

## Design and Synthesis of Polymerizable Cumulated Double Bond System. -Living Coordination Polymerization of Alkylallenes by $\pi$ -Allylnickel Catalyst-

Takeshi Endo\*, Koji Takagi, and Ikuyoshi Tomita

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226, Japan

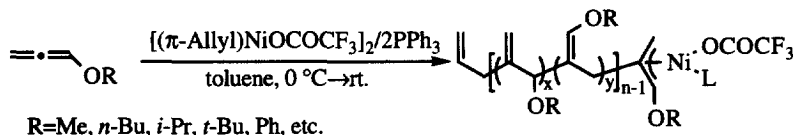
**Abstract:** The coordination polymerization of monoalkylallenes (**2a**; 1,2-nonadiene, **2b**; 1,2-heptadiene, **2c**; cyclohexylallene, **2d**; *t*-butylallene) was carried out by  $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$  (**1**). The polymerization was found to proceed through a living process without any side reactions to yield soluble polymers in high yields, where the resulting polymers had predictable molecular weights and narrow molecular weight distributions. The coordination polymerization of dialkylallene (**2e**; 3-methyl-1,2-nonadiene, **2f**; 2,3-nonadiene) was also carried out to obtain soluble polymers, although the polymerization rate of **2f** was found to be considerably low compared with those of monoalkylallenes. © 1997 Elsevier Science Ltd.

### INTRODUCTION

Development of a living polymerization system is one of the most attractive and important research fields in polymer synthetic chemistry, because it provides a promising route for well-defined polymers with predictable molecular weights and narrow molecular weight distributions. Block copolymers, telechelic polymers, macromonomers, star polymers, etc. could be also designed by using living techniques. For the last decade, numerous kinds of living polymerization methods have been reported including the ionic<sup>1</sup>, the coordination<sup>2</sup>, and the radical<sup>3</sup> polymerization, by which versatile monomers have become available for the living polymerizations. However, each of the reported living polymerization methods has a strict limitation on the monomer substituents. The lack of the diversity of monomer types in the living system causes a crucial problem for applications to macromolecular designs such as block copolymerizations. Accordingly, it is desirable to develop a novel living polymerization system tolerant of the monomer substituents. In particular, it is of importance to construct a living polymerization system which can afford reactive polymers with controlled architecture (i.e., molecular weight, molecular weight distribution, and stereoregularity), because they could be converted to various functional materials by their subsequent polymer reactions such as addition reactions toward reactive groups.

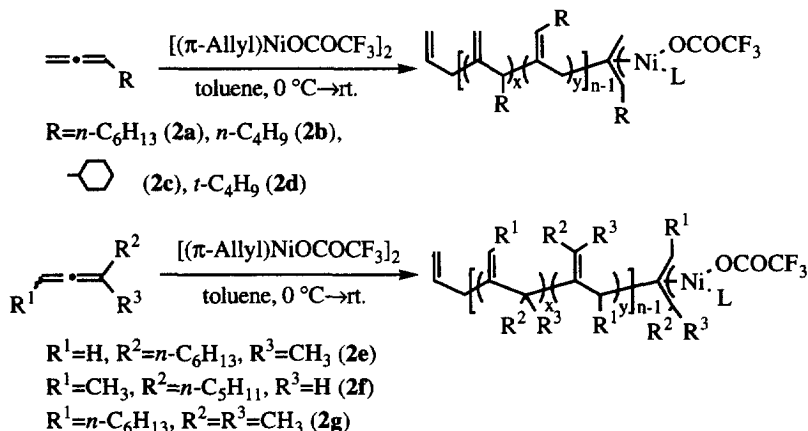
Recently, we have developed a living coordination polymerization of alkoxyallenes by  $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2/2\text{PPh}_3$  system. The coordination polymerization proceeds under mild conditions to give polymers in high yields, whose molecular weights can be controlled by the feed ratios of monomer to initiator and molecular weight distributions are always narrow ( $< 1.1$ ) (Scheme 1).<sup>4</sup> The obtained polymers were soluble in organic solvents and were consisted both of 1,2- and 2,3-polymerization unit (ca. 3:7) and the double bonds in the polymer chain could be detected completely. Because the propagating end of the polymerization is stable under nitrogen atmosphere, block copolymers of various alkoxyallenes<sup>5</sup> and those of alkoxyallenes with

isocyanides<sup>6</sup> have been obtained by the two-stage copolymerization of the allene monomers with the corresponding monomers. To demonstrate the reactivity of poly(allene)s, we have independently reported some polymer reactions of poly(allene)s.<sup>7</sup>



Scheme 1.

Herein, the coordination polymerization of various alkylallenes (**2a–2g**) was carried out with  $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$  (**1**) as an initiator to examine the effect of the monomer substituents on the polymerization behavior (e.g., the number and the position of the substituents) and to increase the number of monomers adaptable to the living polymerization of allene derivatives (Scheme 2).



Scheme 2.

## RESULTS AND DISCUSSION

*Coordination Polymerizations of 1,2-Nonadiene (2a) by  $[(\pi\text{-Allyl})\text{NiOCOCF}_3]_2$  (1).* The coordination polymerization of **2a** (100 equiv. relative to **1**) was carried out by **1** in toluene at 0 °C to ambient temperature. As a result, **2a** was consumed quantitatively within several hours to obtain a polymer ( $M_n=11,100$ ,  $M_w/M_n=1.05$ ) in 96 % yield after precipitation with H<sub>2</sub>O/MeOH ( $v/v=1/1$ ). By the polymerization under various feed ratios of **[2a]**/**[1]**, the polymers with narrow molecular weight distributions were obtained in high yields regardless of the feed ratio and a good linear relationship between the molecular weight of the resulting polymer and the monomer feed ratio was obtained (Figure 1).

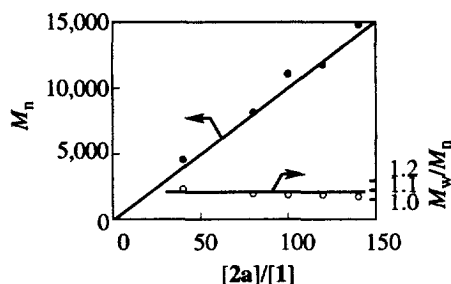


Figure 1.  $M_n$  and  $M_w/M_n$  vs. the feed ratio ( $[2a]/[1]$ ).

The relationship between the monomer conversion and the molecular weight of the resulting polymer was elucidated by GC and GPC under the condition of  $[2a]/[1]=80$ . The molecular weight of the resulting polymer was found to increase linearly as the increase of the monomer conversion, while the molecular weight distribution was constantly narrow ( $\cong 1.1$ ) (Figure 2).

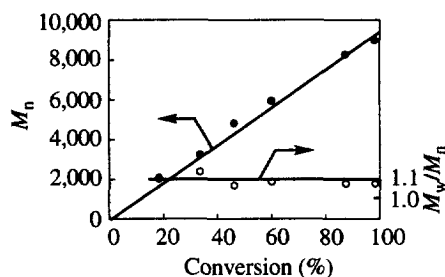
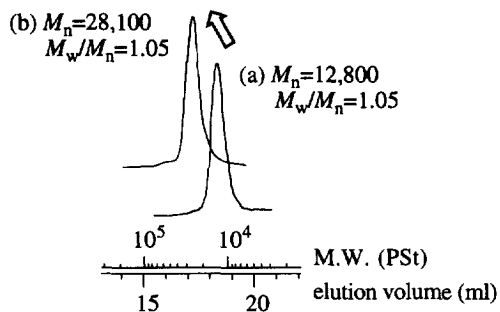


Figure 2.  $M_n$  and  $M_w/M_n$  vs. the conversion of **2a** ( $[2a]_0=2.0$  M,  $[1]_0=0.025$  M).

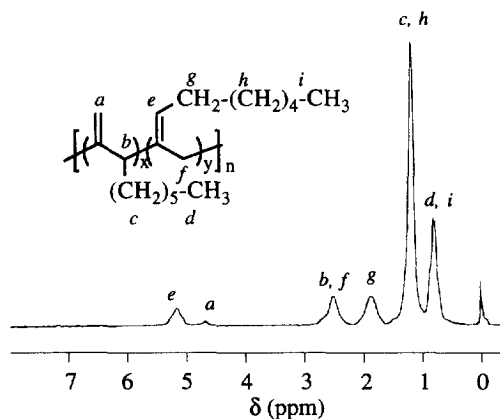
Consequently, the coordination polymerization of **2a** by **1** may be strongly supported to proceed through a living process. The monomer conversion was followed under the condition of  $[2a]_0/[1]=40$  at  $0^\circ\text{C}$  (see Figure 7). As a result, the present polymerization was found to proceed following the first order kinetics of the monomer concentration (equation 1), from which the kinetic coefficient of **2a** was determined as  $33.2\text{ l}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ , which was comparable to that of phenylallene ( $34.4\text{ l}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ ).<sup>8</sup>

To evaluate the stability of the propagating end of the polymerization, the living polymer solution obtained by the polymerization of **2a** (100 equiv.) was kept at ambient temperature for 1 day under nitrogen atmosphere, to which 100 equiv. of **2a** was added again to re-initiate the polymerization. As a result, the monomer consumed quantitatively and the elution peak of the resulting polymer shifted completely to the higher molecular weight region without broadening of the molecular weight distribution in GPC (Figure 3). Therefore, the propagating end of the polymer, the allylnickel species, was confirmed to be stable enough under the examined conditions.



**Figure 3.** GPC traces of poly(**2a**) produced by the reaction of 100 equiv. of **2a** by **1** (a) and that obtained by the further polymerization of 100 equiv. of **2a** (b).

From the  $^1\text{H}$  NMR spectrum, the obtained polymer was found to contain both 1,2- and 2,3-polymerized unit (Figure 4). The ratio of 1,2- to 2,3-polymerization was estimated as 91:9 on the basis of the integral ratio of the peaks for double bonds (5.09 and 4.60 ppm, for 1,2- and 2,3-polymerized unit, respectively). The double bonds on the polymer backbone were observed quantitatively by the comparison of the integral ratios of the protons of double bonds to those of the other aliphatic protons.



**Figure 4.**  $^1\text{H}$  NMR spectrum of poly(**2a**).

*Coordination Polymerization of 1,2-heptadiene (2b), cyclohexylallene (2c), and t-butylallene (2d) by 1.* The coordination polymerization of **2b-2d** (100 equiv. relative to **1**) was also carried out in toluene using **1** as an initiator. The polymerization proceeded homogeneously to obtain polymers with narrow molecular weight distributions in high yields (Table 1). No significant difference in the polymerization rate was observed in these monoalkylallenes.

**Table 1.** Coordination Polymerization of **2a-2d** by **1**<sup>a</sup>.

run	<b>2</b>	yield (%) <sup>b</sup>	$M_n$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	x : y ratio <sup>d</sup>
1	<b>2a</b>	96	11,100	1.05	9 : 91
2	<b>2b</b>	99	11,500	1.07	9 : 91
3	<b>2c</b>	93 <sup>e</sup>	11,300	1.05	8 : 92
4	<b>2d</b>	98	10,200	1.05	0 : 100

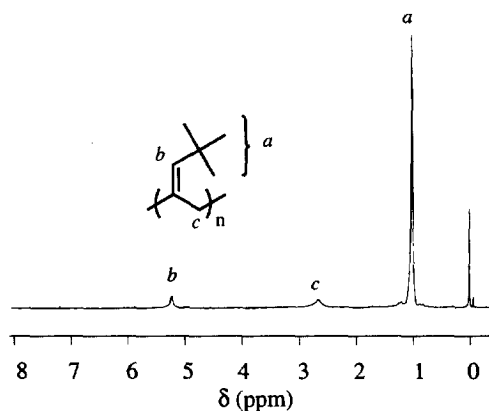
a) Conditions ; [1]= $2.0 \times 10^{-2}$  mol, [2]<sub>0</sub>/[1]=100, at 0 °C→rt., for 24 h, in toluene.

b) Isolated yield after the precipitation with H<sub>2</sub>O/MeOH (v/v=1/1).

c) Estimated by GPC (THF, PSt Std). d) Determined by <sup>1</sup>H NMR.

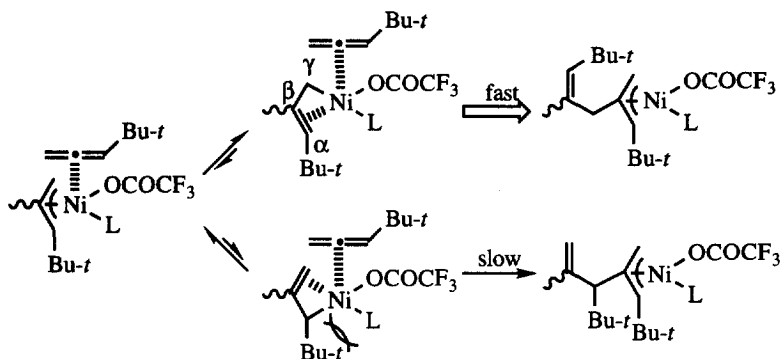
e) Isolated yield after the precipitation with MeOH.

From the <sup>1</sup>H NMR spectra of the resulting polymers, the proportion of the 1,2-polymerization was found to increase a little as the increase of the bulkiness of the substituents. The results are in good accordance with the previously reported ones obtained from various alkoxyallenes, in which sterically hindered substituents reduced the polymerization at the substituted olefinic part. Especially in the case of poly(**2d**), no peak assignable to the *exo*-methylene moiety in the 2,3-polymerized unit was observed at 4.7 ppm (Figure 5). The selective 1,2-polymerization is probably due to the steric repulsion of the *tert*-butyl group on the propagating end. That is, the coordinated monomer inserts specifically into the  $\gamma$ -carbon-nickel bond in the case of **2d** (Scheme 3).



**Figure 5.** <sup>1</sup>H NMR spectrum of poly(**2d**) (Table 1, run 4).

*Coordination Polymerization of 3-Methyl-1,2-nonadiene (2e), 2,3-Nonadiene (2f), and 2-Methyl-2,3-decadiene (2g) by 1.* The coordination polymerization of **2e-2g** (100 equiv. relative to **1**) was carried out similar to the case of monoalkylallenes. Although it required much longer reaction times for the complete consumption of the monomers, the polymerizations of **2e** and **2f** proceeded completely to produce soluble polymers with narrow



Scheme 3.

molecular weight distributions ( $< 1.1$ ) in high yields. On the other hand, no polymerization took place in the case of **2g** even at higher polymerization temperature (e.g., 40 °C) (Table 2).

Table 2. Coordination Polymerization of **2e-2g** by **1**<sup>a</sup>.

run	<b>2</b>	yield (%) <sup>b</sup>	$M_n^c$	$M_w/M_n^c$	x : y ratio <sup>d</sup>
1	<b>2e</b> <sup>e</sup>	93	10,700	1.06	0 : 100
2	<b>2f</b> <sup>f</sup>	100	10,500	1.08	45 : 55
3	<b>2g</b>	0	-	-	-

a) Conditions :  $[1]=2.0 \times 10^{-2}$  mol,  $[2]_0/[1]=100$ , at 0 °C  $\rightarrow$  rt., in toluene.

b) Isolated yield after the precipitation with H<sub>2</sub>O/MeOH (v/v=1/1).

c) Estimated by GPC (THF, PSt Std). d) Determined by <sup>1</sup>H NMR.

e) Polymerization was carried out for 2 days.

f) Polymerization was carried out for 7 days.

As expected from the monomer structure of **2f**, which possesses primary alkyl groups on both sides, both the units from the polymerization of the 2,3- and 3,4-double bonds were observed in the <sup>1</sup>H NMR spectrum of poly(**2f**), while **2e** was found to undergo the specific 1,2-polymerization (Figure 6). The specific 1,2-polymerization of **2e** can be also explained by the steric effect originated from  $\alpha,\alpha$ -dialkyl groups, similar to the case of **2d**.

The polymerization rates of these monomers were evaluated by the monomer consumption curves under the condition of  $[2]_0/[1]=40$  as mentioned above (Figure 7). All polymerization's were found to proceed following the first order kinetics of the monomer concentration (see, equation 1), from which the kinetic coefficients for **2e** and **2f** were determined as 8.0 and 0.8 l $\cdot$ mol<sup>-1</sup> $\cdot$ h<sup>-1</sup>, respectively. Obviously, the polymerization of  $\alpha,\gamma$ -dialkylallene (**2f**) was found to proceed much slower than that of the monoalkylallene (**2a**) by ca. 40 times, while the difference was not significant in the case of  $\alpha,\alpha$ -dialkylallene (**2e**). These results may probably suggest that the introduction of the substituent at both  $\alpha$ - and  $\gamma$ -position makes the monomer insertion more difficult (Scheme 4), while  $\alpha,\alpha$ -dialkyl and monoalkylallenes have less hindered  $\gamma$ -position for the monomer insertion process.

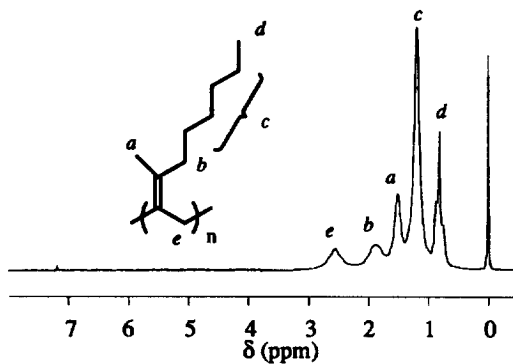


Figure 6.  $^1\text{H}$  NMR spectrum of poly(2e). (Table 2, run 1).

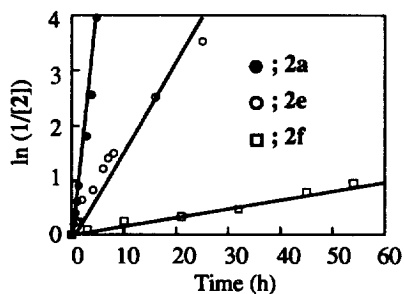
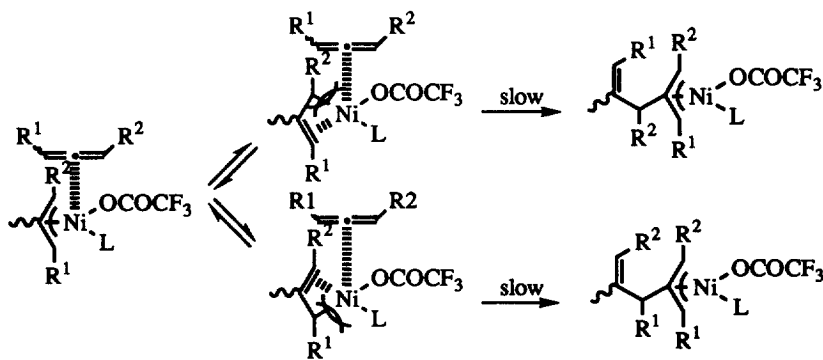


Figure 7. Time vs.  $\ln(1/[2])$  curves of 2a, 2e, and 2f ( $[2]_0=1.0\text{ M}$ ,  $[2]_0/[1]=40$ ).



Scheme 4.

## CONCLUSIONS

The coordination polymerization of monoalkylallenes (**2a-2d**) by  $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$  was found to proceed through a living process. The molecular weight of the obtained polymers could be controlled by the feed ratio of  $[2]/[1]$  and the molecular weight distributions were constantly narrow. The propagating end of the polymer (i.e., allylnickel species) was found to be quite stable under nitrogen atmosphere. The polymers from monoalkylallenes had the 1,2-polymerized unit predominantly and the population of the 1,2-polymerization increased as the bulkiness of the substituent increased. The coordination polymerization of dialkylallenes (**2e-2f**) also proceeded successfully to produce polymers with narrow molecular weight distribution. However, the polymerization rate was largely effected by the position of the substituent. Namely, the polymerization rate of  $\alpha,\alpha$ -dialkylallene is larger than  $\alpha,\gamma$ -isomer.

## EXPERIMENTAL SECTION

**Materials and Instruments.** Propargyl methyl ether was prepared from propargyl alcohol according to the previously reported method<sup>9</sup>. **2b** was obtained by the reaction of propargyl methyl ether with *n*-butylmagnesium chloride in the presence of catalytic amount of CuBr as described previously (23.5 % yield, 45-49 °C/100 mmHg) (lit.<sup>10</sup>, 105 °C/760 mmHg). **2c** was obtained similarly from cyclohexylmagnesium chloride (10.7 % yield, 53-55 °C/17 mmHg) (lit.<sup>10</sup> 55 °C/ 17 mmHg). **2d** was obtained by the reaction of propargyl chloride with *t*-butylmagnesium chloride in the presence of catalytic amount of CuBr as described previously (20.4 % yield, 79-81 °C/760 mmHg) (lit.<sup>11</sup> 79-82 °C/760 mmHg). The initiator (i.e.,  $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$ ) was prepared from bis(1,5-cyclooctadiene)nickel ( $\text{Ni}(\text{cod})_2$ ) and equimolar amount of allyltrifluoroacetate under nitrogen atmosphere and was used without isolation. Diethyl ether, toluene, and tetrahydrofuran (THF) were dried over sodium and distilled under nitrogen before use. 1-Chlorobutane, 1-chlorohexane, cyclohexyl chloride, *t*-butyl chloride, methyltriphenylphosphonium bromide, 2-octanone, 2-octene, 3-chloro-3-methyl-1-butyne, bromoform, sodium hydroxide, and other reagents (for precipitations and analyses) were used as received. All the reactions for monomer synthesis and polymerization were carried out under nitrogen.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL EX-90 or a JEOL EX-400 instrument (tetramethylsilane as an internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. Gel permeation chromatographic analyses were carried out on a HLC-8020 (TSK gel G2500H<sub>XL</sub>, G3000H<sub>XL</sub>, G4000H<sub>XL</sub>, and G5000H<sub>XL</sub>, THF as an eluent) or on a SPD-6A (TSK gel G4000H<sub>XL</sub>, CHCl<sub>3</sub> as an eluent) on the basis of standard polystyrene samples. Gas chromatographic analyses were performed on a Shimadzu GC-4A equipped with a FID detector using *n*-tetradecane as an internal standard (SE-30, 1 m, gradient temperature of 80 °C to 230 °C, 10 °C/min).

### Monomers:

**Synthesis of 2a.** To a mixture of propargyl methyl ether (29.4 g, 0.42 mol), CuBr (0.20 g, 1.40 mmol) and diethyl ether (60 ml) placed in a three necked flask equipped with a mechanical stirrer and a dropping funnel, was added *n*-hexylmagnesium chloride (obtained from 56.7 g (0.47 mol) of 1-chlorohexane) from a dropping funnel at 0 °C (it required ca. 30 min). After stirring for further 30 min at that temperature, the reaction mixture was poured into a mixture of excess cold NH<sub>4</sub>Cl aq and hydrochloric acid. The mixture was extracted three times with diethyl ether and the combined organic layer was dried over MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, diethyl ether) followed by distillation (77-78 °C/52 mmHg) to give 1,2-nonadiene (**2a**) in 62.4 % yield (32.5 g, 0.26 mol); <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm) 0.89 (-CH<sub>3</sub>, t, 3H, *J*=6.2Hz), 1.13-1.60 (- (CH<sub>2</sub>)<sub>4</sub>-, 8H), 2.00 (=C-CH<sub>2</sub>-, m, 2H), 4.60 (H<sub>2</sub>C=C=, m, 2H), 5.09 (-CH=C=, m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm) 14.1, 22.6, 28.3, 28.8, 29.1, 31.7, 74.5, 90.1, 208.5; IR (neat, cm<sup>-1</sup>) 2926, 2857, 1958, 1688, 1379, 1343, 1312, 1109.



**Synthesis of 2e and 2f.** To a mixture of 2-methyl-1-octene (19.6 g, 0.16 mol, obtained from 25.6 g (0.20 mol) of 2-octanone and 71.4 g (0.20 mol) of methyltriphenylphosphonium bromide), bromoform (78.6 g, 0.31 mol), and tetrabutylammonium bromide (0.16 g, 0.51 mmol), was added dropwise a solution of sodium hydroxide (77.5 g, 1.90 mol) in 90 ml of water at ambient temperature (it required ca. 1.5 h). After pouring the reaction mixture into the excess amount of water, the mixture was extracted three times with diethyl ether and the combined organic layer was dried over MgSO<sub>4</sub>. The crude dibromocyclopropane derivative obtained by the evaporation was used for the following reaction without further purification. To a solution of the dibromocyclopropane (44.6 g, 0.15 mol) in diethyl ether (75 ml), was added dropwise *n*-butyllithium in *n*-hexane (1.66 N, 90 ml, 0.15 mmol) at -50 °C (it required ca. 1 h). After stirring for additional several hours at that temperature, the reaction mixture was poured into cold saturated NH<sub>4</sub>Cl aq. The mixture was extracted three times with diethyl ether and the combined organic layer was dried over MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, *n*-hexane) followed by distillation (74-75 °C/25 mmHg) to give 3-methyl-1,2-nonadiene (**2e**) in 62.9 % yield (13.1 g, 0.09 mol); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.88 (-C-CH<sub>3</sub>, t, 3H, *J*=6.2Hz), 1.10-1.60 (-(CH<sub>2</sub>)<sub>4</sub>-, 8H), 1.67 (=C-CH<sub>3</sub>, t, 3H, *J*=3.1Hz), 1.93 (=C-CH<sub>2</sub>-, br, 2H), 4.57 (H<sub>2</sub>C=C=, m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 14.1, 18.7, 22.6, 27.4, 28.9, 31.7, 33.5, 73.7, 98.5, 206.2; IR (neat, cm<sup>-1</sup>) 2957, 2928, 2859, 1962, 1697, 1460, 1377, 1153. 2,3-Nonadiene (**2f**): 67.4 % yield; 78-79 °C/63 mmHg; <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.89 (-C-CH<sub>3</sub>, t, 3H, *J*=5.6Hz), 1.05-1.50 (-(CH<sub>2</sub>)<sub>3</sub>-, 6H), 1.64 (=C-CH<sub>3</sub>, m, 3H), 1.97 (=C-CH<sub>2</sub>-, m, 2H), 5.02 (-CH=C=CH-, m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 14.1, 14.6, 22.5, 28.8, 31.3, 85.3, 90.4, 204.7; IR (neat, cm<sup>-1</sup>) 2959, 2928, 2859, 1966, 1460, 1373, 1279.

**Synthesis of 2g.** To a flask containing PdCl<sub>2</sub> (1.73 g, 9.70 mmol) and PPh<sub>3</sub> (5.09 g, 19.4 mmol), diisobutylaluminum hydride (1.73 g, 9.70 mmol) was added dropwise at room temperature. After stirring the reaction mixture for further 30 min, 3-chloro-3-methyl-1-butyne (9.95g, 0.097mol) was added dropwise in ca. 30 min. Then *n*-hexylmagnesium chloride (0.23 mol, obtained from 18.0 g (0.15 mol) of *n*-hexyl chloride) in THF (70 ml) was added from a dropping funnel at 0 °C (it required ca. 1 h). After stirring for further 30 min at that temperature, the reaction mixture was poured into the mixture of excess cold NH<sub>4</sub>Cl aq and hydrochloric acid. The mixture was extracted several times with diethyl ether and the combined organic layer was dried over MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, diethyl ether) followed by distillation (74-77 °C/12 mmHg) to give 2-methyl-2,3-decadiene (**2g**) in 38.3 % yield (5.60 g, 0.04 mol); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.88 (-CH<sub>3</sub>, t, 3H, *J*=6.2Hz), 1.13-1.60 (-(CH<sub>2</sub>)<sub>4</sub>-, 8H), 1.67 (=C-CH<sub>3</sub>, d, 6H, *J*=2.9Hz), 2.00 (=C-CH<sub>2</sub>-, m, 2H), 4.93 (-CH=C=, m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 14.1, 20.8, 22.7, 28.7, 29.2, 31.8, 88.8, 94.7, 201.7; IR (neat, cm<sup>-1</sup>) 2959, 2926, 2857, 1970, 1453, 1377, 1364, 1231, 1190.

**Coordination Polymerization (Typical Procedure).** To a flask containing a 1.00 ml toluene solution of **1** (2.0x10<sup>-2</sup> mmol) and a magnetic stirrer bar, **2a** (0.124 g, 1.00 mmol, 50 equiv. relative to **1**) was added at 0 °C and the mixture was kept stirring at ambient temperature. After the complete conversion of **2a** in gas chromatography (it required ca. 6 h), the solvent was removed under the reduced pressure and the viscous product was dissolved in THF (2 ml) and was precipitated with H<sub>2</sub>O/MeOH (v/v=1/1) (100 ml) to give poly(**2a**) in 100 % yield (0.124 g, 1.00 mol); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.87 (-CH<sub>3</sub>, br, 3H), 1.05-1.65 (-(CH<sub>2</sub>)<sub>4</sub>-, >C-CH<sub>2</sub>-, 8H+2Hx0.09), 1.65-2.25 (=C-CH<sub>2</sub>-, 2Hx0.91), 2.25-3.10 (=C-CH<sub>2</sub>-C=, >CH-, 2Hx0.91+1Hx0.09), 4.78 (=CH<sub>2</sub>, br, 2Hx0.09), 5.24 (=CH-C-, br, 1Hx0.91); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 14.1, 22.8, 28.2, 29.3, 30.2, 32.0, 37.8, 127.0, 134.1; IR (neat, cm<sup>-1</sup>) 2957, 2926, 2855, 1638, 1460, 1377, 1231, 1157.

**Poly(2b):** 99 % yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.87 (-CH<sub>3</sub>, br, 3H), 1.05-1.65 (-(CH<sub>2</sub>)<sub>2</sub>-, >C-CH<sub>2</sub>-, 4H+2Hx0.09), 1.65-2.25 (=C-CH<sub>2</sub>-, 2Hx0.91), 2.25-3.10 (=C-CH<sub>2</sub>-C=, >CH-, 2Hx0.91+1Hx0.09), 4.78 (=CH<sub>2</sub>, br, 2Hx0.09), 5.24 (=CH-C-, br, 1Hx0.91); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 14.1, 22.7, 27.8, 29.1, 32.2, 37.8, 126.9, 133.9; IR (neat, cm<sup>-1</sup>) 2957, 2926, 2859, 1638, 1464, 1377, 1231, 1157.

**Poly(2c):** 93 % yield; <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm) 0.40-2.30 (-C<sub>6</sub>H<sub>11</sub>, 11H), 2.25-3.10 (=C-CH<sub>2</sub>-C=, >CH-, 2Hx0.92+1Hx0.08), 4.88 (=CH<sub>2</sub>, br, 2Hx0.08), 5.05 (=CH-C-, br, 1Hx0.92); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm) 21.1, 25.6, 26.1, 30.3, 31.9, 33.6, 34.2, 36.9, 37.7, 128.3, 133.3; IR (neat, cm<sup>-1</sup>) 2922, 2849, 2666, 1636, 1447, 1375, 1350, 1262, 1213.

**Poly(2d):** 98 % yield;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 1.00 ( $-(\text{CH}_3)_3$ , br, 9H), 2.65 ( $=\text{C}-\text{CH}_2-\text{C}=\text{C}$ , br, 2H), 5.21 ( $=\text{CH}-\text{C}-$ , br, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 14.1, 22.7, 25.6, 31.4, 32.6, 40.1, 133.0, 137.5; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2905, 2866, 1647, 1464 1433, 1362, 1259, 1200.

**Poly(2e):** 93 % yield;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 0.89 ( $-\text{CH}_3$ , br, 3H), 1.10-1.51 ( $-(\text{CH}_2)_4-$ , 8H), 1.58 ( $=\text{C}-\text{CH}_3$ , br, 3H), 1.98 ( $=\text{C}-\text{CH}_2-$ , br, 2H), 2.66 ( $=\text{C}-\text{CH}_2-\text{C}=\text{C}$ , br, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 14.2, 19.5, 22.8, 28.3, 30.2, 32.0, 33.7, 35.5, 129.8, 132.0; IR (neat,  $\text{cm}^{-1}$ ) 2959, 2926, 2857, 1522, 1458, 1157.

**Poly(2f):** 100 % yield;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 0.30-1.00 ( $-\text{CH}_3$ , 3H+3Hx0.55), 1.00-1.45 ( $-(\text{CH}_2)_3-$ ,  $-(\text{CH}_2)_4-$ , 6Hx0.55+8Hx0.45), 1.45-1.90 ( $=\text{C}-\text{CH}_3$ , 3Hx0.45), 1.90-2.40 ( $=\text{C}-\text{CH}_2-$ , 2Hx0.55), 2.40-3.65 ( $>\text{CH}-$ , 1H), 5.00-5.90 ( $=\text{CH}-$ , 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 14.1, 21.2, 30.3, 32.1, 34.2, 128.3, 135.8; IR (neat,  $\text{cm}^{-1}$ ) 2957, 2926, 2857, 2253, 1640, 1377, 1262, 1233, 1157.

**Estimation of the Kinetic Coefficient (Typical Procedure).** The polymerization of **2a** ( $[\mathbf{2a}]_0=1.0\text{ M}$ ,  $[\mathbf{1}]=0.025\text{ M}$ ) was performed in toluene containing *n*-tetradecane (0.038M) as an internal standard at  $0^\circ\text{C}$  similar to the above mentioned procedure. After the designated reaction period at  $0^\circ\text{C}$ , a small portion of the reaction mixture was sampled up by the syringe (ca, 10  $\mu\text{l}$ ) and the monomer conversion was estimated by GC analyses.

## REFERENCES AND NOTES

- For the review, see, for example: (a) Sawamoto, M. *Petrotech (Tokyo)* **1996**, *19*, 814. (b) Aida, T. *Petrotech (Tokyo)* **1996**, *19*, 811, and references cited therein.
- (a) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664. (b) Schllard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (c) Schrock, R. R.; Luo, S.; Lee, J. C., Jr; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3383. (d) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 1906. (e) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633, and see also the review in ref. 1.
- (a) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070. (b) Chung, T. C.; Janvikul, W.; Lu, H. L. *J. Am. Chem. Soc.* **1996**, *118*, 705. (c) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (d) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722. (e) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S. *Macromolecules* **1995**, *28*, 2093, and for the review, see, for example: (a) Matyjaszewski, K. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 769. (b) Sawamoto, M.; Kamigaito, M. *Trends in Polym. Sci.* **1996**, *4*, 371, and references cited therein.
- (a) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413. (b) *idem*, *Acta Polymerica* **1995**, *46*, 432.
- Tomita, I.; Abe, T.; Takagi, K.; Endo, T. *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 2487.
- Tomita, I.; Taguchi, M.; Takagi, K.; Endo, T. *J. Polym. Sci.: Part A: Polym. Chem.* in press.
- (b) Aggour, Y. A.; Tomita, I.; Endo, T. *J. Polym. Sci.: Part A: Polym. Chem.*, **1994**, *32*, 1991. (b) Tomita, I.; Igarashi, T.; Endo, T. *J. Jpn. Soc. Colour Mater. (SHIKIZAI)* **1994**, *67*, 754.
- (a) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* submitted. (b) *idem*, *Polym. Prepr. Jpn.* **1995**, *44*, 1296.
- (a) Roppe, W. *Ann. Chem.* **1955**, *74*, 596. (b) Hoff, S.; Brandsma, L.; Arens, J. K. *Trav. Chim. Pays-Bas* **1968**, *87*, 916.
- Moreau, J.-L.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *108*, 159.
- Brandsma, L.; Verkruisje, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Brandsma, L.; Verkruisje, H. D., Ed.; Elsevier: New York, 1984.

(Received 29 April 1997; revised 19 June 1997; accepted 1 August 1997)