additions of monomers. Monomer **7** (M/C = 200) was treated with catalyst **4**, followed by the addition of monomer **5** (M/C = 200) after 30 minutes (Table 2, entry 1). The resulting polymer had almost twice the $\bar{M}_n$ of the initial homopolymer **7**, and the PDI of 1.10. The ^{1}H NMR spectrum of this product shows only two sets of overlaying signals identical to those of the two homopolymers. To confirm that **4** produces diblock copolymers, another block copolymer was synthesized by treating monomer **6** (M/C = 50) with catalyst **4**, followed by monomer **7** (M/C = 200). The well-resolved GPC traces for the diblock copolymer of entry 2 (Table 2) show the complete shift to higher molecular weights (Figure 2a).

The $\bar{M}_n$ value of the final copolymer (73000) agrees with the value obtained by adding the $\bar{M}_n$ of individually synthesized homopolymers of **6** and **7** (10000 + 60000 = 70000). One can also make ABC-triblock copolymers by the sequential addition of three different monomers (entry 3). Figure 2b displays well-resolved GPC traces of monodisperse triblock copolymer. No fractions are observed in the low-molecular-weight regions, which indicates that no termination processes occurred during the course of the two sequential additions of monomers. In all cases, the ratios of the monomers, obtained by ^{1}H NMR studies of the final block copolymers, are in good agreement with the added feed ratios.

In conclusion, we have demonstrated that catalyst **4** bearing an N-heterocyclic carbene, which greatly enhances the activity, and a 3-bromopyridine[16] ligand, which significantly increases the initiation process, effects controlled living polymerization of norbornene and oxo-norbornene derivatives, even those derivatives that do not undergo living polymerization with other catalysts.

Table 2: Synthesis of block copolymers.[a]

Entry	First Monomer	M/C	$\bar{M}_n$[b] [×10³]	Second monomer	M/C	$\bar{M}_n$[b] [×10³]	Yield[c] [%]	PDI[b]
1	**7**	200	60.6	**5**	200	115.1 (143.5)	90	1.10
2	**6**	50	10.0	**7**	200	72.7 (75.9)	86	1.07
3	**6**	15	5.1	**7**	75	37.4 (27.9)		1.06
		third	monomer	**5**	370	154.8 (169.5)	90	1.05

[a] 0.2 M in CH_2Cl_2 at 23 °C for 30 min for each monomer. [b] Determined by GPC with CH_2Cl_2 relative to polystyrene standards. [c] Yield of product isolated by precipating into methanol.

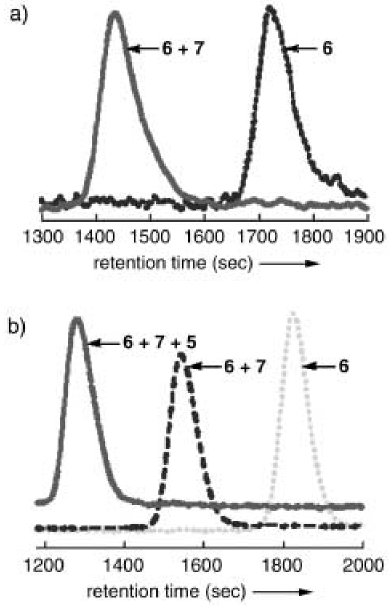


Figure 2. GPC traces for diblock (a) and triblock (b) copolymers.

Experimental Section

Representative procedure for the ROMP of monomer **7**: A solution of **7** (150 mg, 0.45 mmol) in CH_2Cl_2 (0.5 mL) was added rapidly by syringe to a vial charged with **4** (1.0 mg, 1.1 μmol) in CH_2Cl_2 (1 mL) under an argon atmosphere at room temperature. After 30 minutes excess ethyl vinyl ether was added and the polymer was precipitated by pouring the reaction mixture into methanol. Yield 135 mg (90%, 59% *cis* olefin). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.25$ (brs, 10H), 5.25 (brm, 2H), 4.30 (brm, 4H), 3.45 (brs, 4H), 2.76 (brs, 1.2H for *cis*), 2.38 (brs, 0.8H for *trans*), 2.03 (3H, brm), 1.12 ppm (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.9$ (brm), 134.0 (brm), 128.5, 127.7, 127.6, 73.2, 70.7, 70.4, 48.0, 47.7, 45.4 (brm), 41.3 (brm), 40.3 ppm. Other homopolymers referred to herein are known and characterized.

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[1] For recent reviews on ROMP, see: a) B. M. Novak, W. Risse, R. H. Grubbs, *Adv. Polym. Sci.* **1992**, *102*, 47; b) K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, CA, **1997**; c) R. H. Grubbs, E. Khosravi, *Mater. Sci. Technol.* **1999**, *20*, 65; d) M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565; e) U. Frenzel, O. Nuyken, *J. Polym. Sci. Part A* **2002**, *40*, 2895.

[2] a) R. R. Schrock, *Acc. Chem. Res.* **1990**, *23*, 158; b) G. C. Bazan,

R. R. Schrock, H. N. Cho, V. C. Gibson, *Macromolecules* **1991**, *24*, 4495.

[3] a) S. Kanaoka, R. H. Grubbs, *Macromolecules* **1995**, *28*, 4707; b) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100; c) M. Weck, P. Schwab, R. H. Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789.

[4] a) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrman, *Angew. Chem.* **1998**, *110,* 2631; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490; b) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrman, *Angew. Chem.* **1999**, *111,* 2573; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416; c) J. Huang, E. D. Stevnes, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2675.

[5] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.

[6] a) A. K. Chatterjee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 1751; b) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783; c) T.-L. Choi, A. K. Chatterjee, R. H. Grubbs, *Angew. Chem.* **2001**, *113*, 1317; *Angew. Chem. Int. Ed.* **2001**, *40*, 1277; d) A. K. Chatterjee, T.-L. Choi, R. H. Grubbs, *Synlett* **2001**, 1034; e) T.-L. Choi, C. W. Lee, A. K. Chatterjee, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 10417; f) T.-L. Choi, R. H. Grubbs, *Chem. Commun.* **2001**, 2648; g) C. W. Lee, T.-L. Choi, R. H. Grubbs, *J. Am. Chem. Soc.* **2002**, *124*, 3224.

[7] a) M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749; b) M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543.

[8] a) C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, *112,* 3025; *Angew. Chem. Int. Ed.* **2000**, *39*, 2903; b) C. W. Bielawski, D. Benitez, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8610; c) O. A. Scherman, H. M. Kim, R. H. Grubbs, *Macromolecules* **2002**, *35*, 5366.

[9] T.-L. Choi, I. M. Rutenberg, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 3995; *Angew. Chem. Int. Ed.* **2002**, *41*, 3839.

[10] ROMP with catalyst **3** gives extremely high-molecular-weight polymers that are often insoluble, but low PDIs have been observed in some special cases, see: H. D. Maynard, S. Y. Okada, R. H. Grubbs, *Macromolecules* **2000**, *33*, 6239.

[11] J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 4207; *Angew. Chem. Int. Ed.* **2002**, *41*, 4035.

[12] For ROMP with other fast-initiating catalysts (but slower than **4**), see: a) U. Frenzel, T. Weskamp, F. J. Kohl, W. C. Schattenmann, O. Nuyken, W. A. Herrmann, *J. Organomet. Chem.* **1999**, *586*, 263; b) C. Slugovc, S. Demel, F. Stelzer, *Chem. Commun.* **2002**, 2572.

[13] ROMP of *endo-n*-alkyl norbornene dicarboxyimides with catalyst **1** gave polymers with PDI of 1.3, see: E. Khosravi, W. J. Feast, A. A. Al-Hajaji, T. Leejarkpai, *J. Mol. Catal. A* **2000**, *160*, 1. Crude solutions of polymers (i.e. without precipitation) were subjected to GPC analysis resulting in clean traces that displayed low PDIs. These traces show that the low PDIs are not a consequence of fractionation of polymers of low molecular weight by precipitation.

[14] This PNB contained 61 % of the *cis*-olefin isomer and is much higher than PNB produced with **3** (35 % *cis*), which undergoes chain-transfer reactions.[8b]

[15] Ten equivalents of **8** were mixed with **4** at −10 °C resulting in complete initiation (the only propagating carbene signal in the corresponding ^{13}C NMR spectrum was observed at $\delta = 18.2$ ppm) and 13 % product conversion. Based on the assumption of at least 99 % initiation, a minimum value of $k_i/k_p = 19$ is calculated by using the Gold equation. See reference [1b] page 232.

[16] Complexes with other substituted-pyridine ligands can show similar rapid initiation rates A. Hejl, R. Grubbs, unpublished results.