Air-Stable (Phenylbuta-1,3-diynyl)palladium(II) Complexes: Highly Active Initiators for Living Polymerization of Isocyanides

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Ⓢ *Supporting Information*

ABSTRACT: A family of air-stable (phenylbuta-1,3-diynyl)-palladium(II) complexes were designed and prepared in a facile synthetic procedure. Their structures were characterized by ^{1}H and ^{13}C NMR, MS, and X-ray analysis. These Pd complexes were revealed to efficiently initiate the polymerization of phenyl isocyanides in a living/controlled chain growth manner, which led to the formation of poly(phenyl isocyanide)s with

controlled molecular weights and narrow molecular weight distributions. ^{13}C NMR analysis indicated the isolated poly(phenyl isocyanide) was of high stereoregularity. The Pd unit at the end of the polymer chain could undergo further copolymerization with phenyl isocyanide monomers to give block copolymers. It was also found that incorporation of an electron-donating group on the phenyl group of the Pd complex could improve the catalytic activities. Furthermore, these Pd complexes were tolerant to most organic solvents and applicable to a wide range of isocyanide monomers including alkyl and phenyl isocyanides and even phenyl isocyanide with bulky substituents at the ortho position and diisocyanide monomers. Therefore, this polymerization system is versatile in the preparation of well-defined polyisocyanides with controlled sequence. Bi- and trifunctional Pd complexes with two and three Pd units incorporated onto the same phenyl ring were designed and synthesized. They were also able to initiate the living polymerization of phenyl isocyanide to afford telechelic linear and star-shaped polyisocyanides with controlled molecular weights and narrow molecular weight distributions.
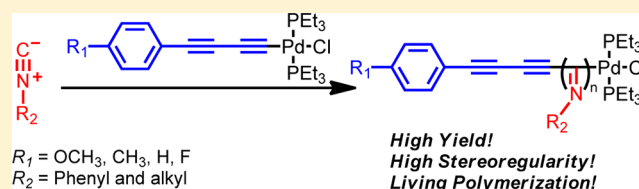
■ INTRODUCTION

The helix is the central structural motif in biological macro-molecules, such as DNA,[1] proteins,[2] and polysaccharides,[3] and is also the ubiquitous object in nature from microscopic to macroscopic points of view. Inspired by sophisticated biological helices and related unique functions, chemists have been challenged to develop artificial helical polymers[4] and oligomers (foldamer)[5] not only to mimic biological helices and functions but also for their potential applications as materials.[6] Among the synthetic helical polymers, polyisocyanides have been the focus of intense efforts in recent decades due to their unique rigid helical structures.[4f,g,j,q,s,7] They have a distinctive π-conjugated system with C═N double bonds at the carbons that connect the monomer units, which twist along the polymer backbone to create a helical conformation. In addition to their interesting rigid helical structure, polyisocyanides have exhibited wide applica-tions in enantiomeric separation, asymmetric catalysis, and chiral recognition as well as in material sciences.[8] Well-defined polyisocyanides are commonly prepared by the polymerization of appropriate isocyanide monomers with transition metal complexes as catalyst or initiator.[4s,7d] Although several transition metal complexes have been discovered to promote the polymerization of isocyanides, as nonliving polymerization

systems they cannot control the sequence and molecular weights of the resulting polyisocyanides.[9]

Among the transition metal complexes, organonickel com-plexes have been widely used for isocyanide polymerizations. For example, Notle et al. have reported that some Ni(II) salts are efficient catalysts for the polymerization of alkyl and aryl isocyanides through the so-called "merry-go-round" mecha-nism,[4g,10] while Deming et al. revealed that π-allylnickel complexes are effective catalysts for living polymerization of alkyl isocyanides in noncoordinating solvents.[11] Very recently, Asaoka et al. disclosed a fast, living/controlled polymerization of isocyanide by using aromatic isocyanide as monomer and aromatic nucleophile adduct of tetra(tert-butylisocyano)nickel-(II) complex as initiator.[12] We found that poly(3-hexylthio-phene) with a nickel complex residing at the chain end can initiate the block copolymerization of phenyl isocyanide,[13] alkyl isocyanide,[14] and 4,5-dimethyl-1,2-diisocyanobenzene mono-mers[15] in controlled chain extension fashions. Suginome and co-workers demonstrated that arylnickel complexes are effective initiators for the living polymerization of both phenyl isocyanide and 1,2-diisocyanobenzenes.[16] In contrast to the widely used

Ni(II) complexes, the utilization of other transition metal complexes as catalysts or initiators for isocyanide polymerization are relatively limited. Onitsuka et al. have found that arylrhodium complexes can promote the polymerization of aryl isocyanides in a living/controlled manner. Nevertheless, a large amount of phosphine ligands were needed to stabilize the living chain end, which made product purification difficult.[17]

Palladium complexes have been widely used in organic synthesis and polymer preparation,[18] and for promoting the polymerization of 1,2-diisocyanobenzenes.[19] However, examples of the polymerization of isocyanide and its derivatives with a Pd complex as catalyst or initiator are limited. The challenge in designing Pd catalysts for this purpose may be their great tendency in forming a trimer intermediate involving intramolecular N—Pd coordination to terminate the polymerization progress.[9,16,20] Two decades ago, Onitsuka et al. reported that a dinuclear Pd—Pt μ-ethynediyl complex can catalyze the living polymerization of aryl isocyanide.[21] Although isocyanides were demonstrated to exclusively insert into the carbon—Pd bond, Pt played an important role since no polymerization occurred with a similar (phenylethynyl)palladium(II) complex.[21c] In our previous studies, we found that such a Pd—Pt μ-ethynediyl complex was sensitive to air and hard to synthesize.[22] Moreover, it is ineffective for the polymerization of bulky phenyl and alkyl isocyanides. Therefore, the development of a novel air-stable, facile accessible Pd complex for efficient living polymerization of different isocyanides is highly desirable.

We herein describe the synthesis of a new kind of (phenylbuta-1,3-diynyl)palladium complexes from the reaction of phenylbuta-1,3-diynyl with trans-bis(triphenylphosphine)palladium(II) dichloride in high yields. In contrast to their analogues (phenylethynyl)- and ethynylpalladium complexes, which are inactive for the polymerization of isocyanides,[21b] these new complexes can efficiently initiate the living polymerization of phenyl isocyanide to afford poly(phenyl isocyanide) with controlled molecular weight (M_n) and narrow molecular weight distribution (M_w/M_n). They can tolerate most organic solvents and are applicable to a wide range of isocyanide monomers, including phenyl and alkyl isocyanides and bulky phenyl isocyanides as well as diisocyanobenzene monomers. Furthermore, we further prepared bi- and trifunctional Pd complexes by attaching two or three Pd atoms to a straight or triangular ligand. We demonstrate that these multifunctional complexes can also initiate the living polymerization of phenyl isocyanide to yield well-defined telechelic linear and star-shaped polyisocyanides with controlled M_n and narrow M_w/M_n.

■ RESULTS AND DISCUSSION

(Phenylbuta-1,3-diynyl)palladium complexes **1a–e** with various substituents on the para position of the benzene ring was prepared in the same procedure as outlined in Scheme 1. The synthesis of **1a** is briefly described here. First, 1-ethynyl-4-methylbenzene was brominated by NBS with AgNO$_3$ as catalyst in acetone at room temperature to afford **5a** in almost quantitative yield. The isolated **5a** was then reacted with ethynyltrimethylsilane (TMSA) by Sonogashira coupling reaction to afford **6a**, and removal of the TMS group with potassium carbonate gave **7a** in 83% yield over two steps. Complex **1a** was then obtained in 65% yield by treating **7a** with trans-dichlorobis(triethylphosphine)palladium(II) in dichloromethane in the presence of diethylamine as base and copper chloride as catalyst at room temperature.[23] By using similar procedures, **1b–d** could be prepared and isolated in high yields.

Scheme 1. Synthesis of (Phenylbuta-1,3-diynyl)palladium(II) Complexes 1a–e
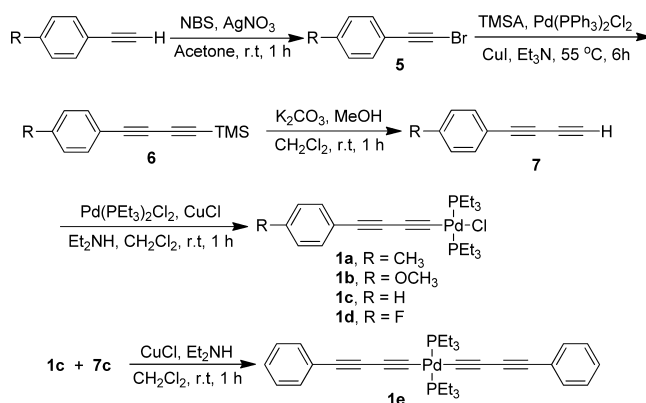
Compound **1c** was further reacted with **7c** in dichloromethane in the presence of copper chloride at room temperature to produce complex **1e** in 75% yield. All complexes **1a–e** were soluble in common organic solvents, such as chloroform, n-hexane, toluene, and THF. Their structures were completely characterized by ^{1}H and ^{13}C NMR, MS, FT-IR, and elemental microanalysis. It is noteworthy that, the precursors **7a–d** are unstable, their colorless chloroform solutions easily turn to brown and eventually to dark within one week. Straight-phase thin layer chromatography analysis indicated new spots were formed on the plate (Figure S1, see Supporting Information [SI]). In sharp contrast, **1a–e** are very stable; their ^{1}H NMR spectra in CDCl$_3$ showed no changes after the samples were deposited for two weeks at ambient temperature.

Single crystals of **1a**, **1b**, **1c**, and **1e** suitable for X-ray analysis were obtained by slow evaporation of their solutions in the mixture of ethyl acetate and petroleum ether at room temperature, and their crystal structures are shown in Figure 1. It can be found that for all the complexes, the benzene ring is perpendicular to the Pd coordination plane, probably to minimize the steric hindrance between the phenyl ring and the ethyl groups on the phosphine ligands. For **1a–c**, the linear phenyldiynyl moiety is not straight, but a little bent. In contrast, **1e** adopts a straight linear conformation.

The catalysis of **1a–e** for the polymerization of decyl 4-isocyanobenzoate **2**[13a] was then investigated. The activity of **1a** was first examined by treating it with 100 equiv of **2** in THF at room temperature ($[2]_0 = 0.2$ M, $[2]_0/[1a]_0 = 100$) (Scheme 2). No polymeric product was isolated after even 20 h, and monomer **2** was recovered. At 55 °C, the polymerization could take place, the originally colorless solution turned to brown-yellow, and the viscosity of the solution also increased considerably. After 10 h, methanol was added, and the formed precipitate was isolated by centrifugation to give poly-**a2**$_{100}$ (the footnote indicates the initial feed ratio of monomer to initiator) as a yellow solid in almost quantitative yield. The M_n and M_w/M_n values of poly-**a2**$_{100}$ were determined to be 2.9×10^4 and 1.11, respectively, by size exclusion chromatography (SEC) with polystyrene (PSt) standards (Scheme 2). The FT-IR spectrum of poly-**a2**$_{100}$ showed an absorption band at 1599 cm^{-1} due to $\nu_{(C=N)}$, which is characteristic for polyisocyanides (Figure S2, SI),[17b] but no absorption of the monomer around 2260 cm^{-1}. ^{1}H, ^{13}C, and ^{31}P NMR and UV−vis spectra of the polymer also confirmed its structure (Figures S3−S6, SI). It is worthy to note that the polymerization could be carried out in an open system to give the same polymer.
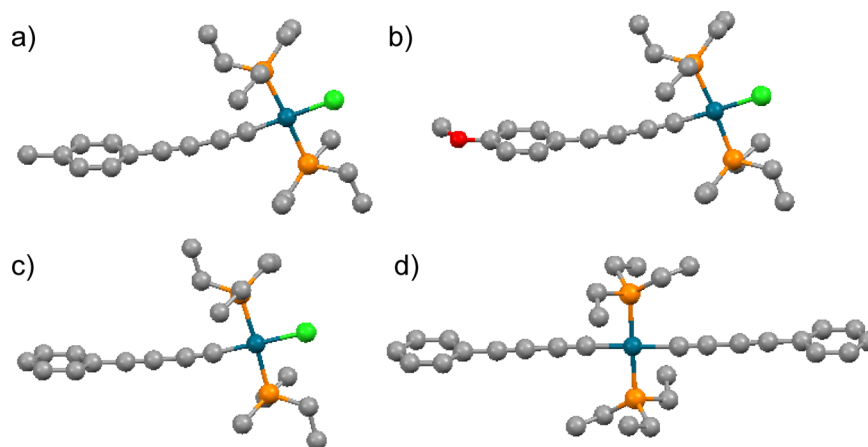
Figure 1. Crystal structures of Pd complex **1a** (a), **1b** (b), **1c** (c), and **1e** (d). The H atoms were omitted for clarity.

Scheme 2. Polymerization of Phenyl Isocyanide 2 with Pd Complex 1a in THF at 55 °C and Block Copolymerization of 2 with Poly-a2$_m$ As Macroinitiator, and the SEC Chromatograms of Poly-a2$_{50}$, poly-a2$_{100}$ and the Resulting Block Copolymer Poly(a2$_{100}$-b-2$_{100}$)
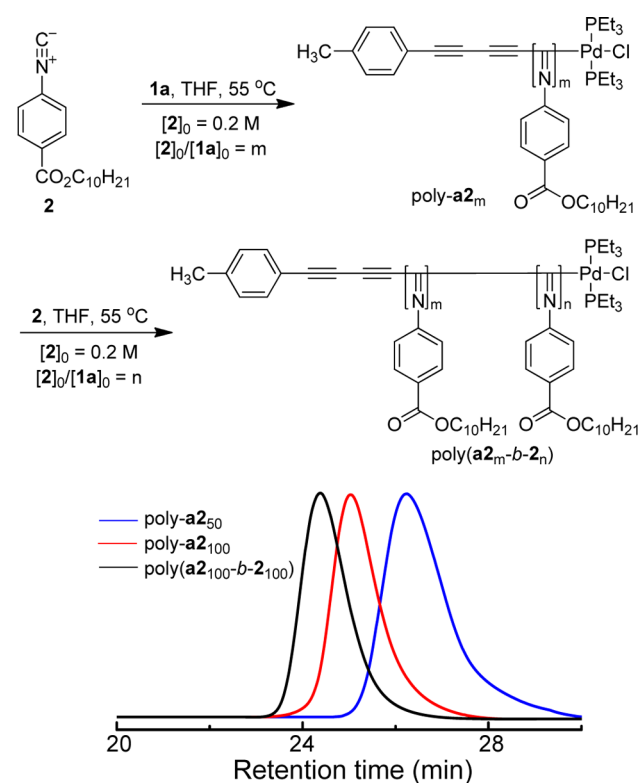

Stereoregularity is one of the most important parameters for natural and synthetic polymers and has significant influence on the optical activity for helical polyisocyanides. It is thus worth examining the stereoregularity of the polymer prepared through this new method. The stereoregularity of poly-a2$_{100}$ was evaluated through a calculation of half-bandwidth of the main chain imino carbon signal on ^{13}C NMR spectroscopy in CDCl$_3$ at room temperature.[17b,24] A relatively sharp resonance corresponding to the imino carbons of the polymer backbone was displayed at δ 162.56 ppm, and the half-bandwidth was estimated to be 30 Hz (Figure S4, SI), which suggested that poly-a2$_{100}$ had a high stereoregularity of the imino groups. In contrast, poly(aryl isocyanide)s prepared with nickel complexes as catalyst have low stereoregularity of the imino groups.[25]

The narrow molecular weight distribution of poly-a2$_{100}$ suggested that the polymerization of **2** initiated by **1a** might proceed in a living or controlled chain growth fashion. To test this, **1a**-initiated polymerizations of **2** in different initial feed ratios (m) were performed under the same conditions ([**2**]$_0$ = 0.2 M, [**2**]$_0$/[**1a**]$_0$ = m, THF, 55 °C). SEC chromatograms of the prepared polymers were shown in Figure 2a. All the polymers exhibited symmetric and single model SEC traces. The M_n of the produced poly-a2$_m$ was found to increase linearly and in proportion to the initial feed ratio of **2** to **1a** up to 180 (Figure 2b). All the samples showed narrow molecular weight distribution (M_w/M_n < 1.20) which became narrower with the increase of the polymerization degree. The absolute M_n value was determined by ^{1}H NMR from the integral ratio of the methyl signal of the Pd complex on the polymer chain end to the OCH$_2$ signal on the polymer repeat units. The M_n (^{1}H NMR) values of poly-a2$_m$ were consistent with the M_n (SEC) and in good agreement with the ideal M_n values calculated from the initial feed ratio of [**2**]$_0$/[**1a**]$_0$, suggesting the polymerization did proceed in a living/controlled chain growth manner. This result also revealed the initiation efficiency of **1a** was extremely high and almost quantitative. Due to the living nature of the polymerization, a range of poly-a2$_m$'s with different molecular weights and narrow molecular weight distributions could be prepared using this new initiator by simply varying the initial feed ratio of monomer and initiator. The polymerization results are shown in Table 1.

To further confirm the living nature of the generated poly(phenyl isocyanide) and also to examine the stability of the living chain end of the Pd moiety of the synthetic polyisocyanide, block copolymerization was carried out for the isolated poly-a2$_{100}$ (M_n = 2.9 × 10^4, M_w/M_n = 1.11) and **2** in THF at 55 °C ([**2**]$_0$ = 0.2 M, [**2**]$_0$/[poly-2$_{100}$]$_0$ = 100/1). SEC analysis of the resulting product demonstrated that block copolymerization did take place because the SEC chromatogram of the product shifted to the higher-molecular weight region (Scheme 2). The molecular weight of the obtained copolymer increased by 1 time and also kept narrow distribution (M_n = 5.8 × 10^4, M_w/M_n = 1.07). This result supported the fact that the isolated poly-a2$_{100}$ was still stable to keep the active living chain end group −Pd(PEt$_3$)$_2$Cl to initiate the copolymerization.

We then carried out the polymerizations in various organic solvents to investigate the influence of the solvent. The results are
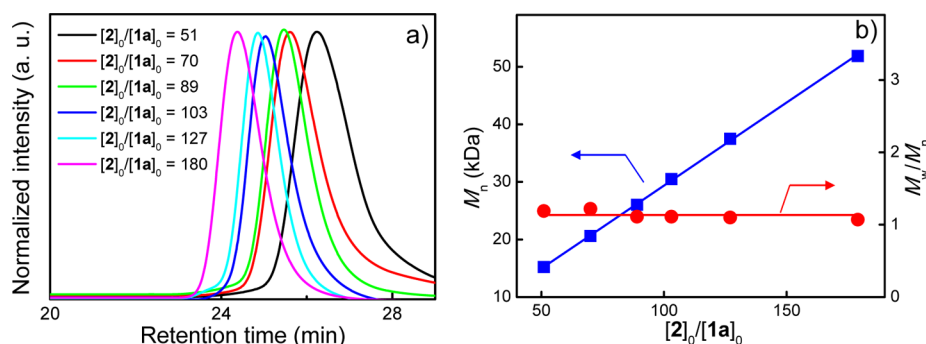
Figure 2. (a) SEC chromatograms of poly-a2$_m$ prepared from **2** with **1a** as initiator in THF at 55 °C with different initial feed ratios. (b) Plot of M_n and M_w/M_n values of poly-a2$_m$ as a function of the initial feed ratios of **2** to **1a**. M_n and M_w/M_n were determined by SEC with PSt standard (eluent = THF, temperature = 40 °C).

Table 1. Polymerization Results of Phenyl Isocyanide 2 with Pd Complex 1a as Initiator at 55 °C[a]

run	$[2]_0/[1a]_0$[b]	solvent	polymer	M_n[c]	M_w/M_n[c]	yield,[d] %
1	50	THF	poly-a2$_{50}$	1.5×10^4	1.19	96
2	100	THF	poly-a2$_{100}$	2.9×10^4	1.11	96
3	200	THF	poly-a2$_{200}$	5.8×10^4	1.07	91
4	50	toluene	poly-a2$_{50}$(t)	1.4×10^4	1.29	94
5	100	toluene	poly-a2$_{100}$(t)	2.6×10^4	1.32	96
6	50	CHCl$_3$	poly-a2$_{50}$(c)	1.5×10^4	1.21	94
7	100	CHCl$_3$	poly-a2$_{100}$(c)	2.7×10^4	1.11	90
8	50	DMF	poly-a2$_{50}$(d)	1.5×10^4	1.36	90
9	50	Acetone	poly-a2$_{50}$(a)	9.5×10^3	1.38	68

[a]The poly-a2$_m$ was synthesized according to Scheme 2. [b]The initial feed ratio. [c]The M_n and M_w/M_n were determined by SEC and reported as equivalent to standard PSt. [d]Isolated yield.

summarized in Table 1. It can be seen that the polymerization proceeded smoothly at 55 °C in most of the solvents of varying polarity, including toluene, CHCl$_3$, acetone, THF, and DMF (runs 4−9 in Table 1, Figures S7−S9, SI). In *n*-hexane and methanol, the polymerization also took place, but the resulting polymers were not soluble, and thus only short oligomers or polymers were obtained as precipitates. The polymers formed in acetone and DMF exhibited a little bit larger M_w/M_n probably due to the poor solubility of the Pd complex and the polymers, and poly-a2$_m$ with higher M_n could not be obtained in these solvents.

To get deep insight into the new polymerization system, the relationship between the conversion of monomer **2** and M_n of the obtained poly-a2$_m$ was also investigated. The polymerization ($[2]_0 = 0.2$ M, $[2]_0/[1a]_0 = 90$) was performed in THF in the presence of PSt ($M_n = 2630$, $M_w/M_n = 1.06$) as internal standard to facilitate the calculation of the monomer conversion.[22a] The process was followed by SEC analyses of aliquots of the reaction solution at appropriate time intervals to estimate the M_n and M_w/M_n of the generated polyisocyanide as well as the monomer conversion. The results are shown in Figure 3. It can be found that the polymerization was relatively fast and >80% of the monomer was consumed within 5.5 h. Both conversion-M_n and conversion-M_w/M_n relationships are plotted in Figure 4a. The M_n values of the isolated polymers are linearly correlated with the conversion of **2** and kept a narrow distribution, further confirming the living nature of the polymerization. Kinetic studies revealed that the polymerization obeyed the first-order rate law. The rate constant was estimated to be ~7.58×10^{-5} s^{-1} according to the kinetic plot (Figure 4b), which is comparable to that of the analogous initiator Pd−Pt μ-ethynediyl complex in the polymerization of phenyl isocyanides.[21c]
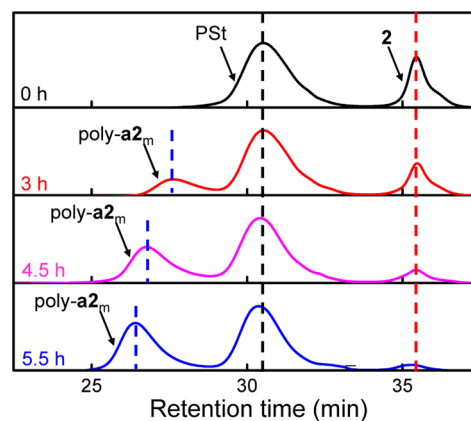
Figure 3. Time-dependent SEC chromatograms for **1a**-initiated polymerization samples of **2** in THF at 55 °C with PSt ($M_n = 2630$, $M_w/M_n = 1.06$) as internal standard ($[2]_0 = 0.2$ M, $[2]_0/[1a]_0 = 90$; SEC condition: eluent = THF; temperature = 40 °C).

Pd complexes **1b−d** (Scheme 1) were further synthesized to investigate their activity for polymerization of **2**. The reactions were also followed by SEC as used for **1a**-initiated reaction. It was found that these complexes also exhibited high activity to lead to the formation of polyisocyanide in high isolated yield and with designed M_n and narrow M_w/M_n. Time-dependent SEC chromatograms of the polymerizations with **1b**, **1c**, and **1d** (Figures S10−15 in SI) indicated the polymerizations all proceeded in a living chain growth fashion. Kinetic studies revealed the polymerizations also obeyed the first-order rate law, and the reaction rate constants for **1b**, **1c**, and **1d** were estimated to be 1.61×10^{-4}, 6.51×10^{-5}, and 4.78×10^{-5} s^{-1}, respectively (Figure 4b). The sequence of the polymerization rate is **1b** > **1a** >
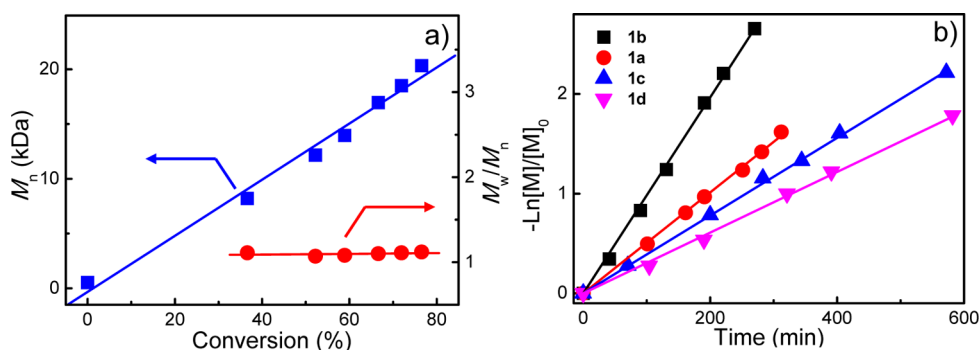
Figure 4. (a) Plot of M_n and M_w/M_n values as a function of **1a**-initiated conversion of **2** in THF at 55 °C ($[2]_0 = 0.2$ M, $[2]_0/[1a]_0 = 90$). (b) First-order kinetics plots for polymerizations of **2** initiated by **1a** (red ●), **1b** (black ■), **1c** (blue ▲), and **1d** (magenta ▼).

1c > 1d, demonstrating the incorporation of an electron-donating group to the benzene ring of the complex improved the polymerization activity. However, the difference in rate constants was not prominent, and decreased with the increase of the polymerization degree because the substituent on the benzene ring is far away from the living chain end. Even at higher temperature and with longer time, **1e** did not initiate the polymerization of **2**. This result suggested that the chloride counterion of complexes **1a−d** might play an important role in the polymerization and is indispensable for this series of Pd complexes. The polymerization of **2** with **1a−d** may take place through multiple and successive insertion of isocyanides into a Pd−C bond following the mechanism proposed for the polymerization of the dinuclear Pd−Pt μ-ethynediyl complex.[21b] The insertion was believed to proceed by nucleophilic substitution of the chloride with an isocyanide monomer to form a cationic intermediate in which both isocyanide and phenylbuta-1,3-diynyl groups are bonded to the Pd atom, and simultaneously the phenylbuta-1,3-diynyl group migrates to the isocyanide. In **1a−d**, the phenylbuta-1,3-diynyl group may promote the nucleophilic attack and facilitate its migration from Pd to isocyanide. The two phenylbuta-1,3-diynyl groups on **1e** hampered the nucleophilic substitution, and thus it could not initiate the polymerization. The electron-donating group on the phenyl ring should promote the migration. Therefore, **1b** exhibited the highest reaction rate.

The above results clearly demonstrate **1a−d** were effective in initiating the polymerization of phenyl isocyanide in a living/controlled chain growth fashion. Because the conformational stability of helical poly(aryl isocyanide)s should be affected by the steric factor of the pendants, helical poly(aryl isocyanide)s with a substituent at the ortho position of its benzene ring are attractive targets to prepare. We thus further investigated the ability of **1a−d** for initiating the polymerization of 2-(2-(trimethylsilyl)ethynyl)benzenisocyanide **3a**, which bears a bulky (trimethylsilyl)ethynyl group at the ortho position of the benzene ring. Due to steric hindrance, **3a** could only be polymerized with aryl rhodium complexes as an initiator in the presence of an excess of phosphine ligands as additives.[17b] Because **1b** was the most active among the new Pd complexes, polymerization of **3a** was investigated in THF at 55 °C with **1b** as initiator (Scheme 3). However, no polymeric product was isolated after 20 h. When the reaction was run in toluene at 90 °C ($[3a]_0/[1b]_0 = 50$, $[3a]_0 = 0.2$ M), polymerization took place to lead to the formation of yellow-brown poly-**b3a**$_{50}$ with $M_n = 5.0 \times 10^3$ and $M_w/M_n = 1.18$ as determined by SEC (Figure 5a).

The polymerization of 1-isocyanohexadecane **3b** could also be initiated in toluene by **1b** at 90 °C ($[3c]_0/[1b]_0 = 50$, $[3c]_0 = 0.2$

Scheme 3. Polymerization of Isocyanides 3a−f and Diisocyanide 4 Initiated by 1b
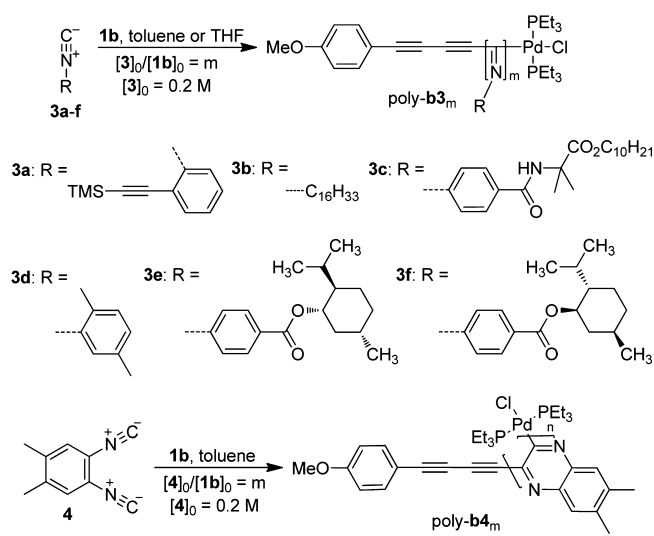
M). The M_n (3.8×10^3) and M_w/M_n (1.08) of the resulting product poly-**b3b**$_{50}$ were determined by SEC. The yield of poly-**b3b**$_{50}$ was very low, and polymers of higher M_n could not be obtained due to poor solubility of the product in toluene. The polymerization of isocyanides **3c−f** could also be initiated by **1b**. The structures of the resulting polymers were confirmed by ^{1}H NMR, FT-IR, and SEC (Figure 5a) and the results are summarized in Table 2. The polymerization of enantiomers **3e** and **3f** gave optically active poly-**b3e**$_{100}$ and poly-**b3f**$_{100}$, which respectively exhibited positive and negative Cotton effects at 364 nm in the circular dichroism (CD) spectra (Figure 5b). The $\Delta\varepsilon_{364}$ of poly-**b3e**$_{100}$ and poly-**b3f**$_{100}$ were estimated to be −11.8 and +12.8, respectively. These results indicated that a single-handed helical polyisocyanide was formed through the induction of the chiral pendants. To extend the reaction scope, we further prepared diisocyanobenzene 4,5-dimethyl-1,2-diisocyanobenzene **4**,[14] and found that, although **1b** did not initiate its polymerization in THF at 55 °C, the polymerization could take place in toluene at 90 °C to give poly-**b4**$_{50}$ with $M_n = 5.4 \times 10^3$ and $M_w/M_n = 1.19$ as estimated by SEC (Table 2).

Telechelic polymers represent a class of chain-end functionalized polymers. In contrast to monofunctional polymers which are widely applied for surface functionalization[26] or drug immobilization,[27] telechelic polymers offer an additional functional group on the other chain end and thus can combine different molecules such as biomacromolecules with, for
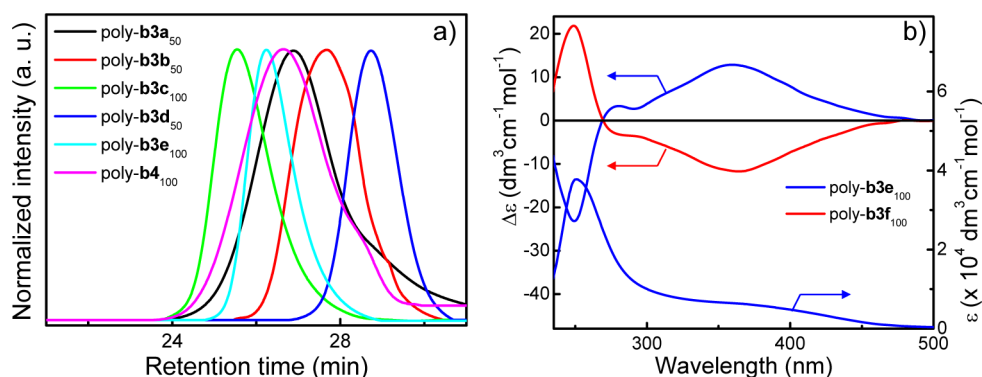
Figure 5. (a) SEC chromatograms of the polymerization of **3a–e** and **4** prepared by using **1b** as initiator (SEC conditions: eluent = THF; temperature = 40 °C). (b) CD and UV–vis spectra of poly-**b3e**$_{100}$ and poly-**b3f**$_{100}$ measured in CHCl$_3$ at 25 °C (c = 0.10 mg/mL).

Table 2. Polymerization Results of Isocyanide 3a–f and Diisocyanide 4 with 1b as Initiator.[a]

| run	monomer	[M]$_0$/[1b]$_0$[b]	solvent	T, °C	polymer	M_n[c]	M_w/M_n[c]	yield,[d] %
1	**3a**	50	toluene	90	poly-**b3a**$_{50}$	5.0×10^3	1.18	70
2	**3a**	100	toluene	90	poly-**b3a**$_{100}$	8.3×10^3	1.08	83
3	**3b**	50	toluene	90	poly-**b3b**$_{50}$	3.8×10^3	1.04	30
4	**3c**	50	THF	55	poly-**b3c**$_{50}$	1.1×10^4	1.22	90
5	**3c**	100	THF	55	poly-**b3c**$_{100}$	1.7×10^4	1.14	89
6	**3d**	50	toluene	90	poly-**b3d**$_{50}$	3.6×10^3	1.05	59
7	**3e**	50	THF	55	poly-**b3e**$_{50}$	1.0×10^4	1.29	95
8	**3e**	100	THF	55	poly-**b3e**$_{100}$	1.9×10^4	1.22	93
9	**3f**	50	THF	55	poly-**b3f**$_{50}$	1.1×10^4	1.16	97
10	**3f**	100	THF	55	poly-**b3f**$_{100}$	2.2×10^4	1.21	95
11	**4**	50	toluene	90	poly-**b4**$_{50}$	5.4×10^3	1.19	75
12	**4**	100	toluene	90	poly-**b4**$_{100}$	7.4×10^3	1.20	58

[a]The polymers were synthesized according to Scheme 3. [b]The initial feed ratio of monomer to initiator. [c]The M_n and M_w/M_n were determined by SEC and reported as equivalent to standard PSt. [d]Isolated yield.

Scheme 4. Synthesis of Bi- and Trifunctional Pd Complexes 1f and 1g and Their Initiation for the Polymerization of 2
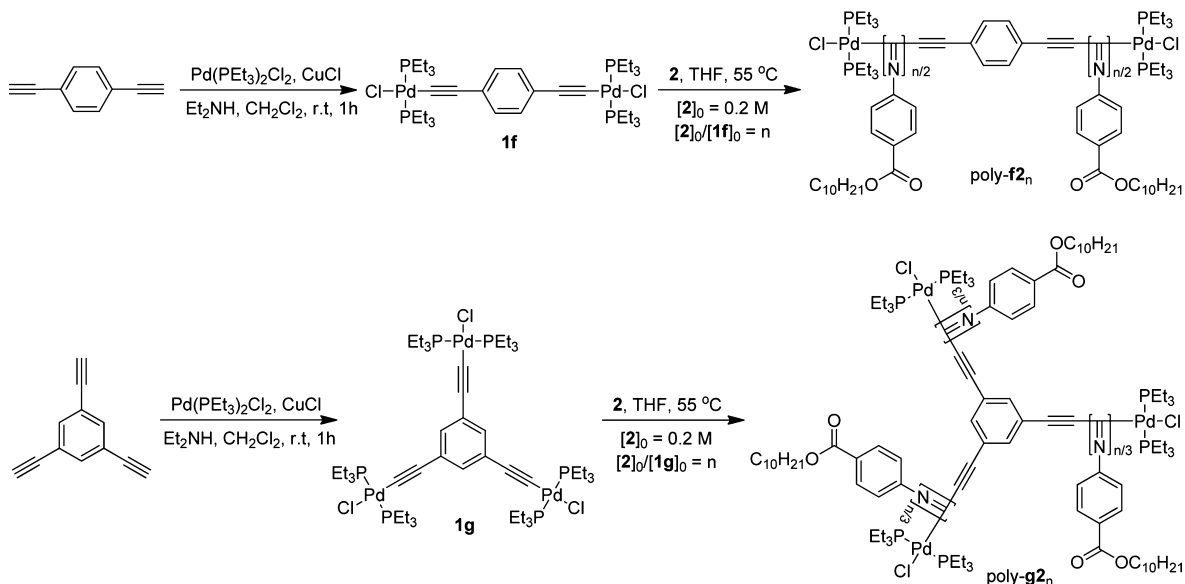
example, dyes or inorganic tracers to produce intriguing properties or functions.[28,29] We envisioned that introducing more than one Pd unit to the benzene ring might produce a multifunctional initiator for preparing telechelic polyisocyanides. We thus further synthesized Pd complexes **1f** and **1g** by attaching two and three Pd(PEt$_3$)$_2$Cl moieties to 1,4-diethynylbenzene or

1,3,5-triethynylbenzene (Scheme 4). The polymerizations of **2** initiated by **1f** and **1g** were then investigated in THF at 55 °C. Both complexes displayed high activity (Figures S16 and S17 and Table S1, SI). The reaction in the initial feed ratio of 60 gave poly-**f2**$_{60}$ with $M_n = 1.5 \times 10^4$ and $M_w/M_n = 1.19$ (Figure 6a). The narrow M_w/M_n also supported a living/controlled polymer-
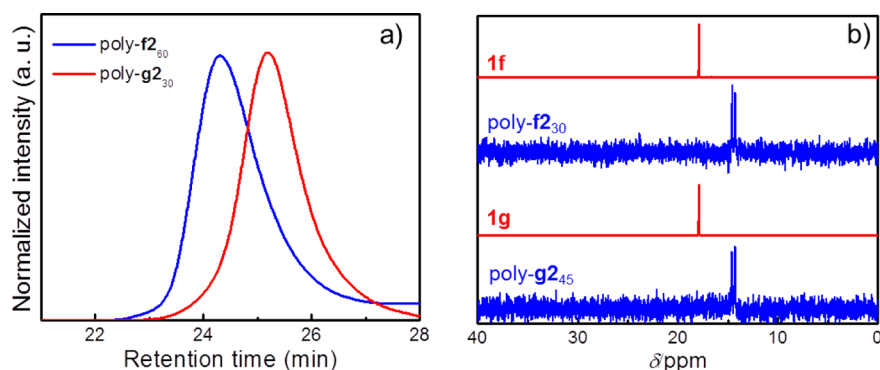
Figure 6. (a) Representative SEC chromatograms of the polymerization of **2** initiated by **1f** and **1g** in THF at 55 °C (SEC conditions: eluent = THF; temperature = 40 °C). (b) ^{31}P NMR spectra of **1f** and **1g** and the resulting poly-**f2**$_{30}$ and poly-**g2**$_{45}$ in CDCl$_3$ at room temperature.

ization mechanism, and the M_n of the resulting polymers could be controlled by varying the initial feed ratio (Figures S18 and S19, SI). With **1g** as initiator, living polymerization also took place because linear dependence of the M_n values of the resulting star polymers with the initial feed ratio was also observed (Figures S20 and S21, SI).

The structures of these two- and three-armed polymers were characterized by ^{1}H and ^{31}P NMR, SEC, and FT-IR. The ^{1}H NMR spectra of the telechelic polymers were similar to that of poly-**a2**$_{100}$ (Figures S3, S61, and S62, SI). The formation of such multiarmed polymers were also tracked and confirmed with ^{31}P NMR spectroscopy.[30] For comparison, ^{31}P NMR spectra of **1a** and the resulting poly-**a2**$_{50}$ were further recorded (Figure S6, SI). The spectrum of **1a** displayed a single peak at δ 18.8 ppm. This peak disappeared after the polymerization of **2** took place, which was accompanied with a new doublet at 14.4 ppm, corresponding to the formation of poly-**a2**$_{50}$. Di- and trifunctional initiators **1f** and **1g** exhibited a single peak around δ 17.9 ppm in ^{31}P NMR spectra. The peak disappeared after polymerization, while a new doublet at δ 14.4 ppm was observed, again supporting the formation of desired polymers (Figure 6b). All these results suggested that the Pd units in these multifunctional initiators functioned as reactive points for the polymerization to afford the well-defined multiarmed telechelic polymers.

CONCLUSION

In summary, we have designed and synthesized a series of air-stable (phenylbuta-1,3-diynyl)palladium(II) complexes and demonstrated their robust ability for initiating the polymerization of phenyl isocyanides in living and controlled chain growth manner. The poly(phenyl isocyanide)s prepared using the new initiators possess controlled M_n and narrow M_w/M_n and high stereoregularity, which is important for maintaining the helical sense of the polymer main chain. The obtained polymers can keep the activity of the living chain end of Pd(PEt$_3$)$_2$Cl complex to further undergo block copolymerization with isocyanide monomers. The new Pd complexes can promote the living polymerization of a broad range of isocyanides and diisocyanides in a number of solvents, which leads to the formation of a variety of polymers. Furthermore, the bi- and tri-Pd catalysts can be used to prepare multifunctional polyisocyanides with the same arm length. We believe that the present systematic studies will provide not only a useful living polymerization method for facile preparation of a broad range of polyisocyanides with controlled M_n and narrow M_w/M_n but also a clue for designing novel catalysts and initiators.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, spectral data of palladium complexes, isocyanide monomers and polymers, SEC chromatograms of polyisocyanides, and details of X-ray analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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