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Facile synthesis of stereoregular helical poly(phenyl isocyanide)s and poly(phenyl isocyanide)-*block*-poly(L-lactic acid) copolymers using alkylethynylpalladium(II) complexes as initiators

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ABSTRACT. Development of novel synthetic methods for facile preparation of well-defined stereoregular helical polyisocyanides and their block copolymers in living/controlled fashion is of great interest. In this contribution, a family of air-stable alkylethynyl Pd(II) complexes were unexpectedly found to promote the living polymerization of phenyl isocyanide, afforded poly(phenyl isocyanide)s with controlled molecular weights, narrow molecular weight distributions and high stereoregularity. Interestingly, such alkylethynyl Pd(II) complex exhibit very high helix-sense-selectivity in the living polymerization of an optically active phenyl isocyanide bearing an L-alanine pendant with a long decyl chain, and a single handed helical poly(phenyl isocyanide)s with controlled helical sense was selectively produced. Moreover, Pd(II) complex bearing a hydroxyl group can initiate the living polymerization of both phenyl isocyanide and L-lactide in one-pot lead to the formation of well-defined poly(phenyl isocyanide)-*b*-poly(L-lactic acid) copolymers in high yields with controlled molecular weights and tunable compositions. Although the two monomers were polymerized via distinct mechanisms, the block copolymerization was revealed to proceed under living/controlled manners.

Introduction

Helix is the prevalent structural motif for biological macromolecules and plays important roles in their sophisticated functions.[1] Since the discovery of biological helices, extensive studies have been conducted on the development of artificial helical polymers with a controlled helix-sense to mimic the structure of biomacromolecules and also to exploit new materials with novel functions.[2] Representative examples of synthetic helical polymers including sterically restricted poly(methacrylate ester),[3] polyacrylamides[4] and poly(aryl vinyl),[5] polyisocyanide,[6] polyisocyanate,[7] polycarbodiimide[8] and polyacetylene.[9] Among them, optically active polyisocyanides with a controlled helical sense has been the focus of the intense research efforts owning to theirs fascinating rigid helical structures and widely applications.[10] Well-defined polyisocyanides were usually prepared through the polymerization of appropriate isocyanide monomers with transition metal complexes as catalyst.[11] Nevertheless, approaches for facile synthesis of well-defined, stereoregular helical polyisocyanides in living/controlled manner are rare. Nickel(II) complexes are by far the most used catalyst for isocyanide polymerizations although the generated polyisocyanides may possessing low stereoregularity in some cases.[12]

Living polymerization of isocyanide promoted by organopalladium complexes is still a pristine area.[13] Takahashi et al. disclosed a unique dinuclear Pd−Pt μ-ethynediyl complex that can imitate the living polymerization of aryl isocyanide two decades ago.[14] We previously found that polymerization of an optically active phenyl isocyanide bearing an L-alanine pendant with the achiral Pd−Pt μ-ethynediyl complex produced both right- and left-handed helical polyisocyanides at once with different molecular weights and yields, which could be separated into each helix by fractionation with acetone.[15] Very recently, air-stable phenylbuta-1,3-diynyl Pd(II) and phenylethynyl Pd(II) complexes were reported to initiate the living polymerization of some isocyanides lead to the formation of well-defined polyisocyanides with high stereoregularity.[16] In contrast to these conjugated arylethynyl Pd(II) complexes, utilization of non-conjugated alkylethynyl Pd(II) complexes in the preparation of stereoregular polyisocyanides and their block copolymers have rarely been explored yet. However, substituents on the Pd(II) initiator may affect the polymerization activity and the chiroptical property of the afforded polymers. Optically active helical polyisocyanides were usually obtained through the polymerization of chiral isocyanide monomers with achiral initiator through the helix-sense-selective manner. Thus, development of novel initiator for highly selective synthesis of a single handed helical polyisocyanides with controlled helical sense is of great desired.

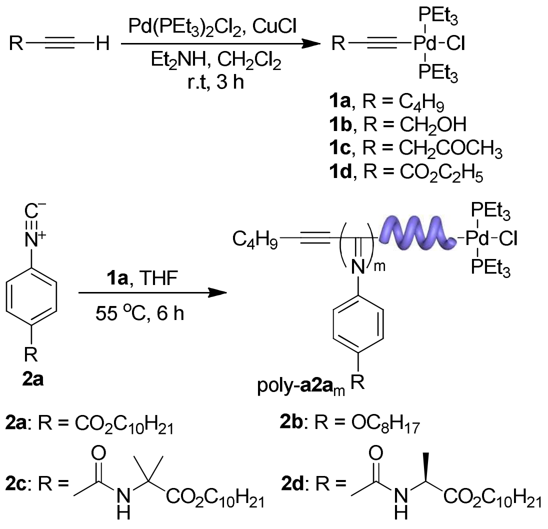
Facile preparation of polyisocyanide hybrid block copolymers under controlled manners is of great interest owning to theirs applications in many fields such as biosensor, scaffolds for tissue engineering, and materials with new properties.[17] Actually, synthesis of block copolymers composed of two segments that cannot be prepared by the same polymerization mechanism still remains a challenge in synthetic polymer chemistry.[18] Notle and coworkers prepared polystyrene-*b*-polyisocyanide block copolymers via the polymerization of isocyanide using a amine-terminated polystyrene as macroinitiator with nickel salt as catalyst.[19] Cornelissen and coworkers prepared a rod-rod poly(γ-benzyl L-glutamate)-*b*-polyisocyanide hybrid block copolymer through the sequential polymerization of the two respective monomers.[20] However, facile syntheses of hybrid block copolymers containing stereoregular polyisocyanide via distinct polymerization mechanism in one-pot are really rare.

In this contribution, we report a family of alkylethynyl Pd(II) complexes (**1a**-**1d**, Scheme 1) which were found to promote the living polymerization of various isocyanides (**2a**-**2d**), produced polyisocyanides with high stereoregularity. Very interestingly, polymerization of optically active chiral phenyl isocyanide (**2d**) with such Pd(II) complex exhibit very high helix-sense-selectivity as comparing with other Pd(II) complexes, and a single handed helical poly(phenyl isocyanide) (PPI) was readily obtained. Moreover, Pd(II) complex bearing an hydroxyl group can catalyze the living polymerizations of both L-lactide and phenyl isocyanides in one-pot lead to the formation of well-defined PPI-*b*-poly(L-lactic acid) (PPI-*b*-PLLA) block copolymers with controlled M_ns and tunable compositions. Poly(L-lactic acid) (PLLA) is an aliphatic polyester thermoplastic derived from corn starch or sugarcane. Because of its appealing biodegradability, biocompatibility and renewability, materials based on PLLA have attracted considerable attentions in recent years.[21] However, to the best of our knowledge, the block copolymers containing polyisocyanides and PLLA have never been reported.

Results and Discussion

Polymerization of Isocyanides with Alkylethynyl Pd(II) Initiators. As illuminated in Scheme 1, alkylethynyl Pd(II) complexes **1a-d** were readily prepared according to the procedure reported by our group previously with slightly modification.[15] The synthesis of *trans*-

bis(triethylphosphine)-hex-1-yn-1-ylpalladium(II) chloride (**1a**) was described here briefly. Hex-1-yne was treated with *trans*-dichlorobis(triethylphosphine)palladium(II) in dichloromethane at room temperature in the presence of diethylamine and copper chloride. The generated Pd(II) complex **1a** was isolated as a yellow solid in 85% yield. Similarly, Pd(II) complexes **1b**-**1d** with different substituents were readily obtained in high yields (>80%). These Pd(II) complexes are air and moisture stable in solid state and even in solution. All the complexes behave good solubility in most common organic solvents including *n*-hexane, toluene, THF, and $CHCl_3$. The chemical structures were verified by ^{1}H and ^{13}C NMR, FT-IR, mass spectroscopies as well as elemental analysis (Fig. S1-S12, see ESI†).



Scheme 1 Synthesis of Pd(II) Complexes **1a-d** and Polymerization of Phenyl Isocyanides with Pd(II) Complexes as Initiators.

After the Pd(II) complexes were successful achieved, polymerization behaviors of these complexes with isocyanide were then investigated. As depicted in Scheme1, **1a** was treated with decyl 4-isocyanobenzoate (**2a**) in THF at 55 °C for 6 h ($[\mathbf{2a}]_0$ = 0.2 M, $[\mathbf{2a}]_0/[\mathbf{1a}]_0$ = 55). The polymeric product was firstly analyzed by size exclusion chromatography (SEC). As shown in

Fig. 1a, the isolated poly-**a2a**$_{55}$ (the footnote denotes the initial feed ratio of monomer to initiator) exhibit a single model elution peak on size exclusion chromatogram. The M_n and M_w/M_n were estimated to be 1.51 × 10^4 Da and 1.19, respectively, which indicate the polymerization take place. To examine the living nature of the polymerization, a series of polymerizations of **2a** with **1a** were performed in different initial feed ratios (Table 1). All the isolated polymers exhibit single modal elution peaks on the recorded SEC (Fig. 1a). The M_ns of the polymers are linearly correlated to the initial feed ratios of monomer to initiator and the M_w/M_ns are narrow (Fig. 1b). Thus, the polymerizations of **2a** with **1a** as initiator was proceed in living/controlled manner. The structures of the afforded polymers were confirmed by ^{1}H and ^{13}C NMR and FT-IR spectroscopies. ^{1}H NMR spectrum of isolated poly-**a2a**$_m$ was displayed in Fig. S13 in ESI†. The resonances are relatively broad due to the restrict motion of the helical conformation. Nevertheless, the signals can be clearly assigned including phenyl protons at 7.31 and 5.74 ppm, and $-CO_2CH_2-$ at 4.50–3.50 ppm. ^{13}C NMR studies of the isolated polyisocyanides revealed the half-band width of the imino carbons of the backbone is narrow. For example, the half-band width of poly-**a2a**$_{55}$ is about 30 Hz, suggesting the generated polymer has high stereoregularity (Fig. S14, see ESI†).[12] FT-IR spectrum of poly-**a2a**$_m$ shows an intense characteristic C=N vibration at 1600 cm^{-1}, confirm the formation of expected polyisocyanide with high stereoregularity (Fig. S15, see ESI†). These studies suggest that the alkylethynyl Pd(II) complex can initiate the polymerization of phenyl isocyanide under a living/controlled chain-growth manner, afford the desired polymers in high yields with controlled M_n, narrow M_w/M_n, and high stereoregularity.

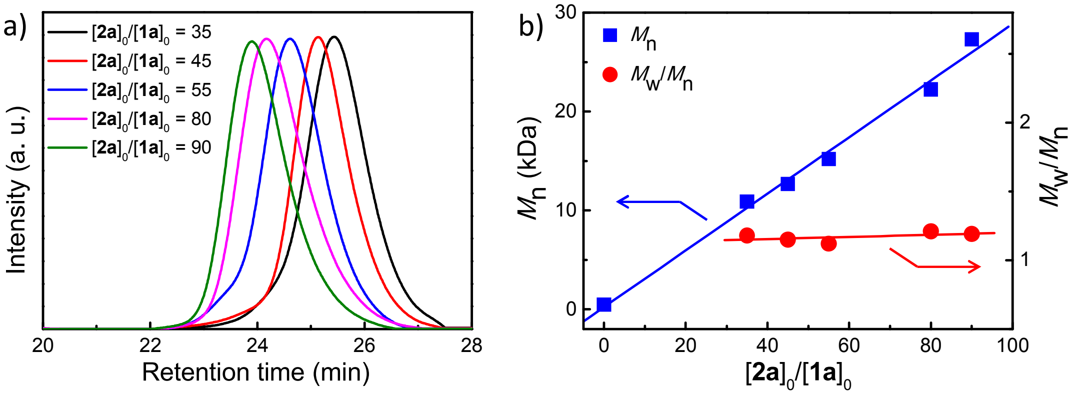


Fig. 1 (a) SEC chromatograms of poly-**a2a**$_m$ prepared from the polymerization of **2a** with **1a** as initiator in THF at 55 °C with different initial feed ratios of **2a** to **1a**. (b) Plot of M_n and M_w/M_n values of poly-**a2a**$_m$ as a function of the initial feed ratios of **2a** to **1a**. M_n and M_w/M_n were determined by SEC with polystyrene standard (eluent = THF, temperature = 40 °C).

To get more detail, the polymerization of **2a** with **1a** as initiator was traced by SEC analyses of small aliquots take from the polymerization solution at appropriate time intervals. It was found that all the polymers isolated at different polymerization stages showed single modal elution peaks on SEC chromatogram and shifted to higher-molecular weight region with the increase of monomer conversion (Fig. S16, see ESI†). The polymerization was relative fast and more than 90% of **2a** was consumed within 5 hours. The correlations of M_n and M_w/M_n values of the isolated polymers with the conversions of **2a** were summarized in Fig. 2a. The M_n increased linearly to the conversion of monomer **2a**, further confirm the living nature of the polymerization. Kinetic studies revealed that the polymerization obeyed the first-order reaction rule. The reaction rate constant was estimated to be 1.12×10^{-4} s^{-1}, larger than that initiated by aryl conjugated phenylethynyl Pd(II) complex which is 8.87×10^{-5} s^{-1} (Fig. 2b).[19b] The faster reaction rate of **1a** probably due to the less steric hindrance of the alkyl substituent.

Table 1 Selected Results for the Polymerization of **2a**-**2c** with **1a**-**1d** as Initiator in Various Solvents at 55 °C[a]

run	Monomer	Initiator.	[**M**]$_0$/[**I**]$_0$[b]	solvents	polymer	M_n[c] (Da)	M_w/M_n[c]	Yield[d]
1	**2a**	**1a**	35	THF	poly-**a2a**$_{35}$	1.12×10^4	1.18	87 %
2	**2a**	**1a**	45	THF	poly-**a2a**$_{45}$	1.31×10^4	1.15	95 %
3	**2a**	**1a**	55	THF	poly-**a2a**$_{55}$	1.51×10^4	1.19	90 %
4	**2a**	**1a**	80	THF	poly-**a2a**$_{80}$	2.21×10^4	1.18	85 %
5	**2a**	**1a**	100	THF	poly-**a2a**$_{100}$	3.01×10^4	1.14	95 %
6	**2a**	**1b**	60	THF	poly-**b2a**$_{60}$	1.81×10^4	1.14	93%
7	**2a**	**1b**	100	THF	poly-**b2a**$_{100}$	3.02×10^4	1.09	89%
8	**2a**	**1b**	150	THF	poly-**b2a**$_{150}$	4.31×10^4	1.09	87%
9	**2a**	**1c**	50	THF	poly-**c2a**$_{50}$	1.51×10^4	1.15	91%
10	**2a**	**1c**	85	THF	poly-**c2a**$_{85}$	2.50×10^4	1.17	89%
11	**2a**	**1d**	55	THF	poly-**d2a**$_{55}$	1.61×10^4	1.27	90%
12	**2a**	**1d**	90	THF	poly-**d2a**$_{90}$	2.70×10^4	1.25	93%
13	**2a**	**1b**	50	$CHCl_3$	poly-**a2a**$_{50}$	1.52×10^4	1.14	92%
14	**2a**	**1b**	100	$CHCl_3$	poly-**a2a**$_{100}$	2.51×10^4	1.16	80%
15	**2a**	**1b**	50	toluene	poly-**a2a**$_{50}$	1.51×10^4	1.16	90%
16	**2a**	**1b**	100	toluene	poly-**a2a**$_{100}$	2.60×10^4	1.18	86%
17	**2a**	**1b**	50	DMF	poly-**a2a**$_{50}$	1.51×10^4	1.17	88%
18	**2a**	**1b**	100	DMF	poly-**a2a**$_{100}$	2.66×10^4	1.19	87%
19	**2b**	**1b**	50	THF	poly-**b2b**$_{50}$	1.18×10^4	1.18	90%
20	**2b**	**1b**	100	THF	poly-**b2b**$_{100}$	2.41×10^4	1.19	91%
21	**2c**	**1b**	50	THF	poly-**b2c**$_{50}$	1.74×10^3	1.13	86%
22	**2c**	**1b**	100	THF	poly-**b2c**$_{100}$	3.71×10^4	1.20	94%

[a] The polymers were prepared according to Scheme 1. [b] Initial feed ratio of monomer to initiator. [c] M_n and M_w/M_n values were determined by SEC analyses with equivalent to polystyrene standard. [d] Isolated yields.

The polymerization behaviors of Pd(II) complexes **1b**-**1d** with **2a** were then investigated in THF at 55 °C. It was found that all these Pd(II) complexes can promote the living polymerization of **2a**, afforded the corresponding polyisocyanides in high yields with controlled M_ns, narrow M_w/M_ns. (Table 1, and Fig. S17-S19, see ESI†). These results indicate that the polymerization can be tolerant to hydroxyl, ketone, and ester groups. The influence of solvents on the polymerizations were investigated by perform the polymerization of **2a** with **1b** in various solvents with different polarity such as toluene, $CHCl_3$, DMF, methanol and *n*-hexane (Table 1, and Fig. S20-S22, see ESI†). All polymerizations proceeded very well in these solvents except for those in methanol and *n*-hexane, because the generated polymers were precipitated during the polymerization. Phenyl isocyanides **2b**-**2c** can also be polymerized by these Pd(II) complexes in THF at 55 °C. The results of the polymerizations initiated by **1b** were summarized in Table 1. The SEC chromatograms of the afforded polymers were shown in Fig. S23-S24 (see ESI†). It is worthy to note that polymerization of monomer **2b** bearing an electron-denoting group usually require higher temperature when using phenylethynyl Pd(II) complexes as catalyst due to its low reactivity (higher than 100 °C in toluene).[16b] Thus, the polymerization activity of the alkylethynyl Pd(II) complexes is higher than that of the conjugated arylethynyl Pd(II) complexes.

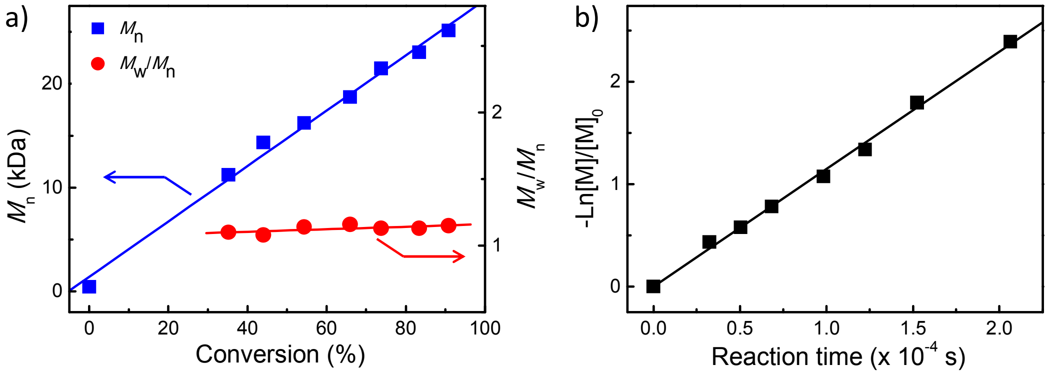


Fig. 2 (a) Plot of M_n and M_w/M_n values as a function of **1a**-initiated conversion of **2a** in THF at 55 °C ($[\mathbf{2a}]_0$ = 0.2 M, $[\mathbf{2a}]_0/[\mathbf{1a}]_0$ = 90). (b) First-order kinetics plot for polymerization of **2a** initiated by **1a**.

Helix-Sense-Selective Polymerization of Chiral Isocyanide. The helix-sense-selectivity of the polymerization was investigated through the polymerization of an optically active phenyl isocyanide bearing L-alanine pendant with a long decyl chain (**2d**) using Pd(II) complex **1a** as initiator. The helix-sense controlled polymerization of **2d** has been well described using *μ*-ethynediyl Pt-Pd complex as catalyst, which produced two diastereomers with different M_ns and yields at once.[15] Here, helix-sense-selectivity of the polymerization of chiral **2d** initiated by achiral Pd(II) complexes were performed in $CHCl_3$ at 50 °C. For comparison, polymerization of **2d** with phenylethynyl Pd(II) complex (**1e**) and phenylbuta-1,3-diynyl Pd(II) complex (**1f**) were also performed to disclose influences of the substituent on the helix-sense-selectivity (Figure 3). The polymerizations of chiral **2d** with achiral **1a**, **1e** and **1f** as initiators were carried out under the same experimental conditions with fixed initial feed ratios of monomer to initiator. The polymerization results were summarized in Table 2. Normalized SEC traces of the isolated polymers were displayed in Fig. 4. It was found that the poly-**e2d**$_{100}$ prepared from the polymerization of **1e** and **2d** showed two elution peaks similar to that prepared using *μ*-ethynediyl Pt-Pd complex as catalyst as we reported previously (Fig. 4a).[15] Circular dichroism (CD) and UV-vis absorption spectra of the produced poly-**e2d**$_{100}$ were shown in Fig. 5. Strong Cotton effect at 364 nm corresponding the n-π* transition of C=N imino chromophore of the polyisocyanide backbone was observed, suggesting a left-handed helical polyisocyanide was preferentially formed. The intensity of the molar circular dichroism at 364 nm ($\Delta\varepsilon_{364}$) of poly-**e2d**$_{100}$ was estimated to be –12.1 M^{-1} cm^{-1}. Collectively, these results demonstrated that both left-handed and right-handed helical polyisocyanides were produced at once with left-handed helix predominated. According to our previous work, two diastereomers was then separated into left-handed helical poly-**e2d**(–) and right-handed helical poly-**e2d**(+) by acetone fractionation (Fig. 3).[15] Each single handed helical polyisocyanide exhibit a monomodal elution peak in SEC chromatograms (Fig. 4b and 4c). The values of $\Delta\varepsilon_{364}$ of poly-**e2d**(–) and poly-**e2d**(+) were estimated to be –20.8 and +20.6 M^{-1} cm^{-1}, respectively (Fig. 5). Similar to Pd(II) complex **1e**, polymerization of **2d** with **1f** as initiator also produced both left- and right-handed helical polyisocyanides at once as confirmed by SEC chromatogram and CD spectrum (Fig. 4d and Fig.

5), while the helix-sense-selectivity was improved because the $\Delta\varepsilon_{364}$ of poly-**f2d**$_m$ was increased to –14.2 M^{-1} cm^{-1}.

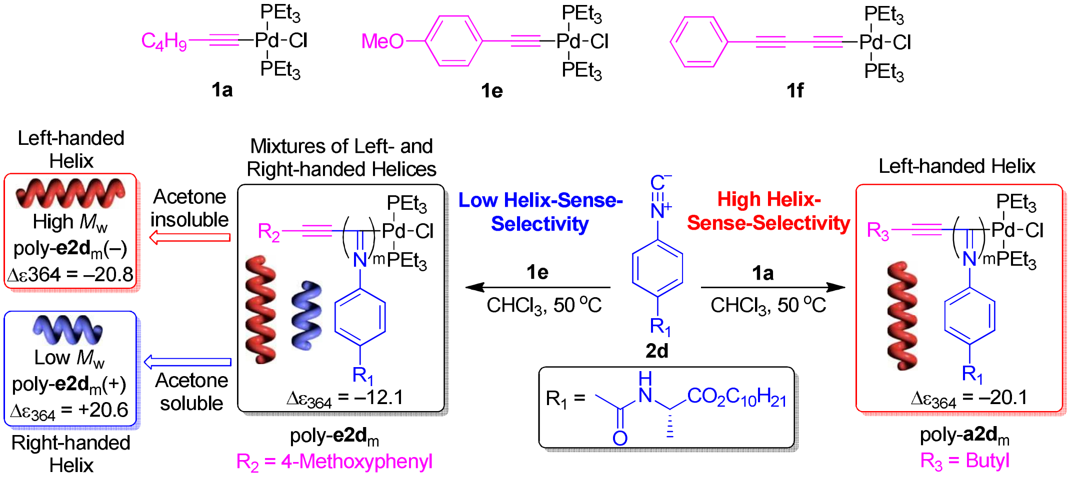


Fig. 3 Polymerization of optically active chiral monomer **2d** with Pd(II) complexes as initiators in $CHCl_3$ at 50 °C. The mixture of the diastereomers were separated into left-handed helical poly-**e2d**$_{100}$(–) and right-handed helical poly-**e2d**$_{100}$(+) by acetone fractionation.

Table 2. Selected results for the polymerization of **2d** with different Pd(II) initiators in $CHCl_3$ at 50 °C[a]

run	Initiator	$[M]_0/[I]_0$[b]	polymer	M_n (Da)[c]	M_w/M_n[c]	yield[d]	$\Delta\varepsilon_{364}$[e]	$[\alpha]^{25}_D$[f]
1	**1e**	100	poly-**e2d**$_{100}$	5.2×10^4	1.43	92%	–12.1	–1156
2	**1e**	150	poly-**e2d**$_{150}$	7.5×10^4	1.35	96%	–11.8	–1113
3	**1e**	--	poly-**e2d**$_{100}$(–)[g]	5.5×10^4	1.21	--	–20.8	–1986
4	**1e**	--	poly-**e2d**$_{100}$(+)[g]	1.0×10^4	1.07	--	+20.6	+1876
5	**1f**	100	poly-**f2d**$_{100}$	5.3×10^4	1.41	95%	–14.2	–1285
6	**1f**	150	poly-**f2d**$_{150}$	7.4×10^4	1.33	94%	–14.5	–1244
7	**1a**	100	poly-**a2d**$_{100}$	5.4×10^4	1.23	93%	–20.1	–1879
8	**1a**	150	poly-**a2d**$_{150}$	7.3×10^4	1.21	95%	–20.0	–1804

[a] The polymers were prepared according to Figure 3. [b] Initial feed ratio of monomer to initiator. [c] The M_n and M_w/M_n data were determined by SEC and reported as equivalent to standard polystyrene. [d] Isolated yield. [e] The molar circular dichroism were measured in $CHCl_3$ at 25 °C. [f] The optical rotations were measured in $CHCl_3$ at room temperature (c = 1). [g] The single-handed helical polymers were obtained through the acetone fractionation of poly-**e2d**$_{100}$.

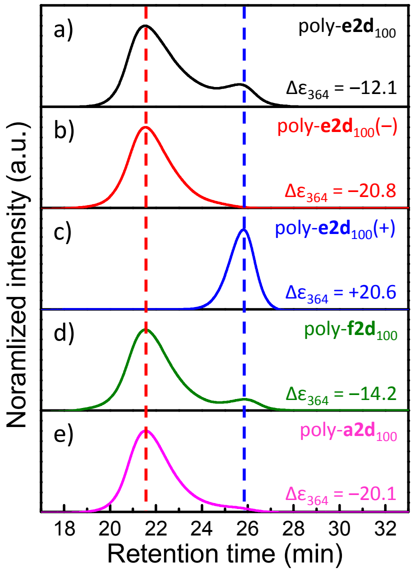


Fig. 4 Size exclusion chromatograms of polymers obtained from the polymerization of chiral **2d** with different achiral Pd(II) complexes as initiators in $CHCl_3$ at 50 °C.

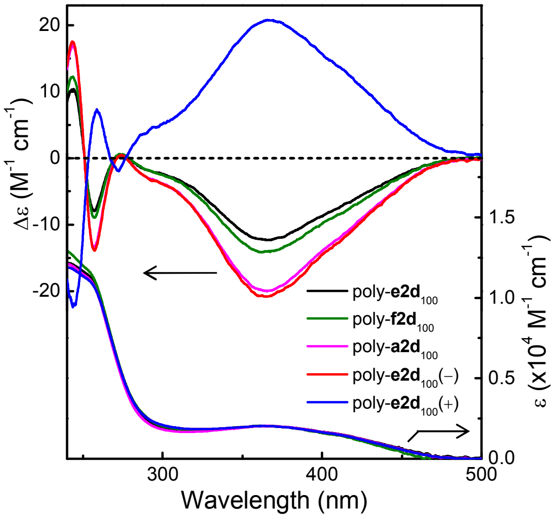
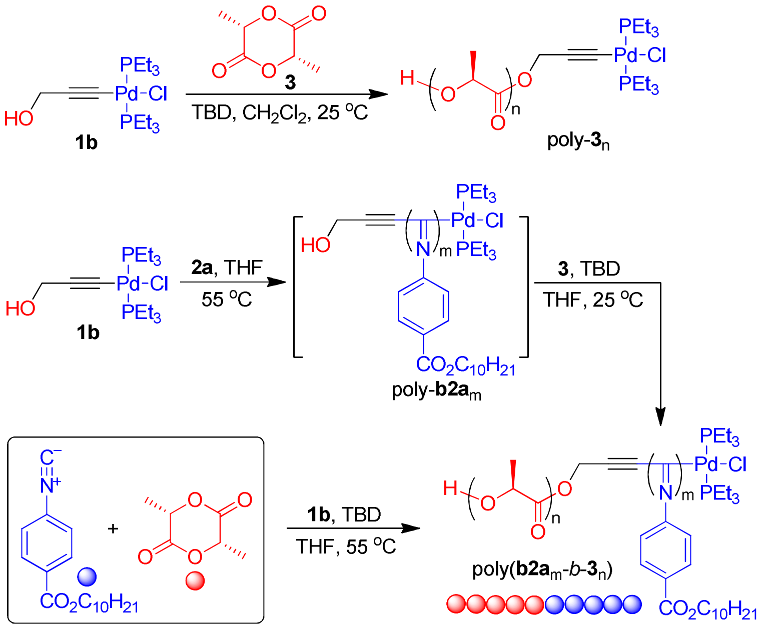


Fig. 5 CD and UV-vis absorption spectra of polymers obtained from the polymerization of chiral **2d** with different achiral Pd(II) complexes as initiators in $CHCl_3$ at 50 °C (*c* = 0.2 mg/mL).

Helix-sense-selectivity of the polymerization of **2d** with **1a** was conducted under the same conditions to that of **1e** and **1f**. The recorded SEC chromatogram of the isolated poly-**a2d**$_m$ was depicted in Fig. 4e. Very interestingly, in sharp contrast to the bimodal elution peaks of the polymers prepared using **1e** and **1f** as initiators, poly-**a2d**$_m$ showed a monomodal elution peak on the SEC chromatogram. The SEC profile is very similar to that of the acetone fractionated poly-**e2d**$_m$(–), suggests only left-handed helical polyisocyanide was selectively produced. CD and UV-vis absorption spectra of the isolated poly-**a2d**$_m$ also support this conclusion. As shown in Fig. 5, a strong Cotton effect around $\lambda = 364$ nm was observed on the CD spectrum. The $\Delta\varepsilon_{364}$ was estimated to be –20.1 M^{-1} cm^{-1} which almost identical to that of the left-handed helical poly-**e2d**$_m$(–) obtained through acetone fractionation ($\Delta\varepsilon_{364} = -20.8$). Thus, it can be concluded that the Pd(II) complex **1a** has a higher helix-sense-selectivity in the polymerization of chiral phenyl isocyanide as comparing with the other two Pd(II) complexes of **1e** and **1f**. The sequence of the helix-sense-selectivity of the Pd(II) complexes is **1a** > **1f** > **1e**. The optical rotation data of the afforded helical polymisocyanides using different Pd(II) complexes as initiator were summarized in Table 2, which show similar results to those obtained from CD and UV-vis spectra. For example, the optical rotation of the isolated poly-**a2d**$_{100}$ was estimated to be –1879, very close to that of the left-handed helical poly-**e2d**$_{100}$(–) (–1986). In contrast, the optical rotations of the poly-**e2d**$_{100}$ and poly-**f2d**$_{100}$ were estimated to be only –1156 and –1285, respectively, confirm the higher helix-sense-selectivity of **1a**. Considering the structure of these Pd(II) complexes, it was found that the substituent on the Pd(II) complexes play important role not only on the polymerization activity but also on the helix-sense-selectivity of the living polymerization of chiral phenyl isocyanide. The reason for the higher helix-sense-selectivity of **1a** than that of **1e** or **1f** is not very clear at current stage. Probably, the key factor for determining the helicity of the isolated polymer is the screw sense of the oligomers formed at the initiating stage of the polymerization. The less steric hindrance of **1a** facilitate the chiral monomer insertion following the same screw sense to produce a single-handed helical oligomer at the beginning stage. The subsequent insertion of monomers at chain-extension stage will following the same screw sense of the oligomers, thus it gives a single-handed helical polymer.

One-pot Copolymerization of Isocyanide and L-Lactide. Hydroxyl group is able to initiate the living polymerization of lactide and caprolactone via the ring-opening polymerization mechanism.[21] Thus, Pd(II) complex **1b** bearing an hydroxyl group may be further used as initiator for the polymerization of lactide. To verify this, as illuminated in Scheme 2, **1b** was treated with L-lactide (**3**) in CH_2Cl_2 at room temperature with the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) ($[\mathbf{3}]_0$ = 1.0 M, $[\mathbf{3}]_0/[\mathbf{1b}]_0$ = 50). The SEC chromatogram of the isolated PLLA poly-$\mathbf{3}_{50}$ was shown in Fig. 6a. A single modal elution peak appeared at high-molecular weight region was observed. M_n and M_w/M_n of poly-$\mathbf{3}_{50}$ were estimated to be 5.51×10^3 Da and 1.23, respectively. Further studies revealed the polymerization of **3** with **1b**/TBD was proceed in a living manner because the M_ns of the afforded PLLAs can be easily controlled through the variation on the initial feed ratio of **3** to **1b** (Fig. 6b). The afforded polymers exhibit single modal elution peaks on SEC chromatograms and the M_w/M_ns are narrow. These results suggest the Pd(II) complex **1b** is an effective initiator for the living polymerization of L-lactide. Thus, a series of poly-$\mathbf{3}_n$s with different M_ns and narrow M_w/M_ns were facilely prepared via the polymerization of **3** with **1b** in different initial feed ratios of monomer to initiator (Table S1, see ESI†). The structure of poly-$\mathbf{3}_n$ was confirmed by ^1H NMR and FT-IR spectroscopies. As shown in Fig. 7a, intense resonances at 5.16 and 1.58 ppm assignable to CH and CH_3 of the main chain were clearly observed on the ^1H NMR spectrum. FT-IR spectrum of the afforded polymer shows a strong absorption at 1760 cm^{-1} corresponding to the vibration of C=O (Fig. S25, see ESI†).



Scheme 2 Polymerization of L-Lactide and one-pot copolymerization of phenyl isocyanides and L-Lactide with Pd(II) complex **1b** as Initiator.

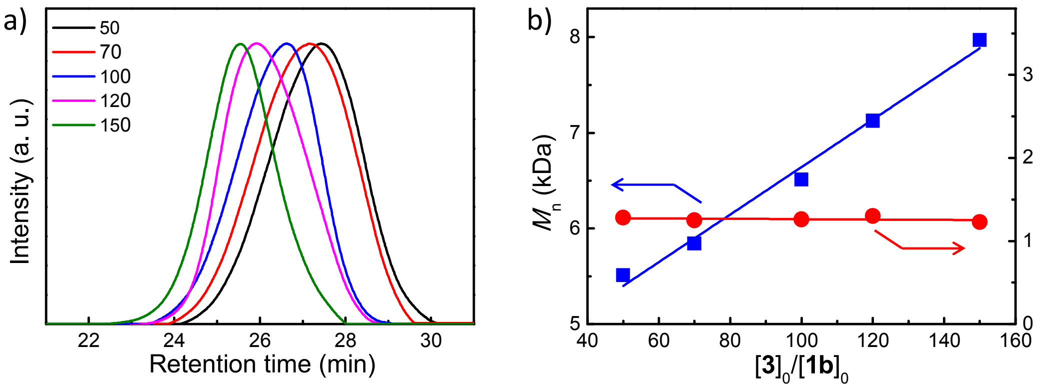


Fig. 6 (a) SEC chromatograms of poly-$\mathbf{3}_n$s prepared from the polymerization of L-Lactide **3** with hydroxyl-terminated Pd(II) complex **1b** as initiator with different initial feed ratios of **3** to **1b**. (b) Plots of M_n and M_w/M_n values of poly-$\mathbf{3}_n$s as a function of the initial feed ratios of **3** to **1b**. M_n and M_w/M_n data were determined by SEC with polystyrene standard (eluent = THF, temperature = 40 °C).

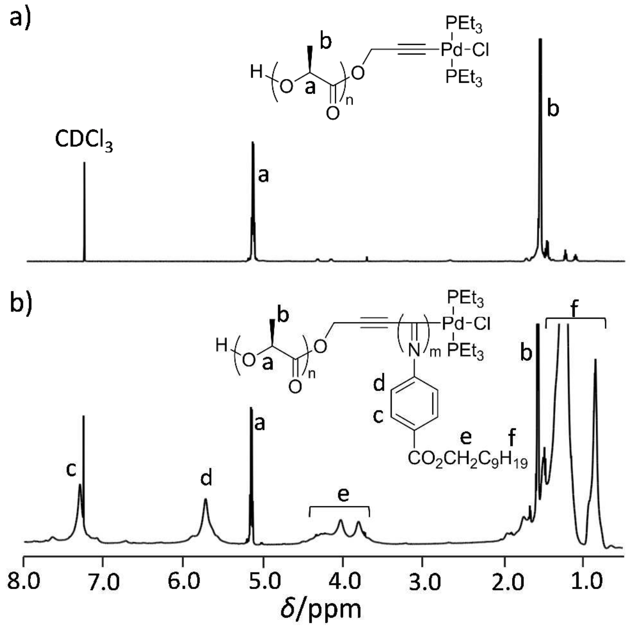


Fig. 7 ^{1}H NMR (600 MHz) spectra of poly-$\mathbf{3}_n$ (a) and poly($\mathbf{b2a}_m$-*b*-$\mathbf{3}_n$) block copolymer (b) measured in CDCl$_3$ at 25 °C.

Since Pd(II) complex **1b** is able to initiate the living polymerizations of both phenyl isocyanide and L-lactide. Block copolymers containing poly(phenyl isocyanide) and PLLA blocks may be facilely prepared in one-pot through copolymerization of the two monomers using **1b** as a single catalyst. Initially, the one-pot block copolymerization was conducted via two-feed procedure by copolymerization the two monomers sequentially. Monomer **2a** was first polymerized with **1b** in THF at 55 °C ($[\mathbf{2a}]_0/[\mathbf{1b}]_0 = 90$, $[\mathbf{2a}]_0 = 0.2$ M) to afford hydroxyl-terminated poly-$\mathbf{b2a}_{90}$ macroinitiator. After **2a** was completely consumed as indicated by SEC (M_n of the afforded polymer ceased to increase), an aliquot was removed for further analysis, **3** and TBD were then added to the polymerization vessel ($[\mathbf{3}]_0/[\mathbf{1b}]_0 = 30$). After 12 h, the mixture was poured into excess methanol, and the precipitated solids were collected in 88% isolated yield (over the two polymerization steps) via filtration. The recorded SEC chromatograms of macroinitiator poly-$\mathbf{b2a}_{90}$ and poly($\mathbf{b2a}_{90}$-*b*-$\mathbf{3}_{30}$) block copolymer were shown in Fig. 8a. The block polymer showed a single modal elution peak and was located at higher-molecular weight region as compared to its precursor poly-$\mathbf{b2a}_{90}$. The M_n and M_w/M_n of poly($\mathbf{b2a}_{90}$-*b*-$\mathbf{3}_{30}$) were respectively estimated to be 2.91×10^4 Da and 1.20 which are larger than that of the poly-$\mathbf{b2a}_{90}$ precursor ($M_n = 2.56 \times 10^4$, $M_w/M_n = 1.19$). ^{1}H NMR spectrum of poly($\mathbf{b2a}_{90}$-*b*-$\mathbf{3}_{30}$) block copolymer was shown in Fig. 7b. The resonances assignable to both segments can be clearly observed, including signals of phenyl protons (at 7.31 and 5.74 ppm) and $–CO_2CH_2–$ (at 4.50–3.50 ppm) originate from polyisocyanide, and resonances of CH (at 5.16 ppm) and CH_3 (at 1.58 ppm) ascribe to PLLA block. The block ratio of the two segments deduced from the integral analysis of ^{1}H NMR spectrum is 3:1, which agrees well with initial feed ratio of the two monomers added to the polymerization vessel. FT-IR spectrum of the block copolymer shows a series of characteristic vibrations including the $\upsilon_{C=N}$ (at 1600 cm^{-1}) and $\upsilon_{C=O}$ (at 1720 cm^{-1}) come from poly-**b2a**$_m$ segment, and $\upsilon_{C=O}$ (at 1760 cm^{-1}) come from poly-**3**$_n$ block (Fig. S26, see ESI†). These studies confirm the formation of expected PPI-*b*-PLLA block copolymer under controlled manner. By using this synthetic method, a series of PPI-*b*-PLLA block copolymers with different block ratios, controlled M_n and narrow M_w/M_n were readily prepared in high yields by just varying the initial feed ratio of the two monomers to initiator **1b** (Table 3, and Fig. S27, see ESI†).

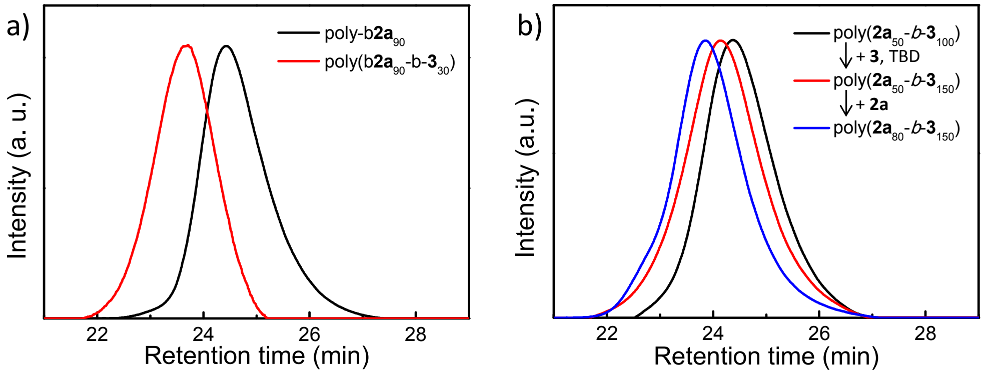


Fig. 8 (a) Representative size exclusion chromatograms of macroinitiator poly-**b2a**$_{90}$ and the respective one-pot synthesized poly(**b2a**$_{90}$-*b*-**3**$_{30}$) block copolymer. (b) Size exclusion chromatograms of the chain-extended poly(**b2a**$_{50}$-*b*-**3**$_{150}$) and poly(**b2a**$_{80}$-*b*-**3**$_{150}$) block copolymers prepared through the sequential copolymerization of **3** and **2a** with poly(**b2a**$_{50}$-*b*-**3**$_{100}$) as macroinitiator in THF at 55 °C.

Table 3. Selected results for the one-pot copolymerization of 2a and 3 with 1b as initiator via two-feed procedure[a]

run	Macroinitiator[b]			$[\mathbf{3}]_0/[\mathbf{Pd}]_0$[d]	Block copolymer				
	polymer	M_n (Da)[c]	M_w/M_n[c]		copolymer	M_n (Da)[c]	M_w/M_n[c]	yield[e]	ratio[f]
1	poly-$\mathbf{b2a}_{90}$	2.56×10^4	1.19	30	poly($\mathbf{b2a}_{90}$-*b*-$\mathbf{3}_{30}$)	2.91×10^4	1.20	88%	3:1
2	poly-$\mathbf{b2a}_{50}$	1.48×10^4	1.19	100	poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{100}$)	2.06×10^4	1.20	82%	1:2
3	poly-$\mathbf{b2a}_{60}$	1.87×10^4	1.16	40	poly($\mathbf{b2a}_{60}$-*b*-$\mathbf{3}_{40}$)	2.23×10^4	1.21	83%	3:2
4	poly-$\mathbf{b2a}_{80}$	2.38×10^4	1.14	20	poly($\mathbf{b2a}_{80}$-*b*-$\mathbf{3}_{20}$)	2.69×10^4	1.19	88%	4:1
5	poly-$\mathbf{b2a}_{100}$	2.96×10^4	1.20	150	poly($\mathbf{b2a}_{100}$-*b*-$\mathbf{3}_{150}$)	3.78×10^4	1.23	87%	2:3

[a]The block copolymers were prepared according to Scheme 2 by first preparing macroinitiator poly-$\mathbf{b2a}_m$ of different M_ns, followed by addition of **3** and TBD. [b]The M_n of the macroinitiator poly-$\mathbf{b2a}_m$ was determined by analysis via SEC of aliquots removed from the respective reaction mixtures prior to the addition of **3**. [c]M_n and M_w/M_n were determined by SEC with polystyrene standard. [d]The initial feed ratio of monomer to initiator. [e]Isolated yield over the two steps as indicated. [f]Block ratio of PPI to PLLA segments determined by ^{1}H NMR spectroscopy.

Interestingly, the one-pot block copolymerization of **2a** and **3** can be performed via one-feed procedure by treated a mixed solution of **2a** and **3** in THF with **1b** and TBD at 55 °C. The afforded block copolymers showed almost the same structure to that prepared via two-feed procedure as confirmed by SEC, ^{1}H NMR, ^{13}C NMR and FT-IR spectra (Fig. S28-S31, see ESI†). ^{1}H NMR spectrum of the resulted block copolymer was shown in Fig. S29 (see ESI†), which exhibit the same profile to that prepared via two-feed procedure. The resonances attributable to the two blocks can be clearly observed and the block ratio deduced from 1H NMR analysis is consistent to the initial feed ratio of the two monomers, indicates the two monomers were orthogonally polymerized at the same time. Remarkably, the ^{13}C NMR analysis of the resulting block copolymer shows a sharp signal at 162.53 ppm corresponding to the imino carbons of the main chain. The half-band width is about 30 Hz, suggesting the polyisocyanide segment of the block copolymer still possessing high stereoregularity (Fig. S30, see ESI†). Although phenyl isocyanide and chiral L-lactide were simultaneously polymerized in a single pot, the afforded block copolymers were CD silent at the absorption region of the polyisocyanide backbone even the sample was annealed in toluene at 100 °C for one weak. Probably the chiral LA cannot provide a sufficient asymmetric environment to induce the bias of the polymerization of phenyl isocyanide in this case.

To verify the living nature of chain ends of the one-pot synthesized block copolymer, chain-extension experiments were performed by sequential copolymerization of **3** and **2a** with poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{100}$) as macroinitiator. Firstly, poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{100}$) was treated with **3** to verify the living nature of the hydroxyl terminus of the PLLA segment ($[\mathbf{3}]_0/[\mathbf{1b}]_0 = 50$). As shown in Fig. 8b, the elution peak of the resulting chain-extended poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{150}$) was shifted to higher-molecular weight region as comparing to the macroinitiator poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{100}$) precursor. The M_n of poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{150}$) was increased to 2.43×10^4 Da ($M_w/M_n = 1.22$). The afforded poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{150}$) was then treated with **2a** to examine the living nature of the Pd(II) complex terminus of the polyisocyanide block ($[\mathbf{2a}]_0/[\mathbf{1b}]_0 = 30$). As shown in Fig. 8b, the single modal elution peak of the resulting polymer was shifted to shorter retention-time region, suggesting copolymerization of **2a** with poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{150}$) also take place. The resulting chain-extended poly($\mathbf{b2a}_{80}$-*b*-$\mathbf{3}_{150}$) has a M_n of 3.63×10^4 Da and M_w/M_n of 1.21. The M_n was larger than that of the poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{150}$) and poly($\mathbf{b2a}_{50}$-*b*-$\mathbf{3}_{100}$) precursors, but kept narrow M_w/M_n. These results demonstrated that one-pot copolymerization of **2a** and **3** with **1b** as catalyst were both proceed in living/controlled manners. Based on the established synthetic method, a range of PPI-*b*-PLLA block copolymers with controlled M_n, narrow M_w/M_n and tunable compositions were facilely prepared by just varying the initial feed ratio of monomers to initiator (Table S2 and Fig. S28, see ESI†).

Morphology of the one-pot synthesized block copolymer was then investigated in film state by atomic force microscopy (AFM). A solution of poly(**b2a**$_{100}$-*b*-**3**$_{150}$) in THF was spin-casted onto a clear, precleaned silicon wafers. After the sample was annealed under the vapor of the same solvent at room temperature for 12 h and slowly dried in air, it was subjected to AFM observation. The height and phase AFM images acquired in tapping-mode were shown in Fig. 9. Well-defined spherical nanoparticles were clearly observed owning to the immiscibility of the two blocks. The average diameter of the particles was estimated to be ca. 35 nm with good homogeneity due to the narrow M_w/M_n of the block copolymer. For comparison, investigations on the morphology of thin films prepared from the corresponding homopolymers of poly-**b2a**$_{100}$ and poly-**3**$_{150}$ were performed under the same experimental conditions to that of the poly(**b2a**$_{100}$-*b*-**3**$_{150}$) block copolymer. Although many efforts were conducted, no similarly well-defined morphologies could be observed. These results further confirmed the success of the one-pot living copolymerization of two different monomers with hydroxyl-terminated Pd(II) complex as a single catalyst via distinct polymerization mechanisms.

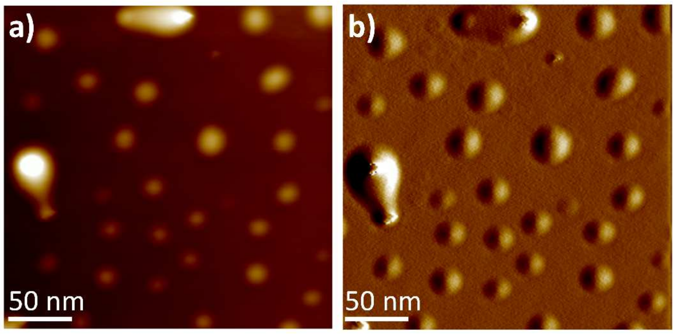


Fig. 9 AFM height (a) and phase (b) images of the self-assembled structures of poly(**b2a**$_{100}$-*b*-**3**$_{150}$).

Conclusion

In summary, a family of easily accessible and air-stable alkylethynyl Pd(II) complexes were designed and synthesized. These Pd(II) complexes were found to promote the polymerization of phenyl isocyanides in living/controlled chain-growth manner, afforded well-defined poly(phenyl isocyanide)s in high yields with controlled M_ns, narrow M_w/M_ns and high stereoregularity. The Pd(II) complexes showed very high activity and can be applied to the polymerization of isocyanide monomer with low reactivity in mild conditions. Very interestingly, such alkylethynyl Pd(II) complexes exhibit extremely high helix-sense-selectivity in polymerization of chiral phenyl isocyanide as comparing with other Pd(II) initiators, lead to the formation of single handed helical polymers. Moreover, Pd(II) complex bearing an hydroxyl group can initiate the orthogonal polymerization of both L-lactide and phenyl isocyanide in one-pot. Although the two monomers were polymerized under distinct mechanisms, the copolymerization was revealed to proceed in living/controlled manners, afforded well-defined block copolymers in high yields with controlled M_ns and tunable compositions. Given the modifications on monomers and Pd(II) complexes, we believe the present study will provide a convenient synthetic method for synthesis of optically active helical polyisocyanides with controlled helical sense and high stereoregularity and also for a broad range of hybrid block copolymers.

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