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One-Pot Synthesis of Brush Copolymers Bearing Stereoregular Helical Polyisocyanides as Side Chains through Tandem Catalysis

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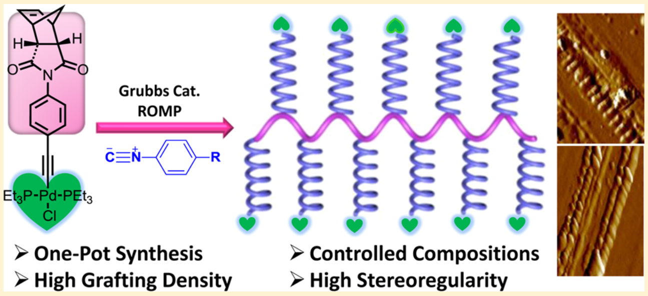
Supporting Information

ABSTRACT: An air-stable phenylethynyl Pd(II) complex containing a polymerizable norbornene unit was designed and synthesized. Such a Pd(II) complex can initiate the living/controlled polymerization of phenyl isocyanide, giving stereoregular poly(phenyl isocyanide)s in high yields with controlled molecular weights and narrow molecular weight distributions. The norbornene unit on the Pd(II) complex can undergo ring-opening metathesis polymerization (ROMP) with Grubbs' second-generation catalyst, affording polynorbornene bearing Pd(II) complex pendants under a living/controlled manner. Interestingly, the Pd(II) complex pendants on the isolated polynorbornene are active enough to initiate the living/controlled polymerization of phenyl isocyanides, yielding well-defined brush-like copolymers with polynorbornene backbone and helical poly(phenyl isocyanide) as side chains. ^{31}P NMR analyses indicate almost all the Pd(II) units on the polynorbornene participated in the polymerization, and the grafting density of the brush copolymer is high. Further studies revealed the brush copolymer can be readily achieved in one-pot via tandem catalysis. By using this method, a range of brush copolymers with different structures and tunable compositions were facilely prepared in high yields with controlled molecular weights and narrow molecular weight distributions. The synthesized brush copolymers were revealed to form worm-like cylindrical morphologies and helical rod architectures in film state by atomic force microscope observations.



■ INTRODUCTION

The helix is one of the most important secondary structures of biological macromolecules and is closely related to the characteristic functions.[1] Inspired by sophisticated biological helices and related unique functions, chemists have been challenged to develop artificial helical polymers not only for mimic biological helices and functions but also for their applications in the field of material science.[2] Although some investigations have been carried out in recent decades, the number of artificial polymers with stable helical conformation is still limited. Examples of such artificial helical polymers include sterically restricted poly(methacrylate ester)s[3] and poly(aryl vinyl)s,[4] polyisocyanides,[5] polyisocyanate,[6] polyguanidines,[7] and polyacetylenes.[8] Among them, polyisocyanides have attracted considerable research interests in recent years owing to their unique fascinating rigid helical structures and wide applications in many fields.[9] Well-defined polyisocyanides can be obtained through the polymerization of appropriate isocyanide monomers with transition metal complexes as catalysts or initiators. The nickel(II) complex is by far the most used catalyst for the isocyanide polymerization; even the Ni(II) species reside on a polymer chain end.[5,9] We found that the Ni(II)-terminated regioregular poly(3-hexylthiophene) can initiate the living polymerization of isocyanide, affording well-defined conjugated block copolymers with controlled molecular weights and tunable compositions.[10] However, polyisocyanides prepared with Ni(II) complexes usually possess low stereoregularity, which is important to the optical activity of a helical polymer.[11] Besides the nickel complexes, other metal complexes for living/controlled polymerization of isocyanide are very limited. The aryl−rhodium complex and μ-ethynediyl Pt−Pd binuclear complex have been reported to promote the living/controlled polymerization of aryl isocyanide.[12] By using the μ-ethynediyl Pt−Pd complex as catalyst, we developed a facile synthetic method for preparation of single-handed helical poly(phenyl isocyanide)s.[13] Nevertheless, their applications in preparation of brush copolymers containing polyisocyanide segment have been difficult because of their narrow tolerance to initiator and terminator structures and polymerization conditions. Very recently, we reported a class of air-stable (phenylbuta-1,3-diynyl)- and phenylethynylpalladium(II) complexes which were unexpectedly found to promote the living/controlled polymerization of isocyanides, leading to the formation of well-defined polyisocyanides with controlled

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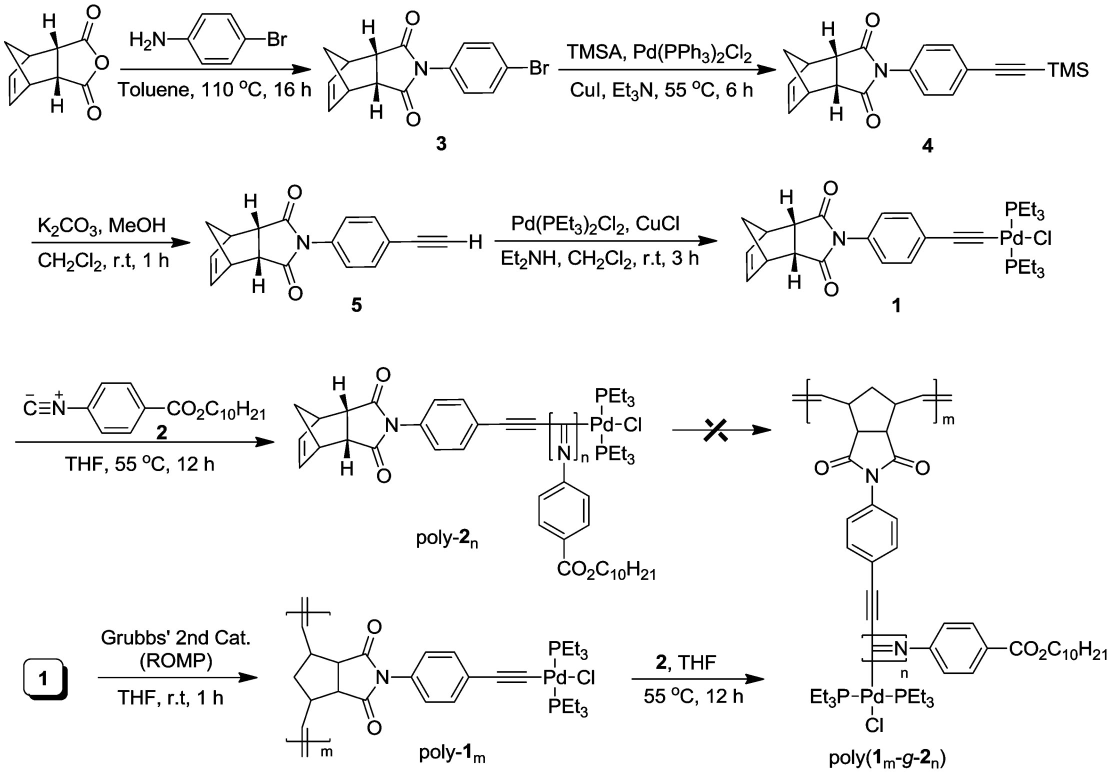
Scheme 1. Synthesis of Pd(II) Complex 1 and Brush Copolymer Poly(1_m-*g*-2_n)



molecular weight (M_n), narrow molecular weight distribution (M_w/M_n), and high stereoregularity.[14] Utilization of these synthetic methods, block and star-shaped copolymers containing well-defined stereoregular polyioscyanide segments have been successfully developed. We envision that this polymerization method may be further applied to the preparation of brush copolymers bearing well-defined polyisocyanide as side chains through modification on the structure of the Pd(II) complex.

Brush copolymer is a class of one-dimensional macromolecules containing a high density of side chains connected to a linear backbone.[15] Because of their crowding arrangement, those side chains are stretched away from the backbone to form a brush-like or a worm-like cylindrical conformation.[16] Thus, brush copolymers with controlled structures are expected to provide relatively precise shape and size control in each dimension. They can afford unique nanoscale morphologies that are unavailable by self-assembly of block copolymers.[17] Because of the unique interesting helical structure and functions, brush copolymers containing helical polymers as side chains have attracted considerable research attentions in the past few years.[18] Chen et al. developed a series of brush copolymers with polynorbornene backbone bearing helical poly(γ-benzyl-L-glutamate) branches through integrated ring-opening metathesis polymerization (ROMP) and the polymerization of amino acid *N*-carboxyanhydrides.[19] Deming and coworkers reported the preparation of cylindrical polypeptide brushes via the tandem catalysis approach.[20] Maeda and coworkers synthesized chiral polymer brushes with helical polyacetylene backbone and helical polyisocyanates as side chains.[21] However, to the best of our knowledge, well-defined brush copolymers bearing rigid helical polyisocyanides as side chains have never been reported to date, probably due to the limited synthetic method.

In this contribution, we designed and synthesized a new class of air-stable phenylethynyl Pd(II) complexes (**1**, Scheme 1) that are connected with a polymerizable norbornene unit. Such Pd(II) complex can initiate the living/controlled polymerization of phenyl isocyanides, leading to the formation of well-defined, stereoregular poly(phenyl isocyanide)s in controlled M_ns and narrow M_w/M_ns. In addition, the norbornene unit on the Pd(II) complex can undergo ROMP with Grubbs' second-generation catalyst (G2), affording well-defined polynorbornene containing multiple Pd(II) complexes. Combination of the ROMP and the polymerization of phenyl isocyanide, well-defined brush copolymers with polynorbornene backbone bearing helical poly(phenyl isocyanide)s as side chains with tunable compositions and high grafting density were readily achieved in a single-pot via tandem catalysis. The synthesized brush copolymer was founded to form worm-like cylindrical morphologies and helical rod architectures by atomic force microscope observations.

■ RESULTS AND DISCUSSION

Synthesis of Pd(II) Complex. The phenylethynyl Pd(II) complex **1** containing a polymerizable norbornene unit was prepared in a synthetic procedure similar to that we reported previously and was briefly described here.[14] As depicted in Scheme 1, *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride reacted with 4-bromoaniline in toluene at 110 °C to give **3** in 72% yield. The isolated **3** was then reacted with trimethylsilylacetylene (TMSA) by Sonogashira coupling reaction to afford **4**. Removal of the TMS group with potassium carbonate gave **5** in 81% yield over the two steps. The norbornene incorporated phenylethynyl Pd(II) complex **1** was obtained in 60% yield by treating **5** with *trans*-dichlorobis(triethylphosphine)palladium(II) in dichloromethane in the presence of diethylamine as base and copper chloride as catalyst at room temperature. The Pd(II) complex **1** is air-stable and shows good solubility in most common organic solvents such as *n*-hexane, chloroform, THF, toluene, and ethyl acetate. The structures of **1** and the related intermediates were characterized by ^{1}H and ^{13}C NMR, FT-IR, and mass spectroscopies as well as microanalysis (Figures S1−S7, Supporting Information). As shown in Figure 1a, ^{1}H NMR analysis of **1** showed a series of characteristic resonances, including those of phenyl protons (*a* at 7.28 and *b* at 6.99 ppm), norbornene alkene protons (*c* at 6.24 ppm), and the protons of PCH_2CH_3 on the Pd unit (*f*, at 1.93 ppm). The integration area ratios of *a*:*c*:*f* are 2:2:12, which were in good agreement with the proton number ratios of the proposed structure. The ^{31}P NMR spectrum of the Pd(II) complex shows a singlet at 17.80 ppm (Figure 2), which is almost the same as that of the reported (phenylbuta-1,3-diynyl)palladium(II) and phenylethynyl Pd(II) complexes, confirming the chemical structure of **1**.

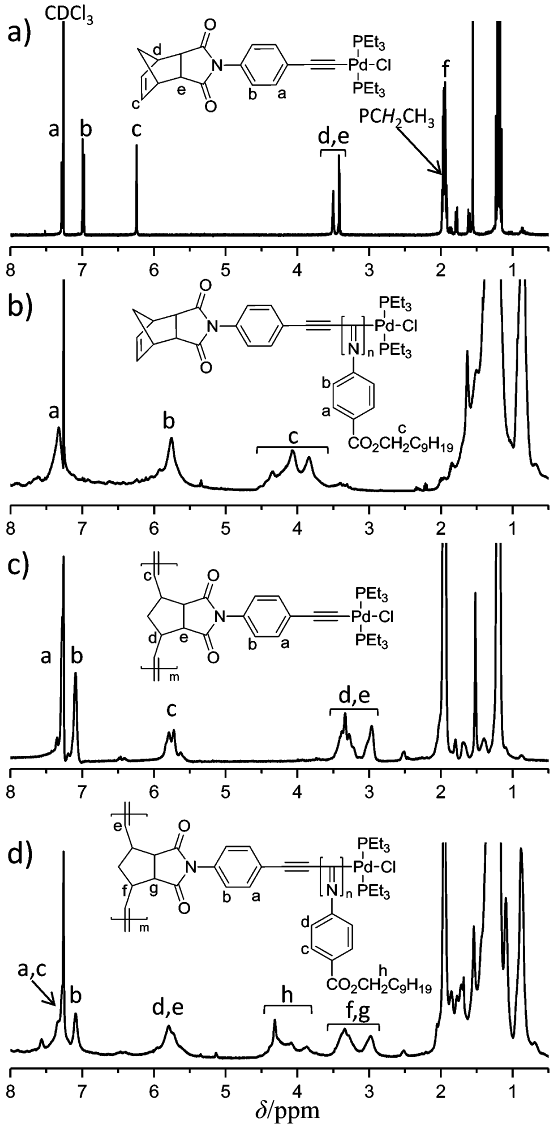


Figure 1. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **1** (a), poly-$\mathbf{2}_n$ (b), poly-$\mathbf{1}_m$ (c), and poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$) (d) at 25 °C.

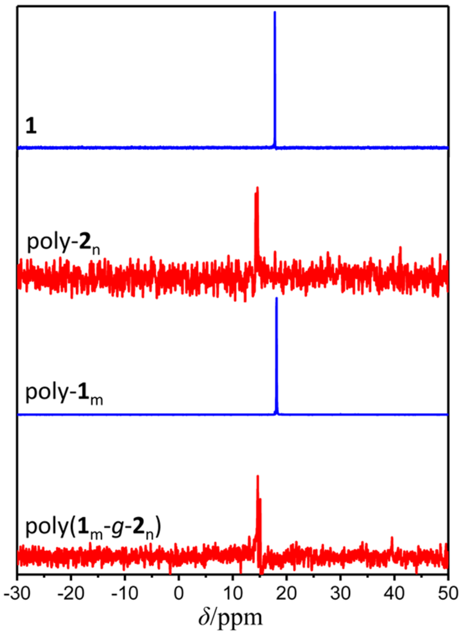


Figure 2. ^{31}P NMR spectra of the Pd(II) complex **1**, poly-$\mathbf{2}_n$, poly-$\mathbf{1}_m$, and poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$) measured in $CDCl_3$ at room temperature.

Polymerization of Isocyanide. The polymerization behavior of Pd(II) complex **1** with phenyl isocyanide was investigated by treating **1** with decyl 4-isocyanobenzoate (**2**) in THF with $[\mathbf{2}]_0$ = 0.2 M and $[\mathbf{2}]_0/[\mathbf{1}]_0$ = 55. The polymerization failed at room temperature because no polymeric product could be isolated even though the polymerization time was elongated to 20 h, and the monomer was recovered. However, the polymerization succeeded at 55 °C as confirmed by size exclusion chromatography (SEC) analysis. As shown in Figure 3a, the recorded SEC chromatogram of the isolated poly-$\mathbf{2}_{55}$ (the footnote indicates the initial feed ratio of monomer to catalyst) showed a monomodal elution peak at the high molecular weight region. The M_n and M_w/M_n of poly-$\mathbf{2}_{55}$ were estimated to be 1.7×10^4 and 1.19, respectively, based on SEC analysis with polystyrene standard. The FT-IR spectrum of poly-$\mathbf{2}_{55}$ in KBr showed an absorption band at 1600 cm^{-1} due to the $\upsilon_{(C=N)}$, which is characteristic for poly(phenyl isocyanide)s (Figure S8, Supporting Information). The ^{1}H NMR spectrum of the isolated poly-$\mathbf{2}_{55}$ is depicted in Figure 1b. The resonances of phenyl and $-CO_2CH_2-$ protons coming from the isocyanide repeating units appeared at 7.33, 5.76 and 3.45−4.50 ppm, respectively. All the resonances are relatively broad due the rigid helical conformation of the main chain which restricted motion of the backbone. ^{13}C NMR of the resulting poly-$\mathbf{2}_{55}$ measured in $CDCl_3$ at room temperature also confirmed the structure of the isolated polymer. Moreover, a relatively sharp resonance corresponding to the imino carbons of the polymer backbone was displayed at δ 162.5 ppm, and the half-bandwidth was estimated to be 29 Hz (Figure S9, Supporting Information), which suggested that the isolated polyisocyanide had a high stereoregularity of the imino groups of backbone. To further confirm the polymerization of phenyl isocyanide with **1** as initiator proceeded in a living/controlled chain-growth manner, a series of polymerizations of **2** with **1** as catalyst were then carried out with different initial feed ratios of monomer to catalyst. The SEC chromatograms of the isolated poly-$\mathbf{2}_n$s are displayed in Figure 3a. It was found that all the polymers exhibited single modal elution peaks. The M_n and M_w/M_n values of the afforded poly-$\mathbf{2}_n$s estimated from SEC analyses were plotted against the initial feed ratios of monomer to catalyst and are summarized in Figure 3b. All the isolated

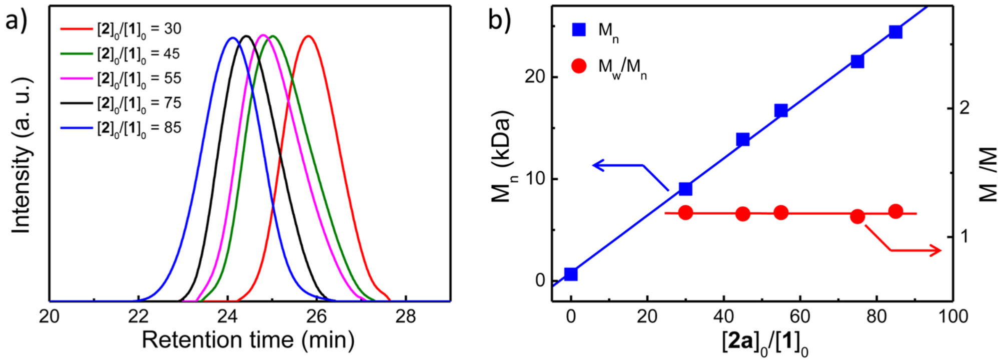


Figure 3. (a) Size exclusion chromatograms of poly-$\mathbf{2}_n$s prepared from phenyl isocyanide **2** with Pd(II) complex **1** as initiator in THF at 55 °C with different initial feed ratios of **2** to **1**. (b) Plot of M_n and M_w/M_n values of the isolated poly-$\mathbf{2}_n$s as a function of the initial feed ratios of **2** to **1**. M_n and M_w/M_n values were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

polymers exhibited narrow M_w/M_n. A linear correlation between the M_n and the initial feed ratios was observed, suggesting the polymerization of phenyl isocyanide **2** with Pd(II) complex **1** as initiator did proceed in a living/controlled chain-growth manner. These results demonstrated that incorporation of a polymerizable norbornene unit on the phenylethynyl Pd(II) complex has no negative influence on the living/controlled polymerization of phenyl isocyanide. The double bonds of the norbornene did not interfere with the isocyanide polymerization, and no side reaction took place during the polymerization. Thus, a range of poly-$\mathbf{2}_n$s with different M_n and narrow M_w/M_n were readily prepared by just varying the initial feed ratio of monomer to catalyst (Table 1).

Table 1. Selected Results for the Polymerization of 2 with 1 as Initiator in THF at 55 °C[a]

run	[**2**]$_0$/[**1**]$_0$[b]	polymer	M_n[c]	M_w/M_n[c]	yield[d] (%)
1	30	poly-$\mathbf{2}_{30}$	9.0 × 10^3	1.19	90
2	45	poly-$\mathbf{2}_{45}$	1.4 × 10^4	1.18	94
3	55	poly-$\mathbf{2}_{55}$	1.7 × 10^4	1.19	92
4	75	poly-$\mathbf{2}_{75}$	2.2 × 10^4	1.16	92
5	85	poly-$\mathbf{2}_{85}$	2.4 × 10^3	1.20	89

[a] The polymers were synthesized according to Scheme 1. [b] The initial feed ratio of **2** to **1**. [c] The M_n and M_w/M_n data were determined by SEC and reported as equivalent to standard polystyrene. [d] Isolated yield.

ROMP of Pd(II) Complex 1. The ROMP behavior of the norbornene unit of Pd(II) complex **1** was examined by treating **1** with Grubbs' catalyst G2 in THF at room temperature with $[\mathbf{1}]_0 = 0.2$ and $[\mathbf{1}]_0/[\mathrm{G2}]_0 = 20$ (Scheme 1). The polymerization was relatively fast, and **1** was almost completely consumed within 1 h. SEC and ^{1}H NMR analyses of the isolated poly-$\mathbf{1}_{20}$ suggest the successful transformation of **1** into expected polynorbornene bearing Pd(II) complexes pendants. As shown in Figure 4a, SEC chromatogram of the isolated material exhibited a monomodal elution peak at high molecular weight region. Based on SEC calculations, poly-$\mathbf{1}_{20}$ was found to have a M_n of 1.2 × 10^4 Da and M_w/M_n of 1.37. The ^{1}H NMR spectrum of the isolated poly-$\mathbf{1}_{20}$ is shown in Figure 1c, which revealed that **1** was nearly completely consumed (>99%) as the essential absence of the sharp resonances of alkene protons at 6.24 ppm. In addition, a series of characteristic resonances assignable to the proposed polynorbornene structure were observed, including those of the phenyl protons (*a* at 7.28 ppm and *b* at 7.01 ppm), alkene protons of the polynorbornene-based main chain (*c*, at 5.50−6.95 ppm), and PCH_2CH_3 protons (CH_2 at 1.95 ppm and CH_3 at 1.20 ppm). The integration area ratio of *a*:*b*:*c* is 2:2:2, which agreed very well with the proton number ratio of the proposed structure, indicating almost quantitatively one Pd(II) functionality per repeating unit of poly-$\mathbf{1}_{20}$. As depicted in Figure 2, the ^{31}P NMR spectrum of poly-$\mathbf{1}_m$ showed a sharp resonance appearing at 17.8 ppm—the same as that of monomer **1**. No other peaks could be detected on the ^{31}P NMR spectrum, suggesting no side reaction occurred on the Pd(II) unit during the

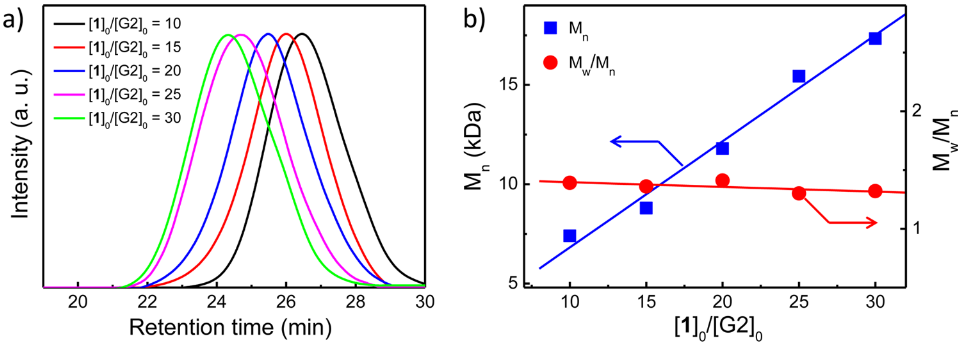


Figure 4. (a) Size exclusion chromatograms of poly-$\mathbf{1}_m$s prepared from Pd(II) complex **1** with G2 as catalyst in THF at room temperature with different initial feed ratios of **1** to G2. (b) Plots of M_n and M_w/M_n values of the isolated poly-$\mathbf{1}_m$s as a function of the initial feed ratios of **1** to G2. M_n and M_w/M_n were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).

polymerization of norbornene. Further studies revealed that the ROMP of **1** in THF at room temperature also proceeds in a living/controlled fashion. A range of poly-$\mathbf{1}_m$s were synthesized by the ROMP method with different initial feed ratios of **1** to G2. All the isolated polymers showed single modal elution peaks on SEC chromatograms and exhibited narrow M_w/M_ns. The M_ns of the synthesized poly-$\mathbf{1}_m$s showed a linear relationship with the initial feed ratios of monomer to catalyst (Figure 4b). Thus, a series of poly-$\mathbf{1}_m$s with different M_n and narrow M_w/M_n can be facile prepared in high yields under controlled manner (Table 2). These results demonstrated that the G2 catalyst and the polymerization condition have no negative influence on the Pd(II) complex units. That is, the Pd(II) complex is robust enough to tolerate the polymerization condition and the structure of the Pd(II) complexes was maintained during the ROMP.

Table 2. Selected Results for ROMP of 1 with G2 as Catalyst in THF at 25 °C[a]

run	$[\mathbf{1}]_0/[\mathrm{G2}]_0$[b]	polymer	M_n[c]	M_w/M_n[c]	yield[d] (%)
1	10	poly-$\mathbf{1}_{10}$	7.4×10^3	1.39	87
2	15	poly-$\mathbf{1}_{15}$	8.6×10^3	1.36	92
3	20	poly-$\mathbf{1}_{20}$	1.2×10^4	1.37	93
4	25	poly-$\mathbf{1}_{25}$	1.5×10^4	1.30	89
5	30	poly-$\mathbf{1}_{30}$	1.7×10^4	1.32	85

[a] The polymers were synthesized according to Scheme 1. [b] The initial feed ratio of monomer **1** to catalyst G2. [c] The M_n and M_w/M_n were determined by SEC and reported as equivalent to standard polystyrene. [d] Isolated yield.

Synthesis of Brush Copolymers. The experiments mentioned above have demonstrated that the polymerizable norbornene incorporated phenylethynyl Pd(II) complex **1** is applicable to both living/controlled polymerization of phenyl isocyanide and ROMP by using G2 as catalyst. Therefore, brush copolymer with polynorbornene as backbone and helical polyisocyanide as side chains may be readily prepared through the combination of ROMP and the living polymerization of phenyl isocyanides. To verify, we initially attempt to prepare such brush copolymer using "grafting through" strategy by ROMP of the norbornene-terminated poly-$\mathbf{2}_{55}$ as macromonomer with G2 as catalyst in THF at room temperature—the same condition as the polymerization of Pd(II) complex **1**. However, SEC analysis indicated the polymerization was failed because no molecular weight increase was observed. The elution peak of recorded SEC did not shift to higher molecular weight region as compared to the corresponding macromonomer, and poly-$\mathbf{2}_{55}$ was recovered. Probably, the steric hindrance of the rigid helical poly(phenyl isocyanide)s prevents the ROMP of the norbornene terminus.

The brush copolymer was then attempt to be prepared through the polymerization of phenyl isocyanide with the isolated poly-$\mathbf{1}_m$ bearing Pd(II) complexes pendants as multiple macroinitiators. First, a test reaction of small amount of **2** with poly-$\mathbf{1}_{20}$ was investigated in THF at 55 °C. The ^{1}H NMR spectrum of the isolated polymer is shown in Figure 1d. In addition to the resonances come from the polynorbornene backbone, broad signals ascribe to the phenyl isocyanide units were clearly observed, including phenyl peaks located at 7.45 and 5.80 ppm and $-CO_2CH_2-$ resonance at 3.61−4.50 ppm. This result indicates the Pd(II) units on the poly-$\mathbf{1}_m$ are active enough to reacted with phenyl isocyanide. Then, the polymerization of **2** with poly-$\mathbf{1}_{10}$ as macroinitiator was performed to achieve brush copolymers with long side chains. The recorded SEC chromatogram of the obtained materials (poly($\mathbf{1}_{10}$-*g*-$\mathbf{2}_{10}$)) is shown in Figure 5. As expected, the brush polymer exhibited a monomodal elution peak on SEC chromatogram and was shifted to higher molecular weight region as compared with the respective polyfuntional initiator poly-$\mathbf{1}_{10}$. No elution peaks corresponding to macroinitiator poly-$\mathbf{1}_{10}$ and monomer **2** could be observed on the SEC chromatogram, suggesting the phenyl isocyanide monomer was completely participated in the polymerization. The M_n of the isolated poly($\mathbf{1}_{10}$-*g*-$\mathbf{2}_{10}$) was estimated to be 3.1×10^4 Da based on SEC analysis, larger than that of the poly-$\mathbf{1}_{10}$ precursor ($M_n = 7.4 \times 10^3$ Da, $M_w/M_n = 1.25$). Although the M_n was considerably increased, the M_w/M_n was kept narrow which was estimated to be 1.28 by SEC analysis. The FT-IR spectrum of the brush copolymer showed a characteristic absorption band of imino backbone at 1600 cm^{-1} (Figure S10, Supporting Information). The ^{1}H NMR spectrum of a brush copolymer with long side chains is similar to that of the poly-$\mathbf{2}_n$ homopolymer. Signals assignable to the polynorbornene backbone protons are difficult to observe, probably due to the high grafting density (Figure S11, Supporting Information). The ^{13}C NMR spectrum is also similar to that of the poly-$\mathbf{2}_n$ homopolymer and showed a sharp resonance of the imino carbons of the backbone of side chains at 162.5 ppm with the half-bandwidth of 30 Hz, suggesting the poly(phenyl isocyanide) side chains of the brush copolymer also possess

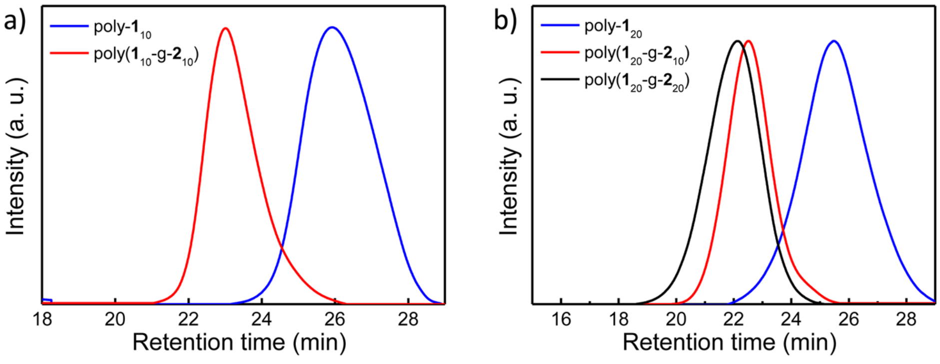


Figure 5. (a) SEC chromatograms of poly-$\mathbf{1}_{10}$ and the respective brush copolymer poly($\mathbf{1}_{10}$-*g*-$\mathbf{2}_{10}$). (b) SEC chromatograms of poly-$\mathbf{1}_{20}$ and the respective brush copolymer poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{10}$) and the side-chain-extended poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{20}$) prepared from the polymerization of **2** with poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{10}$) as macroinitiator in THF at 55 °C.

Table 3. Selected Polymerization Results for Brush Copolymer Poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$)[a]

run	polymer[b]	M_n[c] (Da)	M_w/M_n[c]	yield (%)[d]	$[\mathbf{2}]_0/[\mathbf{1}]_0$	brush copolymer[b]	M_n[c] (Da)	M_w/M_n[c]	yield[d] (%)
1	poly-$\mathbf{1}_{10}$	7.4×10^3	1.25	92	10	poly($\mathbf{1}_{10}$-*g*-$\mathbf{2a}_{10}$)	3.1×10^4	1.28	84
2	poly-$\mathbf{1}_{15}$	9.4×10^3	1.38	89	10	poly($\mathbf{1}_{15}$-*g*-$\mathbf{2a}_{10}$)	4.0×10^4	1.27	78
3	poly-$\mathbf{1}_{20}$	1.2×10^4	1.37	87	10	poly($\mathbf{1}_{20}$-*g*-$\mathbf{2a}_{10}$)	5.9×10^4	1.25	75
4	poly-$\mathbf{1}_{25}$	1.5×10^4	1.40	89	20	poly($\mathbf{1}_{25}$-*g*-$\mathbf{2a}_{20}$)	1.7×10^5	1.25	76
5	poly-$\mathbf{1}_{15}$	9.4×10^3	1.30	85	5	poly($\mathbf{1}_{15}$-*g*-$\mathbf{2b}_{5}$)	3.5×10^4	1.23	84
6[e]	poly-$\mathbf{1}_{15}$	9.1×10^3	1.31		10	poly($\mathbf{1}_{15}$-*g*-$\mathbf{2b}_{10}$)	5.1×10^4	1.19	80
7[e]	poly-$\mathbf{1}_{10}$	7.6×10^3	1.30		10	poly($\mathbf{1}_{10}$-*g*-$\mathbf{2c}_{10}$)	3.3×10^4	1.29	70
8[e]	poly-$\mathbf{1}_{10}$	7.6×10^3	1.30		20	poly($\mathbf{1}_{10}$-*g*-$\mathbf{2c}_{20}$)	5.4×10^4	1.31	76
9[e]	poly-$\mathbf{1}_{30}$	1.8×10^4	1.38		50	poly($\mathbf{1}_{30}$-*g*-$\mathbf{2c}_{50}$)	5.3×10^5	1.20	80

[a] The brush copolymers were prepared according to Scheme 1. [b] The footnotes indicate the initial feed ratios of the monomer to initiator. [c] M_n and M_w/M_n data were estimated by SEC with polystyrene standard. [d] Isolated yield. [e] Prepared in one-pot via tandem catalysis.

high stereoregularity. The ^{31}P NMR spectrum of the isolated brush copolymer is shown in Figure 2, which shows multiple peaks at 14.7 ppm; no peaks could be detected at 17.8 ppm, corresponding to the unreacted Pd complex in the current experimental conditions. These results undoubtedly demonstrated that most of the Pd(II) complexes pendants on the poly-$\mathbf{1}_m$ take part in the phenyl isocyanide polymerization. Thus, the grafting density of the afforded brush polymer is high. By using this synthetic approach, a range of brush copolymers of polybornene backbone bearing well-defined, stereoregular helical poly(phenyl isocyanide)s as side chains were facilely prepared in high yields (Table 3). It is worthy to note that the Pd(II) complexes reside at the side chain end of the isolated brush copolymers are still active and can undergo further copolymerization with phenyl isocyanide to give a brush copolymer with extended poly(phenyl isocyanide) side chains. For example, adding monomer **2** to a THF solution of poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{10}$) at 55 °C ($[\mathbf{2}]_0/[\text{Pd}]_0 = 10$), SEC analysis of the resulting polymer poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{20}$) indicated the chain extension polymerization occurred. As shown in Figure 5b, the isolated side-chain-extended poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{20}$) showed a single modal elution peak and was shifted to the higher molecular weight region as compared with the poly($\mathbf{1}_{20}$-*g*-$\mathbf{2}_{10}$) precursor and also kept a narrow molecular weight distribution ($M_w/M_n = 1.28$).

The synthesis of the brush copolymer of poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$)s was then investigated to be accomplished in one-pot via tandem catalysis. To verify, Pd(II) complex **1** was added to the mixture solution of G2 and monomer **2** in THF, and the mixture was first stirred at room temperature for the ROMP of **1** with G2. After **1** was completely consumed, the M_n ceased to increase as indicated by SEC analyses of the aliquots removed from the polymerization mixture; the polymerization solution was then heated up to 55 °C to allow the polymerization of phenyl isocyanide. In the aforementioned experiments, we have demonstrated that, catalyzed by G2, ROMP of **1** was a very fast process and could reach near complete conversion within 1 h at room temperature, whereas polymerization of **2** with **1** required higher temperature (55 °C) and longer time (usually several hours) to obtain significant polymerization rate and monomer conversion. Therefore, with much faster polymerization rate for ROMP of **1** than that for the polymerization of **2** under the same conditions, essentially ROMP and isocyanide insertions should occurred sequentially. SEC analysis of the isolated materials indicated the one-pot polymerizations were succeeded. All the isolated brush copolymers exhibited single modal elution peaks on the SEC chromatograms (Figures S15–S18, Supporting Information). The structures of the one-pot synthesized brush copolymers were also confirmed by ^{1}H, NMR, and FT-IR spectra, which were the same to that prepared via two steps. These results demonstrated the well-defined brush copolymers with polynorbornene backbone bearing rigid helical poly(phenyl isocyanide)s as side chains can be readily achieved in one-pot via tandem catalysis (Table 3). Moreover, the molecular weights and the compositions of the brush copolymer are easily controlled through the variation on the ratios of monomer to catalyst.

The morphology of the synthesized brush copolymers in the film state was investigated using atomic force microscopy (AFM). The thin film for AFM observation was prepared by spin-casted a solution of poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$) in appropriate solvent onto silicon wafers. After the sample was annealed under the vapor of the corresponding solvent and slowly dried in air, it was subjected to AFM observation. The tapping-mode phase and height images of the thin film spin-casted from brush copolymer poly($\mathbf{1}_{30}$-*g*-$\mathbf{2}_{50}$) in diluted toluene are shown in Figures 6a and 6b. As expected, worm-like cylindrical structures with ca. 160 nm in length and ca. 80 nm in width were clearly

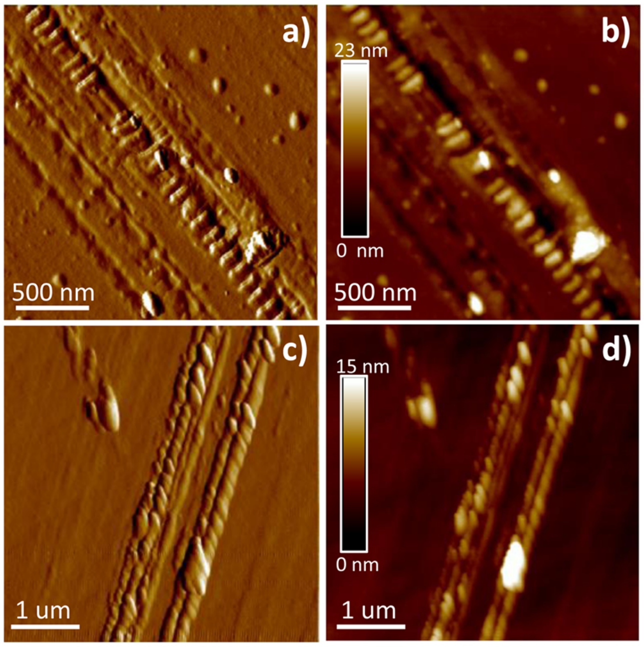


Figure 6. AFM phase (a) and height (b) images of thin film spin-casted from a solution of brush copolymer poly($\mathbf{1}_{30}$-*g*-$\mathbf{2}_{50}$) in toluene ($c = 0.10$ mg/mL) and AFM phase (c) and height (d) images of the thin film spin-casted from a solution of poly($\mathbf{1}_{30}$-*g*-$\mathbf{2}_{50}$) in THF at room temperature ($c = 0.10$ mg/mL).

observed. The average height of the worm-like supramolecular structures was estimated to be ca. 12.4 nm. Interestingly, the worm-like structures were further self-assembled into a well-defined ladder-like supramolecular architecture on the silicon wafer. However, the morphology of the self-assembly architecture was dependent on the solvent used. When the thin film was spin-casted from a diluted THF solution, rigid-rod helical structures with distinct handedness were clearly observed (Figures 6c and 6d). The dimensions of the assembled helical rods were estimated to have several micrometers in lengths, ca. 150 nm in width, and ca. 9.0 nm in height. For comparison, the morphology of the linear poly-$\mathbf{1}_{30}$ precursor was examined by AFM under the identical conditions. However, in sharp contrast to the brush copolymers poly($\mathbf{1}_{30}$-*g*-$\mathbf{2}_{50}$), no well-defined morphology was observed by AFM on the thin film spin-casted from corresponding poly-$\mathbf{1}_{30}$ (Figure S19, Supporting Information). Probably, the distinct morphology of the synthesized brush copolymers in film state was ascribed to the rigid-rod structure of the polynorbornene backbone and steric congestion offered by the densely populated and rigid stereoregular helical poly(phenyl isocyanide) side chains.

■ CONCLUSION

In summary, we have designed and synthesized a simple phenylethynyl Pd(II) complex containing a polymerizable norbornene unit. Such a Pd(II) complex was found to promote the living/controlled polymerization of phenyl isocyanide, affording well-defined helical poly(phenyl isocyanide)s with controlled M_n, narrow M_w/M_n, and high stereoregularity. The norbornene unit on the Pd(II) complex can undergoROMP by using Grubbs' second-generation catalyst in living/controlled manner. Combination of these two polymerizations, brush copolymers with polynorbornene backbone bearing well-defined, stereoregular helical poly(phenyl isocyanide) side chains can be readily achieved in high yields with controlled molecular weights and tunable compositions. The synthesis of these brush copolymers can be readily accomplished in one-pot via tandem catalysis. Worm-like morphologies and helical rod architectures formed from the brush copolymer were clearly observed by AFM. Given the modifications on the structure of Pd(II) complex and isocyanide monomers, we believe this novel polymerization technique will allow easily access to numerous hybrid materials with novel functions and broad applications.

■ EXPERIMENTAL SECTION

Instruments. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker 600 or 400 MHz (H) spectrometer. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. SEC was performed on Waters 1515 pump and a Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel columns (HR1, HR2, and HR4) with THF as eluent (flow rate is 0.3 mL/min). M_n and M_w/M_n data are reported relative to polystyrene standards. FT-IR spectra were recorded on PerkinElmer Spectrum BX FT-IR system using KBr pellets at room temperature. AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 scanning probe microscope using standard silicon cantilevers with a nominal spring constant of 50 N/m and resonance frequency of ~300 kHz.

Materials. All solvents were obtained from Sinopharm. Co. Ltd. and were purified by the standard procedures before use. 4-Bromoaniline, *exo*-norbornene anhydride, trimethylsilylacetylene, copper(I) iodide, copper(I) chloride, *trans*-dichlorobis(triphenylphosphine)palladium(II), *trans*-dichlorobis(triethylphosphine)palladium(II), and Grubbs second-generation Ru catalyst were purchased from Aladdin and Sigma-Aldrich Co. Ltd. and were used as received without further purification. The phenyl isocyanide **2** was prepared according to the literatures and the structure was confirmed by ^{1}H NMR.[10]

Synthesis of 3. This compound was synthesized according to the literature with slight modification.[22] Anhydrous toluene (15 mL) was added to the mixture of *exo*-norbornene anhydride (0.50 g, 3.05 mmol) and 4-bromoaniline (0.35 mL, 3.05 mmol) under a dry nitrogen atmosphere. After the reaction mixture was stirred at 110 °C for 16 h, the solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography with ethyl acetate and petrol ether (v/v = 5/1) as eluent to yield **3** as a white solid (0.70 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, J = 9.0 Hz, 2H, aromatic), 7.03 (d, J = 9.0 Hz, 2H, aromatic), 6.25 (s, 2H, CH of double bond), 3.51 (s, 2H, CH), 3.44−3.43 (m, 2H, CH), 1.79 (d, J = 8.4 Hz, 1H, CH_2), 1.61 (d, J = 8.4 Hz, 1H, CH_2).

Synthesis of 4. A mixture of **3** (1.85 g, 5.84 mmol), CuI (32 mg, 0.17 mmol), and $Pd(PPh_3)_2Cl_2$ (0.12 g, 0.17 mmol) in a 100 mL three-neck flask was degassed and refilled with N_2. After this procedure was repeated three times, triethylamine (30 mL) and trimethylsilylacetylene (0.90 mL, 6.43 mmol) were added via a syringe. The reaction solution was stirred at 55 °C for 6 h, and then the solvent was evaporated to dryness under reduced pressure. The residue was further purified by column chromatography with ethyl acetate and petrol ether (v/v = 4/1) as eluent to afford **4** as white solid (1.63 g, 83%); mp 108.2−109.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 2H, aromatic), 7.09 (d, J = 8.4 Hz, 2H, aromatic), 6.25 (s, 2H, CH of double bond), 3.51−3.49 (m, 2H, CH), 3.43−3.41 (m, 2H, CH), 1.79 (d, J = 8.8 Hz, 1H, CH_2), 1.61 (d, J = 8.8 Hz, 1H, CH_2), 0.24 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 176.53, 134.66, 132.52, 132.28, 131.74, 128.23, 126.40, 123.49, 104.13, 95.47, 52.31, 45.84, 45.56. FT-IR (KBr, cm^{-1}): 2160 ($\nu_{C\equiv C}$), 1710 ($\nu_{C=O}$). HRMS *m/z* calcd for $C_{20}H_{22}NO_2Si$ $[M + H]^+$: 336.1342; Found: $C_{20}H_{22}NO_2Si$, 336.1419. Anal. Calcd (%) for $C_{20}H_{21}NO_2Si$: C, 71.60; H, 6.31; N, 4.18; Found (%): C, 71.31; H, 6.60; N, 4.00.

Synthesis of 5. To a solution of **4** (0.89 g, 2.65 mmol) in dichloromethane (20 mL) and methanol (20 mL) was added K_2CO_3 (0.70 g, 5.3 mmol). After the mixture was stirred at room temperature for 1 h, the solvent was evaporated to dryness under reduced pressure. The afforded residue was extracted with ether and washed successively with H_2O (10 mL × 3) and brine (10 mL × 3). The organic layer was dried over Na_2SO_4. After filtration and evaporation, the resulting crude product was purified by column chromatography with petrol ether as eluent to afford **5** as a white solid (0.68 g, 97%). The isolated **5** was directly used in next step without further characterization due to instability.

Synthesis of 1. To a solution of **5** (110 mg, 0.42 mmol) in diethylamine (15 mL) and dichloromethane (15 mL) was added *trans*-dichlorobis(triethylphosphine)palladium (178 mg, 0.43 mmol) and copper(I) chloride (3 mg, 0.03 mmol). The mixture solution was stirred at room temperature for 3 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by column chromatography with ethyl acetate and petrol ether (v/v = 2/1) as eluent. The afforded product was recrystallized from petrol ether and methanol to give **1** as a white solid (160 mg, 60%); mp 112.5−113.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.8 Hz, 2H, aromatic), 6.99 (d, J = 8.8 Hz, 2H, aromatic), 6.24 (s, 2H, CH of double bond), 3.51−3.50 (m, 2H, CH of norbornene), 3.42−3.41 (m, 2H, CH of norbornene), 1.99−1.91 (m, 12H, PCH_2CH_3), 1.80−1.77 (m, 1H, CH_2 of norbornene), 1.62−1.60 (m, 1H, CH_2 of norbornene), 1.23−1.15 (m, 18H, PCH_2CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 177.01, 134.70, 131.33, 128.98, 128.42, 126.35, 106.22, 97.60, 52.36, 45.90, 45.62, 15.46, 8.44. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 17.80. FT-IR (KBr, cm^{-1}): 2970 (ν_{C-H}), 2930 (ν_{C-H}), 2880 (ν_{C-H}), 2120 ($\nu_{C\equiv C}$), 1720 ($\nu_{C=O}$). HRMS *m/z* calcd for $C_{29}H_{43}ClNO_2P_2Pd$ $[M + H]^+$: 640.1414. Found: $C_{29}H_{43}ClNO_2P_2Pd$, 640.1922. Anal. Calcd (%) for $C_{29}H_{42}ClNO_2P_2Pd$: C, 54.38; H, 6.61; N, 2.19. Found (%): C, 54.09; H, 6.90; N, 2.00.

Typical Procedure for Polymerization of 2 with 1 as Initiator (Poly-$\mathbf{2_{55}}$). A 10 mL oven-dried flask was charged with monomer **2** (50 mg, 0.17 mmol), THF (0.77 mL), and a stir bar. To this stirring solution was added a solution of **1** in THF (0.035 M, 0.09 mL) via a microsyringe at room temperature. The concentrations of monomer **2** and catalyst **1** were 0.2 and 0.0036 M, respectively ($[\mathbf{2}]_0/[\mathbf{1}]_0 = 55$). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight to afford poly-$\mathbf{2}_{55}$ as a yellow solid (45 mg, 89% yield). SEC: $M_n = 1.7 \times 10^4$, $M_w/M_n = 1.19$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.33 (br, 2H, aromatic), 5.76 (br, 2H, aromatic), 4.50−3.45 (br, 2H, CO_2CH_2), 1.63−0.83 (br, 19H, CH_2 and CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 164.95, 162.54, 150.34, 129.63, 127.22, 117.03, 64.87, 31.87, 29.72, 29.64, 29.59, 29.42, 29.30, 28.60, 25.07, 22.62, 14.03. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 14.70. FT-IR (KBr, cm^{-1}): 2965 (ν_{C-H}), 2928 (ν_{C-H}), 2851 (ν_{C-H}), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Typical Procedure for ROMP of 1 with G2 as Catalyst (Poly-$\mathbf{1_{20}}$). A solution of G2 in THF (0.0039 M, 0.1 mL) was added to a degassed solution of Pd(II) complex **1** (50 mg, 0.08 mmol) in THF (0.30 mL) via a microsyringe. The initial concentrations of **1** and catalyst G2 were 0.2 and 0.01 M, respectively ($[\mathbf{1}]_0/[G2]_0 = 20$). After the reaction mixture was stirred at room temperature for 1 h, thin-layer chromatography (TLC) analysis indicated **1** was completely consumed. The polymerization was then quenched by addition of ethyl vinyl ether (1.0 mL) and poured into a large amount methanol. The precipitated solid was collected by centrifugation, washed with methanol, and dried under vacuum to afford poly-$\mathbf{1}_{20}$ (44 mg, 88% yield). SEC: $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.37$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.28 (br, 2H, aromatic), 7.01 (br, 2H, aromatic), 5.92−5.50 (br, 2H, norbornene−CH═CH), 3.50−3.22 (br, 2H, norbornene−CH), 3.20−2.91 (br, 2H, norbornene−CH), 1.95 (br, 12H, PCH_2CH_3), 1.80−1.68 (br, 1H, norbornene−CH_2), 1.52−1.40 (br, 1H, norbornene−CH_2), 1.20 (br, 18H, PCH_2CH_3). FT-IR (KBr, cm^{-1}): 2970 (ν_{C-H}), 2930 (ν_{C-H}), 2880 (ν_{C-H}), 2190 ($\nu_{C\equiv C}$), 1710 ($\nu_{C=O}$).

Typical Procedure for Preparation of Brush Copolymerization (Poly($\mathbf{1_{20}}$-*g*-$\mathbf{2_{10}}$)). A 10 mL oven-dried flask was charged with poly-$\mathbf{1}_{20}$ ($M_n = 1.2 \times 10^4$, $M_w/M_n = 1.37$, 44 mg), THF (1.70 mL), and a stir bar. To this stirring solution was added a solution of **2** (195 mg, 0.68 mmol) in THF (1.70 mL) via a microsyringe at room temperature. The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 h. After being cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in a vacuum at room temperature overnight, affording brush copolymer poly($\mathbf{1}_{20}$-g-$\mathbf{2}_{10}$) as a yellow solid (179 mg, 75% yield). SEC: $M_n = 5.9 \times 10^4$, $M_w/M_n = 1.25$. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.33 (br, 2H, aromatic), 5.76 (br, 2H, aromatic), 4.50−3.45 (br, 2H, CO_2CH_2), 1.63−0.83 (br, 19H, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2960 (ν_{C-H}), 2930 (ν_{C-H}), 2850 (ν_{C-H}), 2120 ($\nu_{C\equiv C}$), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Typical One-Pot Polymerization Procedure for Brush Copolymer Poly($\mathbf{1}_m$-*g*-$\mathbf{2}_n$). A 10 mL oven-dried flask was charged with Pd(II) complex **1** (50 mg, 0.078 mmol), **2** (230 mg, 0.80 mmol), THF (2.00 mL), and a stir bar. The solution was degassed and refilled with N_2. After this procedure was repeated three times, G2 in THF (0.0039 M, 0.1 mL) was added via a microsyringe. The initial feed ratio of **1** to G2 is 20; **2** to **1** is 10 ($[\mathbf{1}]_0/[G2]_0 = 20$, $[\mathbf{2}]_0/[\mathbf{1}]_0 = 10$). The reaction mixture was stirred at room temperature for 1 h, then immersed into an oil bath at 55 °C, and stirred for 12 h. The polymerization was poured into a large amount methanol. The precipitated solid was collected by centrifugation, washed with methanol, and dried under vacuum to afford the expected brush copolymers. The structures of the isolated brush copolymers were characterized by SEC and ^{1}H NMR.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional spectral data and SEC chromatograms. 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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■ REFERENCES

(1) (a) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737. (b) Pauling, L.; Corey, R. B.; Branson, H. R. *Proc. Natl. Acad. Sci. U. S. A.* **1951**, *378*, 205.

(2) (a) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (b) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (c) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745. (d) Lockmam, J. W.; Paul, N. M.; Parquette, J. R. *Prog. Polym. Sci.* **2005**, *30*, 423. (e) Aoki, T.; Kaneko, T.; Teraguchi, M. *Polymer* **2006**, *47*, 4867. (f) Pijper, D.; Feringa, B. L. *Soft Matter* **2008**, *4*, 1349. (g) Yashima, E.; Maeda, K.; Furusho, Y. *Acc. Chem. Res.* **2008**, *41*, 1166. (h) Rudick, J. G.; Percec, V. *Acc. Chem. Res.* **2008**, *41*, 1641. (i) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102. (j) Zhang, D.-W.; Zhao, X.; Li, Z.-T. *Acc. Chem. Res.* **2014**, *47*, 1961.

(3) (a) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013.

(4) (a) Zhi, J. G.; Zhu, Z. G.; Liu, A. H.; Cui, J. X.; Wan, X. H.; Zhou, Q. F. *Macromolecules* **2008**, *41*, 1594. (b) Wang, R.; Li, X.; Bai, J.; Zhang, J.; Liu, A.; Wan, X. *Macromolecules* **2014**, *47*, 1553. (c) Wang, Y.; Sakamoto, T.; Koyama, Y.; Takanashi, Y.; Kumaki, J.; Cui, J. X.; Wan, X. H.; Nakano, T. *Polym. Chem.* **2014**, *5*, 718.

(5) (a) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785. (b) Schwartz, E.; Koepf, M.; Kitto, H. J.; Nolte, R. J. M.; Rowan, A. E. *Polym. Chem.* **2011**, *2*, 33. (c) Kajitani, T.; Onouchi, H.; Sakurai, S.-i.; Nagai, K.; Okoshi, K.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2011**, *133*, 9156. (d) Xu, A.; Hu, G.; Hu, Y.; Zhang, X.; Liu, K.; Kuang, G.; Zhang, A. *Chem.—Asian J.* **2013**, *8*, 2003.

(6) (a) Green, M. M.; Park, J. W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3139. (b) Maeda, K.; Wakasone, S.; Shimomura, K.; Ikai, T.; Kanoh, S. *Chem. Commun.* **2012**, *48*, 3342.

(7) (a) Nieh, M.-P.; Goodwin, A. A.; Stewart, J. R.; Novak, B. M.; Hoagland, D. A. *Macromolecules* **1998**, *31*, 3151. (b) Reuther, J. F.; Bhatt, M. P.; Tian, G.; Batchelor, B. L.; Campos, R.; Novak, B. M. *Macromolecules* **2014**, *47*, 4587.

(8) (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683. (b) Chen, L.; Chen, Y. W.; Yao, K.; Zhou, W. H.; Li, F.; Chen, L. P.; Hu, R. R.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4723. (c) Makiguchi, W.; Kobayashi, S.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2013**,

52, 5275. (d) Song, C.; Liu, X.; Liu, D.; Ren, C. L.; Yang, W. T.; Deng, J. P. *Macromol. Rapid Commun.* **2013**, *34*, 1426.

(9) (a) Reggelin, M.; Doerr, S.; Klussmann, M.; Schultz, M.; Holbach, M. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5461. (b) Yamamoto, T.; Suginome, M. *Angew. Chem., Int. Ed.* **2009**, *121*, 547. (c) Tamura, K.; Miyabe, T.; Iida, H.; Yashima, E. *Polym. Chem.* **2011**, *2*, 91. (d) Gowda, C. M.; Van Eck, E. R. H.; Van Buul, A. M.; Schwartz, E.; Van Pruissen, G. W. P.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Kentgens, A. P. M. *Macromolecules* **2012**, *45*, 2209. (e) Hu, G.; Li, W.; Hu, Y.; Xu, A.; Yan, J.; Liu, L.; Zhang, X.; Liu, K.; Zhang, A. *Macromolecules* **2013**, *46*, 1124. (f) Asaoka, S.; Joza, A.; Minagawa, S.; Song, L.; Suzuki, Y.; Iyoda, T. *ACS Macro Lett.* **2013**, *2*, 906.

(10) (a) Wu, Z.-Q.; Ono, R. J.; Chen, Z.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 14000. (b) Wu, Z.-Q.; Radcliffe, J. D.; Ono, R. J.; Chen, Z.; Li, Z.; Bielawski, C. W. *Polym. Chem.* **2012**, *3*, 874. (c) Liu, N.; Qi, C.-G.; Wang, Y.; Liu, D.-F.; Yin, J.; Zhu, Y.-Y.; Wu, Z.-Q. *Macromolecules* **2013**, *46*, 7753. (d) Wu, Z.-Q.; Qi, C.-G.; Liu, N.; Wang, Y.; Yin, J.; Zhu, Y.-Y.; Qiu, L.-Z.; Lu, H.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2939. (e) Wu, Z.-Q.; Liu, D.-F.; Wang, Y.; Liu, N.; Yin, J.; Zhu, Y.-Y.; Qiu, L.-Z.; Ding, Y.-S. *Polym. Chem.* **2013**, *4*, 4588.

(11) Takei, F.; Onitsuka, K.; Takahashi, S. *Macromolecules* **2005**, *38*, 1513.

(12) (a) Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed.* **1992**, *31*, 851. (b) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. *Organometallics* **1994**, *13*, 3862. (c) Onitsuka, K.; Mori, T.; Yamamoto, M.; Takei, F.; Takahashi, S. *Macromolecules* **2006**, *39*, 7224. (d) Onitsuka, K.; Yamamoto, M.; Mori, T.; Takei, F.; Takahashi, S. *Organometallics* **2006**, *25*, 1270.

(13) (a) Wu, Z.-Q.; Nagai, K.; Banno, M.; Okoshi, K.; Onitsuka, K.; Yashima, E. *J. Am. Chem. Soc.* **2009**, *131*, 6708. (b) Banno, M.; Wu, Z.-Q.; Nagai, K.; Sakurai, S.-i.; Okoshi, K.; Yashima, E. *Macromolecules* **2010**, *43*, 6553.

(14) (a) Xue, Y.-X.; Zhu, Y.-Y.; Gao, L.-M.; He, X.-Y.; Liu, N.; Zhang, W.-Y.; Yin, J.; Ding, Y.; Zhou, H.; Wu, Z.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 4706. (b) Xue, Y.-X.; Chen, J.-L.; Jiang, Z.-Q.; Yu, Z.; Liu, N.; Yin, J.; Zhu, Y.-Y.; Wu, Z.-Q. *Polym. Chem.* **2014**, *5*, 6435.

(15) (a) Sheiko, S. S.; Möller, M. *Chem. Rev.* **2001**, *101*, 4099. (b) Hadjichristidis, N.; P Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747. (c) Zhang, M.; Müller, A. H. E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3461. (d) Kang, H. A.; Bronstein, H. E.; Swager, T. M. *Macromolecules* **2008**, *41*, 5540. (e) Nyström, A. M.; Wooley, K. L. *Acc. Chem. Res.* **2011**, *44*, 969. (f) Liu, L.; Li, W.; Liu, K.; Yan, J.; Hu, G.; Zhang, A. *Macromolecules* **2011**, *44*, 8614.

(16) (a) Ding, L.; Huang, Y.; Zhang, Y.; Deng, J.; Yang, W. *Macromolecules* **2011**, *44*, 736. (b) Chen, Y. *Macromolecules* **2012**, *45*, 2619. (c) Xie, C.; Ju, Z.; Zhang, C.; Yang, Y.; He, J. *Macromolecules* **2013**, *46*, 1437. (d) Finnegan, J. R.; Lunn, D. J.; Gould, O. E. C.; Hudson, Z. M.; Whittell, G. R.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2014**, *136*, 13835. (e) Gao, A. X.; Liao, L.; Johnson, J. A. *ACS Macro Lett.* **2014**, *3*, 854. (f) Deshmukh, P.; Gopinadhan, M.; Choo, Y.; Ahn, S.-k.; Majewski, P. W.; Yoon, S. Y.; Bakajin, O.; Elimelech, M.; Osuji, C. O.; Kasi, R. M. *ACS Macro Lett.* **2014**, *3*, 462. (g) Shi, Y.; Zhu, W.; Yao, D.; Long, M.; Peng, B.; Zhang, K.; Chen, Y. *ACS Macro Lett.* **2014**, *3*, 70.

(17) (a) Djalali, R.; Li, S.-Y.; Schmidt, M. *Macromolecules* **2002**, *35*, 4282. (b) Tang, C.; Dufour, B.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6199. (c) Huang, K.; Rzayev, J. *J. Am. Chem. Soc.* **2009**, *131*, 6880. (d) Gunkel, G.; Weinhart, M.; Becherer, T.; Haag, R.; Huck, W. T. S. *Biomacromolecules* **2011**, *12*, 4169. (e) Li, Y.; Zhang, J.; Liu, W.; Li, D.; Fang, L.; Sun, H.; Yang, B. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2126. (f) Yu, Y.; Chen, C.-K.; Law, W.-C.; Mok, J.; Zou, J.; Prasad, P. N.; Cheng, C. *Mol. Pharmaceutics* **2013**, *10*, 867. (g) Deshmukh, P.; Ahn, S.-k.; Gopinadhan, M.; Osuji, C. O.; Kasi, R. M. *Macromolecules* **2013**, *46*, 4558.

(18) (a) Kikuchi, M.; Lien, L. T. N.; Narumi, A.; Jinbo, Y.; Izumi, Y.; Nagai, K.; Kawaguchi, S. *Macromolecules* **2008**, *41*, 6564. (b) Nguyen, L.-T.; Ardana, A.; Brinke, G. t.; Schouten, A. J. *Langmuir* **2010**, *26*, 6515. (c) Fruth, A.; Klapper, M.; Müllen, K. *Macromolecules* **2010**, *43*, 467. (d) Chen, P.; Li, C.; Liu, D.; Li, Z. *Macromolecules* **2012**, *45*, 9579. (e) Miyake, G. M.; Weitekamp, R. A.; Piunova, V. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 14249.

(19) (a) Lu, H.; Wang, J.; Lin, Y.; Cheng, J. *J. Am. Chem. Soc.* **2009**, *131*, 13582. (b) Zhang, Y.; Yin, Q.; Lu, H.; Xia, H.; Lin, Y.; Cheng, J. *ACS Macro Lett.* **2013**, *2*, 809.

(20) Rhodes, A. J.; Deming, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 19463.

(21) (a) Maeda, K.; Wakasone, S.; Shimomura, K.; Ikai, T.; Kanoh, S. *Chem. Commun.* **2012**, *48*, 3342. (b) Maeda, K.; Wakasone, S.; Shimomura, K.; Ikai, T.; Kanoh, S. *Macromolecules* **2014**, *47*, 6540.

(22) Kim, K. O.; Choi, T.-L. *ACS Macro Lett.* **2012**, *1*, 445.