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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b07431 • Publication Date (Web): 02 Sep 2019

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Living Cyclocopolymerization Through Alternating Insertion of Isocyanide and Allene via Controlling the Reactivity of the Propagation Species: Detailed Mechanistic Investigation

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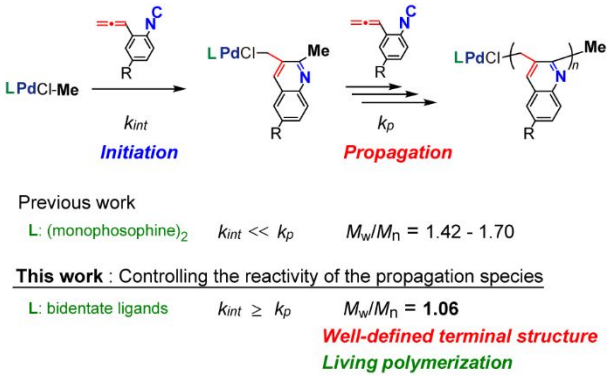
ABSTRACT: Living cyclocopolymerization through the alternating insertion of an isocyanide and allene into palladium–carbon bond was developed based on the controlling the reactivity of the propagation species using bidentate ligands. We revealed that the rate of the presented cyclocopolymerization was depended on the ligands of Pd-initiator. When the palladium–methyl complexes having appropriate cis-chelating ligand, such as 1,3-bis(diphenylphosphino)propane (dppp), were used as initiator, the cyclocopolymerization of bifunctional aryl isocyanides (**1**) that contain both isocyano and allenyl moieties polymerized to afford poly(quinolylene-2,3-methylene)s with controlled molecular weight and narrow molecular weight distributions. The resulting polymer was characterized by ^{1}H and ^{13}C NMR analyses, which clearly showed that the terminal moiety of the polymer formed well-defined organopalladium complex as the resting state for the polymerization, which could undergo further polymerization; not only cyclocopolymerization with **1** but also homopolymerization of simple aryl isocyanide. In the analysis of the cyclocopolymerization mechanism, we conclusively demonstrated that the insertion reaction of isocyanide is the rate-determination step in the cyclocopolymerization, which proceeds via a five-coordinate intermediate with a geometrical change. The cis-chelating ligand controls the site interchange reaction, which dominates the reactivity of propagation species.

Introduction

The precise design of polymer structures has received significant attention because many factors influence the chemical and physical properties the primary structure and its constituent units, associated molecular weights, and the final structure of the polymer. The development of precise synthesis of novel polymer architectures is an important subject in polymer chemistry. Cyclopolymerization of bifunctional monomers is one of the efficient method of synthesizing new types of polymer materials.[1] The resulting polymer has a cyclic structure in the backbone, exhibiting unique properties compared to those of the corresponding linear polymers. To date, various precise cyclopolymerization systems have been developed using bifunctional monomers with unsaturated hydrocarbons as substituents, such as non-conjugated dienes and divinyl compounds.[2] In most cyclopolymerization systems, the same type of reactive site is used as a substituent on the bifunctional monomer, resulting in mechanistically similar reactions successively proceeded. Cyclocopolymerization via the combination of different types of substituents by an alternating intra- and intermolecular mechanisms is challenging and has therefore hardly been achieved, despite the expanding range of polymer designs.[3] Controlling the reactivity of each substituent is generally difficult, which prevents intermolecular homopolymerization and promotes the alternate reaction. Additionally, it is necessary to regulate head-to-tail selectivity.

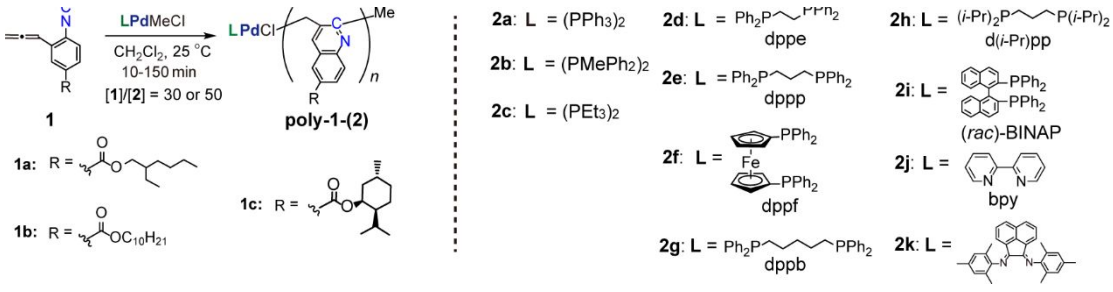
Isocyanide is an important monomer in polymer chemistry, which is known to undergo polymerization in the presence of an organometallic catalyst through multiple isocyanide insertions into a metal-carbon bond.[4] Polymerization systems with isocyanides have been designed to afford various types of polyisocyanides, and these polymers have been developed in many fields.[5] Previously, we studied cyclocopolymerization systems involving the intramolecular alternating insertion of isocyanides and unsaturated hydrocarbons into a palladium–carbon bond using bifunctional aryl isocyanides **1** bearing unsaturated hydrocarbons at the *ortho*-position.[6] Recently, we focused on an allene[7] as the unsaturated molecules during our polymerization, and aryl isocyanide containing allenyl moiety at the *ortho*-position was designed and synthesized.[8] The molecules polymerized rapidly within 10 min in the presence of $(PPh_3)_2PdMeCl$ through completely alternating insertions of the isocyanide and allene moieties into the palladium–carbon bond with perfect head-to-tail selectivity. This is a novel example of cyclocopolymerization involving completely different types of substituents. The resulting polymers, poly(quinolylene-2,3-methylene)s, are completely new architecture and hold potential for a new polymer design. However, in this reaction system, the molecular weight distribution of the resulting polymer is relatively broad (M_w/M_n = 1.42–1.70), and control of the polymerization reaction has not been achieved (Scheme 1). This is because the propagation reaction is quite faster than the initiation reaction, and the structure of the propagation species is unclear due to the instability of the terminal palladium complex, leaving the detailed reaction mechanism unclarified. In order to control the polymerization reaction, it is necessary to determine the terminal structure and mechanism, and to regulate the reactivity of the propagation species.

Scheme 1. Cyclocopolymerization Based on Alternating Insertion of Isocyanide and Allene



In the past decades, living polymerization systems have been developed, which allow not only to control the molecular weight and molecular weight distributions but also to realize a wide variety of polymer design, such as block copolymers, via the well-defined terminal structure.[9] Herein, we report a novel living polymerization based on our cyclocopolymerization system involving the alternating incorporation of isocyanides and allene moieties. When the appropriate bidentate ligands were used, the reactivity of the propagation species was controlled to achieve living polymerization, and a well-defined palladium complex was remained at the growth end. The resulting propagation species maintained its reactivity, which can be utilized for the block copolymerization. In the latter part of this paper, the polymerization mechanism was investigated, and we conclusively demonstrated that insertion reaction of isocyanide is rate-determination step in the cyclocopolymerization, which proceeds via the five-coordinate intermediate with a conformational change to the appropriate configuration depending on the bidentate ligands.

Table 1. Cyclocopolymerization of Monomer 1 with Pd Complex Bearing Various Ligands [a]



entry	1	2	[1] / [2]	time (min.)	conv. (%)	M_n (DP_n)		M_w/M_n [b]
						$M_{n(SEC)}$ [b]	$M_{n(NMR)}$ [c]	
1	**1a**	**2a**	50	< 10	>99	7800	15 200 (51)	1.44
2	**1a**	**2b**	50	< 10	>99	7500	15 000 (51)	1.52
3	**1a**	**2c**	50	< 10	>99	6700	15 000 (51)	1.65
4	**1a**	**2e**	50	30	45	3200	-	1.11
5	**1a**	**2e**	50	150	>99	7800	15 000 (51)	1.15
6	**1b**	**2e**	30	120	>99	6900	9800 (30)	1.06
7	**1b**	**2c**	15	90	>99	2700	5200 (16)	1.20
8	**1b**	**2d**	30	120	10	6900	- [e]	- [e]
9	**1b**	**2d**	30	900	>99	7500	- [e]	1.72
10	**1b**	**2f**	30	120	96	7500	9500 (29)	1.10
11	**1b**	**2g**	30	120	96	12 000	- [e]	1.56
12	**1b**	**2h**	30	120	82	18 000	- [e]	2.20
13	**1b**	**2i**	30	120	>99	7200	- [e]	4.29
14	**1b**	**2j**	30	30	>99	7100	10 000 (31)	1.06
15	**1b**	**2k**	30	30	>99	7500	10 000 (31)	1.06

[a] [**1**] = 0.1 M ([**1**]/[**2**] = 30) at CH_2Cl_2 (5.0 mL) at 25 °C , [**1**]/[**2**] = 30 or 50, [b] Determined by SEC using polystyrene standards. [c] Determined by ^{1}H NMR spectroscopy based on the terminal methyl group. The polymerization degrees (DP) is shown in parenthesis. [e] Not Determined.

Results and Discussion

Living Cyclocopolymerization Through Alternating Insertion of Isocyanide and Allene. Initially, the polymerization of aryl isocyanide **1a** (R = 2-ethylhexyloxycarbonyl) that contains isocyano and allenyl moieties in the presence of several palladium complexes **L**PdMeCl (**2**) with different types of ligands was examined in CH_2Cl_2 ([**1**] = 0.1 M, [**1**]/[**2**] = 50) at 25 °C (Table 1). The resulting polymers were analyzed by size-exclusion chromatography (SEC) in $CHCl_3$ with polystyrene standard calibration. When mono phosphines, PPh_3, PPh_2Me, and PEt_3 (**2a-2c**) were used as a ligand, polymerization was completed within only 10 min at 25 °C, and poly(quinolylene-2,3-methylene)s (**poly-1a-(2a–2c)**) were obtained with broad molecular weight distributions (M_w/M_n) (entries 1–3). The use of cis-chelating ligands affected the polymerization reaction significantly. When 1,3-bis(diphenylphosphino)propane (dppp) was used as a ligand (**2e**), the reaction slowed down and the resulting polymer exhibited a narrower molecular weight

distribution (M_w/M_n = 1.15 in entry 5) than **poly-1a-(2a–2c)**. The resulting polymer was characterized by NMR spectroscopy (Figure S9, see the Supporting Information (SI)). The ^{1}H NMR spectrum of **poly-1a-(2e)** exhibited signals associated with the quinolylene-2,3-methylene backbone [δ 8.34 (s, 1H), 7.78 (s, 1H), 7.62 (d, 1H), 7.41 (d, 1H)] that was generated by the alternating insertion of isocyanide and allene, and the allenyl protons of **1a** [δ 6.53 (t, 1H), 5.33 (d, 2H)] had been clearly consumed. The results indicate that the cyclocopolymerization of **1a** also proceeded via the alternating insertion of isocyanide and allene when using dppp as a ligand. The molecular weight ($M_{n(NMR)}$) of the resulting polymer was calculated from the ^{1}H NMR signal of the terminal methyl group and methylene moieties on the backbone ($M_{n(NMR)}$ = 15 000, n = 51), and was in good agreement with the ideal M_n value calculated on the basis of [**1**]/[**2**] ratio of 50. When **1b** (R = decyloxycarbonyl) and **1c** (R = l-menthyl) were used as a monomer ([**1**] = 0.1 M, **1b**; [**1**]/[**2**] = 30, **1c**; [**1**]/[**2**] = 15),[10] the polymerization also proceeded to yield **poly-1b-(2e)** and **poly-1c-(2e)** with narrow M_w/M_n (entries 6 and 7). Subsequently, other types of cis-chelating phosphine ligands with different bite angles[11] were investigated using the conditions in entry 6. The cyclocopolymerization of **1** was affected by the bite angle. When 1,3-bis(diphenylphosphino)ethane (dppe) (**2d**), which has a narrower bite angle (85°)[12] than 91° of **2e**, was used as the ligand, the polymerization rate markedly decreased with increasing the reaction time and the molecular weight distribution became broad (entries 8 and 9). In the case of 1,3-bis(diphenylphosphino)ferrocene (dppf) (**2f**) which has larger bite angle (95°) than that of **2e**, a similar M_w/M was also obtained with **2e** (M_w/M = 1.10, entry 10), whereas, when the complexes of 1,3-bis(diphenylphosphino)butane (dppb) (**2g**), which has much larger bite angle (98°) was used, the molecular weight distribution was broad (M_w/M_n = 1.56, entry 11). On the other hand, even when ligand with a similar bite angle to that of **2e** but more bulky substituents on phosphorus or twist spacer of cis-chelating ligand, for example, 1,3-bis(di-*i*-propylphosphino)propane (d(*i*-Pr)pp) (**2h**) or 2,2′-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) (**2i**; 92°), were used, the molecular weight distributions were broad (entries 11–13). These results indicate that not only the simple bite angle of the ligand but also appropriate direction of the phosphorous lone pair electrons toward the metal is crucial for achieving narrow molecular weight distributions in the cyclocopolymerization of **1**. Next, we examined cis-chelating nitrogen ligands. When 2,2′-bipyridine (**2j**) was used, the polymerization reaction completed in 30 min, and the desired polymer with a narrow molecular weight distribution (M_w/M_n = 1.06) was obtained (entry 14), even though the bite angle (78°)[13] of **2j** is smaller than that of **2d**. A similar trend was also observed in other rigid bidentate nitrogen ligands, such as bis(arylimino)acenaphthene ligands (**2k**), which was used for olefin polymerization (entry 15). The differences in the tendency of the polymerization between phosphorous and nitrogen ligands can be attributed to the coordination ability or the trans effect.[14]

The polymerization of **1b** initiated by **2e** (L = dppp) or **2j** (L = bpy) at different initial feed ratios ([**1**]/[**2**] = 10–50) was examined (Table 2) under the conditions described above. In all cases, after consumption of the monomer, all the polymer exhibited a monomodal elution peak with a narrow molecular weight distribution. Furthermore, the $M_{n(NMR)}$ values of the resulting polymers were in good agreement with the ideal M_n values calculated from [**1**]/[**2**] feed ratio, suggesting that all of the initial palladium complex participated in the polymerization (Figure 1).[15] The $M_{n(SEC)}$ values of **poly-1b-(2)**, which were calculated by size-exclusion chromatography (SEC) using polystyrene standards, were different from the $M_{n(NMR)}$ values, although they exhibited a linear relationship. This phenomenon was attributed to the difference in hydrodynamic radius between polystyrene and **poly-1b-(2)**.[8] Interestingly, in the ^{1}H NMR spectra of **poly-1b-(2e)**, several small peaks assigned to a quinolylmethyl-palladium complex were clearly observed (Figure 2a and S10). The phosphine ligand (f-H, h-H, and g-H) and methylene protons (a-H) adjacent to the palladium were clearly observed, and two doublet peaks derived from dppp ligand of the terminal palladium complex were also recorded in ^{31}P NMR spectrum (Figure 2b). Additionally, several units adjacent to the Pd complex can be clearly distinguished by ^{1}H NMR (b-H, c-H, d-H). These peaks were assigned by ^{1}H 2D-ROESY, and ^{1}H, ^{13}C-HSQC experiments of the resulting polymers (Figure S17 and S18). The corresponding methylene protons (*b*-H, *c*-H, and *d*-H) were assigned. These results clearly indicate that palladium complex remained on the terminal moiety of the polymer. This propagation complex survives quantitatively based on a comparison of the integral of both terminal signals in the ^{1}H NMR spectrum. Similar results were also found in the cases of **2f** and **2j** (Figure S14 and S15).

Table 2. Cyclocopolymerization using Pd Complex 2e and 2j with the Different Initial Feed Ratios of Monomer 1b[a]

entry	2	[**1b**]/[**2**]	time (min.)	M_n (DP$_n$)		M_w/M_n[b]
				$M_{n(SEC)}$[b]	$M_{n(NMR)}$[c]	
1	**2e**	10	30	2100	3400 (11)	1.20
2	**2e**	20	90	4800	7200 (22)	1.09
3	**2e**	30	120	6900	9800 (30)	1.06
4	**2e**	50	150	13 000	17 000 (53)	1.15
5	**2j**	10	30	2700	3600 (10)	1.16
6	**2j**	20	30	5100	7200 (22)	1.08
7	**2j**	30	30	7100	10 000 (31)	1.06
8	**2j**	50	40	12 200	17 300 (53)	1.06

[a] [**1**] = 0.1 M in CH_2Cl_2 (5.0 mL) at 25 °C. [b] Determined by SEC using a polystyrene standard. [c] Determined by ^{1}H NMR spectroscopy based on the integral intensity of the terminal methyl group. The polymerization degrees (DP) is shown in parenthesis.

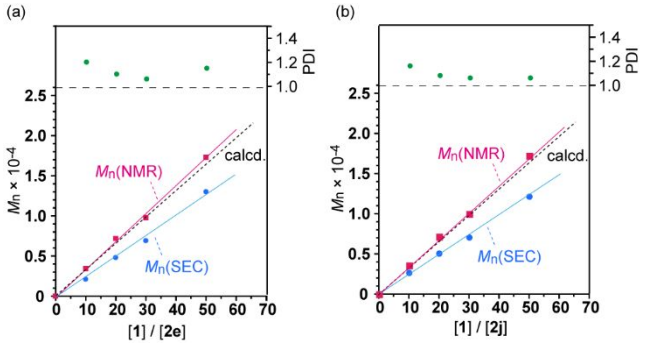


Figure 1. Relationship between M_n, M_w/M_n and feed ratio of monomer **1** to initiator (a) **2e** and (b) **2j** in polymerization

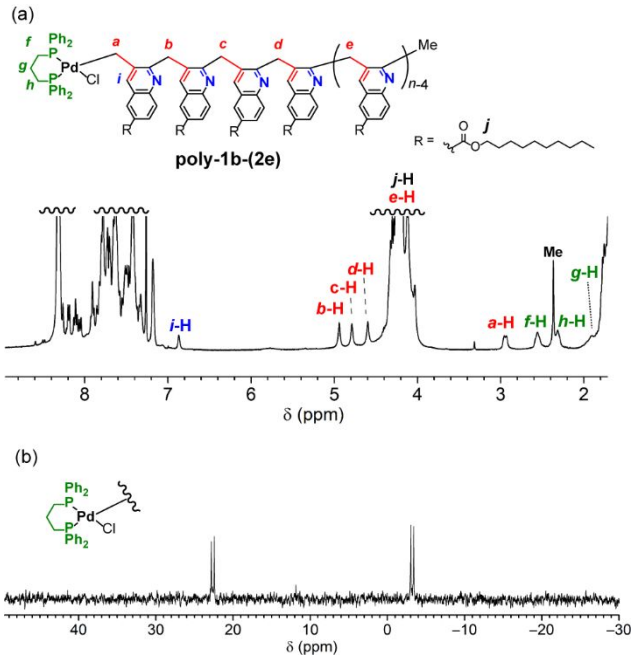


Figure 2. (a) ^{1}H NMR (400 MHz) and (b) ^{31}P NMR spectra of **poly-1b-(2e)** ([**1b**]/[**2e**] = 20, entry 2 in Table 2 in $CDCl_3$.

To investigate the living nature of the polymerization, stepwise addition of the monomer was conducted. A five-step addition of 10 equiv of **1b** to a dichloromethane solution of initiator (**2e** or **2j**) resulted in the stepwise formation of the corresponding polymers. The polymers exhibited a narrow molecular weight distribution and a linear relationship between M_n and cumulative addition of **1b** (Table S1 and Figure 3). These results indicated that each propagation chain end group of **poly-1b-(2e)** or **poly-1b-(2j)** remained active after the monomer was depleted, and all polymer chains grew at the same rate without chain transfer and termination. Therefore, the system is a living polymerization.

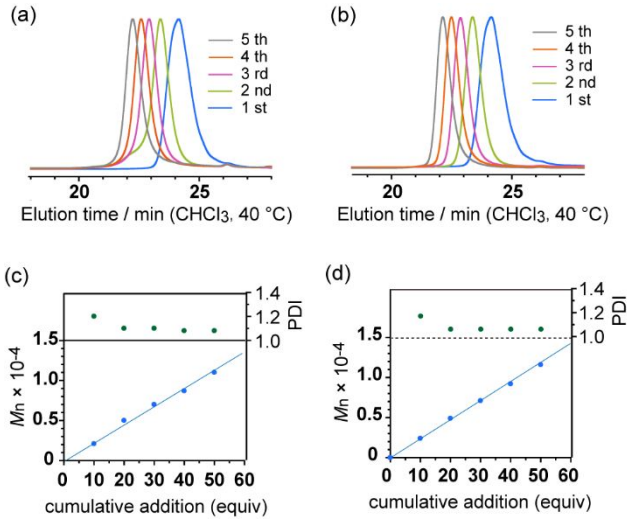
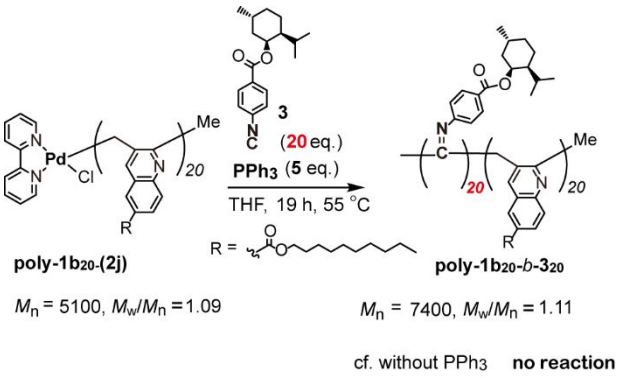


Figure 3. (a) and (b) SEC trace of **poly-1b** following each addition step using **2e** and **2j** as an initiator. (c) and (d) M_n(SEC) as a function of the cumulative addition of **1b** using **2e** and **2j** as an initiator.

Because the living polymer presented herein contains a Pd-σ alkyl bond at the growing polymer end, further polymerization using a different monomer was conducted.[16] Thus, we attempted the block copolymerization of isocyanide using **poly-1b$_{20}$-(2j)** ($M_{n(SEC)}$ = 5100, M_w/M_n = 1.09) as an initiator (Scheme 2). According to a general method, the block polymerization of menthyl-4-isocyanobenzoate **3** (20 equiv) was performed in THF at 55 °C. Unfortunately, the polymerization did not proceed, because the bpy ligand of **2j** was likely replaced by the excess isocyanide.[17] Therefore, a ligand exchange reaction was conducted using phosphine that was previously in the polymerization of isocyanide. In the presence of excess triphenylphosphine (5 equiv), the desired block copolymer (**poly-1b$_{20}$-*b*-3$_{20}$**) was successfully formed with a narrow molecular weight distribution. The prepared block copolymer exhibited a unimodal SEC trace (Figure 4), and the corresponding ^{1}H NMR spectrum contained the expected signals (Figure S16).

Scheme 2. Block Copolymerization with Isocyanide 3



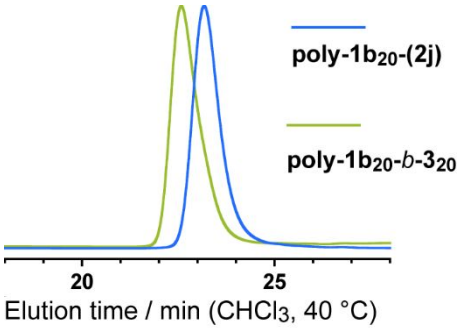


Figure 4. SEC curves of **poly-1b$_{20}$-(2j)** and **poly-1b$_{20}$-*b*-3$_{20}$**.

Investigation of the Polymerization Mechanism

Kinetic Study of the Polymerization. n previous studies of the cyclocopolymerization system, the polymerization kinetic information was not obtained at all, because the propagation reaction was too fast. To gain further insight into the polymerization mechanism, we performed a trace experiment on the polymerization of **1b** with **2e** ([**1**] = 0.06 M, [**2**] = 0.002) in CD_2Cl_2 at 25 ˚C using ^{1}H NMR spectroscopy. When the concentration of **1b** was plotted against reaction time, a linear relationship was obtained, which indicated that the rate

of the present polymerization was independent of the concentration of monomer **1b**; the rate was found to be zero order with respect to monomer concentration (Figure 5a, k_{obs}(25 °C) = 1.3 × 10^{-5} s^{-1}). Similar experiments were also conducted using **2j**. The zero-order polymerization of **1b** using **2j** also proceeded at 10 °C (Figure 5b, k_{obs}(10 °C) = 2.1 × 10^{-5} s^{-1}). These results were in sharp contrast with the first-order kinetics observed for the polymerization of aryl isocyanides with organopalladium complexes.[4i,4l] Additionally, the rate constants for polymerization were determined at several temperatures (Table S2), and the thermodynamic activation parameters were calculated from the Arrhenius plots of the rate constants. The thermodynamic activation parameters are $\Delta H^{\ddagger}$ = 56.2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = –150.0 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$ = 100.9 kJ mol^{-1} at 25 °C on **2e** and $\Delta H^{\ddagger}$ = 58.1 kJ mol^{-1}, $\Delta S^{\ddagger}$ = –129.1 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$ = 94.6 kJ mol^{-1} at 10 °C on **2j**.

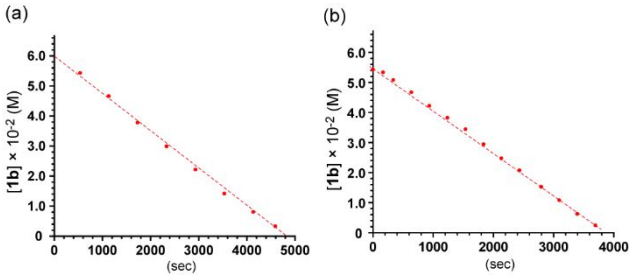
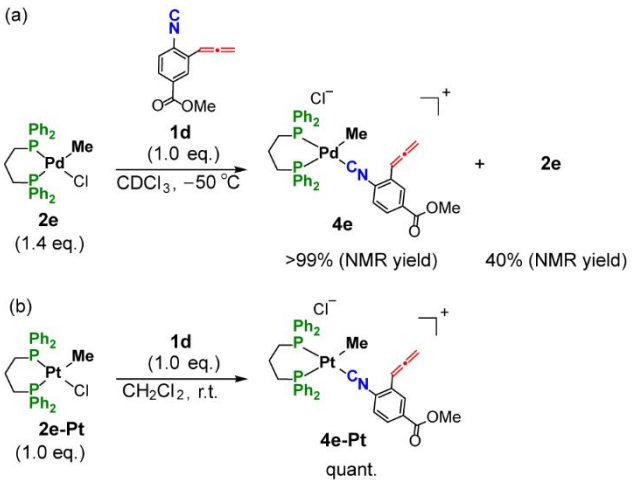


Figure 5. Plots of the concentration of **1b**. Initial concentration: [**1**] = 0.06 M, [**2**] = 0.002 M; CD_2Cl_2, (a) 25 °C (**2** = **2e**), (b) 10 °C (**2** = **2j**).

Stoichiometric Reaction. To understand the successive insertion mechanism of the isocyanides and allenes, a series of stoichiometric reactions was performed. Initially, **1d** (R = 2-methyloxycarbonyl) was allowed to react with 1.4 equiv of Pd(dppp)MeCl (**2e**) in $CDCl_3$ at –50 °C (Scheme 3a), which was monitored by NMR spectroscopy. In the ^{1}H NMR spectra, the signals of **1d** were quantitatively consumed, and new signals arising from the coordinated isocyanide appeared (Figure 6c). The resulting isocyanide-coordinated complex **4e** was stable at –50 °C, and no further reaction was observed. The methylene protons (h-H and f-H) of the phosphine ligand (–$CH_2CH_2PPh_2$, 3.19–3.12 ppm) are present in a lower magnetic field region than those of other four-coordinate complexes bearing dppp [**2e** (2.47 and 2.33 ppm)]. Yamamoto and co-workers reported five-coordinate nickel complexes with isocyanide, chloride, and dppp, formulated as [NiCl(dppp)(3,5-$Me_2C_6H_3NC)_2$](PF_6),[18] and the chemical shifts of the methylene protons on the phosphine ligand (–$CH_2CH_2PPh_2$, 3.21 ppm) are similar to those of **4e**. To determine the geometry of **4e** experimentally, a similar stoichiometric reaction was carried out using a more inert platinum complex (**2e-Pt**: Pt(dppp)MeCl) (Scheme 3b). The isocyanide-coordinated **4e-Pt** could be prepared in a quantitative yield by combining **2e-Pt** (1.0 equiv) with **1e** (1.0 equiv) in CH_2Cl_2 at room temperature, and the resulting **4e-Pt** was stable at room temperature. The ^{1}H NMR spectrum of **4e-Pt** resembles that of **4e** showing a characteristic downfield shift of the methylene protons of the phosphine ligand (–$CH_2CH_2PPh_2$, 3.34-3.25 ppm) like that of **4e** (Figure 6d). Furthermore, X-ray quality single crystals were obtained by the slow diffusion of diethyl ether into a chloroform solution. The molecular structure of **4e-Pt** is shown in Figure 7. This structure has a square planar geometry around the Pt center. The Cl^- anion forms C-H···Cl^- hydrogen bonds from methylene and phenyl protons of the dppp ligand, which is closed to the platinum center in the square plane without a Pt-Cl^- bond ($d_{Pt\text{-}Cl^-}$ ≈ 4.3 Å). This result implies that the downfield shifts of the methylene protons in **4e** and **4e-Pt** are caused by the C-H···Cl^- hydrogen bonds, and the Cl^- anion is also located in the binding pocket created by four protons of the dppp ligand in $CDCl_3$. Additionally, the downfield shift of the methylene protons of the dppp ligand is supported by the simulation of the chemical shifts using DFT calculations based on the crystal structure of **4e-Pt** (Figure S29).

Scheme 3. Stoichiometric Reaction of 1d with (a) 2e and (b) 2e-Pt



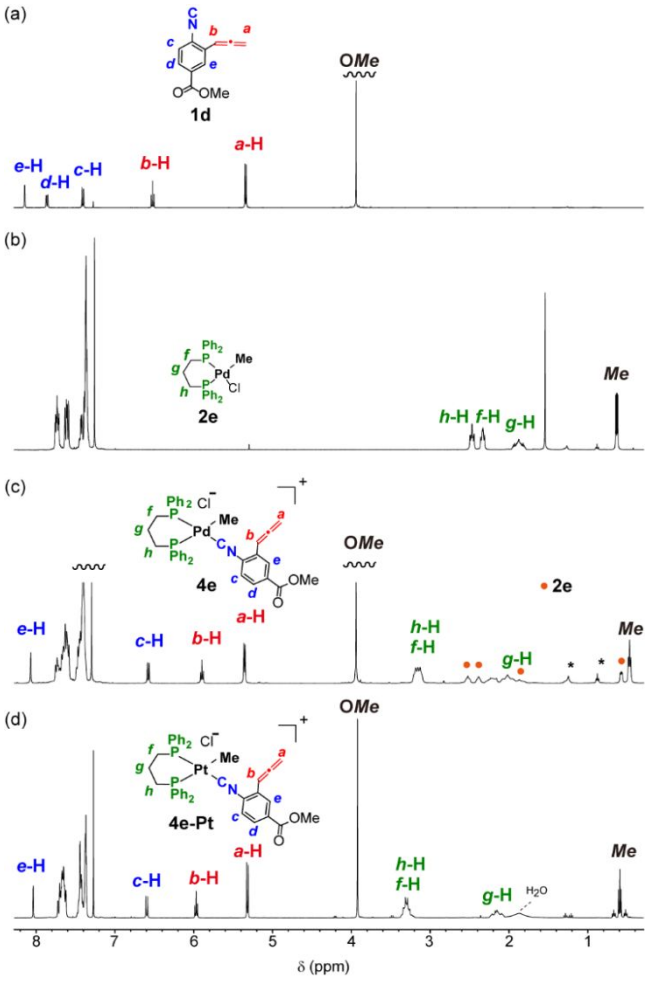


Figure 6. ^{1}H NMR (400 MHz) spectra of (a) **1d** and (b) **2e** in $CDCl_3$ at 25 °C, (c) **4e** in $CDCl_3$ at –50 °C, and (d) **4e-Pt** in $CDCl_3$ at 25 °C.

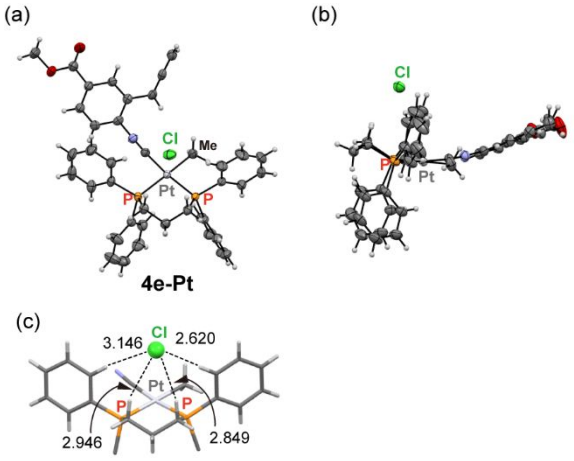
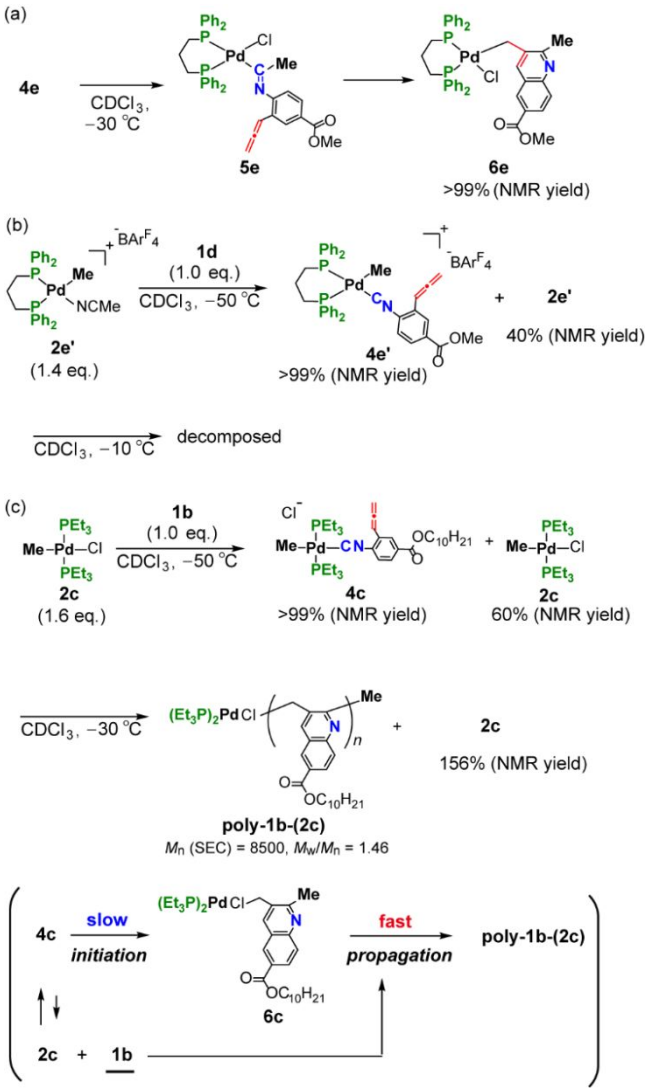


Figure 7. X-ray structure of the **4e-Pt** complex viewed from (a) the top, and (b) the side of the square plane. (c) Expansion of the region relevant to the C-H···Cl⁻ hydrogen bonds with dppp. The schematic drawings indicates selected bond distances (Å) of C-H···Cl⁻ hydrogen bonds.

Upon warming the reaction mixture in Figure 6c, up to –30 °C, the succeeding reactions of **4e** slowly proceed (Scheme 4a), which was monitored by ^{1}H NMR spectroscopy (Figures 8, and S19–S23). The initial reaction, the insertion of isocyanide, followed a first-order kinetic with a rate constant of 8.8×10^{-4} s^{-1} with respect to the concentration of **4e**. At low conversions of **4e**, iminoacyl complex **5e** and quinolylmethyl-palladium complex **6e** were observed (Figure 8b). Because **5e** is consumed as soon as it is produced, the insertion reaction of isocyanide is the rate-determining step of the successive insertion reactions of isocyanide and allene (Figure S23).

Scheme 4. Consecutive Insertion Reactions of Isocyanide and Allene



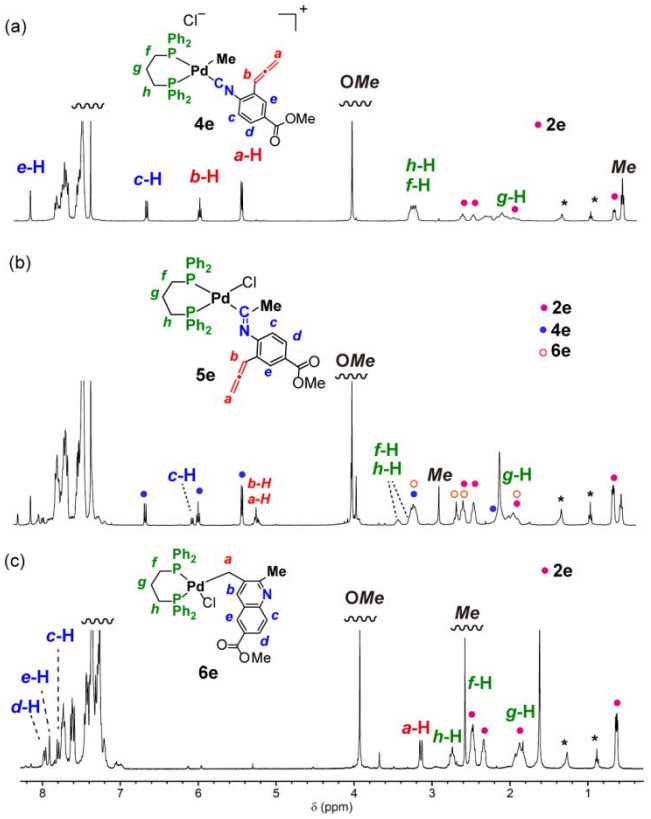


Figure 8. ^{1}H NMR spectra of stoichiometric reaction of **2e** with **1d** producing **4e** (a) at –50 °C in $CDCl_3$ (identical to Figure 6c), (b) after warming up to –30 °C for 30 min., and (c) 130 min.

Similar stoichiometric experiments were performed using other palladium complexes. When the ionic complex [Pd(dppp)Me(MeCN)](BAr^F_4) (**2e'**) having $^-BAr^F_4$ [Ar^F = 3,5-$(CF_3)_2C_6H_3$] as a non-coordinating counter anion instead of chloride was allowed to react with **1d** at –50 °C, isocyanide coordination complex **4e'** was also formed (Scheme 4b); however, the successive insertion reaction did not proceed at –30 °C. Upon heating warming to –10 °C, **4e'** slowly decomposed, resulting in no insertion products. To reveal the role of the chloride anion, a stoichiometric reaction to that shown in Scheme 4a was performed in the presence of NBu_4Cl (1.4 equiv), but the reaction proceeded similarly without changes in the reaction rate. Thus, it can be concluded that the weakly interacting chloride anion of **4e**, located near the palladium center, is necessary to promote the insertion reaction. For the monophosphine complexation **2c** with **1b** (Scheme 4c), coordination complex **4c** was also formed at –50 °C. When the reaction temperature was increased to –30 °C, polymerization proceeded slowly to produce the corresponding polymer (**poly-1b-(2c)**; $M_{n\,(SEC)}$ = 8500, M_w/M_n = 1.46). These results suggest that **1b**, generated by the dissociation from **2c**, preferentially reacted with the propagation chain end. The insertion reaction of **1b** with the resulting quinoline-methyl complex bearing trans-phosphorus ligands **6c** or **poly-1b-(2c)** was much faster than that the reaction with **2c**.

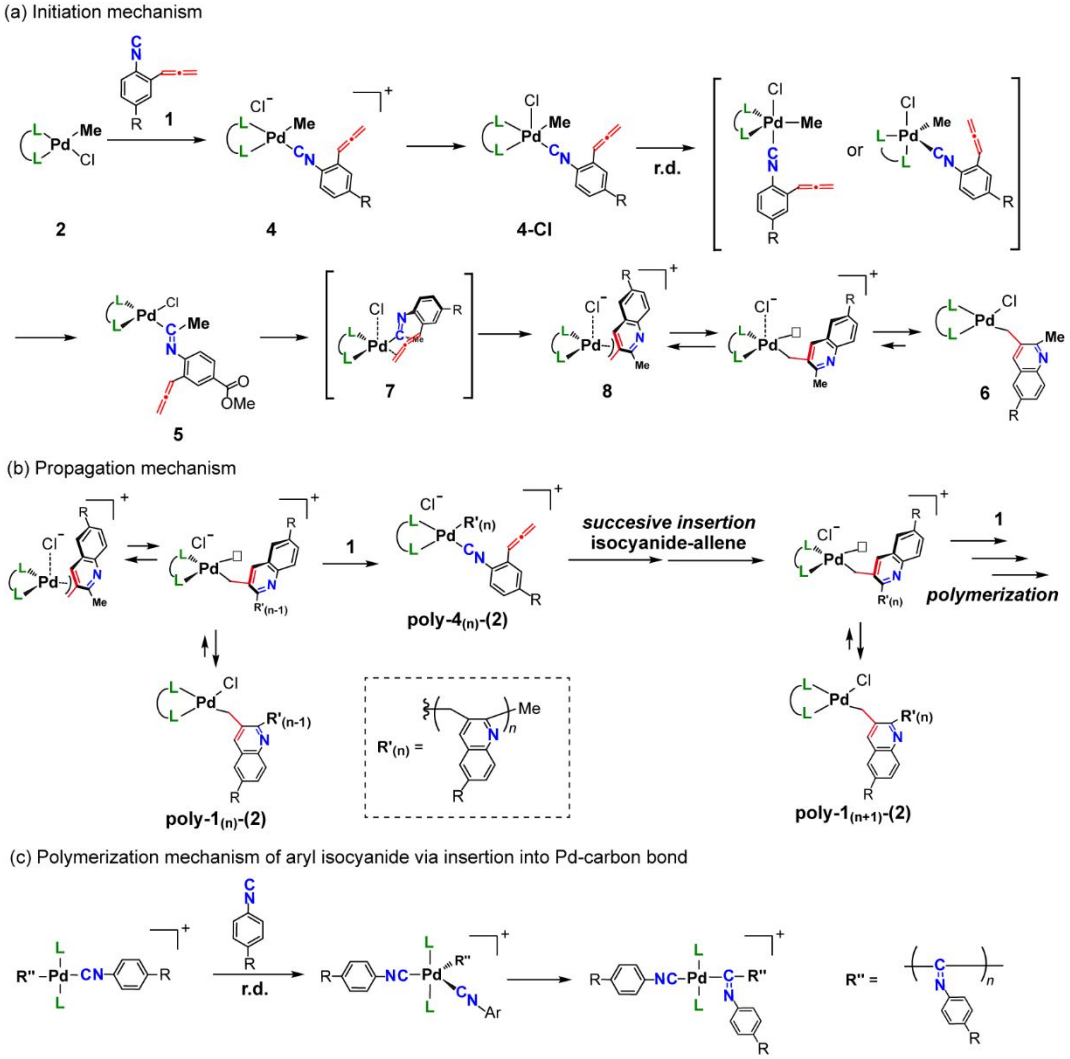
Reaction Mechanism. The initiation and propagation mechanisms of the above experiments are summarized in Schemes 5a and 5b. In this cyclocopolymerization system, the insertion reaction of isocyanide was determined to be the rate-determining step of the successive isocyanide and allene reactions. In the initiation step, the isocyanide-coordination complex **4** was rapidly formed from the reaction of initiator **2** with **1**, and subsequently, the insertion reaction of isocyanide proceeds to form iminoacyl complex **5** (Scheme 5a). Generally, it has been proposed that the insertion of an isocyanide into Pd–C bonds involves the formation of a five-coordinate intermediate that facilitates the migratory insertion of isocyanide (Scheme 5c).[19] Based on of the stoichiometric reaction (Scheme 4b), chloride as a coordinating anion is needed to promote the insertion of isocyanide **1**, allowing the cyclocopolymerization to proceed via the five-coordinate intermediate for isocyanide insertion. Presumably, after the formation of the five-coordinate complex **4-Cl** via coordination of the chloride anion, conformational rearrangements involving pseudorotation are required to achieve a suitable configuration, such as trigonal bipyramidal, for alkyl migration to the coordinated isocyanide.[20] Additionally, the polymerization reactions were dependent on the type of phosphine ligands (*vide supra*). These differences can be attributed to the conformational rearrangements of **4-Cl** required for isocyanide insertion. For the monophosphine ligands, because the conformational change is rapid, the propagation reaction cannot be controlled. In contrast, because the rigid cis-chelating phosphine ligands prevent ligand site-interchange reactions, the reaction rate decreased. The ligands dppp and dppf exhibit a much more flexible backbone and larger bite angle than those of dppe, which likely allowed the site-interchange reaction to occur, resulting in successful polymerization. The same trend has also been reported in the context of CO insertion into an organopalladium complex containing bidentate phosphine ligands.[21] However, when bpy was used as the ligand, the polymerization proceeded smoothly, despite the narrower bite angle in bpy (~81°) than in dppe.[22] This result suggests that the successive insertion proceeds via a different mechanism in the case of bpy. The insertion reaction of isocyanide likely occurs via palladium–nitrogen bond dissociation and subsequent conformational rearrangements of **4**.[23]

After the insertion of isocyanide, the iminoacyl complex **5** was formed. Subsequently, intramolecular insertion of the allene moiety proceeded to form **6**. Because the allene moiety insertion is quite rapid compared to the isocyanide insertion step, the reaction details remain unclear. Therefore, DFT calculations were performed using B3LYP to gain further insight into the reaction mechanism of allene insertion.[24] The detailed procedures and the optimized structures are shown in the Supporting Information (Figure S29). Initially, the model structure of **4e** (L = dppp) was constructed based on the X-ray structure (**4e-Pt**). The iminoacyl model **5e** was composed from **4e** and subsequently optimized. Based on the optimized structure of **5e**, suitable constraints to constract the palladium-allene coordination model (**7e**; L = dppp, R′ = Me), followed by distance constraints to form the quinolyl moiety, resulted in reasonable molecular structure. Finally, the removal constraints and structural optimization yielded **8e** (L = dppp, R′ = Me) with η^3 coordination of the quinolyl methylene moiety to the palladium center, which was more stable than the optimized structure of **4e** (ΔE_{8e-4e} = –63.9 kcal/mol). The Pd–C(3) bond (2.14 Å) is much shorter than Pd–C(1) (2.49 Å) and Pd–C(2) (2.31 Å), which may be due to the contribution of an η^1 structure (Figure 9a). Furthermore, the η^1-quinolyl methyl complex **6e**, formed by moving the chloride anion of **8e** to form a square planar complex, is slightly more stable compared to **8e** (ΔE =

4.8 kcal/mol) (Figure 9b). These results suggest that the insertion of the allene occurs in coordination complex **7**, and the insertion reaction subsequently proceeds rapidly to form the more stable η^3 coordination complexes **8** followed by complex **6** (Scheme 5a).

During the polymerization, excess isocyanide easily coordinates to the vacant site produced by η^3–η^1 isomerization (**poly-1$_{(n)}$**) to form a square planar isocyanide-coordination complex (**poly-4$_{(n)}$-(2)**). Further polymerization occurs via a five-coordinate intermediate with a geometrical change, as shown in the initiation mechanism (Scheme 5b). This is consistent with the finding that the rate of the cyclocopolymerization shows a zero-order dependence on the monomer concentration and results in a negative entropy activation value[25] (Figure 5). After consumption of **1**, the chloride anion coordinates to the palladium center, resulting in η^3–η^1 isomerization to form η^1-quinolyl methyl complex (**poly-1$_{(n+1)}$**). The complex represents the resting state for the cyclocopolymerization, which corresponds to the well-defined terminal structure of the resulting polymers (**poly-1-(2)**).

Scheme 5. Proposed Mechanism in Cyclocopolymerization



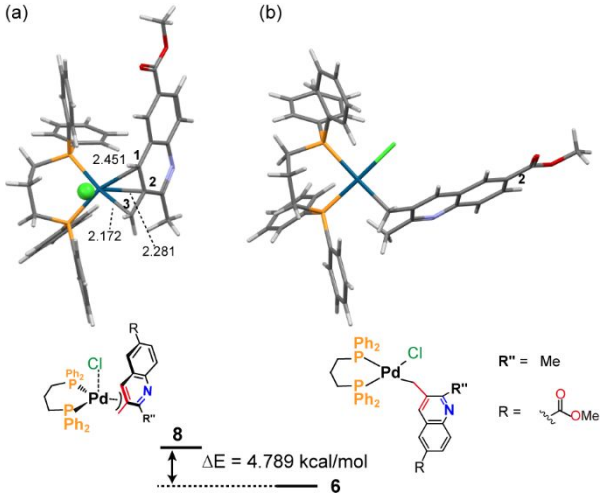


Figure 9. Optimized structures of (a) η^3 and (b) η^1-coordination quinolyl methyl complex.

Conclusions

In conclusion, a new living cyclocopolymerization reaction through the alternating insertion of isocyanide and allene into a palladium-carbon bond was demonstrated. When bidentate ligands, such as dppp and bpy, were used, the propagation reaction was controlled to afford the desired polymer, poly(quinolylene-2,3-methylene)s, with a narrow molecular weight distribution. The resulting polymer has a well-defined palladium complex at the propagation terminal and the polymer structure near the propagation terminal was clearly distinguished. The terminal palladium complex maintained its reactivity, which can be extended to block copolymerization with isocyanide. Kinetic studies and the results of stoichiometric reactions elucidated the mechanistic aspects of polymerization: the insertion reaction of isocyanide is the rate-determining step, and the reaction proceeds via a five-coordinate intermediate with a conformation change to the appropriate configuration. In the case of the cis-chelating ligand, because the site interchange reaction can be controlled, the reactivity of the propagation species is dominated. The presented living polymerization reaction greatly expands the possibility of cyclocopolymerization based on alternating insertion of isocyanides and allenes, and further molecular design becomes possible. Additionally, these results and mechanistic investigation provide new insight for designing other types of cyclocopolymerization system via the combination of completely different types of substituents. Studies focusing on the synthesis of new functional polymers based on the resulting living polymerization and the development of new cyclocopolymerization system are currently in progress.

Experimental Procedures

General. All reactions were carried out under an Ar atmosphere, whereas the workup was performed in air. NMR spectra were recorded in $CDCl_3$ and benzene-d_6 on JEOL JNM-ECS400, JEOL JNM-ECA500 and spectrometers. In ^1H and ^{13}C NMR, $SiMe_4$ was used as an internal standard, and an external 85% H_3PO_4 reference was used for ^{31}P NMR. HR-MS measurement was carried out on Thermo Fisher Scientific LTQ-Orbitrap XL. The molecular weights (M_n) and its distributions (M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in chloroform at 40 °C with polystyrene gel column [Tosoh; TSKgel GMH_{HR}-M × 3 (exclusion molecular weight = 4×10^6); flow rate 0.7 mL min^{-1}] connected to Shimadzu LC6-AD and Shimadzu SPD-10A UV-vis detectors. IR spectra were recorded on SHIMADZU IR Prestige-21 using KBr tablet.

Standard Method of the Cyclocopolymerization. To a dichloromethane solution (3.0 mL) of **2e** (0.01 mmol) was added the dichloromethane solution (2.0 mL) of **1b** (97.8 mg, 0.3 mmol) at 0 °C. The mixture was warmed to 25 °C and stirred for 120 min. After the completion of polymerization reaction, the reaction mixture was concentrated in vacuo to give yellow solid (quant.).

Elongation of the Polymer Chain. To a dichloromethane solution (3.0 mL) of **2** (0.01 mmol) was added a dichloromethane solution (2.0 mL) of **1b** (32.6 mg, 0.10 mmol) at 0 °C. The mixture was warmed to 25 °C and stirred for 30 min. The resulting solution was added a dichloromethane solution (2.0 mL) of **1b** (32.6 mg, 0.10 mmol) by syringe at 30 min interval for four times. The resulting solution was concentrated in vacuo to give a yellow solid.

The procedure for the Kinetic Study. To a solution of **2j** (0.62 mg, 2.0 μmol), 1,4-dimethoxybenzene (internal standard, 1.38 mg, 10.0 μmol), in CD_2Cl_2 (0.8 mL) was added **1b** (19.6 mg, 60.0 μmol) in CD_2Cl_2 (0.4 mL) at –78 °C. The reaction mixture was warmed to reaction temperature, and the reaction course was monitored by ^1H NMR spectra.

Stoichiometric reaction of 2e and 1d. To a solution of **2e** (7.1 mg, 12.5 μmol) in $CDCl_3$ (0.6 mL) was added **1d** (2.0 mg, 10.0 μmol) in $CDCl_3$ (0.2 mL) at –78 °C. The reaction mixture was warmed to –50 °C, which was monitored by ^1H NMR spectroscopy. After 10 min. the reaction mixture was warmed to –40 °C. The insertion reaction proceeded, and time course was monitored by ^1H NMR spectra.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI:
Experimental details and characterization data (PDF)
Crystallographic data for **4e-Pt** (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by a grant-in-aid for JSPS KAKENHI Grant JP16K21154, 19K05582, and the financial support from the Tokuyama Science Foundation and the TonenGeneral Sekiyu Foundation. We thank Jun Ikegami for assistance of the synthesis of **1c**, and Manami Narukawa for assistance with some of the experiments in block copolymerization with isocyanide.

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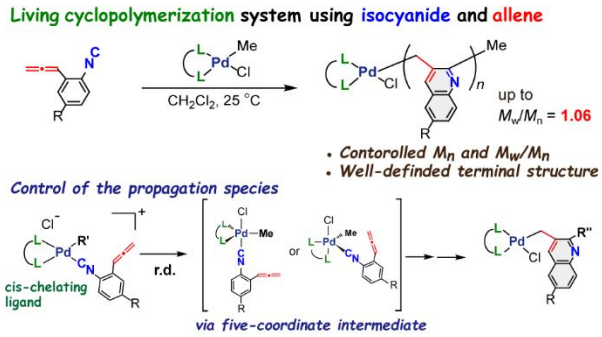
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