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A Novel Living Coordination Polymerization of Phenylallene Derivatives by π-Allylnickel Catalyst

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ABSTRACT: Coordination polymerizations of *para*-substituted phenylallenes (**2a**−**2e**) were carried out by using [(π-allyl)NiOCOCF$_3$]$_2$ (**1**) as an initiator. The polymerizations were found to proceed through a living mechanism to yield polymers exclusively composed of 2,3-polymerized units in high yields, where the resulting polymers have predictable molecular weights and narrow molecular weight distributions. From kinetic studies, the polymerization rate was found to increase with the electron-donating character of the *para* substituent in **2**. The coordination polymerizations of α-methylphenylallene (**2f**) and γ-methylphenylallene (**2g**) were also carried out to produce soluble polymers. In these cases, the methyl substituent on the allene moiety (especially at the γ-position) was found to reduce the polymerizability. A plausible polymerization mechanism was also discussed based on the results obtained in the study.

Introduction

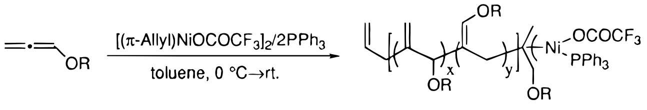
Reactive polymers are important synthetic precursors for various kinds of the functional materials by the subsequent polymer reactions. The versatility of the polymer reactions has made it possible to construct desired functional materials for application. Because the applicable polymer reactions are very much dependent on the character (i.e., the reactivity) of the functional groups in the starting polymers, it is desirable to develop a new type of reactive polymer bearing various reactive moieties. Among the reactive polymers known, polymers bearing unsaturated systems such as polybutadiene are some of the most attractive synthetic precursors for the functional materials because of the versatility of the addition reactions toward double bonds.[1]

It is preferable to control the synthesis of reactive polymers, since many of the properties such as molecular weights, molecular weight distributions, and stereoregularities of the main chain cannot be changed by the polymer reactions such as addition reactions toward the reactive groups.

The polymerization of allene derivatives in place of butadiene may provide interesting reactive polymers bearing double bonds on the main chain through 1,2- and/or 2,3-polymerization. Therefore, we have developed the polymerizations and the reactions[2] of allene derivatives. Although the radical[3] and the cationic[4] polymerizations of allene derivatives can give soluble polymers containing the objective structures, they are limited in the monomer structure and the polymerization conditions.

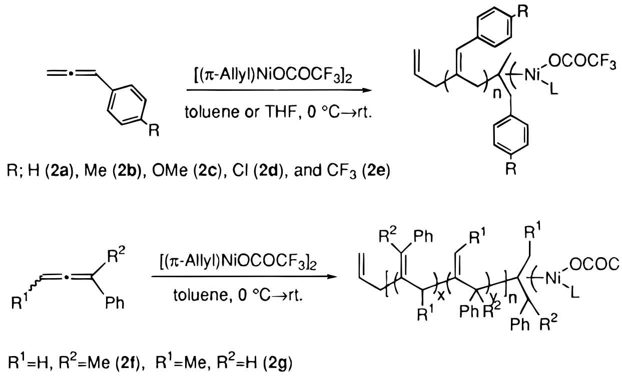
To obtain polyallenes having well-defined structures, controlled molecular weights, and molecular weight distributions, we have recently developed a living coordination polymerization of alkoxyallenes by the [(π-allyl)NiOCOCF$_3$]$_2$/PPh$_3$ system, in which the molecular weight of the resulting polymer can be controlled by the feed ratio of monomer to initiator (Scheme 1).[5] The polymers obtained in this system have narrow molecular weight distributions (<1.1), especially when the polymerization is carried out in the presence of PPh$_3$ (a slight excess relative to nickel). The resulting polymers consist of both 1,2- and 2,3-polymerized units, and the double bonds in the polymers are still present quantitatively. Block copolymers from two kinds of alkoxyallenes have been successfully obtained by two-stage block copolymerization, because the propagating end group in the polymerization is remarkably stable under nitrogen.[6] Herein, the coordination polymerization of phenylallene derivatives **2a**−**2g** was carried out by using [(π-allyl)NiOCOCF$_3$]$_2$ (**1**) as an initiator to investigate the effect of the electronic character of monomers on the polymerization behavior and to extend the adaptable monomers for this coordination polymerization system (Scheme 2).

Scheme 1



R; Me, *n*-Bu, *i*-Pr, *t*-Bu, Ph, etc.

Scheme 2



Results and Discussion

Coordination Polymerization of Phenylallene (2a) by [(π-Allyl)NiOCOCF$_3$]$_2$ (1). The coordination

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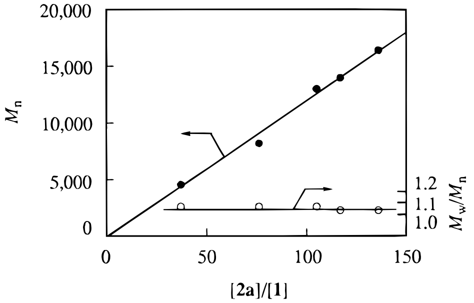


Figure 1. M_n and M_w/M_n vs the feed ratio ([**2a**]/[**1**]).

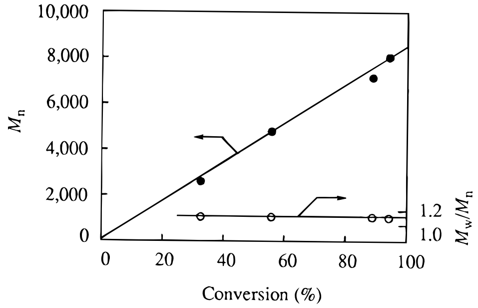


Figure 2. M_n and M_w/M_n vs the conversion of **2a** ($[\mathbf{2a}]_0 = 1.0$ M, $[\mathbf{1}]_0 = 0.025$ M).

polymerization of **2a** (80 equiv relative to **1**) by **1** was performed from 0 °C to ambient temperature in toluene. As a result, **2a** was consumed quantitatively within several hours to give a polymer ($M_n = 8230$, $M_w/M_n = 1.06$) in 97% yield after precipitation in H_2O/MeOH (v/v = 1/1).[7] Using various feed ratios of [**2a**]/[**1**], polymers with narrow molecular weight distributions were obtained in high yields regardless of the feed ratio and their molecular weights had a good linear relationship with the feed ratio (Figure 1).

Monomer conversion and polymer molecular weight were monitored as a function of time by GC and GPC, respectively. The number average molecular weight of the resulting polymer (M_n) was found to increase linearly with the monomer conversion (Figure 2), which means no significant chain transfer occurred throughout the polymerization.

To estimate the stability of the propagating end group of the polymerization, the polymerization mixture was kept at ambient temperature for 1 day under nitrogen atmosphere after the complete consumption of **2a** (100 equiv relative to **1**). After that, 100 equiv of **2a** was added to the polymerization system, which was consumed quantitatively after the further reaction for 12 h, and M_n of the polymer increased significantly without broadening of the molecular weight distribution, as determined by the GPC analyses (Figure 3). Consequently, the propagating end group of the polymerization, the allylnickel moiety, was confirmed to be sufficiently stable under nitrogen at room temperature. Moreover, these results support the living character of the present polymerization.

From the ^{1}H NMR spectrum, the resulting polymer was found to have only the 2,3-polymerized unit (Figure 4). No peak at 5.1 ppm assignable to the *exo*-methylene moiety in the 1,2-polymerized unit was observed. The number of double bonds in the polymer was determined quantitatively on the basis of the integral ratio of the peaks of the double bonds to those of other moieties (i.e., phenyl and methylene groups). Thus, the double bonds in the polymer did not undergo any side reactions throughout the polymerization.

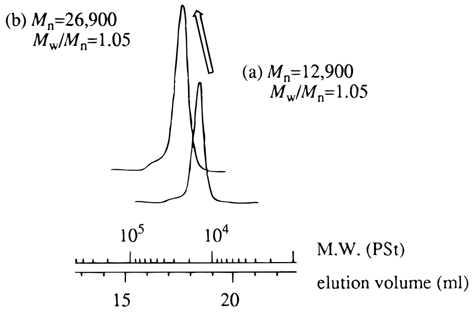


Figure 3. GPC traces of poly(**2a**) produced by (a) the reaction of 80 equiv of **2a** with **1** and (b) the further addition of 80 equiv of **2a**.

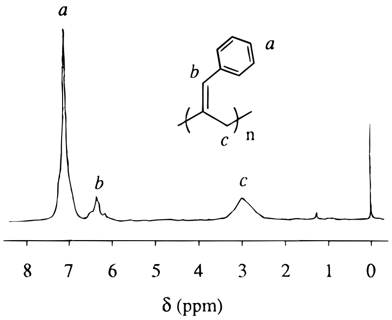


Figure 4. ^{1}H NMR spectrum of poly(**2a**) (Table 1, run 3).

Table 1. Coordination Polymerization of 2a under Various Polymerization Temperatures[a]

run	temp (°C)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	rt[d]	97	8230	1.06
2	40	96	9090	1.09
3	80	98	9020	1.09

[a] Conditions: $[\mathbf{2a}]_0/[\mathbf{1}] = 80$, $[\mathbf{2a}]_0 = 1.0$ M, in toluene. [b] Isolated yield after the precipitation in H_2O/MeOH (v/v = 1/1). [c] Estimated by GPC (THF, PSt standard). [d] Room temperature.

Table 2. Coordination Polymerization of 2a–2e by 1[a]

run	[2]	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**2a**	97	13 000	1.06
2	**2b**	97	12 800	1.05
3	**2c**	98	12 600	1.06
4	**2d**	97	12 800	1.11
5[d]	**2e**	95[e]	12 600[f]	1.11[f]

[a] Conditions: $[\mathbf{2}]_0/[\mathbf{1}] = 100$, $[\mathbf{2}]_0 = 1.0$ M. [b] Isolated yield after the precipitation in H_2O/MeOH (v/v = 1/1). [c] Estimated by GPC (THF, PSt standard). [d] Polymerization was carried out in THF. [e] Isolated yield after the precipitation in *n*-hexane. [f] Estimated by GPC ($CHCl_3$, PSt standard).

To examine the effect of polymerization temperature, the polymerization of **2a** (80 equiv relative to **1**) was also carried out at 40 or 80 °C (Table 1). At higher reaction temperatures, the conversion of **2a** was much faster (e.g., after the reaction for 30 min, the conversion reached 56, 87, and 100%, at room temperature, 40 °C, and 80 °C, respectively). At all the examined reaction temperatures, the polymers with the narrow molecular weight distribution (<1.1) could be obtained in high yields after the complete conversion of **2a**.[8]

Coordination Polymerization of *para*-Substituted Phenylallenes (2b–2e) by 1. Similar to the case of **2a**, the coordination polymerizations of **2b–2e** (100 equiv relative to **1**) were carried out using **1** as an initiator (Table 2).[9] The polymerization of **2b–2d** proceeded homogeneously in toluene, and polymers with narrow molecular weight distributions were obtained in high yields after precipitation in H_2O/MeOH (v/v =

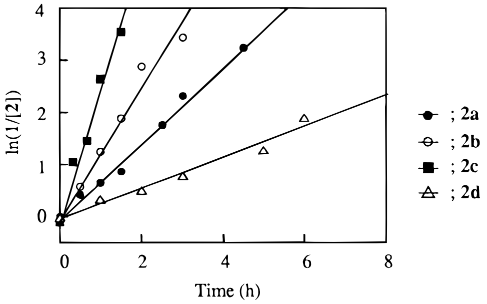


Figure 5. Kinetic plots of **2a**–**2d** in the polymerization using **1** as an initiator ($[\mathbf{2}]_0 = 1.0$ M, $[\mathbf{1}]_0 = 0.025$ M).

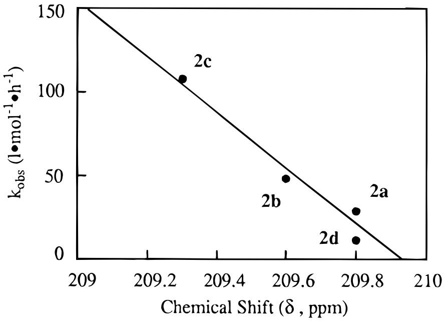


Figure 6. Correlation between the first-order kinetic coefficients and the chemical shifts of the center carbon of the allene monomers in ^{13}C NMR spectra.

1/1). In the case of **2e**, a polymer precipitated from the toluene solution during the polymerization. However, the polymerization of **2e** in THF proceeded homogeneously to produce a polymer with narrow molecular weight distribution in high yields. From the ^{1}H NMR spectra, the resulting polymers consist of only 2,3-polymerization units, irrespective of the substituent on the monomers.

The polymerization rates of **2a**–**2d** were determined from the kinetic plots (Figure 5). In all cases, the monomer conversion agreed well with first-order kinetic equations. The first-order kinetic coefficients of **2a**, **2b**, **2c**, and **2d** were estimated to be 29.0, 48.5, 108, and 11.6 L·mol^{-1}·h^{-1}, respectively. Thus, the polymerization rate was found to increase in the order of **2d** < **2a** < **2b** < **2c**, which is in good agreement with the increasing order of the electron-donating character of the *para* substituent. According to the ^{13}C NMR studies on allene derivatives, the chemical shift of the center carbon has been correlated well with the electron density of allene moieties.[10] Thus the observed kinetic coefficients were plotted in regard to their chemical shift, from which a good correlation was obtained (Figure 6). Because the electron-donating substituent in the *para* position tends to accelerate the polymerization rate, the propagation step in this polymerization is most probably explained by the electrophilic reaction of the π-allylnickel propagating end toward the allene monomers.

Coordination Polymerizations of α-Methylphenylallene (2f) and γ-Methylphenylallene (2g) by 1. The coordination polymerizations of **2f** and **2g** (100 equiv relative to **1**) were also carried out at ambient temperature using **1** as an initiator. The monomer was consumed quantitatively within several hours in the case of **2f**, but **2g** required several days. However, both **2f** and **2g** produced polymers with narrow molecular weight distributions in high yields when the reactions were taken to complete monomer conversion (Table 3).

Table 3. Coordination Polymerization of 2f and 2g by 1[a]

run	[2]	polymerizn time	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**2f**	12 h	95	13 000	1.07
2	**2g**	7 days	93	11 700	1.08

[a] Conditions: $[\mathbf{2}]_0/[\mathbf{1}] = 100$, $[\mathbf{2}]_0 = 1.0$ M, in toluene. [b] Isolated yield after the precipitation in H_2O/MeOH (v/v = 1/1). [c] Estimated by GPC (THF, PSt standard).

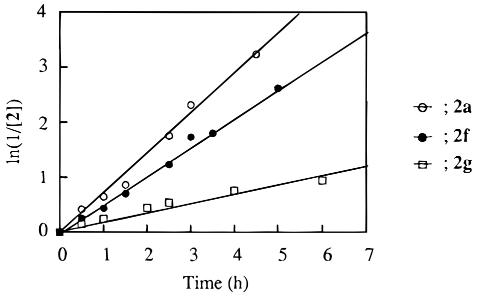
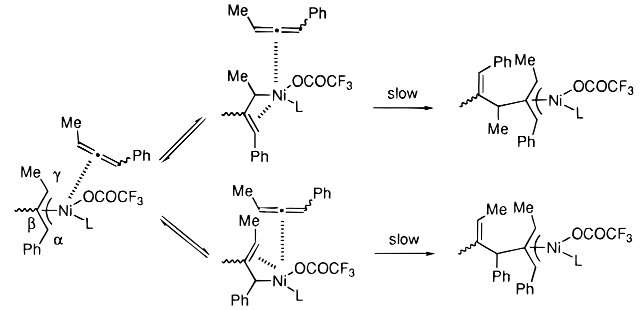
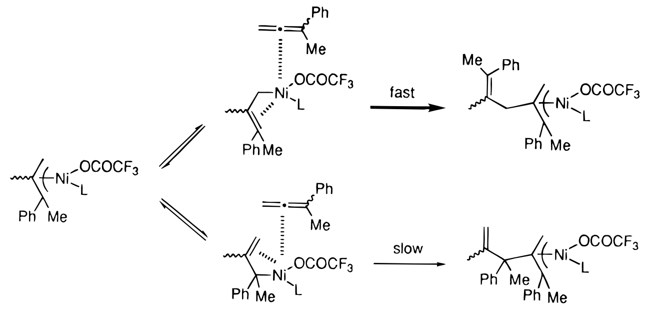


Figure 7. Kinetic plots of **2a**, **2f**, and **2g** in the polymerization using **1** as an initiator ($[\mathbf{2}]_0 = 1.0$ M, $[\mathbf{1}]_0 = 0.025$ M).

Scheme 3



Scheme 4



As shown in Figure 7, the polymerization rates of these monomers were evaluated by the monomer consumption curves and the kinetic plot. The polymerization of **2g** was found to be much slower than that of **2f** or **2a**, and the first-order kinetic coefficient of **2g** was estimated to be 6.28 L·mol^{-1}·h^{-1} (ca. 4.6 times smaller than that of **2a**). Thus, the introduction of the methyl group at the γ-position dramatically reduces the polymerizability of the monomer. The decrease of the polymerizability in the case of **2g** may not be due to the electronic effect because the methyl substituent in both **2f** and **2g** should increase the electron density of the allene moieties similarly. The difference in the polymerizability between **2g** and **2a** (or **2f**) is most probably due to the steric effect. That is, the propagating end generated from **2g** has substituents on both α- and γ-positions (Scheme 3), while the propagating ends of **2a** and **2f** do not have any substituents on the γ-position (Scheme 4), from which the insertion of the monomer (**2a** and **2f**) may smoothly take place.

Conclusions

The coordination polymerization of phenylallene derivatives (**2a**−**2g**) by $[(\pi\text{-allyl})NiOCOCF_3]_2$ was found to be living. The propagating allylnickel species was found to be quite stable under nitrogen at room temperature. The polymerization rate increased with the electron density of the allene monomers, which can be taken to mean that the insertion step is the electrophilic reaction of the propagating end. The steric effects of substituents on the monomer also effected the polymerizability. The γ-unsubstituted phenylallene derivatives (i.e., monosubstituted or α,α-disubstituted monomer) were found to polymerize much faster than the γ-substituted monomer.

Experimental Section

Materials and Instruments. Propargyl methyl ether was prepared according to the previously reported method.[11] Phenylallene (**2a**) was synthesized from propargyl methyl ether and phenylmagnesium bromide in the presence of a catalytic amount of CuBr, as reported previously[12] (39% yield, 61−62 °C/12 mmHg). Diethyl ether, toluene, and tetrahydrofuran (THF) were dried over sodium and distilled before use under nitrogen. *p*-Chlorostyrene, bromobenzene, 4-bromotoluene, *p*-(trifluoromethyl)bromobenzene, α-methylstyrene, β-methylstyrene, bromoform, sodium hydroxide, and other reagents (for precipitation and analyses) were used as received. All the polymerization reactions were carried out under nitrogen.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ 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$_{XL}$, G3000H$_{XL}$, G4000H$_{XL}$, and G5000H$_{XL}$, THF as the eluent), or on a SPD-6A (TSK gel G4000H$_{XL}$, $CHCl_3$ as the eluent), calibrated against standard polystyrene samples. Gas chromatographic analyses were performed on a Shimadzu GC-4A equipped with a FID detector using tetradecane as an internal standard (SE-30, 1 m, gradient temperature of 80−230 °C, 10 °C/min).

Syntheses of Monomers 2b, 2c, and 2e. To a mixture of propargyl methyl ether (16.1 g, 0.23 mol), CuBr (0.80 g, 5.60 mmol), and diethyl ether (30 mL) placed in a three-necked flask equipped with a mechanical stirrer and a dropping funnel was added (*p*-methylphenyl)magnesium bromide (0.29 mol, obtained from 50 g (0.29 mol) of 4-bromotoluene) from a dropping funnel at 0 °C (ca. 30 min). After stirring for a further 30 min at that temperature, the reaction mixture was poured into an excess of cold aqueous NH_4Cl. The mixture was extracted with diethyl ether (three times), and the combined extracts were dried over $MgSO_4$. The product was purified by column chromatography (silica gel, *n*-hexane), followed by distillation (bp 58−59 °C/6.5 mmHg) to give (*p*-methylphenyl)allene (**2b**) in 31% yield (9.10 g, 0.07 mol): ^{1}H NMR ($CDCl_3$, δ, ppm) 2.32 ($-CH_3$, s, 3H), 5.11 ($H_2C{=}C{=}$, d, 2H, $J = 6.8$ Hz), 6.13 ($-CH{=}C{=}$, t, 1H, $J = 6.8$ Hz), 7.04−7.25 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 21.1, 78.6, 93.7, 126.6, 129.3, 130.9, 136.6, 209.6; IR (neat, cm^{-1}) 3001, 2920, 2866, 1942, 1703, 1512, 1443, 1111.

(*p*-Methoxyphenyl)allene (**2c**): 38% yield; bp 53−54 °C/0.35 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 3.79 ($-OCH_3$, s, 3H), 5.11 ($H_2C{=}C{=}$, d, 2H, $J = 6.9$ Hz), 6.12 ($-CH{=}C{=}$, t, 1H, $J = 6.8$ Hz), 6.76−7.27 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 55.3, 78.9, 93.3, 114.1, 126.1, 127.7, 158.7, 209.3; IR (neat, cm^{-1}) 2955, 2836, 1942, 1609, 1510, 1248, 1111.

[*p*-(Trifluoromethyl)phenyl]allene (**2e**): 37% yield; bp 57−58 °C/8.0 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 5.21 ($H_2C{=}C{=}$, d, 2H, $J = 6.8$ Hz), 6.19 ($-CH{=}C{=}$, t, 1H, $J = 6.8$ Hz), 7.32−7.60 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 79.3, 93.2, 122.9, 125.5, 126.8, 128.9, 137.9, 210.4; IR (neat, cm^{-1}) 2980, 2872, 1942, 1618, 1441, 1325, 1125.

Syntheses of Monomers 2d, 2f, and 2g. To a mixture of *p*-chlorostyrene (25.0 g, 0.18 mol), bromoform (73.3 g, 0.29 mol), and tetrabutylammonium bromide (0.2 g), was added dropwise a solution of sodium hydroxide (52.0 g, 1.30 mol) in 70 mL of water at ambient temperature (ca. 1 h). After the reaction mixture was poured into excess water, the mixture was extracted with diethyl ether (three times), and the combined extracts were dried over $MgSO_4$. The crude product thus obtained was purified by column chromatography (silica gel, *n*-hexane), followed by distillation (bp 95−96 °C/0.5 mmHg) to give 23.2 g (0.08 mol, 41%) of the dibromocyclopropane derivative. To a solution of the dibromocyclopropane (24.0 g, 0.08 mol) in diethyl ether (30 mL), was added dropwise methyllithium in diethyl ether (0.08 mmol) at −50 °C (ca. 1 h). After stirring for 2 h at that temperature, the reaction mixture was poured into an excess of cold aqueous NH_4Cl. The mixture was extracted with diethyl ether (three times), and the combined extracts were dried over $MgSO_4$. The product was purified by distillation (bp 34−36 °C/0.3 mmHg) to give (*p*-chlorophenyl)allene (**2d**) in 56% yield (6.53 g, 0.04 mol); ^{1}H NMR ($CDCl_3$, δ, ppm) 5.15 ($H_2C{=}C{=}$, d, 2H, $J = 6.7$ Hz), 6.12 ($-CH{=}C{=}$, t, 1H, $J = 6.7$ Hz), 7.13−7.35 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 79.2, 93.1, 127.8, 128.2, 128.7, 132.5, 209.8; IR (neat, cm^{-1}) 2980, 1942, 1491, 1435, 1402, 1093.

α-Methylphenylallene (**2f**): 59% yield; bp 37−38 °C/1.8 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 2.10 ($=CCH_3$, t, 3H, $J = 3.2$ Hz), 4.98 ($H_2C{=}C{=}$, q, 2H, $J = 3.2$ Hz), 7.25−7.38 ($-C_6H_5$, 5H); ^{13}C NMR ($CDCl_3$, δ, ppm) 16.8, 77.5, 99.9, 125.8, 126.7, 128.5, 136.9, 209.1; IR (neat, cm^{-1}) 2982, 1942, 1597, 1597, 1493, 1443, 1069, 1026.

γ-Methylphenylallene (**2g**): 52% yield; bp 51−52 °C/3.5 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.78 ($=CCH_3$, dd, 3H, $J = 7.1$, 3.3 Hz), 5.53 (MeCH=, m, 1H), 6.09 (PhCH=, m, 1H), 7.15−7.37 ($-C_6H_5$, 5H); ^{13}C NMR ($CDCl_3$, δ, ppm) 14.0, 89.5, 94.0, 126.6, 128.5, 135.1, 206.0; IR (neat, cm^{-1}) 3030, 2984, 1948, 1599, 1494, 1462, 1369.

Coordination Polymerization (Typical Procedure). The initiator (**1**) (i.e., $[(\pi\text{-allyl})NiOCOCF_3]_2$) was prepared from bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$) and an equimoler amount of allyl trifluoroacetate under a nitrogen atmosphere and was used without isolation. To a flask containing a magnetic stir bar and a toluene solution of **1** (2.5×10^{-2} mmol), was added **2a** (0.116 g, 1.00 mmol, 40 equiv relative to **1**) at 0 °C. The polymerization reaction was stirred at ambient temperature. After the complete conversion of **2a** by gas chromatography (after ca. 3 h) was confirmed, the solvent was removed under reduced pressure, and the viscous product was dissolved in THF (2 mL) and then precipitated in H_2O/MeOH (v/v = 1/1) (100 mL) to give poly(**2a**) in 97% yield (0.113 g, 0.970 mol): ^{1}H NMR ($CDCl_3$, δ, ppm) 2.98 ($-CH_2-$, br, 2H), 6.36 (=CHPh, br, 1H), 6.60−7.80 ($-C_6H_5$, 5H); ^{13}C NMR ($CDCl_3$, δ, ppm) 39.3, 126.3, 128.1, 128.8, 137.2, 137.8; IR (neat, cm^{-1}) 2981, 2911, 1642, 1599, 1493, 1445.

poly(**2b**): 99% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 2.22 ($-CH_3$, br, 3H), 2.97 ($-CH_2-$, br, 2H), 6.29 (=CHp, br, 1H), 6.60−7.70 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 21.1, 37.7, 39.5, 128.3, 128.7, 135.1, 135.7, 135.8, 136.8; IR (neat, cm^{-1}) 2959, 2920, 1642, 1510, 1433.

poly(**2c**): 91% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 3.02 ($-CH_2-$, br, 2H), 3.64 ($-OCH_3$, br, 3H), 6.33 (=CH−, br, 1H), 6.55−7.65 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 37.7, 39.5, 55.0, 113.4, 127.8, 129.6, 130.0, 130.4, 130.5, 136.3; IR (neat, cm^{-1}) 2955, 2909, 2836, 1607, 1510, 1248.

poly(**2d**): 92% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 2.86 ($-CH_2-$, br, 2H), 6.10 (=CH−, br, 1H), 6.40−7.80 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 34.1, 127.7, 128.8, 129.2, 129.6, 130.2, 132.3, 135.7, 137.4; IR (neat, cm^{-1}) 3052, 2967, 1489, 1265, 1092.

poly(**2e**) (the polymerization was carried out in THF, and the resulting polymer was isolated by the precipitation in *n*-hexane): 95% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 2.85 ($-CH_2-$, br, 2H), 6.10 (=CH−, br, 1H), 6.40−8.15 ($-C_6H_4-$, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm) 34.2, 122.6, 127.5, 138.0, 140.5; IR (neat, cm^{-1}) 2965, 1713, 1616, 1412, 1327.

poly(**2f**): 95% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.62 ($=CCH_3$, br, 3H), 2.61 ($-CH_2-$, br, 2H), 6.10−7.80 ($=CC_6H_5$, 5H); ^{13}C NMR ($CDCl_3$, δ, ppm) 21.9, 36.1, 125.7, 128.0, 128.5, 132.7, 145.2; IR (neat, cm^{-1}) 2928, 1597, 1489, 1441, 1067, 1024.

poly(**2g**): 97% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.02 ($-CH_3$, br, 3H), 3.50 (>CHMe, br, 1H), 5.80−7.80 (=CHPh, $-C_6H_5$ 6H); ^{13}C NMR ($CDCl_3$, δ, ppm) 14.3, 34.2, 127.4, 128.3, 135.7; IR (neat, cm^{-1}) 2965, 1676, 1599, 1493, 1445, 1372, 1265.

Estimation of the Kinetic Coefficient (Typical Procedure). The polymerization of **2a** ($[\mathbf{2a}]_0/[\mathbf{1}] = 40$, $[\mathbf{2a}]_0 = 1.0$ M, $[\mathbf{1}] = 0.025$ M) was performed in toluene at 0 °C containing *n*-tetradecane (0.038 M) as an internal standard, similar to the above mentioned procedure. After the designated reaction period at 0 °C, the reaction mixture was sampled by the syringe, and the conversion of the monomer was estimated by GC analysis.

References and Notes

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(7) For a series of the experiments, we have used the catalyst prepared in situ by the reaction of $Ni(cod)_2$ with allyl trifluoroacetate, because the reaction has been reported to proceed in high efficiency (See: Dawans, F.; Marechal J. C.; Teyssie, Ph. *J. Organomet. Chem.* **1970**, *21*, 259) and because the results of the polymerization were comparable to those by the isolated catalyst. For example, the polymerization of **2a** (80 equiv) with the isolated catalyst gives poly(**2a**) ($M_n = 8230$, $M_w/M_n = 1.06$) in 97% yield, while that with in situ catalyst gives the polymer ($M_n = 8850$, $M_w/M_n = 1.05$) in 91% yield.

(8) The polymerization at 80 °C also proceeds by the living mechanism because the molecular weight of the polymer could be controlled by the feed ratio. However, the propagating end was found not to be stable enough on standing the living polymer solution. By the polymerization of **2a** (60 equiv relative to **1**) at 80 °C for 30 min, **2a** was consumed quantitatively to produce a corresponding polymer ($M_n = 6860$, $M_w/M_n = 1.06$). When 60 equiv of **2a** was added again to the polymerization system to carry out further reaction, the added **2a** was consumed quantitatively within 30 min; however, bimodal elution peaks ($M_n = 15100$, $M_w/M_n = 1.05$ and $M_n = 7290$, $M_w/M_n = 1.05$) were observed in the ratio 94:6 by GPC analysis.

(9) In our previous study on the polymerization of alkoxyallenes, we have reported that the addition of PPh_3 to the catalyst system was effective for the synthesis of the polymer with narrow molecular weight distribution (see ref 5). However, the polymerization of **2a**, **2b**, and **2d**−**2g** by **1** did not occur at all in the presence of PPh_3. Hence, we carried out the present polymerization by **1** without the addition of PPh_3.

(10) Theoretical investigations between the chemical shifts and the electron densities have been performed on allene derivatives, from which an excellent correlation ($\rho = 0.983$) has been obtained when the total electron density of the sp carbons was plotted against the corresponding chemical shift. See: Popel, J. A.; Beveridge, D. L. In *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; p 214.

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