Polymer Bulletin 50, 335–342 (2003)
DOI 10.1007/s00289-003-0182-8

Polymer Bulletin

Allylnickel-Catalyzed Living Coordination Polymerization of Allenes with Ester Functionality

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Received: 4 March 2003/Revised version: 22 May 2003/Accepted: 23 May 2003

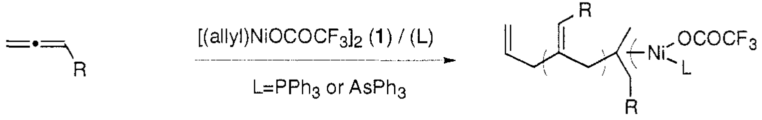
Summary

The coordination polymerization of allenes with ester functionality such as ethyl 2,3-butadienoate (**2a**) and *tert*-butyl 2,3-butadienoate (**2b**) by allylnickel catalysts is described. The catalyst consisting of $[(\text{allyl})\text{NiOCOCF}_3]_2$ (**1**) and an equimolar amount of PPh_3 proved to be suitable to perform the living polymerization of both **2a** and **2b** giving rise to polymers with controlled molecular weight and narrow molecular weight distribution. The kinetic studies indicated that the polymerization of **2a** is faster than **2b** and any other allene derivatives bearing alkoxy, alkyl, and phenyl substituents although **2a** was expected to have much poorer polymerizability judging from its lower electron density on the allene moiety.

Introduction

Living polymerization is one of the most promising methods for a variety of precision macromolecular design, owing to the characteristics of the perfect control of both the molecular weight and the end-structure of polymers. Many living polymerization systems have been developed for monomers with specified substituents. In general, their living behavior is greatly influenced by the substituent on the monomers and their slight modification often provides polymers with irregular structure. This limitation must be overcome in order to facilitate versatile macromolecular design. Therefore, it is of importance to realize a living polymerization system that is tolerant of a wide variety of functional groups. Advances in organometallic chemistry in the design and the synthesis of single-site metal catalysts for olefins [1], ring-opening metathesis [2], and ring-opening polymerization techniques [3] have enabled the preparation of well-defined functional polymers having the predictable molecular weight and controlled end-structure.

We reported the living coordination polymerization of alkoxyallenes [4], arylallenes [5], alkylallenes [6], *N*-allenylamides [7], and hydroxymethylallene [8] by allylnickel catalysts. In these cases, polymers with predictable molecular weight and narrow molecular weight distribution were obtained under mild polymerization conditions. In view of the chemoselective feature of allylnickel complexes in organic synthesis, this polymerization is potentially applicable to a variety of monomers bearing functional groups. Our recent reports on the living coordination polymerization of *N*-allenylamides and hydroxymethylallenes show that the amide and the hydroxy substituents do not interfere with the allylnickel-catalyzed polymerization. Herein, the coordination polymerization of allenes with ester functional groups was carried out by allylnickel catalysts to investigate the possibility of the living polymerization for ester-substituted allenes, which can be regarded as acrylate derivatives having an additional double bond (Scheme 1). It is also of great interest to clarify the polymerizability of these monomers because we have not evaluate the polymerization behavior of allenes carrying electron-withdrawing groups in the series of the coordination polymerization by allylnickel catalysts and because the resulting polymers have potential applications as functional polymers having both double bonds and ester moieties [9].



2a ($R=CO_2C_2H_5$)
2b ($R=CO_2C_4H_9$-*tert*)

Scheme 1. Living Coordination Polymerization of Allenes with Ester Functionality

Experimental

Materials

Bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$) (Cica) was used as received. Triphenylphosphine (PPh_3) was recrystallized from dichloromethane/*n*-hexane. Triphenylarsine ($AsPh_3$) was recrystallized from ethanol. Toluene was dried over sodium, dichloromethane (CH_2Cl_2) was dried over calcium hydride, and they were distilled under nitrogen. Reagents for the monomer synthesis were used as received. All the polymerizations were carried out under nitrogen.

Instruments

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL EX-400 or a JEOL EX-90 instrument using tetramethylsilane as an internal standard. IR spectra were obtained on a JASCO FT/IR-5300 spectrophotometer. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G2500H_{XL} and G3000H_{XL} or G4000H_{XL} and G5000H_{XL} tandem columns, THF as an eluent). The molecular weight of the polymers was calibrated against standard polystyrene samples. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14B equipped with a FID detector using n-tetradecane as an internal standard (SE-30, 3 m, gradient temperature of 100–230 °C, 10 °C/min).

Synthesis of Monomers

Ethyl 2,3-butadienoate (**2a**) was prepared by the reaction of ethyl bromoacetate and ketene generated in situ as previously reported [10] and distilled under nitrogen. *tert*-Butyl 2,3-butadienoate (**2b**) was likewise obtained in 20 % yield from *tert*-butyl bromoacetate and was distilled under reduced pressure (64–65 °C/21–23 mmHg); ^{1}H NMR ($CDCl_3$, ppm): δ = 1.48 ($-C(CH_3)_3$, s, 9H), 5.17 ($H_2C=C=$, d, 2H, J = 6.4 Hz), 5.55 ($-CH=C=$, t, 1H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ = 28.1, 79.0, 81.1, 89.6, 165.1, 215.4; IR (neat, cm^{-1}): 2982, 2254, 1973, 1942, 1456, 1424, 1393, 1345, 1281, 1158.

Coordination Polymerization of 2a by 1/PPh$_3$ (Typical Procedure)

To a CH_2Cl_2 (1.00 mL) solution of **1** [11] (2.00 x 10^{-2} mmol) and PPh_3 (2.00 x 10^{-2} mmol) was added **2a** (0.112 g, 1.00 mmol, 50 equiv relative to the nickel) at 0 °C, which was stirred at ambient temperature for 12 h. After confirming the complete conversion of **2a** by GC, the resulting solution was precipitated into *n*-hexane (100 mL) to give poly(**2a**) in a quantitative yield (0.112 g, 1.00 mol); ^{1}H NMR ($CDCl_3$, ppm): δ = 0.80–1.45 ($-CH_3$, 3H), 2.90–3.85 ($=C-CH_2-C=$, 2H), 3.85–4.50 ($-CO_2CH_2-$, 2H), 5.50–6.10 ($=CH-CO_2-$, 1H); ^{13}C NMR ($CDCl_3$, ppm): δ = 14.2, 40.0, 59.8, 119.7, 154.2, 165.7; IR (neat, cm^{-1}): 2984, 2254, 1707, 1640, 1379, 1246, 1179.

Poly(**2b**) (obtained by **1**/PPh_3, Yield 91 %); ^{1}H NMR ($CDCl_3$, ppm): δ = 1.40-1.50 ($-(CH_3)_3$, 9H), 3.40-3.50 ($=C-CH_2-C=$, 2H), 5.75-5.85 ($=CH-CO_2-$, 1H); ^{13}C NMR ($CDCl_3$, ppm): δ = 28.2, 40.1, 79.6, 120.9, 152.5, 165.4; IR (neat, cm^{-1}): 2978, 2934, 1709, 1638, 1368, 1248, 1150.

Estimation of Kinetic Coefficient (Typical Procedure)

The polymerization of **2a** ([**2a**]$_0$/[Ni] = 40, [**2a**]$_0$ = 0.20 M) was performed in the presence of PPh_3 (1.0 equiv, relative to the nickel) in CH_2Cl_2 at 0 °C containing *n*-tetradecane (8.0 x 10^{-3} M) as an internal standard. After designated reaction periods at 0 °C, a small portion of the reaction mixture was sampled by a syringe (ca. 10 μL), and the monomer conversion was estimated by the GC analyses.

Results and discussion

The coordination polymerization of **2a** (50 equiv) was performed by **1** in CH_2Cl_2. The conversion of **2a** was complete within a few hours at ambient temperature to give a polymer (M_n = 13 900, M_w/M_n = 1.39) in 91 % yield. The ^{1}H NMR spectrum indicates that the resulting polymer consists of a sole unit having trisubstituted olefin moieties and that the double bonds in the repeating units remain quantitatively. The polymerization performed under various ratios of [**2a**]/[Ni] constantly provided polymers in high yields. However, their molecular weight did not increase in proportion to the ratio of [**2a**]/[Ni] and their molecular weight distribution became much broader at the higher monomer concentration (Figure 1). Although allylnickel complexes have been reported to be able to coexist with the ester groups on the basis of the preceding reports on the organic reactions [12], the present result suggests that the propagating end is gradually inactivated in the course of the polymerization.

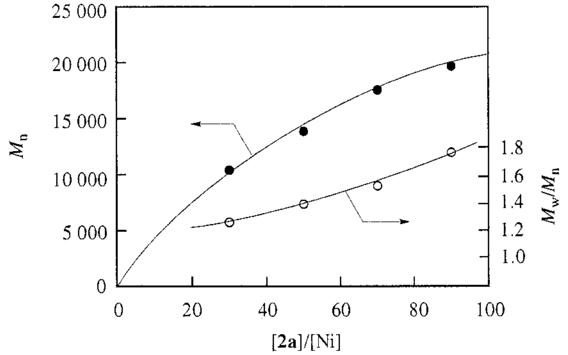


Figure 1. Dependence of M_n and M_w/M_n on the ratio of [**2a**]/[Ni] in the polymerization by **1** (without PPh_3).

The fact that a living poly(alkoxyallene) produced by **1** is gradually inactivated in the presence of an additive containing an ester group also suggests the presence of the side reaction. While the polymerization of 50 equiv of *n*-octyloxyallene (**3**) by **1** provided a narrowly dispersed polymer (M_n = 9 260, M_w/M_n = 1.11) in the presence of ethyl acetate (50 equiv), a part of the growing end proved to be inactivated by keeping this polymer solution for 12 h at ambient temperature under nitrogen. That is, a subsequent addition of 50 equiv of **3** to the polymer solution resulted in the complete consumption of **3** leading to a clear increase of the molecular weight of the polymer (M_n = 18 600) in the GPC measurement. However, its distribution became broader (M_w/M_n = 1.34) and a shoulder elution peak was observed at the position of the elution peak for the initial polymer.

Table 1. Coordination polymerization of **2a** by **1** in the presence of PPh_3 or $AsPh_3$ [a]

run	ligand	[ligand]/[Ni]	poly(**2a**)		
			yield (%) [b]	M_n [c]	M_w/M_n [c]
1	none	-	91	13 900	1.39
2	PPh_3	1	100	6 400	1.18
3	PPh_3	2	27 [d]	1 290 [e]	1.04
4	$AsPh_3$	1	98	5 880	1.25

[a] Conditions: [Ni] = 2.0×10^{-2} mmol, $[\mathbf{2a}]_0$/[Ni] = 50, at 0 °C→rt, for 12 h, in CH_2Cl_2.
[b] Isolated yield after precipitation into *n*-hexane.
[c] Estimated by GPC (THF, polystyrene standard).
[d] Yield did not increase in the prolonged reaction period.
[e] Product has unknown structure without olefinic protons (by ^1H NMR).

In the polymerization of *N*-allenylamides, the addition of PPh_3 to the initiator (**1**) is effective to perform the living polymerization. Thus, the polymerization of **2a** was likewise investigated in the presence of neutral ligands (Table 1). As a result, the addition of PPh_3 to **1** was found to bring about dramatic changes in the yield, the molecular weight, and the molecular weight distribution of the polymers. In the presence of 2 equiv of PPh_3 relative to the nickel, the monomer conversion did not increase sufficiently and oligomers were obtained in low yield (27 %) (run 3). The structure of the oligomeric products thus obtained could not be fully characterized because no peak assignable to the double bonds was detected in its ^{1}H NMR spectrum. The ester-substituted allene (**2a**) was reported to react with a catalytic amount of PPh_3 to afford uncharacterizable oligomers [9a]. In accordance with this report, **2a** was found to give oligomers (M_n = 1 910, M_w/M_n = 1.11) in 19 % yield in the presence of 2 mol% of PPh_3 (i.e., the same quantity added to **1** in run 3). The oligomers might have an identical structure to that obtained in run 3 because no olefinic peak was detected in its ^{1}H NMR spectrum. These results can be taken to mean that the PPh_3-catalyzed oligomerization is predominant under the conditions employed in run 3.

In sharp contrast, a catalyst containing a stoichiometric amount of PPh_3 or $AsPh_3$ proved to give excellent results (runs 2 and 4). For example, the consumption of **2a** was complete within 12 h by the polymerization with **1**/PPh_3 (1 equiv to Ni) and a polymer having a narrow molecular weight distribution (M_w/M_n = 1.18) was obtained in a quantitative yield. The polymer consisted of the unit containing trisubstituted olefin moieties whose double bond could be observed clearly in its ^{1}H and ^{13}C NMR spectra (Figure 2) [13].

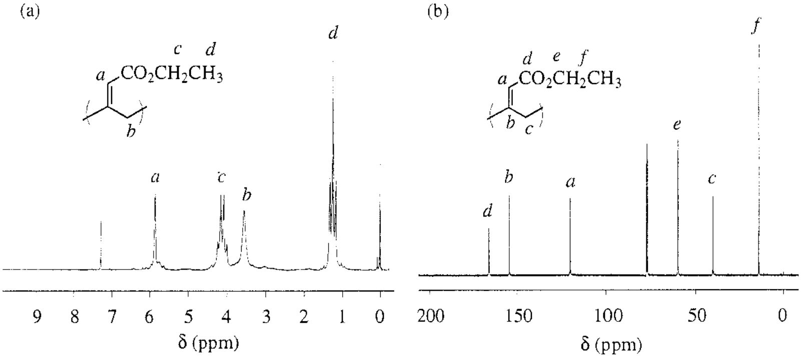


Figure 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of poly(**2a**) obtained by **1**/PPh_3 ($[PPh_3]/[Ni]$ = 1) (Table 1, run 2).

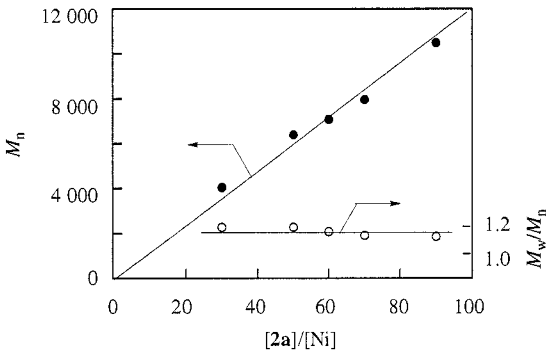


Figure 3. Dependence of M_n and M_w/M_n on the [**2a**]/[Ni] ratio in the polymerization by **1**/PPh_3 ($[PPh_3]/[Ni]$ = 1).

The living nature of the polymerization of **2a** by **1**/PPh_3 ($[PPh_3]/[Ni] = 1$) was confirmed by monitoring the dependence of the molecular weight of the polymer on the ratio of [**2a**]/[Ni]. That is, M_n of the polymer increased linearly by the increase of the [**2a**]/[Ni] ratio where the molecular weight distribution was constantly narrow (Figure 3).

The propagating end of the living poly(**2a**) produced by **1**/PPh_3 was found not to undergo inactivation as evidenced by the post-polymerization experiment. After the polymerization of 40 equiv of **2a** by **1**/PPh_3 was complete, the polymer solution was kept for an additional 12 h at ambient temperature under nitrogen. Afterward, the further polymerization of 40 equiv of **2a** resulted in the quantitative conversion of the added monomer. It is of note that the molecular weight of the polymer increased clearly (M_n = 9 620, M_w/M_n = 1.20) in comparison with that obtained at the first stage (M_n = 5 760, M_w/M_n = 1.22) without broadening the molecular weight distribution. Consequently, it was further confirmed that the addition of PPh_3 contributes to suppress side reactions during and after the polymerization of **2a**.

Coordination Polymerization of 2b

Likewise, the polymerization of a monomer possessing a bulky *tert*-butyl substituent (**2b**) was performed by **1** (without PPh_3) under various ratios of [**2b**]/[Ni]. Polymers were obtained in high yields after the reaction at ambient temperature for 12 h. In this case, the inactivation of the growing end also seems to take place because the observed M_n of the polymer deviated from the theoretical value calculated from the [**2b**]/[Ni] ratio, although the inactivation might occur much less than that observed in the polymerization of **2a**. This result suggests that side reactions of the propagating allylnickel species with the carbonyl group cannot be prohibited completely by the bulky *tert*-butyl substituent. Our attempt to control the polymerization by lowering the polymerization temperature (-20 °C) did not give better results, giving a polymer with a similar polydispersity (Table 2, runs 1 and 2). In contrast, the polymerization by **1**/PPh_3 afforded a polymer with narrower polydispersity (run 3). The polymer was also confirmed to have the trisubstituted olefin unit as a result of the specific polymerization of the less substituted double bond in **2b**.

Table 2. Coordination polymerization of **2b** by **1** with or without PPh_3 [a]

run	catalyst	conditions	yield (%) [b]	M_n [c]	M_w/M_n [c]
1	**1**	0 °C → rt., 12 h	91	15 100	1.38
2	**1**	-20 °C, 24 h	99	11 900	1.40
3	**1**/PPh_3	0 °C → rt., 12 h	98	8 440	1.07

[a] Conditions: $[Ni] = 2.0 \times 10^{-2}$ mmol, $[\mathbf{2b}]_0/[Ni] = 50$, in CH_2Cl_2.

[b] Isolated yield after washing with aqueous HCl (3 %).

[c] Estimated by GPC (THF, polystyrene standard).

The living character of the polymerization of **2b** by **1**/PPh_3 could be supported by the dependence of the molecular weight of the polymer on the ratio of [**2b**]/[Ni]. That is, the linear relationship was observed between the molecular weight of the polymer and the [**2b**]/[Ni] ratio. The propagating end was also demonstrated to be stable enough as convinced by the post-polymerization experiment.

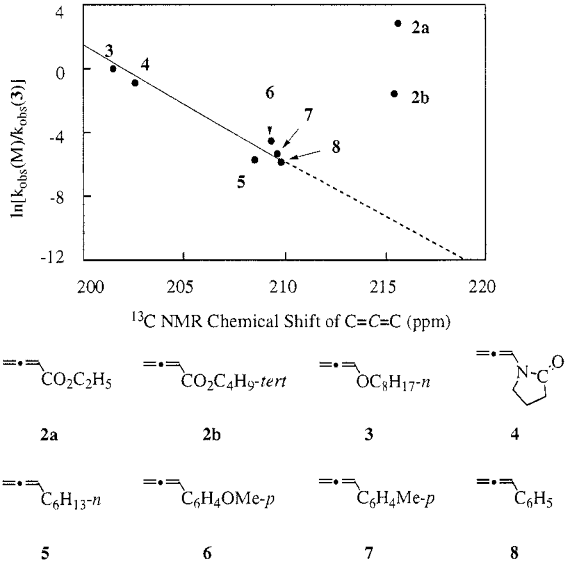


Figure 4. Relationship between the chemical shifts of the center carbon of various allene derivatives in their ^{13}C NMR spectra (in $CDCl_3$) and their kinetic coefficients relative to k_{obs}(**3**).

Kinetic Study

The polymerization rate of **2a** and **2b** by **1**/PPh_3 ($[PPh_3]/[Ni] = 1$) was estimated from the monomer conversion on assuming the first-order kinetic equation ($-d[\mathbf{2}]/dt = k_{obs}[Ni][\mathbf{2}]$). The observed kinetic coefficients (k_{obs}) for **2a** and **2b** were estimated to be 1.06×10^3 $L{\cdot}mol^{-1}{\cdot}h^{-1}$ and 1.28 $L{\cdot}mol^{-1}{\cdot}h^{-1}$, respectively. From our preceding studies on the coordination polymerization of *para*-substituted phenylallenes and other allene derivatives, the electronic character of the allene moiety was found to be a main factor to determine the polymerizability of the monomers where the polymerization rate increased as the electron density of the allene moiety increased [5]. This is also in accordance with the electrophilic nature of the allylnickel complexes [4c]. On the basis of this trend, however, it is difficult to explain the remarkably higher polymerizability of **2a** than that of **3** (k_{obs} = 61.7 $L{\cdot}mol^{-1}{\cdot}h^{-1}$), because the chemical shift of the center carbon in **2a** (δ = 215.6 ppm) indicates that the allene moiety in **2a** is more electron-deficient than that in **3** (δ = 201.5 ppm). The anomalously high polymerizability of **2a** is also clear from Figure 4, which illustrates the relationship between the ^{13}C NMR chemical shifts of the center carbon (i.e., the electron density of the allene moiety) and relative kinetic coefficients in the logarithmic scale. In contrast to **2a**, the coordination polymerization of **2b** by **1**/PPh_3 proceeds much slowly, although the electron density of the allene moiety in **2b** should be comparable to that of **2a** judging from the chemical shift of the central carbon in **2b** (δ = 215.4 ppm). Accordingly, we assume that the difference in the polymerizability between **2a** and **2b** originates from the different coordination ability of the carbonyl group toward the propagating end [14]. That is, a less sterically hindered carbonyl group in **2a** should have stronger interaction with the nickel than that in **2b**, which might accelerate the coordination of the monomer to the nickel center and bring about a higher concentration of the active species (i.e., the allene-coordinated nickel complex).

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