

Ni-Catalyzed Living Coordination Polymerization of Allenes Having Si-Based Functional Groups

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(Received February 10, 1999)

ABSTRACT: Coordination polymerizations of (trimethylsilylmethyl)allene **1** and (*t*-butyldimethylsilyloxy)allene **2** were performed by use of $[(\pi\text{-allyl})\text{NiX}]_2$ as the initiator. The living polymerization was achieved with $[(\pi\text{-allyl})\text{NiBr}]_2$ by the aid of additive ligand, Ph_3As for **1** and Ph_3P or $(\text{PhO})_3\text{P}$ for **2**. The polymers produced from **1** mainly (>95%) consisted of the 2,3-polymerization unit having the allylsilane structure. In the polymerization of **2**, the polymer produced in the absence of the phosphine ligands exclusively consisted of the 2,3-polymerization unit having the silyl enol ether group, while, in the presence of them, the 1,2-polymerization unit was partly involved.

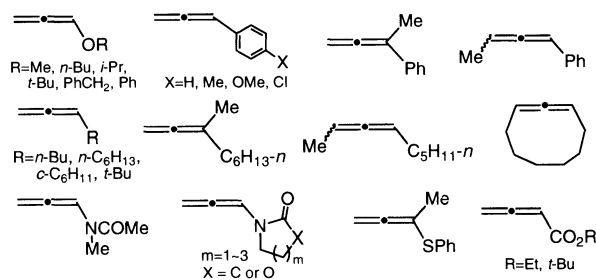
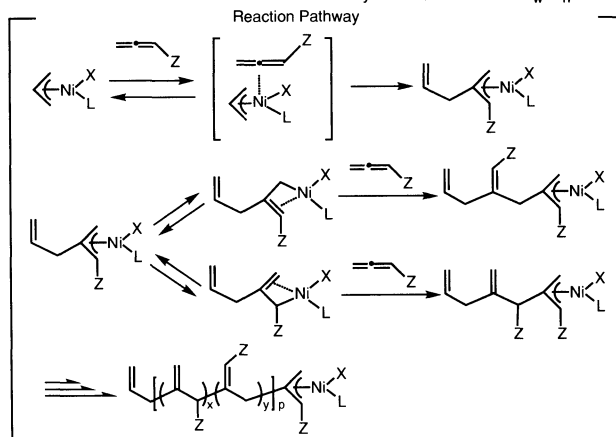
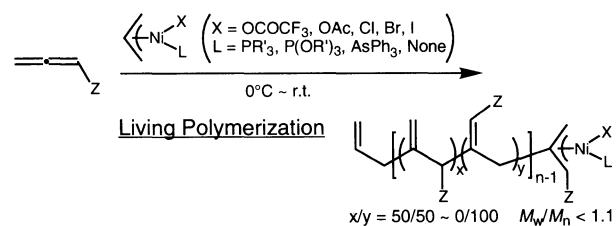
KEY WORDS (Silylmethyl)allene / Silyloxyallene / π -Allylnickel / Coordination Polymerization / Living Polymerization / Polyallene / Reactive Polymer / Allylsilane / Silyl Enol Ether /

Precise control of polymerization is one of important targets in polymer synthesis. In order to expand the scope of this field innovatively, it should be required to investigate polymerization reaction in detail from the standpoint of pure organic chemistry. We have been challenging to this theme in various manners. One of them is the usage of organometallic compounds which are powerful tools to establish a new well-controlled polymerization system because they can be finely tuned for suitable reactivity and good selectivity with the variations of ligand or metal itself.

Our another interest has been focused on reactive monomers and polymers. Recently, a variety of polymerizations of allene derivatives have been developed in our laboratory.¹ Polymers produced from allene derivatives have exomethylene or vinylenic double bonds on the main chains along with substituents as the pendant groups, both of which can act as reactive or functional sites. In other words, polyallenes are novel reactive polymers that can provide versatile materials including various kinds of functional polymers. To enhance the usefulness of polyallenes, we have been exploring the new well-controlled polymerization system of allenes, and π -allylnickel catalysts have been found to conduct the living coordination polymerizations of various allenes effectively.² These polymerizations proceed via the successive insertion of allene monomers to π -allylnickel complexes as the propagating ends (Scheme 1). The monomers undergoing the living polymerization are shown in Chart 1. Not only monosubstituted but also disubstituted allenes are included. The groups such as alkoxy, phenyl, alkyl, phenylthio, acylamino, and alkoxy carbonyl are tolerated as the substituents of allenes. It is noteworthy that both electron-rich and -deficient allenes can undergo the living polymerization. Additionally, this living system has been found to be applicable to the one-pot block copolymerizations between different allenes and between allenes and isonitrile or 1,3-butadiene, which are also known to be polymerized by a π -allylnickel catalyst.²

In order to expand the scope of the above living polymerization, this paper deals with the Ni-catalyzed

polymerizations of allenes having Si-functional groups, which can be converted to other functional groups after the polymerization.³ The monomers investigated herein are (trimethylsilylmethyl)allene **1** and (*t*-butyldimethylsilyloxy)-



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allene **2**, which will be polymerized to produce the allylsilane and silyl enol ether groups on the polymer chains, respectively.

EXPERIMENTAL

Materials and Measurements

(Trimethylsilylmethyl)allene **1** was prepared according to the procedure reported.⁴ Bis(1,5-cyclooctadiene)nickel (Ni(COD)₂) purchased from Kanto Chemicals was used without further purification. Allyl trifluoroacetate, allyl bromide, and triphenylphosphite were purified by distillation under nitrogen. Triphenylphosphine and triphenylarsine were recrystallized from ethanol. Toluene was dried over sodium and distilled under nitrogen. THF and triethylamine were dried over CaH₂ and distilled under nitrogen. Other commercially available reagents were used as received.

GPC analyses were carried out by use of Shodex® K-804L (Showa Denko) as the column and CHCl₃ as the eluent. The GPC calibration curve was made on the basis of polystyrene standards. NMR measurements were performed using a JEOL GSX-500 (500 MHz for ¹H) spectrometer.

Preparation of (*t*-Butyldimethylsilyloxy)allene **2**

The mixture of *t*-butyldimethylsilyl chloride (8.40 g, 55.7 mmol), dry triethylamine (6.88 g, 68.0 mmol), and dry THF (15 ml) was cooled at 0°C and treated dropwise with the THF (15 ml) solution of 2-propyn-1-ol (2.92 g, 52.7 mmol) under nitrogen. The resulting reaction mixture was refluxed for 4.5 h, and the precipitated ammonium salt was filtrated off and washed with diethyl ether (30 ml). The combined filtrate was washed with the saturated NaHCO₃ aqueous solution (50 ml) three times. The aqueous layer combined was extracted with diethyl ether (30 ml), and the organic layer combined was dried over MgSO₄ and evaporated to dryness. The residue was distilled under reduced pressure to give 3-(*t*-butyldimethylsilyloxy)propyne (6.16 g, 65%): bp 45–48°C/8.8 mmHg, ¹H NMR (CDCl₃) δ 0.11 (s, 6H), 0.90 (s, 9H), 2.38 (t, *J* = 2.29 Hz, 1H), 4.30 (d, *J* = 2.29 Hz, 2H).

Under nitrogen, 3-(*t*-butyldimethylsilyloxy)propyne (6.16 g, 36.1 mmol) thus obtained was added to *t*-BuOK (409.2 mg, 3.65 mmol) and the mixture was heated at 70°C for 3.5 h. After the complete conversion was confirmed by gas chromatography, the reaction mixture was distilled to give **2** (2.13 g, 35%): bp 48°C/10.8 mmHg, ¹H NMR (CDCl₃) δ 0.15 (s, 6H), 0.92 (s, 9H), 5.23 (d, *J* = 5.96 Hz, 2H), 6.58 (t, *J* = 5.96 Hz, 1H).

The Typical Procedure for the Polymerization

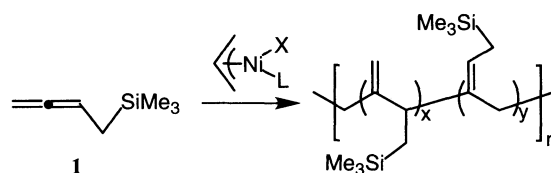
A toluene solution of allyl bromide (1 M, 20 μl, 0.02 mmol) was added to that of Ni(COD)₂ (0.048 M, 420 μl, 0.02 mmol)⁵ at 0°C under nitrogen; the solution became red brown to show the formation of the π-allylnickel complex. After a few minutes, the system was diluted with toluene (540 ml), and a toluene solution of Ph₃As (1 M, 40 μl, 0.04 mmol) and **1** (123.4 mg, 0.979 mmol) were added in this order. The reaction mixture was gradually warmed to room temperature overnight. After the complete conversion of **1** was confirmed by gas chromatography, the reaction mixture was diluted with toluene (5 ml) and stirred under the air; the solution color changed from red brown to pale green. Afterwards, the resulting solution was washed with EDTA-2Na (ethylenediaminetetraacetic acid, disodium salt) aq. (0.01 M, 5 ml). The organic layer was dried over MgSO₄ and the solvent was excluded *in vacuo* to give the colorless waxy polymer.

A similar procedure was applied to the polymerization of **2**.

RESULTS AND DISCUSSION

The Polymerization of **1** (Scheme 2)

As the first experiment, the polymerization of **1** was carried out with [(π-allyl)NiOCOCF₃]₂ as the initiator, which successfully conducted the living polymerization of alkylallenes.² However, in this case, nickel metal deposited soon and the conversion of **1** stopped less than 50% (Table I, run 1). In order to avoid this deactivation of the catalyst, runs 2 and 3 were undertaken, but in vain. We speculated that this deactivation might be caused by the internal attack of CF₃COO⁻ to the silicon atom at the propagating end (Scheme 3). Accordingly, we employed [(π-allyl)NiBr]₂ in which Br⁻ is less nucleophilic than CF₃COO⁻. This idea successfully brought the quantitative conversion of **1** to the polymer, however, whose molecular weight distribution was a little broad (run 4). The effect of the neutral ligand was explored. Addition of 2 equiv. of Ph₃As to Ni induced the quantitative production of the polymer having a narrower molecular weight distribution (*M_w*/*M_n* = 1.12, run 5). On the

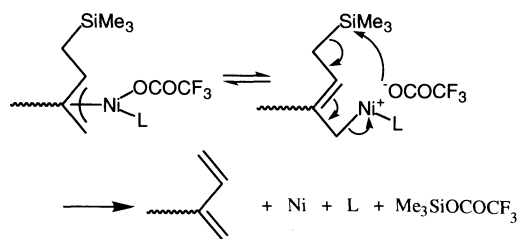


Scheme 2.

Table I. Polymerization of (trimethylsilylmethyl)allene **1**^a

Run	-X	L([L]/[Ni])	Temp. °C	Time h	Conv. %	<i>M_n</i> ^b	<i>M_w</i> / <i>M_n</i> ^b
1	-OCOCF ₃	none	0	45	39	10000	3.69
2		none	-15	26	0	—	—
3		Ph ₃ P (1)	0	45	16	—	—
4	-Br	none	0	3	100	10100	1.29 ^c
5		Ph ₃ As (2)	0→r.t.	overnight	100	9200	1.12 ^c
6		(PhO) ₃ P (2)	0→r.t.	72	14	1300	1.12
7		Ph ₃ P (2)	0→r.t.	47	16	1000	1.02
8		Ph ₃ P (1)	0→r.t.	overnight	100	15700, 6200 ^d	—

^a [1]/[Ni]=50. The polymer yield was quantitative when the conversion of **1** was 100%. ^b GPC (polystyrene standard, eluent CHCl₃). ^c x:y=4:96 (run 4) and 3:97 (run 5), calculated on the basis of ¹H NMR spectra. ^d Molecular weight of the peak tops on the bimodal GPC profile.



Scheme 3. The speculated mechanism of deactivation of the propagating end when $[(\pi\text{-allyl})\text{Ni}(\text{OCOCF}_3)_2]$ was used.

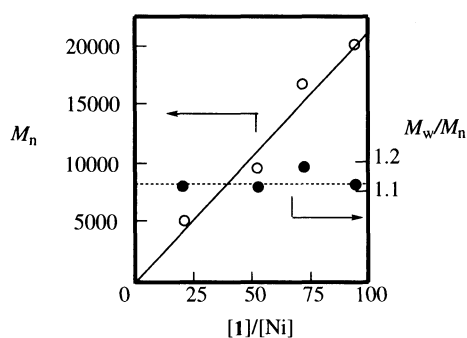


Figure 1. M_n and M_w/M_n vs. the feed ratio of **1** to $(\pi\text{-allyl})\text{NiBr}/2\text{Ph}_3\text{As}$.

other hand, the addition of Ph_3P or $(\text{PhO})_3\text{P}$ in 2 equiv. for Ni considerably retarded the polymerization (runs 6 and 7), which could be due to the stronger coordination power of the phosphine ligand that hinders the coordination of **1** to nickel for the polymerization. When the amount of Ph_3P was reduced to 1 equiv. for Ni, **1** was completely converted (run 8). However, the produced polymer showed a bimodal GPC profile, suggesting that there were two kinds of propagating species.

The living character of the polymerization conducted with the $(\pi\text{-allyl})\text{NiBr}/2\text{Ph}_3\text{As}$ system was supported by experiments varying the monomer-initiator feed ratio (Figure 1). The molecular weight linearly increased with increasing feed ratio $[1]/[\text{Ni}]$, and the M_w/M_n values were almost constant throughout. Figure 2 shows the ^1H NMR spectra of the polymer produced by this living system. There appeared small signals due to the 1,2-polymerization (x) unit along with much bigger signals due to the 2,3-polymerization (y) unit. As shown at the foot note of Table I, the unit ratio of x to y was calculated on the basis of the integral ratio of these signals. The y unit having the allylsilane structure was contained over 95%.

The Polymerization of **2** (Scheme 4)

According to the above study, the polymerization of **2** was

Table II. Polymerization of (*t*-butyldimethylsilyloxy)allene **2**^a

Run	L	$[2]/[\text{Ni}]$	Temp. °C	Time h	M_n^b	M_w/M_n^b	x:y ^c
9	none	21	0	0.5	20800	2.25	0:100
10	none	22	-90→r.t.	3	54900	1.61	0:100
11	Ph_3As	49	0→r.t.	overnight	93000	1.67	0:100
12	Ph_3P	26	0	6	5600	1.17	32:68
13	$(\text{PhO})_3\text{P}$	45	0→r.t.	overnight	7000	1.10	23:77

^a Ni catalyst: $[(\pi\text{-allyl})\text{NiBr}]_2$. $[\text{L}]/[\text{Ni}] = 2$. In all runs, **2** was quantitatively converted to the polymer. ^b GPC (polystyrene standard, eluent CHCl_3).

^c Calculated on the basis of ^1H NMR spectra.

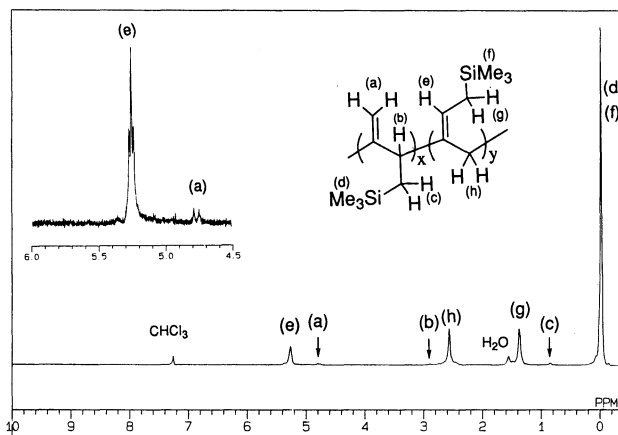
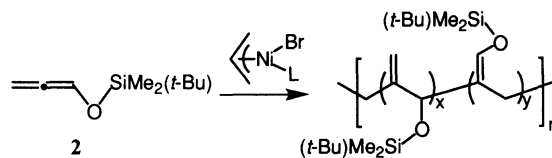


Figure 2. The ^1H NMR spectrum of the polymer produced from **1** at run 5 in Table I.

also investigated by using $[(\pi\text{-allyl})\text{NiBr}]_2$. In contrast to **1**, the controllable polymerization of **2** was achieved by the addition of Ph_3P or $(\text{PhO})_3\text{P}$ to yield the polymer having a narrow molecular weight distribution quantitatively (Table II, runs 12 and 13). This is reasonably ascribable to the higher coordination ability of **2** that is the more electron-rich allene than **1**. In this system, when **2** was sequentially fed to the first polymerization mixture, the GPC elution profile of the product polymer clearly shifted to the higher molecular weight region, which suggested the living character of the polymerization. In contrast, without the above two ligands or with Ph_3As , the efficiency of the initiator was much reduced to produce the high molecular weight polymers having relatively broad molecular weight distributions (runs 9–11). It is noteworthy that the polymer structures produced in the absence of the phosphine ligands (runs 9–11) were different from those produced in the presence of them (runs 12–13), which was clearly revealed by the ^1H NMR spectra (Figures 3 and 4). The former exclusively consisted of the 2,3-polymerization unit having the silyl enol ether moiety, while the latter contained both of the 1,2- and 2,3-polymerization units. A similar selectivity depending on the ligand was previously observed in the polymerization of alkoxyallene.² It is clear that the 2,3-polymerization is predominant in the steric aspect. However, the electronic



Scheme 4.

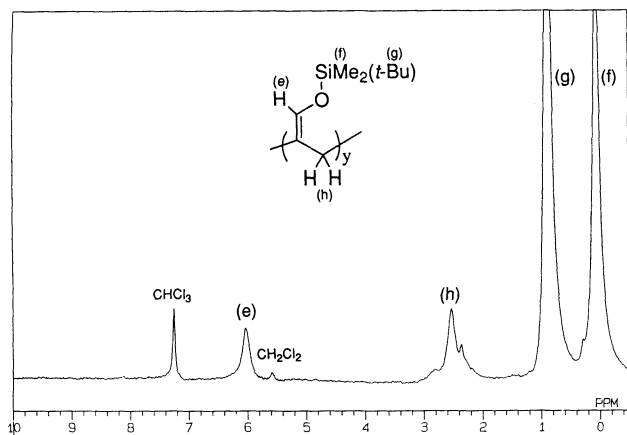


Figure 3. The ^1H NMR spectrum of the polymer produced from **2** at run 9 in Table II.

effect of the π -allylnickel complex on the selectivity has not been disclosed yet.

The polymers obtained in this study consist of the allylsilane or silyl enol ether moieties. The transformation of these groups is now under investigation.

Acknowledgment. The authors appreciate the financial support by Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/09246102), from The Ministry of Education, Science, Sports and Culture, Japan.

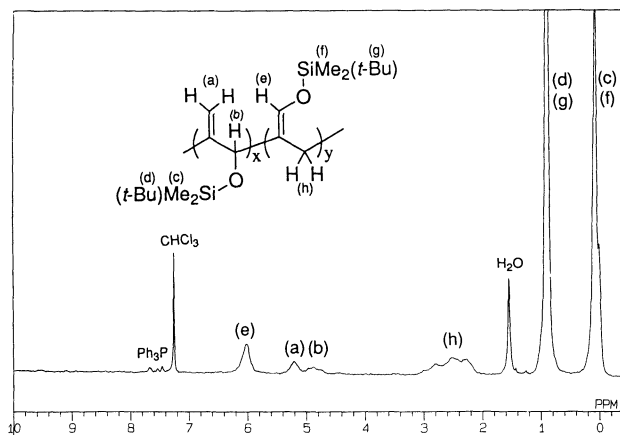


Figure 4. The ^1H NMR spectrum of the polymer produced from **2** at run 12 in Table II.

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5. The concentration of nickel was determined by the chelate titration. The supernatant (5 ml) of the toluene solution of $\text{Ni}(\text{COD})_2$ was evaporated to dryness. The residue was dissolved in 1 M HCl aq. and neutralized with NH_3 aq. The resulting solution was diluted with water in a 50 ml volumetric flask and titrated three times by 0.01 M EDTA-2Na aq. in the presence of murexide as the indicator.