Articles

Living Coordination Polymerization of Allene Derivatives in Protic Solvents: Remarkable Acceleration of Polymerization and Increase of 1,2-Polymerization Selectivity

Tomohiro Kino, Masanori Taguchi, Ayako Tazawa, and Ikuyoshi Tomita*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259-G1-9, Midori-ku, Yokohama, 226-8502 Japan

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ABSTRACT: The allylnickel-catalyzed living coordination polymerization of allene derivatives was carried out in protic solvents such as EtOH to figure out their effect on the polymerization behavior. For example, the coordination polymerization of methoxyallene (**2a**) by $[(allyl)NiOCOCF_3]_2$ (**1**)/PPh_3 in EtOH proved to proceed in a living fashion giving a narrowly dispersed polymer in a high yield. In this case, a remarkable acceleration of the polymerization and the higher selectivity of the 1,2-polymerization were observed compared to the case of the polymerization in aprotic solvents such as toluene. That is, the polymerization of **2a** (50 equiv, $[\mathbf{2a}]_0 = 1.0$ M) was complete within 2 h in EtOH to give a polymer in 95% yield ($M_n = 4400$, $M_w/M_n = 1.10$, 1,2-:2,3-polymerizations = 63:37), while it required 12 h in toluene to obtain a polymer having higher content of the 2,3-polymerized unit in a 99% yield ($M_n = 4100$, $M_w/M_n = 1.07$, 1,2-:2,3-polymerizations = 27:73). In protic solvents, the actual propagating species was supposed to be a cationic π-allylnickel complex on the basis of its ^1H NMR and ^{19}F NMR spectra. The use of protic sources such as pyrrole, indole, and phenol was also found to be effective to accelerate the polymerization and to increase the 1,2-polymerization selectivity.

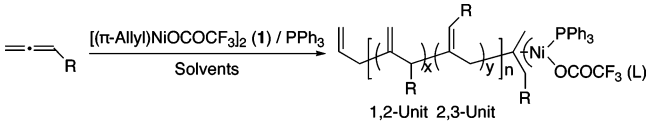
Introduction

Living polymerizations are suitable for precision macromolecular design such as the molecular weight control and preparation of block copolymers, end-functionalized polymers, etc. Up to now, many types of the living systems including the ionic, the radical, and the coordination polymerizations have been established. In most cases, however, the living polymerizations can be performed only if monomers include the limited series of substituents and the limited polymerization conditions such as solvents and additives depending on the nature of the initiating and the growing species. Recently, the living polymerizations for functionalized monomers and those performable under various polymerization conditions have been reported in the controlled radical polymerization[1] and the ring-opening metathesis polymerization.[2] These techniques should be of importance to facilitate versatile macromolecular design based on the living polymerization process.

The π-allylnickel-catalyzed living coordination polymerization of allene derivatives is an attractive candidate for the ideal living polymerization capable of covering monomers carrying many functional groups such as alkyl, aryl, alkoxy, carboalkoxy, hydroxymethyl, and amide to give well-defined polymers bearing a wide variety of functional groups.[3] On the basis of these results, this living polymerization is expected to be performed in the polymerization media containing many functional groups.

* Corresponding author: Tel +81-45-924-5413; Fax +81-45-924-5489; e-mail tomita@echem.titech.ac.jp.

Scheme 1



R; −OMe (**2a**), $-OC_8H_{17}{}^n$ (**2b**), $-C_5H_{11}{}^n$ (**3**), and −Ph (**4**)

Solvents; toluene, DMSO, EtOH, pyrrole, indole, and phenol

In the coordination polymerization of olefins (including nonliving systems), the recent progress of late transition metal catalysts makes it possible to perform the polymerization of monomers carrying polar functional groups and the polymerization in polar media. Nevertheless, the presence of alcohols such as ethanol often brought about the deceleration of the turnover frequencies of the catalysts and the lowering of the molecular weight of the resulting polymers.[4] Compared to the cases of the coordination polymerization of olefins, the initiators and the growing species in those of 1,3-dienes are relatively stable, and some of them are intact toward polar media. For example, the emulsion polymerization of 1,3-butadiene can be performed in water by use of the allylnickel halides as initiators.[5,6]

Herein, we would like to describe the results on the allylnickel-catalyzed living coordination polymerization of some allene derivatives in protic media to find out the unexpected acceleration of the polymerization and the change of the 1,2- to 2,3-polymerization selectivity of the resulting polymers (Scheme 1).

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Experimental Section

Materials and Measurements. A toluene solution of [(π-allyl)-$NiOCOCF_3$]$_2$ (**1**) was prepared as previously reported.[7] Methoxyallene (**2a**),[8] *n*-octyloxyallene (**2b**),[8] *n*-pentylallene (**3**),[9] and phenylallene (**4**)[9] were prepared by the previously reported methods and were purified by the distillation under nitrogen (52 °C/760 mmHg [lit. 52 °C/760 mmHg], 37 °C/0.45−0.50 mmHg, 53 °C/52 mmHg, and 61−62 °C/10 mmHg [lit. bp 70 °C/14 mmHg], respectively). Toluene was dried over sodium and distilled under nitrogen. Ethanol (EtOH) was dried over magnesium ethoxide and distilled under nitrogen. Dimethyl sulfoxide (DMSO) and pyrrole were dried over CaH_2 and distilled under nitrogen. Allyl trifluoroacetate and phenol were distilled under nitrogen. Indole and triphenylphosphine (PPh_3) were purified by recrystallization from MeOH and from diethyl ether, respectively. Other reagents were used as received. All the polymerizations were carried out under nitrogen.

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300, 75, and 282 MHz for ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR, respectively). Fourier transform infrared (IR) spectra were recorded on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS equipped with Tosoh TSK-gel GMH_{HR}-M tandem columns using $CHCl_3$ as an eluent at 35 °C. Polystyrene standards were used for calibration. Gas chromatography (GC) analyses were performed on a Shimadzu GC-14B instrument (SE-30, 2 m, 100−230 °C, at a heating rate of 10 °C/min).

Polymerization of Allene Derivatives (2a, 2b, 3, and 4) in Protic Solvents (Typical Procedure for Polymerization of 2a in EtOH). To a test tube equipped with a three-way cock and a magnetic stirrer bar were added a toluene solution of **1** (0.10 M, 0.20 mL, 0.020 mmol) and a toluene solution of PPh_3 (1.0 M, 40 μL, 0.040 mmol). After removal of toluene under vacuum, EtOH (1.0 mL) and **2a** (0.070 g, 1.0 mmol, [**2a**]/[**1**] = 50) were added at ambient temperature, and the mixture was kept stirring at that temperature. After the polymerization for 3 h, a small portion of the polymer solution (ca. 40 μL) was sampled by a syringe which was subjected to the GPC measurement. By precipitation into MeOH/water (v/v = 50/50), a polymer (poly(**2a**)) was obtained in a 95% yield (0.067 g, M_n = 4400, M_w/M_n = 1.10). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.50 (=C−CH_2−C=, br, 2H × 0.37), 3.24 (⟩CH−OCH_3, br, 3H × 0.63), 3.57 (=CH−OCH_3, br, 3H × 0.37), 3.91 (⟩CH−OCH$_3$, br, 1H × 0.63), 4.46−5.56 (⟩C=CH_2, br, 2H × 0.63), 5.60−6.35 (=CH−OCH$_3$, br, 1H × 0.37); *x*:*y* (in Scheme 1) = 0.63:0.37. ^{13}C NMR ($CDCl_3$, δ, ppm): 29.2 (−CH$_2$−), 55.4 (⟩CH−O−CH$_3$), 58.8 (=C−O−CH$_3$), 83.9 (⟩C−O−), 113.1 (⟩C=CH$_2$ and ⟩C=C−), 144.8 (⟩C=CH$_2$ and ⟩C=C−). IR (film, cm^{-1}): 2930, 2836, 1668, 1460, 1223, 1127, 1001.

The polymerization of **2b**, **3**, and **4** obeyed this protocol, and the polymers (poly(**2b**), poly(**3**), and poly(**4**)) were isolated by precipitation into MeOH/water (v/v = 50/50), acetone, and MeOH/water (v/v = 50/50), respectively. The spectroscopic data of the polymers are as follows:

Poly(2b) (prepared in EtOH/toluene (v/v = 30/70), from **2b** (0.20 g, 1.20 mmol, [**2b**]/[**1**] = 60)): yield 87% (0.174 g, M_n = 9300, M_w/M_n = 1.03). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.87 (−OCH$_2$-(CH$_2$)$_6$CH_3, br, 3H), 1.26 (−OCH$_2$(CH_2)$_6$CH$_3$, br, 12H), 2.27 (=C−CH_2−C=, br, 2H × 0.44), 3.30 (⟩C−OCH_2−, br, 2H × 0.56), 3.61 (=C−OCH_2−, br, 2H × 0.44), 4.02 (⟩CH−O−, br, 1H × 0.56), 4.69−5.56 (⟩C=CH_2, br, 2H × 0.56), 5.69−6.36 (⟩C=CH−O−, br, 1H × 0.44); *x*:*y* (in Scheme 1) = 0.56:0.44. ^{13}C NMR ($CDCl_3$, δ, ppm): 14.1 (−CH$_3$), 22.7−32.8 (−O−CH$_2$(CH$_2$)$_6$CH$_3$), 30.0 (=C−CH$_2$−C=), 63.0 (⟩CH−O−CH$_2$−), 71.8 (=CH−O−CH$_2$−), 83.7 (⟩CH−O), 114.0 (⟩C=CH$_2$ and ⟩C=C−), 142.4 (⟩C=CH$_2$ and ⟩C=C−). IR (film, cm^{-1}): 2928, 2859, 1664, 1466, 1433, 1377, 1265, 1128.

Poly(3) (prepared in EtOH/toluene (v/v = 50/50), from **3** (0.110 g, 1.00 mmol, [**3**]/[**1**] = 50)): yield 99% (0.109 g, M_n = 8600, M_w/M_n = 1.07). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (−CH_3, br, 3H), 1.29 (−CH$_2$(CH_2)$_3$CH$_3$ and ⟩CH−CH_2− br, 6H + 2H × 0.28), 2.06 (=CH−CH_2−, br, 2H × 0.72), 2.20−2.90 (⟩CH− and =C−CH_2−C=, br, 1H × 0.28 + 2H × 0.72), 4.57−5.17 (⟩C=CH_2, br, 2H × 0.28), 5.17−5.70 (⟩C=CH−, br, 1H × 0.72); *x*:*y* (in Scheme 1) = 0.28:0.72. ^{13}C NMR ($CDCl_3$, δ, ppm): 14.1 (−CH$_3$), 22.7−32.1 (−(CH$_2$)$_4$CH$_3$), 37.7 (=C−CH$_2$−C=), 44.0 (⟩CH−), 110.3 (⟩C=CH$_2$), 126.8 (⟩C=CH−), 140.4 (⟩C=C−), 147.6 (⟩C=CH$_2$). IR (film, cm^{-1}): 2957, 2926, 2857, 1637, 1464, 1377, 1340, 1103, 1065, 895, 862, 770, 725.

Poly(4) (prepared in pyrrole, from **4** (0.116 g, 1.00 mmol, [**4**]/[**1**] = 50)): yield 98% (0.114 g, M_n = 5600, M_w/M_n = 1.05). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.98 (−CH_2−, br, 2H), 6.36 (=CH−, br, 1H), 6.60−7.80 (−C$_6$H$_5$, br, 5H); *x*:*y* (in Scheme 1) = 0:1.00. ^{13}C NMR ($CDCl_3$, δ, ppm): 39.6 (−CH$_2$−), 125.9 (⟩C=C−), 127.1−137.2 (−C_6H$_5$), 137.8 (⟩C=C−). IR (film, cm^{-1}): 3059, 3024, 2981, 2911, 2231, 1642, 1599, 1493, 1445.

^{1}H NMR Studies of Initiating Species (Typical Procedure). To a test tube equipped with a three-way cock and a magnetic stirrer bar were added a toluene solution of **1** (0.10 M, 0.80 mL, 0.080 mmol) and a toluene solution of PPh_3 (1.0 M, 0.080 mL, 0.080 mmol). After removal of toluene in vacuo, the residual complex was dissolved in C_6D_6 (0.50 mL) or in CD_3OD (0.50 mL), and the resulting solution was transferred to a NMR tube under nitrogen. The spectroscopic data taken in these solvents are as follows:

^{1}H NMR (C_6D_6, δ, ppm, the spectrum is also shown in Figure 5a): 2.05 (−CH−CH_2 (syn), d, 2H, J = 13.5 Hz), 2.75 (−CH−CH_2 (anti), d, 2H, J = 6.0 Hz), 4.77 (C−CH−C, m, 1H), 7.07−7.56 (P(C$_6$H$_5$)$_3$, 15H).

^{1}H NMR (CD_3OD, δ, ppm, the spectrum is also shown in Figure 5b): 3.02 (−CH−CH_2 (syn), d, 2H, J = 13.5 Hz), 3.80 (−CH−CH_2 (anti), d, 2H, J = 6.0 Hz), 5.81 (C−CH−C, m, 1H), 7.02−7.89 (P(C$_6$H$_5$)$_3$, 15H).

Results and Discussion

Effect of EtOH on Polymerization Behavior. The coordination polymerization of methoxyallene (**2a**) was carried out by [(allyl)$NiOCOCF_3$]$_2$ (**1**)/PPh_3 ([**2a**]/[**1**] = 50, [**2a**]$_0$ = 1.0 M, [PPh_3]/[Ni] = 2) in EtOH at ambient temperature. The conversion of **2a** was complete within 2 h, and a polymer (poly(**2a**), M_n = 4400, M_w/M_n = 1.10) was obtained in a 95% yield by precipitation into MeOH/water (v/v = 50/50). In EtOH, the

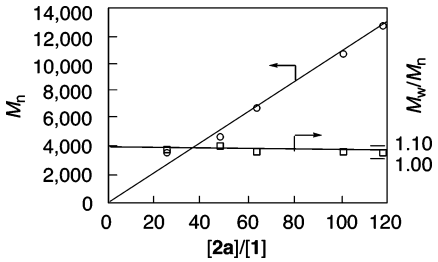

Figure 1. Dependence of M_n and M_w/M_n on the ratio of **2a** to **1**.

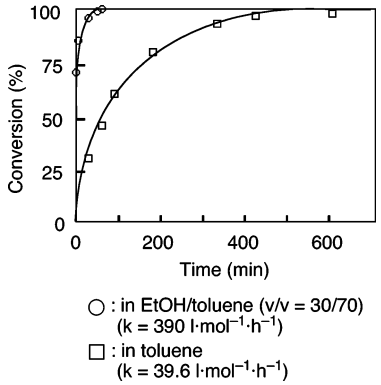

Figure 2. Time−conversion curves of **2b** (conditions: [**2b**]$_0$ = 0.60 M, [**1**]$_0$ = 0.010 M, [PPh_3]$_0$ = 0.010 M, at 25 °C).

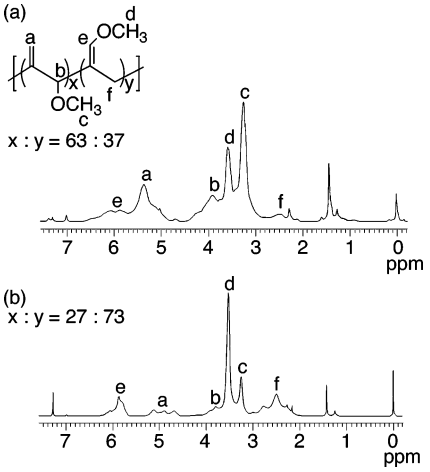

Figure 3. ^{1}H NMR spectra of poly(**2a**) prepared in EtOH (a) and that prepared in toluene (b).

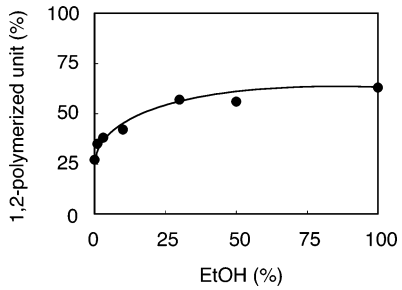

Figure 4. Concentration of EtOH vs the content of the 1,2-polymerized unit (*x* unit).

polymerization was also found to proceed in a living fashion as convinced by the polymerization under various ratios of [**2a**]/[Ni]. In all cases, the polymers with narrow molecular weight distribution were obtained in high yields where a good linear relationship is observed between the ratio of monomer to initiator and the molecular weight of the polymers (Figure 1).

Compared to the case of the polymerization of alkoxyallenes in toluene which requires about 12 h to complete the monomer conversion,[3a] the polymerization proceeds much faster in EtOH as described above for **2a**. Thus, the solvent-dependent nature of the polymerization rate was evaluated in the polymerization of *n*-octyloxyallene (**2b**).[10] From the time−conversion analyses of **2b** in toluene and in EtOH/toluene (v/v = 30/70), the observed kinetic coefficients (k_{obs} in $-d[\mathbf{2b}]/dt = k_{obs}[\mathbf{1}][\mathbf{2b}]$) were estimated as 39.6 and 390 L mol^{-1} h^{-1}, respectively. Not only the acceleration of the polymerization but also the selectivity between the 1,2- and the 2,3-polymerizations proved to be affected by the polymerization solvents. For example, poly(**2a**) prepared in EtOH proved to have a higher content of the 1,2-polymerized unit (1,2-:2,3-polymerizations (*x*:*y* in Scheme 1) = 63:37) than that prepared in toluene (*x*:*y* = 27:73) as can be monitored from their ^{1}H NMR spectra (Figure 3). Using the mixed solvent of EtOH and toluene, the selectivity between the 1,2- and the 2,3-polymerizations was controllable by the concentration of EtOH (Figure 4). That is, the 1,2-polymerized unit in the obtained polymer increased from 27% to 63% by increasing the EtOH content in the mixed solvent, while the molecular weight and its distribution were almost constant.

NMR Studies of the Propagating Species. To study the reason for the acceleration of the polymerization and the increase of the 1,2-polymerization selectivity in the polymerization in EtOH, the NMR studies of the initiating system (**1**/PPh_3) were performed in C_6D_6 and in CD_3OD (Figure 5). In the ^{1}H NMR spectrum of **1**/PPh_3 measured in CD_3OD, all peaks for the allyl protons appeared in the lower magnetic fields by ~1 ppm in comparison with those observed in C_6D_6. Judging from the chemical shifts of the allyl protons reported for π-allylnickel complexes,[11] these changes are ascribable to the formation of the cationic complex in protic solvents such as alcohol. In the ^{19}F NMR spectra of **1**/PPh_3, the peak for the trifluoroacetate also appeared in the higher magnetic field in CD_3OD ($\delta = -79.93$ ppm) in comparison with that in C_6D_6 ($\delta = -77.50$ ppm) which might further support that trifluoroacetate anion dissociates from the complex in the protic solvents to form the cationic complex (Scheme 2).[12] Accordingly, we assume the actual propagating species to be a cationic π-allylnickel complex in EtOH. As we described previously in the polymerization of alkoxyallenes by allylnickel catalysts possessing various anionic ligands, the polymerization rate and the selectivity of the 1,2-polymerization

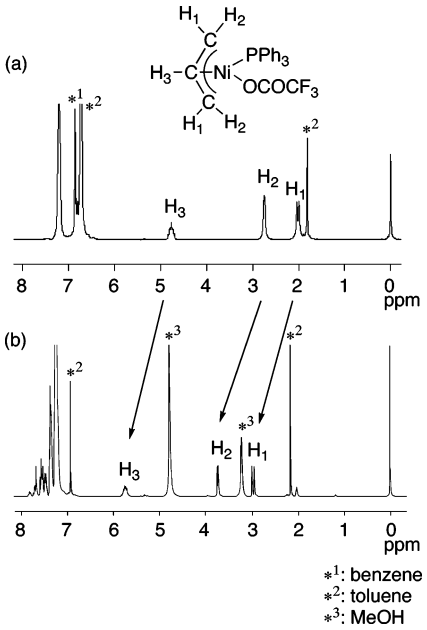

Figure 5. ^{1}H NMR spectra of **1**/PPh_3 ([PPh_3]/[**1**] = 1) in C_6D_6 (a) and that in CD_3OD (b).

Scheme 2

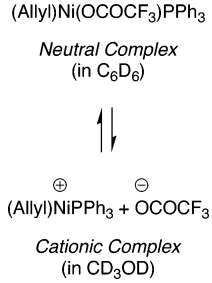

Table 1. Polymerization of 2a (50 equiv) in Various Solvents

run	solvents	yield (%)[a]	*x*:*y*[c]	M_n[d]	M_w/M_n[d]
1	toluene	99	27:73	4100	1.07
2	DMSO/toluene (v/v = 50/50)	99	40:60	3500	1.06
3	EtOH/toluene (v/v = 50/50)	95	56:44	4300	1.08
4	pyrrole/toluene (v/v = 50/50)	90	64:36	3900	1.09
5	indole/toluene (v/v = 50/50)	98	66:34	4600	1.07

[a] Isolated yield after precipitation into MeOH/H_2O (v/v = 50/50). [b] Determined by ^{1}H NMR. [c] Estimated by GPC ($CHCl_3$, polystyrene standard).

Table 2. Polymerization of 3 and 4 (50 equiv) in Various Protic Media

run	monomer	solvents	k_{obs} (L mol^{-1} h^{-1})	yield (%)[a]	*x*:*y*[b]	M_n[c]	M_w/M_n[c]
1	**3**	toluene	0	0			
2[d]	**3**	DMSO/toluene (v/v = 50/50)	2.62	49	27:73	3200	1.03
3	**3**	EtOH/toluene (v/v = 50/50)	16.4	99	28:72	8600	1.07
4	**3**	pyrrole/toluene (v/v = 50/50)	62.2	99	31:69	7100	1.08
5	**3**	indole/toluene (v/v = 50/50)	86.9	94	31:69	7600	1.08
6	**3**	phenol/toluene (v/v = 50/50)	224	93	49:51	7600	1.08
7	**4**	toluene	0	0			
8	**4**	pyrrole	6.24	98[e]	0:100	5600	1.05

[a] Isolated yield after precipitation into acetone. [b] Determined by ^{1}H NMR. [c] Estimated by GPC ($CHCl_3$, polystyrene standard). [d] The polymerization was carried out for 1 week (the conversion of **3** was 53%). [e] Isolated yield after precipitation into MeOH/H_2O (v/v = 50/50).

increased by lowering the electron density on the propagating π-allylnickel species.[3c,d] The results obtained in the present study are in good accordance with this trend: the faster polymerization and the higher 1,2-polymerization content in the polymers are caused by the lower electron density of the Ni atom through the cationic complex formation.[13]

Living Coordination Polymerization in Various Aprotic and Protic Media. The polymerization of **2a** (50 equiv relative to **1**) was likewise performed in the presence of aprotic and protic media such as DMSO, pyrrole, and indole to evaluate the contents of the 1,2-polymerized unit and the polymerization rate. As shown in Table 1, aprotic polar sovents such as DMSO proved to increase the content of the 1,2-polymerized unit in the resulting polymer (run 2). The polymerization of **2a** in the mixture of toluene and various protic sources such as pyrrole and indole was found to complete within a few minutes at ambient temperature to give poly(**2a**) with narrow molecular weight distribution in high yields (runs 4 and 5). Apparently, the polymerization proceeds much faster in the presence of pyrrole and indole compared to the case of EtOH. The content of the 1,2-polymerized unit in the polymer obtained in pyrrole and indole was estimated as 64% and 66%, which was also larger than that obtained in EtOH (56%) or in toluene (27%).

To evaluate the polymerization rates in these reaction media, an alkylallene derivative (pentylallene, **3**) and phenylallene (**4**), which have relatively lower polymerizability than alkoxyallenes, were employed, and their polymerization was performed in these media (Table 2). As expected from the results obtained in alkoxyallenes, the observed kinetic coefficients (k_{obs}) for **3** also increased in the order of DMSO (k_{obs} = 2.62 L mol^{-1} h^{-1}) < EtOH (k_{obs} = 16.4 L mol^{-1} h^{-1}) < pyrrole (k_{obs} = 62.2 L mol^{-1} h^{-1}) < indole (k_{obs} = 86.9 L mol^{-1} h^{-1}). In the polymerization of **3**, phenol/toluene (v/v = 50/50) can also be used because phenol does not react with **3** but **2**. In this case, the k_{obs} was estimated to be the largest (224 L mol^{-1} h^{-1}).[14] Besides, the content of the 1,2-polymerized unit in the resulting polymer also increased in the same order (DMSO < EtOH < pyrrole < indole < phenol).[15,16] In the case of **4**, the acceleration of the polymerization was also observed in the protic media such as pyrrole. However, the resulting polymer was constantly composed of the specific 2,3-polymerization unit, most probably due to the higher thermodynamic stability of the 2,3-units by the conjugation of the olefin unit with the adjacent aromatic substituent.

Conclusions

The coordination polymerization of allene derivatives such as alkoxyallenes (**2a** and **2b**), pentylallene (**3**), and phenylallene (**4**) by [(allyl)NiOCOCF$_3$]$_2$ (**1**)/PPh$_3$ proceeds in a living fashion in both aprotic and protic media such as toluene, DMSO, EtOH, pyrrole, and indole to give polymers with well-defined molecular weight and narrow molecular weight distribution. The remarkable acceleration of the polymerization and the increase of the 1,2-polymerization selectivity were observed especially in the protic polymerization solvents. The actual propagating species of the polymerization was supposed to be the cationic π-allylnickel complex as convinced from the spectroscopic analyses of **1**/PPh$_3$ in protic solvents.

The living polymerizations in protic media such as alcohols and water are still limited and are important to realize precision heterogeneous polymerizations and the green processes for industries. The results obtained through this research may also suggest that the allylnickel-catalyzed living polymerization is potentially applicable to monomers bearing a variety of functional groups. Thus, the possibility of the living polymerization in other media including water and that of functionalized allene derivatives are currently being investigated.

References and Notes

(1) For recent reviews, see for example: (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745. (c) Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3606−3614.

(2) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wieley-VCH: Weinheim, 2003.

(3) (a) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Macromolecules* **1994**, *27*, 4413−4414. (b) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. *Acta Polym.* **1995**, *46*, 432−436. (c) Takagi, K.; Tomita, I.; Nakamura, Y.; Endo, T. *Macromolecules* **1998**, *31*, 2779−2783. (d) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1997**, *30*, 7386−7390. (e) Endo, T.; Takagi, K.; Tomita, I. *Tetrahedron* **1997**, *53*, 15187−15196. (f) Takagi, K.; Tomita, I.; Endo, T. *Chem. Lett.* **1997**, 1187−1188. (g) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules* **1998**, *31*, 6741−6747. (h) Tomita, I.; Ubukata, T.; Endo, T. *React. Funct. Polym.* **1998**, *37*, 27−32. (i) Taguchi, M.; Tomita, I.; Endo, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3667−3669. (j) Takagi, K.; Tomita, I.; Endo, T. *Polym. Bull.* **2003**, *50*, 335−342.

(4) For recent reviews, see for example: (a) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−561. (b) *Late Transition Metal Polymerization Catalysis*; Rieger, B., Baugh, L. S., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003.

(5) (a) Kormer, V. A.; Lyashch, R. S.; Babitskii, B. D.; L'vova, G. V.; Lobach, M. I.; Chepurnaya, T. Ya. *Dokl. Akad. Nauk SSSR* **1968**, *180*, 665−667. (b) Kormer, V. A.; Babitskiy, B. D.; Lobach, M. I. *Adv. Chem. Ser.* **1969**, *91*, 306−316.

(6) Allylnickel complexes have also been reported to be stale in the presence of water in the living polymerization of isocyanides. See: Deming, T. J.; Novak, B. M. *Macromolecules* **1991**, *24*, 6043−6045.

(7) Dawans, F.; Marechal, J. C.; Teyssié, P. *J. Organomet. Chem.* **1970**, *21*, 259−261.

(8) Hoff, S.; Brandsma, R. S.; Arens, J. K. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916−924.

(9) Moreau, J.-L.; Gauder, M. *J. Organomet. Chem.* **1976**, *108*, 159−164.
(10) Because **2b** can also be polymerized in the living mechanism and **2b** could be readily distinguished from the solvents in GC, a series of the time−conversion study has been performed using **2b** as a monomer.
(11) Taube, R.; Gehrke, J. P. *J. Organomet. Chem.* **1985**, *291*, 101−115.
(12) Assuming that the ^{19}F NMR spectrum of **1**/PPh_3 in C_6D_6 represents the chemical shift for the trifluoromethyl group of the neutral complex and that sodium trifluoroacetate dissociates completely in CD_3OD (−80.30 ppm), 87% of the allylnickel is supposed to be dissociated to the cationic complex in CD_3OD (Scheme 2).
(13) The polymerization of **3** by allylnickel complexes having less coordinating anions such as (π-allyl)Ni$(PPh_3)_2^+BPh_4^-$ resulted in the production of polymers having bimodal molecular weight distribution or insufficient conversion of **3**. The results might suggest that the moderate equilibrium between the cationic and the neutral forms might be important to preserve the living nature of the polymerization.
(14) In the ^{1}H NMR study of the initiating system (**1**/PPh_3) in pyrrole/C_6D_6 ([pyrrole]/[**1**] = 20), a clear lower magnetic field shift of the allyl protons was observed (H_1: 2.38 ppm, H_2: 3.02 ppm, H_3: 5.03 ppm), which indicated that the actual propagating species is also a cationic complex similar to the case in alcoholic solvents.
(15) The observed kinetic coefficient (k_{obs}) and the content of the 1,2-polymerized unit are affected by the nature of the catalyst (i.e., the degree of dissociation to the cationic species), which might be influenced by the nature of the solvents. We assume that the acidity of the solvents (i.e., toluene < EtOH < pyrrole < indole < phenol) might be an important factor to control the polymerization behavior.
(16) The polymerization of **3** by **1** without PPh_3 proceeds much faster than that by **1**/PPh_3 in both aprotic and proic solvents. For example, k_{obs} in pyrrole/toluene (v/v = 1/1) and that in phenol/toluene (v/v = 1/1) were 950 and ≥3000, respectively. In these cases, the content of the 1,2-polymerized unit in the polymer (x:y = 12:88 for both solvent systems) was lower than that in the polymer obtained by **1**/PPh_3. These results support that PPh_3 plays an important role of the neutral ligand in these protic polymerization media to control the activity of the catalyst and to determine the microstructure of the resulting polymers.

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