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Living Coordination Polymerization of *N*-Allenylamides by π-Allylnickel Catalysts

Koji Takagi,[†,§] **Ikuyoshi Tomita,**[‡] **and Takeshi Endo***[,†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, 226-8503 Japan, and Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, 226-8502 Japan

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ABSTRACT: The coordination polymerization of *N*-allenylamides was investigated by π-allylnickel catalysts to elucidate the relationship between the amide structure and the polymerization behavior. The polymerization of *N*-allenyl-γ-butyrolactam (**2a**) having a five-membered cyclic amide moiety proceeded smoothly by a π-allylnickel catalyst bearing a trifluoroacetate ligand (**1a**) in the presence of triphenylphosphine (PPh_3), giving a polymer with a narrow molecular weight distribution in high yields. The initiation efficiency of the polymerization was supported quantitatively by measuring the MALDI-TOF mass spectra. The molecular weight of the polymer increased linearly in proportion to the monomer feed ratio ([**2a**]/[Ni]), supporting a living character of the polymerization. The addition of PPh_3 to the initiating system was essential to attain a stable propagating end; otherwise the propagating π-allylnickel species became gradually inactive after the complete monomer conversion. In comparison with **2a**, *N*-allenyl-δ-valerolactam (**2b**), *N*-allenyl-ϵ-caprolactam (**2c**), and *N*-allenyl-*N*-methylacetamide (**2d**) revealed a lower polymerizability by **1a**/PPh_3 under the same conditions. However, the living polymerization of **2b**−**2d** occurred smoothly to give corresponding polymers in high yields by modification of the π-allylnickel catalyst (i.e., by using π-allylnickel iodide (**1b**) in the presence of PPh_3), where the propagating ends were also stable under nitrogen. The observed kinetic coefficients for **2a**, **2b**, and **2d** by **1b**/PPh_3 were estimated as 14.9, 4.21, and 6.54 $L\cdot mol^{-1}\cdot h^{-1}$, respectively. A plausible polymerization mechanism for the different polymerizability of *N*-allenylamides (**2a**−**2d**) was discussed.

Introduction

Generally, the living polymerization technique has advantages over nonliving polymerizations in that it can give macromolecules with regulated structures such as the molecular weight and the molecular weight distribution. Owing to the excellent living systems, precision macromolecular designs have been developed to give many useful block copolymers, multiarmed polymers, macromonomers, telechelic polymers, and so on. Especially, living systems for monomers possessing functional groups have been extensively explored from the viewpoint of the versatile application of the resulting functional polymers.

Transition metal-catalyzed coordination polymerization is one powerful method for the synthesis of well-defined polymers. Several living systems have been established for cyclic olefins,[1] acetylenes,[2] heterocumulenes,[3] and α-olefins,[4] where functional groups of the monomers are reported to behave rather differently. That is, they either assist the stabilization or cause the deactivation of the propagating species. Hence, the role of functional groups in the coordination polymerization is still obscure and should be clarified in each system.

Recently, we have reported the living coordination polymerization of alkoxyallenes by $[(\pi\text{-allyl})NiOCOCF_3]_2/PPh_3$, where the polymers with predictable molecular weights and narrow molecular weight distributions can be obtained in excellent yields (Scheme 1).[5] The role of anionic ligands (X)[6] and phosphine ligands (L)[7] on the allylnickel catalyst ((allyl)Ni(X)L) in the coordination

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[†] Research Laboratory of Resources Utilization.

[‡] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering.

[§] Present address: Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.

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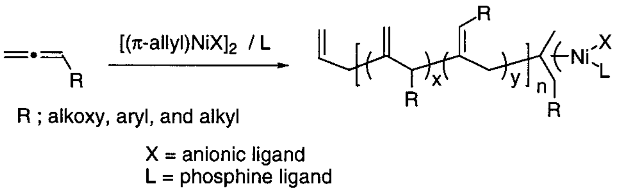
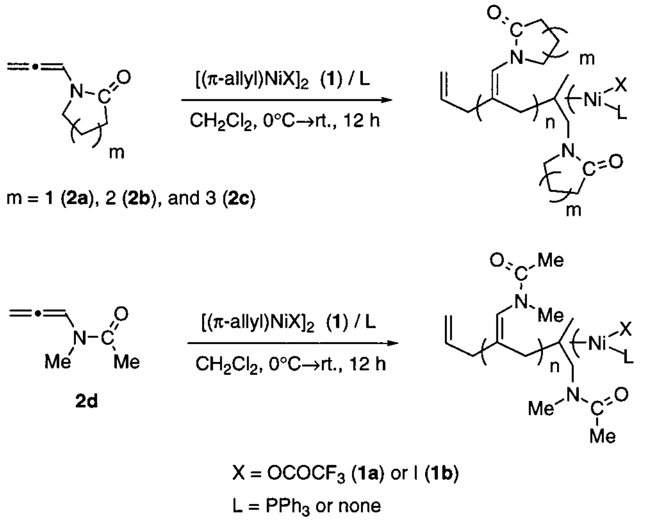
Scheme 1



Scheme 2



polymerization was investigated, where the living nature was supported by the electron-accepting character of the ligands. In addition, the polymerization rate and the content of 1,2-polymerization unit increased as the electron-accepting ability of the ligands increased. The coordination polymerization of alkylallenes[8] and phenylallenes[9] also proceeds in a living mechanism by using [(π-allyl)NiOCOCF$_3$]$_2$ (**1a**) as an initiating system.

Based on the highly chemoselective nature of the allylnickel species, it is expected that the coordination polymerization of allenes carrying various functional groups also proceeds smoothly, although the influence of functional groups on the polymerization behavior is still ambiguous. Herein, we describe the coordination polymerization of *N*-allenylamides by π-allylnickel catalysts to elucidate the relationship between the amide structure and the polymerization behavior (Scheme 2).

Results and Discussion

Coordination Polymerization of *N*-Allenyl-γ-butyrolactam (2a). The coordination polymerization of **2a**[10] (56 equiv) by [(π-allyl)NiOCOCF$_3$]$_2$ (**1a**) was carried out at 0 °C to ambient temperature in CH$_2$Cl$_2$ in the presence of PPh$_3$ (2 equiv to the nickel). By reaction for 12 h, **2a** was consumed completely to give a polymer quantitatively, whose molecular weight and distribution were estimated to be M_n = 11 000 and M_w/M_n = 1.05, respectively (by GPC; DMF as an eluent, calibrated against the standard polystyrene samples).

From the ^{1}H NMR spectrum of poly(**2a**), only the 2,3-polymerization unit was detected and the double bonds in the polymer backbone remained quantitatively by comparing the integral ratios of the double bond protons with those of the aliphatic moieties (Figure 1). These results suggest that both the cyclic five-membered amide moiety and the double bonds in the polymer are intact during the polymerization of **2a** under the examined conditions.

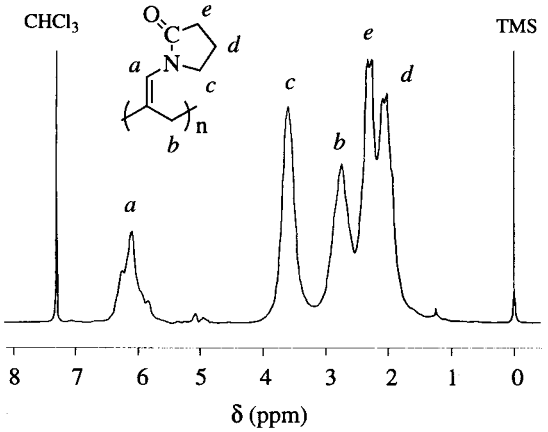


Figure 1. ^{1}H NMR spectrum of poly(**2a**).

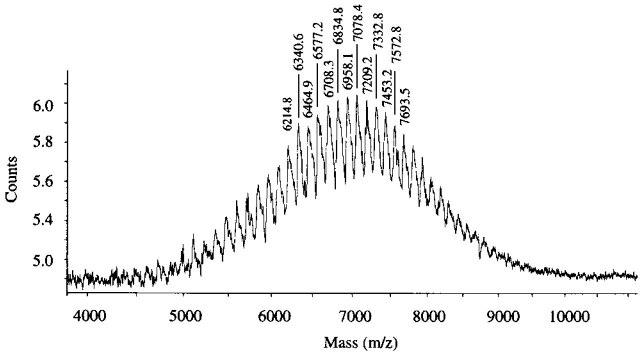


Figure 2. Typical MALDI-TOF mass spectrum of poly(**2a**) obtained under the feed ratio of [**2a**]/[Ni] = 56.

The molecular weight of the polymer (M_n = 11 000) estimated by GPC was much larger than the theoretical one (M_n = 6990) calculated from the feed ratio. One may suspect two possibilities for the observed higher molecular weight: the low initiation efficiency of the catalyst or the factors originating from the estimation by GPC using polystyrene calibration curves. By the measurement of the MALDI-TOF mass spectrum, the absolute molecular weight of the polymer could be determined as M_n = 7120, by which a quantitative initiation efficiency of **1a**/PPh$_3$ (>99%) could be confirmed (Figure 2).

The polymerization of **2a** under various monomer feed ratios ([**2a**]/[Ni]) afforded polymers in high yields, whose molecular weight distributions were constantly narrow (M_w/M_n < 1.09). A linear relationship between the monomer feed ratio and the molecular weight of the polymer was observed, which is a necessary condition for the living polymerization (Figure 3a). By using **1a** as an initiator (without the addition of PPh$_3$), soluble polymers could be also obtained in high yields, where we could observe a linear relationship between the monomer feed ratio and the molecular weight of the polymer. However, the molecular weight distribution of the polymer became a little broader (M_w/M_n = 1.20–1.25) than that obtained by **1a**/PPh$_3$ (Figure 3b).[11]

The stability of the propagating end in the polymerization of **2a** was examined by the reinitiation experiment. After the polymerization of 30 equiv of **2a** by **1a**/PPh$_3$, the solution of the resulting polymer (M_n = 7130, M_w/M_n = 1.03) was kept for an additional 12 h at ambient temperature (ca. 20 °C) under nitrogen. Subsequently, 30 equiv of **2a** was recharged to the polymer solution to conduct a further polymerization. As a

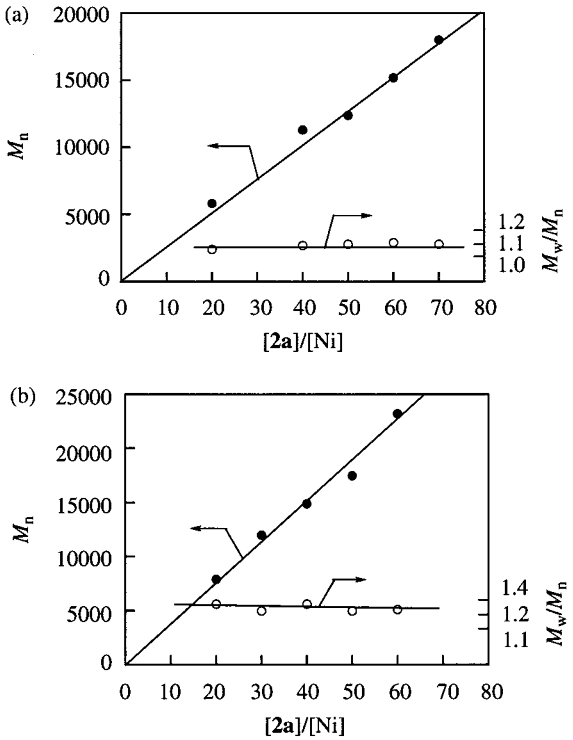


Figure 3. M_n and M_w/M_n vs the feed ratio ([**2a**]/[Ni]) in the polymerization by **1a**/PPh$_3$ (a) and by **1a** (b).

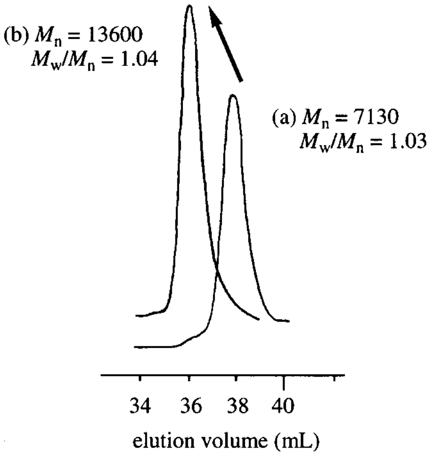


Figure 4. GPC traces of poly(**2a**) produced by the reaction of 30 equiv of **2a** with **1a**/PPh$_3$ (a) and that obtained by the further addition of 30 equiv of **2a** (b).

result, the recharged **2a** was consumed completely within 12 h to provide a polymer with a higher molecular weight (M_n = 13 600, M_w/M_n = 1.04), keeping a narrow molecular weight distribution (Figure 4). On the contrary, when the same experiment was carried out by **1a** without the addition of PPh$_3$, neither the consumption of **2a** nor the increase in the polymer molecular weight was observed in the second stage, indicating that the propagating end is gradually inactivated after the complete monomer conversion.[12] Namely, the addition of PPh$_3$ to the catalyst system is essentially important to stabilize the living propagating end. The present coordination system is believed to proceed via the π-allylnickel intermediate. Reflecting the nature of the π-allylnickel complexes, the propagating ends produced from alkoxyallenes,[5] alkylallenes,[8] and arylallenes[9] were found to be stable both in the absence and presence of PPh$_3$. Although amide moieties seem to be regarded as an inert functional group toward π-allylnickel complexes in organic synthesis, the result obtained here clearly indicates that the amide substituent causes the deactivation of the catalyst. The neutral ligand, PPh$_3$, most probably prevents the side reaction of π-allylnickel species with the amide carbonyl group by the protection of the reaction site for the carbonyl group and/or by the suppression of the activity of the nickel center by the coordination of PPh$_3$.

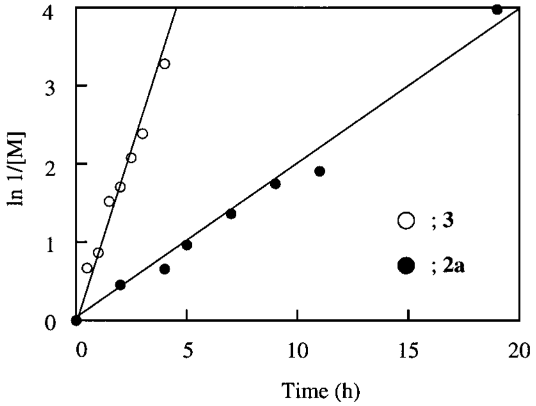


Figure 5. Kinetic plots of **2a** and **3** in the polymerization by **1a**/PPh$_3$ ([**2a**]$_0$/[Ni] = [**3**]$_0$/[Ni] = 40, [**2a**]$_0$ = [**3**]$_0$ = 1.0 M, [PPh$_3$]/[Ni] = 2).

To estimate the polymerization rate of **2a**, the monomer conversion was followed by GC after designated reaction periods. Figure 5 shows the kinetic plots of the polymerization, where the monomer conversion fits well with the first-order kinetic equation in regard to the monomer and the initiator ($-d[\mathbf{2a}]/dt = k_{obs}[\mathbf{1a}][\mathbf{2a}]$). The observed kinetic coefficient (k_{obs}) for **2a** was estimated to be 8.54 L·mol^{-1}·h^{-1}, which is smaller than that of alkoxyallenes (e.g., k_{obs} for *n*-octyloxyallene (**3**) was determined to be 29.6 L·mol^{-1}·h^{-1}).

From our systematic study on the polymerization of *para*-substituted phenylallene derivatives,[9] the polymerization has been proposed to proceed via the electrophilic attack of the propagating π-allylnickel species toward the allene monomer. In other words, the polymerization rate increases as the electron densities on the allene moieties becomes higher. In good accordance with this relationship, the slower polymerization of **2a** in comparison with **3** can be rationally explained by their electronic characters. For instance, the chemical shifts of the center carbon of the allene moieties in ^{13}C NMR spectra, which are known to reflect upon the electron densities of the allenes, are observed at 202.7 and 201.5 ppm for **2a** and **3**, respectively.

Coordination Polymerization of *N*-Allenyl-δ-valerolactam (2b) and *N*-Allenyl-ϵ-caprolactam (2c). The coordination polymerization of **2b** and **2c** (55 and 58 equiv, respectively) having cyclic six- and seven-membered amide moieties, respectively, was carried out by π-allylnickel catalysts. Although the polymerization of **2a** bearing a cyclic five-membered amide moiety proceeded smoothly by **1a**/PPh$_3$, the catalyst (**1a**/PPh$_3$) was not active enough for the polymerization of **2b** and **2c** and polymers with broader molecular weight distributions ($M_w/M_n \sim 1.3$) were produced in lower yields (~60%) (Table 1, runs 2 and 4). As we reported previously, the combination of [(π-allyl)NiI]$_2$ (**1b**) and PPh$_3$ has higher polymerization activity than **1a**/PPh$_3$ (by ca. 3 times) in the polymerization of alkoxyallenes.[6] Accordingly, both **2b** and **2c** were subjected to the

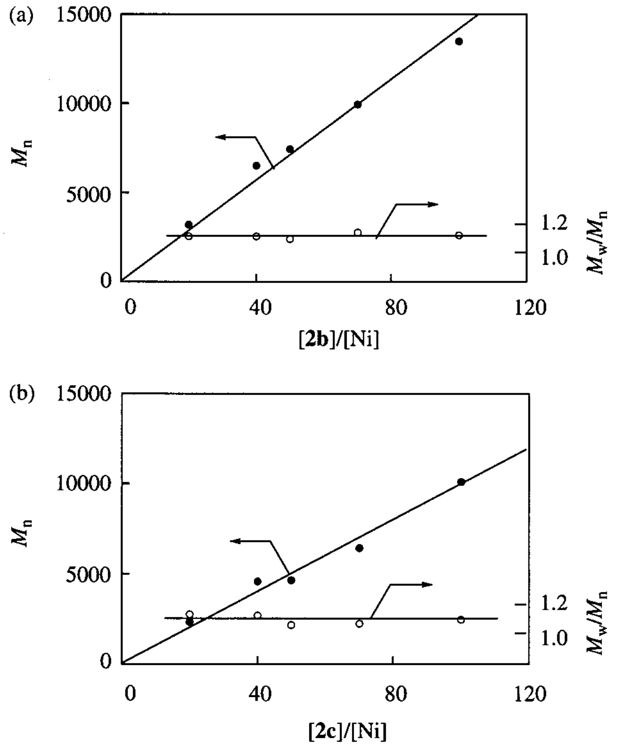


Figure 6. M_n and M_w/M_n vs the feed ratio in the polymerization of **2b** (a) and that of **2c** (b).

polymerization by **1b**/PPh$_3$, from which the polymerization occurred smoothly to give polymers with narrow molecular weight distributions ($M_w/M_n \sim 1.1$) in quantitative yields (runs 1 and 3). These results indicate that the polymerizability of **2b** and **2c** is lower than that of **2a**, despite their similar cyclic amide structures.

The ^{1}H NMR spectra of poly(**2b**) and poly(**2c**) obtained by **1b**/PPh$_3$ indicated that they also consist of only 2,3-polymerization units. The molecular weights of the polymers determined by MALDI-TOF mass spectra confirmed the quantitative initiation efficiencies of **1b**/PPh$_3$ in the polymerizations of **2b** and **2c**.[13]

By the polymerization of **2b** and **2c** by **1b**/PPh$_3$ under various monomer feed ratios, the polymers with narrow molecular weight distributions were constantly obtained in high yields. In both cases, linear relationships between the monomer feed ratio and the molecular weight of the polymer were observed, supporting the living character of the polymerization of **2b** and **2c** (Figure 6a,b).

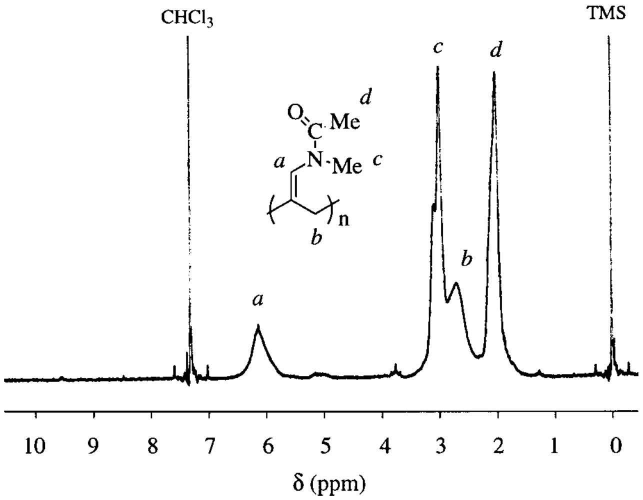


Figure 7. ^{1}H NMR spectrum of poly(**2d**).

Coordination Polymerization of *N*-Allenyl-*N*-methylacetamide (2d). The polymerization behavior of **2d** having an acyclic amide moiety was similar to the cases of **2b** and **2c**, as confirmed by the following experiments. By using **1a**/PPh$_3$ (i.e., the good catalyst for the living polymerization of **2a**), the conversion of **2d** was very slow and a polymer (M_n = 7330, M_w/M_n = 1.19) was obtained in a low yield (27%) when the polymerization was carried out for 12 h (Table 2, run 2). An attempt to overcome the low polymerizability by the reaction at higher temperature resulted in a better yield of the polymer (51%), while its molecular weight distribution became broader (M_w/M_n = 1.48) (run 3). In sharp contrast, the polymerization of **2d** by **1b**/PPh$_3$ completed within 12 h to give a polymer in 99% yield, whose molecular weight distribution was remarkably narrow (M_w/M_n = 1.09) (run 1). The MALDI-TOF mass spectrum of poly(**2d**) also indicated the quantitative initiation efficiency because the molecular weight determined by MALDI (M_n = 5370) was in good accordance with the theoretical one (M_n = 5640). Similar to the cases of poly(**2a**)–poly(**2c**), the ^{1}H NMR spectrum confirmed that poly(**2d**) was composed of the specific 2,3-polymerization unit (Figure 7).

By the polymerization of **2d** by **1b**/PPh$_3$ under various feed ratios ([**2d**]/[Ni]), polymers with narrow molecular

Table 1. Coordination Polymerization of 2b and 2c by 1a/PPh$_3$ or 1b/PPh$_3$[a]

run	2	catalyst[b]	yield (%)[c]	M_n(GPC)[d]	M_w/M_n(GPC)[d]	M_n(MALDI)	M_n(theoretical)[e]
1	**2b**	**1b**/PPh$_3$	97	7460	1.12	7500	7630
2		**1a**/PPh$_3$	64	9070	1.36		
3	**2c**	**1b**/PPh$_3$	97	4650	1.09	8890	8740
4		**1a**/PPh$_3$	60	6850	1.34		

[a] Conditions: [Ni] = 2.0 × 10^{-2} mmol, [**2b**]$_0$/[Ni] = 55, [**2c**]$_0$/[Ni] = 58, at 0 °C → rt, for 12 h, in CH$_2$Cl$_2$. [b] **1a**; [(π-allyl)NiOCOCF$_3$]$_2$, **1b**; [(π-allyl)NiI]$_2$. [c] Isolated yield after precipitation in *n*-hexane. [d] Estimated by GPC (DMF, PSt standard). [e] M_n(theoretical) = (MW of initiator) + (MW of **2**) × [**2**]/[Ni].

Table 2. Coordination Polymerization of 2d by 1a/PPh$_3$ or 1b/PPh$_3$[a]

run	catalyst[b]	yield (%)[c]	M_n(GPC)[d]	M_w/M_n(GPC)[d]	M_n(MALDI)	M_n(theoretical)[e]
1	**1b**/PPh$_3$	99	11 000	1.09	5370	5640
2	**1a**/PPh$_3$	27	7 330	1.19		
3[f]		51	10 200	1.48		

[a] Conditions: [Ni] = 2.0 × 10^{-2} mmol, [**2d**]$_0$/[Ni] = 50, at 0 °C → rt, for 12 h, in CH$_2$Cl$_2$. [b] **1a**; [(π-allyl)NiOCOCF$_3$]$_2$, **1b**; [(π-allyl)NiI]$_2$. [c] Isolated yield after precipitation in *n*-hexane. [d] Estimated by GPC (DMF, PSt standard). [e] M_n(theoretical) = MW of initiator + (MW of **2d**) × [**2d**]/[Ni]. [f] Polymerization was carried out in refluxing ClCH$_2$CH$_2$Cl (at ca. 85 °C).

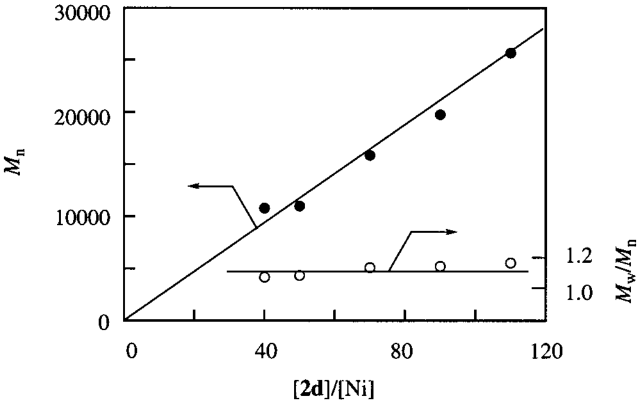


Figure 8. M_n and M_w/M_n vs the feed ratio ([**2d**]/[Ni]).

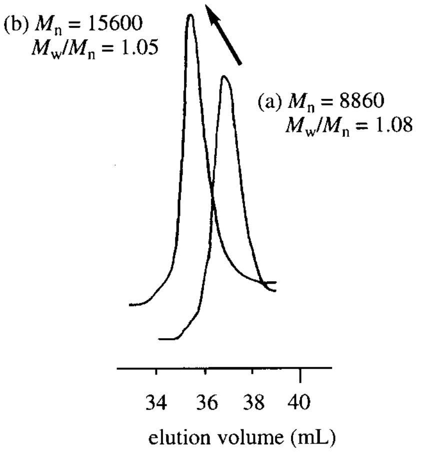


Figure 9. GPC traces of poly(**2d**) produced by the reaction of 30 equiv of **2d** with **1b**/PPh_3 (a) and that obtained by the further addition of 30 equiv of **2d** (b).

weight distributions were likewise obtained in high yields. A linear relationship observed between the monomer feed ratio and the molecular weight of the polymer also supports the living character of the present polymerization (Figure 8).

The stability of the propagating end was examined by the reinitiation experiment. At the first stage, 30 equiv of **2d** was polymerized by **1b**/PPh_3 to give a polymer ($M_n = 8860$, $M_w/M_n = 1.08$). After keeping the polymer solution for an additional 12 h under nitrogen, 30 equiv of **2d** was recharged to conduct the postpolymerization. The recharged **2d** was consumed completely within 12 h and the molecular weight of the polymer increased significantly to the higher molecular weight region without broadening the molecular weight distribution ($M_n = 15\,600$, $M_w/M_n = 1.05$) (Figure 9). Hence, the living propagating end of poly(**2d**) produced by **1b**/PPh_3 also proved to be stable under the examined conditions.

Evaluation of the Polymerizability of *N*-Allenylamides. From the results obtained above, the polymerizability of the four monomers seems to be remarkably different. That is, **2a** undertakes the living polymerization by **1a**/PPh_3, while other monomers (**2b**–**2d**) do not polymerize sufficiently by the same catalyst and require a much more reactive **1b**/PPh_3 for the smooth polymerization.

Since the polymerization of **2a** by **1b**/PPh_3 also proceeds smoothly at 0 °C to ambient temperature,[14] the quantitative evaluation of the polymerizability of **2a**, **2b**, and **2d** was carried out by **1b**/PPh_3.[15] The monomer conversions were monitored by GC after designated reaction periods at 0 °C, from which the kinetic plots of the polymerization could be correlated well with the first-order kinetic equation (Figure 10), where the observed kinetic coefficients for **2a**, **2b**, and **2d** were determined as 14.9, 4.21, and 6.54 $L \cdot mol^{-1} \cdot h^{-1}$, respectively.

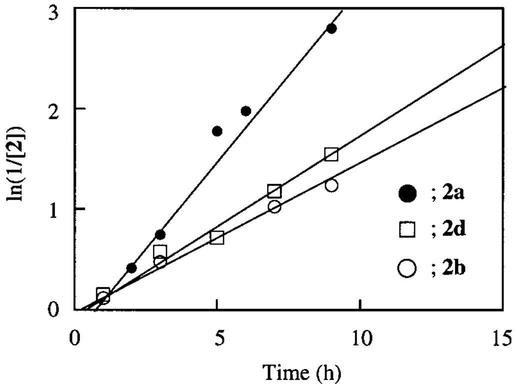


Figure 10. Kinetic plots of **2a**, **2b**, and **2d** in the polymerization by **1b**/PPh_3 ($[2]_0/[Ni] = 40$, $[PPh_3]/[Ni] = 2$).

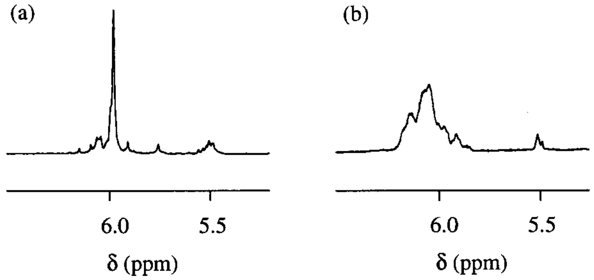


Figure 11. ^1H NMR spectra (δ 4.5–7.0 ppm) of poly(**2b**) (a) and poly(**2a**) (b) obtained by **1b**/PPh_3.

The different polymerizability of the monomers (**2a** > **2b** ≅ **2d**) should be originated from the different nature of the amide substituents. At present, we assume two possible reasons that alter the effect of amides. One is based on the different basicity of the carbonyl groups. According to the literature describing the basicity of various amides, the carbonyl groups in six-membered cyclic and acyclic amides are more basic than that in a five-membered cyclic one.[16] Consequently, the coordination of the carbonyl groups in **2b** and **2d** to the propagating nickel center is expected to be stronger than that of **2a**, which suppresses the monomer coordination toward the nickel atom.[17] In this case, the intermolecular coordination of the carbonyl group can be neglected because **2a** undertook a smooth polymerization by **1a**/PPh_3 in the presence of 1-methyl-2-piperidone or *N*,*N*-dimethylacetamide to afford a polymer whose microstructure was identical to that obtained in the absence of these additives.

Another possible explanation is made by the conformational restriction of the carbonyl group, although we cannot predict which amide moieties have stronger intramolecular coordination. In the ^1H NMR spectrum of poly(**2b**), the peak of the double bond protons appeared much sharper than that in poly(**2a**) (Figure 11). The difference is most probably originated from the distribution of the geometrical isomeric ratio of the trisubstituted olefin unit, and the ratio (i.e., the regularity) is controlled by the intramolecular interaction of the carbonyl group with the nickel center through the polymerization process.

Conclusions

The living coordination polymerization of various *N*-allenylamides (**2a**−**2d**) was attained by using appropriate π-allylnickel catalysts to give narrowly dispersed polymers in excellent yields. The initiation efficiency was confirmed to be quantitative by the MALDI-TOF mass spectra of the polymers. The polymerizability of *N*-allenylamides was found to depend upon the structure of the amide moieties attached to the monomers, in which **2a** having a five-membered cyclic amide moiety revealed a higher polymerizability than **2b**−**2d** having larger cyclic or acyclic amide moieties. The reason for the different polymerizability was discussed by assuming the intramolecular coordination of the amide moieties toward the nickel center.

Experimental Section

Materials and Instruments. Bis(1,5-cyclooctadiene)nickel (Ni(cod)$_2$) was purchased from Cica Chemical Co. and used as received. Allyl trifluoroacetate was purchased from Aldrich Chemical Co. and distilled under nitrogen. Allyl iodide was washed with aqueous sodium thiosulfate, distilled under nitrogen, and used instantly for the catalyst preparation. Triphenylphosphine was recrystallized from dichloromethane/*n*-hexane. The catalysts (**1a** and **1b**) were prepared as described and were used without isolation.[6,18] Toluene and tetrahydrofuran (THF) were dried over sodium, dichloromethane (CH_2Cl_2) was dried over calcium hydride, and they were distilled under nitrogen. Reagents for the monomer syntheses (propargyl bromide, γ-butyrolactam, *N*-methylacetamide, δ-valerolactam, and ϵ-caprolactam) were used as received. *N*-Allenyl-γ-butyrolactam (**2a**) was synthesized according to the previously reported procedure and distilled under nitrogen (80% yield, 53−60 °C/0.25−0.30 mmHg) (lit.[19] 60 °C/0.3 mmHg). 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 Tosoh HLC-8020 (TSK gel G2500H + G4000H + G5000H, DMF as an eluent), calibrated against standard polystyrene samples. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14B equipped with an FID detector using *n*-tetradecane as an internal standard (SE-30, 3 m, gradient temperature of 100−230 °C, 10 °C/min). MALDI-TOF mass spectra were recorded using a Finnigan Mat Ltd. LASERMAT 2000 instrument equipped with a nitrogen laser 9 emission at 337 nm, operating in a linear mode under high vacuum. Samples for MALDI-TOF mass spectroscopic analyses were prepared by mixing 2 μL of the matrix solution (2-[(4-hydroxyphenyl)azo]benzoic acid (HABA) (10 mg in 1 mL of THF)) and 1 μL of the polymer solution (0.2 mg in 1 mL of CH_2Cl_2) on the surface of a stainless steel plate, which was directly introduced into the laser desorption chamber.

Monomer Syntheses. Monomers **2b**−**2d** were synthesized from δ-valerolactam, ϵ-caprolactam, and *N*-methylacetamide, respectively, by the modification of the procedure for **2a**.

N-Allenyl-δ-valerolactam (**2b**): 21% yield; bp 66−70 °C/0.28−0.32 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.79−1.89 (−C−CH_2CH_2−C−, 4H), 2.47 (−CH_2−CO−, t, 2H, J = 6.5 Hz), 3.32 (−CH_2−N<, t, 2H, J = 6.5 Hz), 5.38 (=CH_2, d, 2H, J = 6.6 Hz), 7.62 (=CH−N−, t, 1H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 21.0, 22.6, 32.7, 46.0, 86.9, 99.0, 168.1, 202.3; IR (neat, cm^{-1}) 3047, 2948, 2876, 1958, 1657, 1483, 1449, 1350, 1331, 1290, 1169.

N-Allenyl-ϵ-caprolactam (**2c**): 20% yield; bp 75−76 °C/0.2 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.64−1.75 (−C−$CH_2CH_2CH_2$−C−, 6H), 2.60 (−CH_2−CO−, t, 2H, J = 5.2 Hz), 3.49 (−CH_2−N<, t, 2H, J = 4.8 Hz), 5.38 (=CH_2, d, 2H, J = 5.6 Hz), 7.46 (=CH−N−, t, 1H, J = 5.6 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 23.4, 27.6, 29.7, 37.2, 46.0, 87.3, 99.5, 173.8, 201.6; IR (neat, cm^{-1}) 3044, 2932, 2859, 1958, 1653, 1454, 1406, 1263, 1215, 1192.

N-Allenyl-*N*-methylacetamide (**2d**): 21% yield; bp 52−54 °C/1.5 mmHg; ^{1}H NMR ($CDCl_3$, δ, ppm) 2.18 (−CO−CH_3, s, 3H), 2.98 (>N−CH_3, s, 1.5H), 3.04 (>N−CH_3, s, 1.5H), 5.39 (=CH_2, d, 2H, J = 6.4 Hz), 6.78 (=CH−, t, 0.5H, J = 6.4 Hz), 7.55 (=CH−, t, 0.5H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 21.5, 22.2, 30.6, 33.5, 86.6, 87.0, 99.5, 101.9, 168.4, 168.7, 200.8, 202.2; IR (neat, cm^{-1}) 3050, 2976, 2936, 1960, 1655, 1480, 1453, 1391, 1308, 1142.

Coordination Polymerization of 2a by 1a/PPh$_3$ (Typical Procedure). To a CH_2Cl_2 solution (1.00 mL) of **1a** (2.00 × 10^{-2} mmol) and PPh_3 (4.00 × 10^{-2} mmol), was added **2a** (0.124 g, 1.00 mmol, 50 equiv relative to **1**) at 0 °C, which was stirred at ambient temperature for 12 h. After the complete conversion of **2a** was confirmed by GC, the polymerization mixture was precipitated in *n*-hexane (100 mL) to give poly(**2a**) in 100% yield (0.124 g, 1.00 mol); ^{1}H NMR ($CDCl_3$, δ, ppm) 1.40−2.10 (−C−CH_2−C−, 2H), 2.10−2.55 (−CH_2−CO−, 2H), 2.55−3.20 (=C−CH_2−C=, 2H), 3.20−4.25 (−CH_2−N<, 2H), 5.50−6.60 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.4, 31.4, 34.0, 35.3, 40.2, 48.6, 123.0, 123.7, 124.8, 125.4, 127.8, 128.1, 131.6, 174.4; IR (neat, cm^{-1}) 2982, 2895, 2243, 1688, 1406, 1290.

Poly(**2a**) obtained by **1a**: 99% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.10−2.10 (−C−CH_2−C−, 2H), 2.10−2.60 (−CH_2−CO−, 2H), 2.60−3.20 (=C−CH_2−C=, 2H), 3.20−4.25 (−CH_2−N<, 2H), 5.60−6.60 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.5, 30.3, 35.7, 48.4, 123.0, 124.5, 174.3; IR (neat, cm^{-1}) 2980, 2895, 2241, 1695, 1402, 1288.

Poly(**2a**) obtained by **1b**/PPh_3: 95% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.80−2.20 (−C−CH_2−C−, 2H), 2.10−2.55 (−CH_2−CO−, 2H), 2.60−3.15 (=C−CH_2−C=, 2H), 3.20−3.85 (−CH_2−N<, 2H), 5.65−6.50 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.7, 30.5, 34.3, 35.4, 40.4, 48.8, 49.2, 123.3, 123.7, 124.2, 124.7, 125.6, 174.2, 174.7; IR (neat, cm^{-1}) 2982, 2895, 2245, 1692, 1406, 1290.

Poly(**2a**) obtained by **1a**/PPh_3 in the presence of *N*,*N*-dimethylacetamide: 89% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.80−2.15 (−C−CH_2−C−, 2H), 2.15−2.55 (−CH_2−CO−, 2H), 2.55−3.30 (=C−CH_2−C=, 2H), 3.30−4.10 (−CH_2−N<, 2H), 5.50−6.60 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.6, 30.8, 34.1, 35.6, 40.3, 48.7, 123.2, 123.9, 127.9, 174.5; IR (neat, cm^{-1}) 2982, 2895, 2243, 1684, 1406, 1290.

Poly(**2b**) obtained by **1b**/PPh_3: 97% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.50−2.10 (−C−CH_2CH_2−C−, 4H), 2.10−2.45 (−CH_2−CO−, 2H), 2.45−3.00 (=C−CH_2−C=, 2H), 3.00−3.55 (−CH_2−N<, 2H), 5.70−6.30 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.9, 22.9, 32.3, 34.1, 49.8, 128.1, 131.4, 169.4; IR (neat, cm^{-1}) 2951, 2872, 2240, 1634, 1441, 1414, 1348, 1310, 1167.

Poly(**2b**) obtained by **1a**/PPh_3: 64% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.40−2.10 (−C−CH_2CH_2−C−, 4H), 2.10−2.55 (−CH_2−CO−, 2H), 2.45−2.90 (=C−CH_2−C=, 2H), 2.90−3.60 (−CH_2−N<, 2H), 5.25−6.40 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.9, 22.8, 32.4, 34.3, 44.3, 49.7, 128.2, 131.3, 142.0, 169.7; IR (neat, cm^{-1}) 2947, 2870, 2234, 1634, 1439, 1414, 1348, 1306, 1173.

Poly(**2c**) obtained by **1b**/PPh_3: 97% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.20−2.15 (−C−$CH_2CH_2CH_2$−C−, 6H), 2.20−3.10 (−CH_2−CO−, =C−CH_2−C=, 4H), 3.10−3.90 (−CH_2−N<, 2H), 5.80−6.35 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 23.2, 28.5, 29.6, 33.8, 37.0, 51.7, 129.6, 129.9, 175.5; IR (neat, cm^{-1}) 2934, 2859, 2240, 1638, 1443, 1420, 1352, 1262, 1200.

Poly(**2c**) obtained by **1a**/PPh_3: 60% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.00−2.20 (−C−$CH_2CH_2CH_2$−C−, 6H), 2.20−3.10 (−CH_2−CO−, =C−CH_2−C=, 4H), 3.10−3.95 (−CH_2−N<, 2H), 5.30−6.70 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 23.2, 28.5, 29.7, 37.8, 45.4, 51.3, 129.9, 175.7; IR (neat, cm^{-1}) 2932, 2859, 2240, 1638, 1441, 1418, 1352, 1261, 1198.

Poly(**2d**) obtained by **1b**/PPh_3: 98% yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 1.40−2.25 (−CO−CH_3, 3H), 2.25−3.50 (CH_3−N<, =C−CH_2−C=, 5H), 5.30−6.70 (=CH−N−, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.6, 35.4, 36.0, 38.5, 129.2, 170.3; IR (neat, cm^{-1}) 3056, 2932, 2310, 1644, 1426, 1381, 1342, 1269, 1130.

Poly(**2d**) obtained by **1a**/PPh$_3$: 27% yield; ^{1}H NMR (CDCl$_3$, δ, ppm) 1.40−2.30 (−CO−CH$_3$, 3H), 2.30−3.50 (CH$_3$−N<, =C−CH$_2$−C=, 5H), 5.60−6.70 (=CH−N−, 1H); ^{13}C NMR (CDCl$_3$, δ, ppm) 22.1, 35.4, 36.0, 129.6, 132.7, 170.6; IR (neat, cm^{-1}) 3053, 2928, 2311, 1644, 1426, 1379, 1343, 1273, 1130.

Poly(**2d**) obtained by **1a**/PPh$_3$ in refluxing ClCH$_2$CH$_2$Cl: 51% yield; ^{1}H NMR (CDCl$_3$, δ, ppm) 1.70−2.30 (−CO−CH$_3$, 3H), 2.30−3.30 (CH$_3$−N<, =C−CH$_2$−C=, 5H), 5.30−6.70 (=CH−N−, 1H); ^{13}C NMR (CDCl$_3$, δ, ppm) 22.3, 35.5, 38.4, 129.5, 130.4, 170.3; IR (neat, cm^{-1}) 3054, 2932, 1644, 1426, 1381, 1343, 1271, 1131.

Estimation of the Kinetic Coefficient in the Polymerization of 2a by 1a/PPh$_3$ (Typical Procedure). The polymerization of **2a** ([**2a**]$_0$/[**1a**] = 40, [**2a**]$_0$ = 1.0 M, [**1a**] = 0.025 M) was performed in the presence of PPh$_3$ (2 equiv, relative to the nickel) in CH$_2$Cl$_2$ at 0 °C containing *n*-tetradecane (0.038 M) as an internal standard. After designated reaction periods at 0 °C, a trace amount of the reaction mixture was sampled by the syringe (ca. 10 μL), and the monomer conversions were estimated by the GC analyses.

References and Notes

(1) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Schrock, R. R.; Feldman, J.; Canizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1172. (c) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (d) Schrock, R. R.; Depue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *Ibid.* **1988**, *110*, 1423. (e) Basen, G.; Schrock, R. R.; Khosravi, E.; Feast, W. J.; Gibson, V. C. *Polym. Commun.* **1989**, *30*, 258.

(2) (a) Masuda, T.; Yoshimura, T.; Higashimura, T. *Macromolecules* **1989**, *22*, 3804. (b) Fujimori, J.; Masuda, T.; Higashimura, T. *Polym. Bull.* **1988**, *20*, 1. (c) Tabata, M.; Yang, Y.; Yokota, K. *Polym. J.* **1990**, *22*, 1105. (d) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644. (e) Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054.

(3) (a) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436. (b) Idem. *J. Am. Chem. Soc.* **1991**, *113*, 5065. (c) Hoff, S. M.; Novak, B. M. *Macromolecules* **1993**, *26*, 4067. (d) Deming, T. J.; Novak, B. M. *Ibid.* **1991**, *24*, 326. (e) Shibayama, K.; Seidel, S. W.; Novak, B. M. *Ibid.* **1997**, *30*, 3159.

(4) (a) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008. (b) Killian, C. M.; Temple, D. J.; Johnson, L. K.; Brookhart, M. *Ibid.* **1996**, *118*, 11664. (c) Baumann, R.; Davis, W. M.; Schrock, R. R. *Ibid.* **1997**, *119*, 3830.

(5) (a) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413. (b) Idem. *Acta Polym.* **1995**, *46*, 432.

(6) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1998**, *31*, 2779.

(7) Takagi, K.; Tomita, I.; Endo, T. *Polym. Prepr. Jpn.* **1994**, *43*, 1918.

(8) (a) Endo, T.; Takagi, K.; Tomita, I. *Tetrahedron* **1997**, *53*, 15187. (b) Takagi, K.; Tomita, I.; Endo, T. *Chem. Lett.* **1997**, 1187.

(9) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1997**, *30*, 7386.

(10) Although the thermal or rhodium-catalyzed radical polymerization of *N*-allenyl-γ-butyrolactam has been reported, the polymer yields were relatively low (up to 30%) and the polymer structures were not fully characterized. See: Leland, J.; Boucher, J.; Anderson, K. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 2785.

(11) For instance, the polymerization of 30 equiv of **2a** by **1a** afforded a polymer with M_n = 12 000 and M_w/M_n = 1.20 in 99% yield.

(12) The inactivation of the propagating end observed in the postpolymerization experiment might be one of the reasons for a little broader molecular weight distribution of the polymers by **1a**.

(13) In the case of poly(**2a**), the GPC method proved to overestimate the molecular weight, while poly(**2c**) resulted in the considerable underestimation. Although the reason is not clear, we assume that the difference originates from a little different basicity of the amide moieties and the regularity of the double bond geometry of the repeating units (vide infra).

(14) For example, the reaction of **2a** (50 equiv) by **1b**/PPh$_3$ completed within 12 h in CH$_2$Cl$_2$ to give a soluble polymer (M_n = 12 400, M_w/M_n = 1.08) in 95% yield.

(15) The low solubility of **2c** in CH$_2$Cl$_2$ under the conditions employed for the kinetic investigation (at 0 °C) made it difficult to carry out the quantitative analysis.

(16) The hydrogen-bond basicity scale (pK_{HB}) of 1-methyl-2-pyrrolidone, 1-methyl-2-piperidone, and *N,N*-dimethylacetamide were evaluated to be 2.38, 2.60, and 2.44, respectively. See: Questel, J.-Y. L.; Laurence, C.; Lachkar, A.; Helbert, M.; Berthelot, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2091.

(17) Similar phenomena have been observed in the ring-opening metathesis polymerization of 3-substituted cyclobutenes and 5-substituted cyclooctenes. See, for example: Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459.

(18) (a) Dawans, F.; Marechal, J. C.; Teyssié, Ph. *J. Organomet. Chem.* **1970**, *21*, 259. (b) Semmelhack, M. F. *Org. React.* **1972**, *19*, 115.

(19) Dickinson, W. B.; Lang, P. C. *Tetrahedron Lett.* **1967**, *31*, 3035.

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