Ring-opening Metathesis Polymerization of Norbornene in the Presence of Heteroatom-substituted Vinylic Compounds: Highly Selective Synthesis of End-functionalized Poly(norbornene)s

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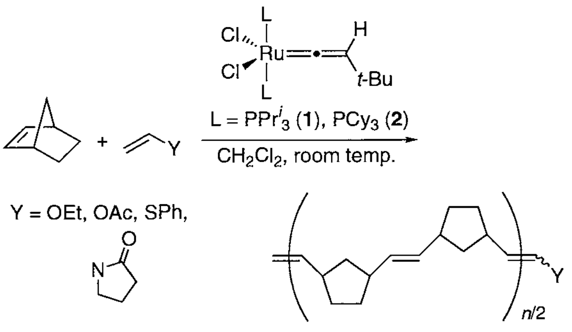
(Received January 13, 1999; CL-990034)

Heteroatom-substituted vinylic compounds including vinyl ether, acetate, sulfide, and pyrrolidinone have been found to serve as efficient chain-transfer agents for ring-opening metathesis polymerization of norbornene in the presence of vinylideneruthenium complexes as the catalyst precursors, leading to selective formation of poly(norbornene)s with end-functionalities.

Ring-opening metathesis polymerization of cyclic olefins (ROMP) in the presence of acyclic olefins bearing heteroatom-based substituents has provided a selective way to synthesize end-functionalized polymers.[1] The acyclic olefins serve not only as the source of end-functionalities but also as a chain-transfer agent (CTA), a part of which is incorporated into the metal carbene species during the chain-transfer process. Since it is generally considered that carbene complexes bearing α-heteroatom substituents (*i.e.* Fischer-type carbene complexes) are poorly reactive toward olefin-metathesis,[2] the acyclic olefins so far employed in ROMP systems have the structures in which heteroatom substituents are separated at least by one methylene group from the olefin moiety to avoid the formation of Fischer-type carbene complexes in the catalytic systems. In contrast, we found in this study that heteroatom-substituted vinylic compounds can be used as efficient CTAs, giving end-functionalized poly(norbornene)s in high selectivities (eq. 1).

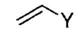
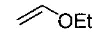
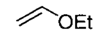
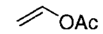
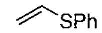
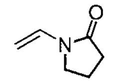


(1)

The present catalytic systems are based on recent our finding that vinylideneruthenium complexes bearing basic tertiary phosphine ligands $RuCl_2(=C=CHBu^t)L_2$ [L = PPr^i_3 (**1**), PCy_3 (**2**)] serve as good catalyst precursors for ROMP of norbornene derivatives.[3] The vinylidene complexes can be easily prepared in high yields from *tert*-butylacetylene.[4]

Table 1 summarizes the results. In the absence of vinylic compounds, the polymerization of norbornene using 2 mol% of **1** rapidly proceeded in CH_2Cl_2 at room temperature to give poly(norbornene) with $M_n = 47.6 \times 10^4$ in 99% yield (entry 1).[5] On the other hand, in the presence of 10 mol% of ethyl vinyl ether, the reaction progress was much slower, and poly(norbornene) with significantly low molecular weight ($M_n = 1.4 \times 10^4$) was obtained in 80% yield after reprecipitation with MeOH (entry 2). ^1H NMR spectrum of the polymer measured in $CDCl_3$ exhibited the following signals assignable to terminal vinyl and ethoxyethenyl groups in a 1 : 1 ratio: δ 5.80 (ddd, J = 17.5, 10.0, 7.5 Hz, 1H), 4.95 (dd, J = 17.5, 2.1 Hz, 1H) and 4.86 (dd, J = 10.0, 2.1 Hz, 1H); δ 5.86 (d, J = 9.0 Hz, 1H), 4.31 (dd, J = 9.0, 7.0 Hz, 1H), 3.77 (q, J = 7.5 Hz, 2H) and 1.24 (t, J = 7.5 Hz, 3H). Based on the relative peak integration between the terminal vinyl protons and the olefinic protons of polymer main chain [δ 5.34, 5.33 (trans) and δ 5.21, 5.19 (cis)],[6] molecular weight of the polymer was estimated to be *ca.* 6400; the value was consistent with the GPC data.[7] Hence the selective formation of poly(norbornene) with vinyl and ethoxyethenyl group at each terminus was evidenced. Almost the same polymer was obtained using **2** in place of **1** as the catalyst precursor (entry 3).

Table 1. Ring-opening metathesis polymerization of norbornene in the presence of vinylic compounds[a]

Entry		Time/h	Yield/%	$M_n{}^b/10^4$	$M_w/M_n{}^b$
1	none	<10 min	99	47.6	1.60
2		24	80	1.4	2.55
3[c]		24	71	1.1	1.67
4		48	61	0.4	1.47
5		2	84	0.4	1.30
6		41	80	1.4	2.20

[a]All reactions were run in CH_2Cl_2 at room temperature using catalyst precursor **1** unless otherwise noted. Initial conditions: $[\text{norbornene}]_0 = 0.10$ M, $[\text{catalyst}]_0 = 2.0$ mM, $[\text{vinylic compound}]_0 = 10$ mM. [b]Determined by GPC based on polystyrene standards. [c]Complex **2** was used in place of **1**.

The molecular weight of polymer could be controlled in extremely wide range ($10^4 M_n = 0.6 - 15.2$) by changing the CTA (ethyl vinyl ether) to monomer ratio (Figure 1). The molecular weight distribution was monomodal for all runs and the M_w/M_n values were within the range of 2.0–2.9.

Vinyl acetate, sulfide, and pyrrolidinone also exhibited the CTA activities, giving the corresponding poly(norbornene)s with end-functionalities (Table 1, entries 4–6). The catalytic system with phenyl vinyl sulfide was particularly reactive and the polymerization was complete within 2 h (entry 5). Reprecipitation with MeOH gave 84% yield of polymer with extremely low

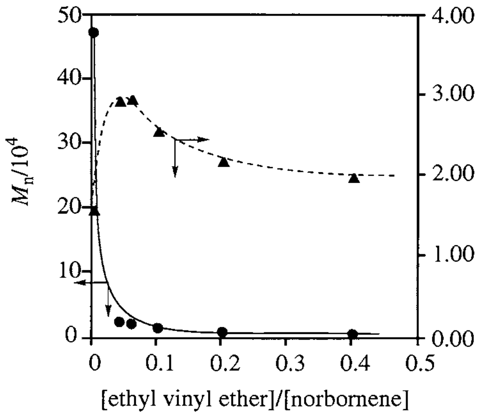
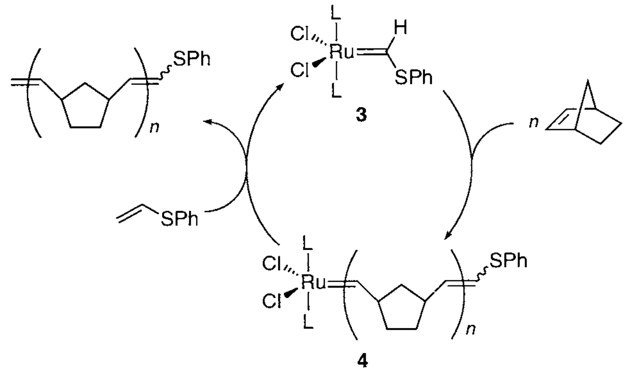


Figure 1. Dependence of the number-average molecular weight (●) and the polydispersity index (▲) of poly(norbornene) on the amount of ethyl vinyl ether added to the polymerization system.

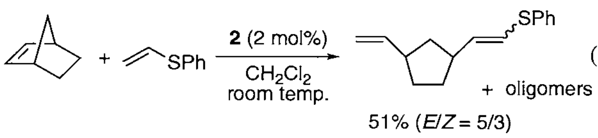
molecular weight (M_n = 4000). The other part of polymerization product was recovered from the MeOH solution.

The catalytic process was examined with phenyl vinyl sulfide, and the catalytic cycle in Scheme 1 emerged. The Fischer-type carbene complex (**3**) generated from the catalyst precursor (**1** or **2**) undergoes successive olefin-metathesis with norbornenes to form a methylideneruthenium intermediate bearing a PhSCH=CH group-capped polymer chain (**4**). Reaction of **4** with phenyl vinyl sulfide gives the product polymer and **3**, and the latter resumes the catalytic cycle.



Scheme 1. Proposed catalytic cycle for the ROMP of norbornene in the presence of phenyl vinyl sulfide.

The elementary processes assumed in this scheme were supported by the following observations. (i) Reaction of Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$[8] with phenyl vinyl sulfide (1 equiv.) in CH$_2$Cl$_2$ at room temperature proceeded in perfect regioselectivity to afford the thiocarbene complex Ru(=CHSPh)Cl$_2$(PCy$_3$)$_2$ (**3a**)[9] and styrene in quantitative yields. (ii) The isolated **3a** catalyzed the polymerization at a comparable reaction rate. (iii) **3a** was detected in the polymerization system using **2** as the catalyst precursor by ^{31}P{^{1}H} NMR spectroscopy.[10] (iv) Treatment of norbornene with an equimolar amount of phenyl vinyl sulfide in CH$_2$Cl$_2$ in the presence of a catalytic amount of **2** (2 mol%) gave 1-(phenylthio)-2-(3-vinylcyclopentyl)ethene (*E/Z* = 5/3) in 51% yield together with oligomeric products (eq. 2).



(2)

In conclusion, we have found a new catalytic system for synthesizing end-functionalized poly(norbornene)s. Various substituents can be selectively introduced at one terminus of the polymer chain by using heteroatom-substituted vinylic compounds. The other terminus remains unsubstituted and is capable of further transformation. Moreover, the present results strongly suggest the catalytic activity of Fischer-type carbene ruthenium complexes in ROMP systems.[11,12] The scope of applications of this novel catalysis is now under investigation.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

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2 Vinyl ethers are commonly used as a terminator of ROMP: M. A. Hillmyer, W. R. Laredo, and R. H. Grubbs, *Macromolecules*, **28**, 6311 (1995); S. Kanaoka and R. H. Grubbs, *Macromolecules*, **28**, 4707 (1995).

3 H. Katayama and F. Ozawa, *Chem. Lett.*, **1998**, 67.

4 H. Katayama and F. Ozawa, *Organometallics*, **17**, 5190 (1998).

5 Owing to low efficiency of the vinylidene initiator, the molecular weight observed in the absence of vinylic compounds was significantly higher than that expected from the monomer to catalyst ratio: see Ref. 3.

6 L. R. Gilliom and R. H. Grubbs, *J. Am. Chem. Soc.*, **108** 733 (1986).

7 Actual M_n values are known to be approximately half of the GPC data based on polystyrene standards: Ref. 6; T. J. Katz, S. J. Lee, and N. Acton, *Tetrahedron Lett.*, **1976**, 4247; T. J. Katz, and N. Acton, *Tetrahedron Lett.*, **1976**, 4251.

8 P. Schwab, R. H. Grubbs, and J. W. Ziller, *J. Am. Chem. Soc.*, **118**, 100 (1996).

9 Spectroscopic data for **3a**: ^{1}H NMR (CDCl$_3$) δ 17.64 (s, 1H, Ru=CH), 7.45–7.36 (m, 5H, Ph), 2.74–2.55, 1.98–1.19 (each m, 66H, Cy); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 280.5 (m, Ru=CH), 141.0 (s, *ipso*-C of Ph), 129.2, 129.1, 128.3 (each s, Ph), 32.5 (virtual triplet, J = 9 Hz, C^1 of Cy), 29.7 (s, C^3 of Cy), 27.7 (virtual triplet, J = 5 Hz, C^2 of Cy), 26.4 (s, C^4 of Cy); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 30.9 (s).

10 This fact indicates that the reaction of **3** with norbornene serves as the rate-determining step of the catalytic cycle in Scheme 1. Therefore, it may be considered that the difference in the polymerization rates dependent upon the CTAs are mainly due to the reactivities of Fischer-type carbene intermediates toward olefin-metathesis. Actually, the isolated thiocarbene complex (**3a**) exhibited much higher reactivity than the oxycarbene analog toward ROMP of norbornene, which is consistent with the particularly high reactivity of the catalytic system using phenyl vinyl sulfide as a CTA (Table 1, run 5): H. Katayama, H. Urushima, T. Nishioka, and F. Ozawa, unpublished results.

11 Grubbs *et al.* reported the lack of ROMP activity of Fischer-type carbene complexes, Ru(O$_2$CCF$_3$)$_2$(=CHY)(PPh$_3$)$_2$ (Y = OCH$_2$Ph, SCH$_2$Ph, NAr$_2$): Z. Wu, S. T. Nguyen, R. H. Grubbs, and J. W. Ziller, *J. Am. Chem. Soc.*, **117**, 5503 (1995). The coordination of chloride ligands as well as basic and bulky phosphine ligands (*i.e.* PPr$^i_3$, PCy$_3$), which are known to enhance the metathesis reactivity of ruthenium carbene complexes,[8] may provide the higher reactivity of the present catalytic systems.

12 For olefin-metathesis reactions of Fischer-type carbene complexes, see: M. Mori, in "Alkene Metathesis in Organic Synthesis," ed by A. Fürstner, Springer-Verlag, Berlin (1998), p. 133; M. Hoffmann, M. Buchert, and H.-U. Reissig, *Angew. Chem., Int. Ed. Engl.*, **36**, 283 (1997).