Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer
Chemistry

www.rsc.org/polymers

ROYAL SOCIETY
OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/polymers

Journal Name

Polymer Chemistry

ARTICLE TYPE

Living polymerization of arylisocyanide initiated by phenylethynyl palladium(II) complex

Ya-Xin Xue, Jia-Li Chen, Zhi-Qiang Jiang, Zhipeng Yu, Na Liu, Jun Yin, Yuan-Yuan Zhu and Zong-Quan Wu*

A family of air-stable phenylethynyl palladium complexes was unexpectedly found to initiate the polymerization of phenyl isocyanide in a living/controlled chain growth manner,
10 affording well-defined, stereoregular poly(phenyl isocyanide)s in high yield with controlled molecular weights and narrow molecular weight distributions.

Polyisocyanides have attracted considerable attention in recent years not only owning to their interesting helical
15 structure but also for the widely applications.[1] They have a π-conjugation system with C=N double bonds at the carbons that connect the monomer units, which twist along the polymer backbone to create a stable helical conformation. Due to the unique rigid helical structures, polyisocyanides have
20 exhibited widely applications in many fields such as enantiomer separation, asymmetric catalysis, chiral recognition, organic solar cell and nuclear magnetic resolution analysis.[2] Thus, the development of living/controlled polymerization method for facile preparation of well-defined
25 polyisocyanide is highly desirable. Polyisocyanides were usually obtained through the polymerization of appropriate isocyanide monomers with transition metal complexes as catalyst/initiator. Nickel(II) complex is the most used catalyst for the isocyanide polymerization since it was disclosed by
30 Notle and coworkers.[1c] Deming et. al have reported that π-allylnickel complexes are effective catalysts for living polymerization of alkyl isocyanides in noncoordination solvents,[3] while Asaoka et al. revealed that aromatic nucleophile adduct of tetra(*tert*-butylisocyano)nickel(II)
35 complex can promote the living polymerization of aryl isocyanide.[4] We found that Ni(II)-terminated poly(3-hexylthiophene) can also initiate the living/controlled polymerization of aryl and alkyl isocyanide.[5] In contrast to nickel complexes, the utilization of other metal complexes as
40 catalyst or initiator for living polymerization of isocyanide are limited. Onitsuka et al. have found that arylrhodium complexes can promote the living polymerization of aryl isocyanides, while the requirement of large amount of phosphine ligand make the product isolation difficult.[6] μ-
45 Ethynediyl Pt-Pd binuclear complex has been demonstrated to be an efficient initiator for the living polymerization of aryl isocyanide, however it is air-unstable and very hard to synthesis.[7] Recently, we reported a class of air-stable

(phenylbuta-1,3-diynyl)palladium (II) complexes for living
50 polymerization of isocyanides with high activity and efficiency.[8] 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] Therefore, the reports
55 on the Pd(II) complexes for living/contrlled polymerization of isocyanide are really rare.
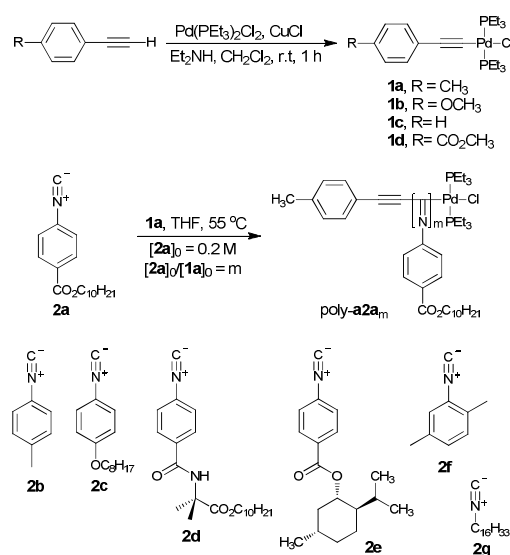
Scheme 1 Synthesis of phenylethynyl Pd(II) complexes **1a-d** and the polymerization of isocyanides with these Pd(II) complexes as initiator.

60 The simply prepared phenyethynyl and ethynyl Pd(II) complexes have been demonstrated to be inactive initiators for isocyanobenzene polymerization in refluxed THF.[7a-b] However, in this contribution, we demonstrate that some phenylethynyl Pd(II) complexes can unexpectedly initiate
65 polymerization of some phenyl isocyanide in living/controlled chain-growth manner, afforded well-defined poly(phenyl isocyanide)s in high yield with controlled molecular weights (M_ns) and narrow molecular weight distributions (M_w/M_ns). As depicted in Scheme 1, phenylethynyl Pd(II) complexes **1a-**
70 **d** with various substituents on the phenyl ring were readily prepared under the similar synthetic procedure we reported previously (see ESI).[8] The structures of **1a-d** were confirmed by ^{1}H, ^{13}C NMR and FT-IR spectroscopy, and **1c** was further

characterized by X-ray analysis of a single crystal (Fig. S1, ESI). All these complexes behave good solubility in common organic solvents such as chloroform, *n*-hexene, THF, toluene and ethyl acetate. It is worthy to note that these Pd(II)
5 complexes are quite stable in air. No significant changes could be observed on their ^{1}H NMR spcetra after the samples were deposited for several weeks at room temperature.
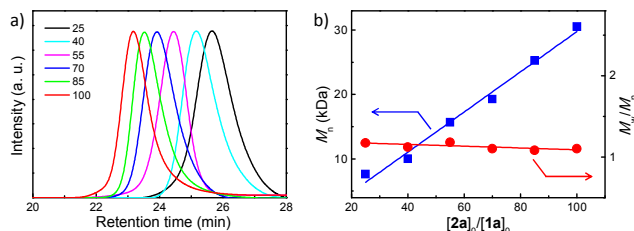

Fig. 1 (a) Size exclusion chromatograms of poly-**a2a**$_m$s prepared from **2a**
10 with **1a** as initiator in THF at 55 °C with different initial feed ratios. (b) Plots of M_n and M_w/M_n values of poly-**a2a**$_m$ as a function of the initial feed ratios of **2a** to **1a**. M_n and M_w/M_n were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

The polymerization behavior of **1a** was investigated by
15 treated **1a** with 100 equivalent of phenyl isocyanide **2a** in THF ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1a**]$_0$ = 100). Although the polymerization was failed at room temperature, it took place smoothly at 55 °C because the colorless solution turned to brown and the viscosity increased considerably. Size
20 exclusion chromatography (SEC) analysis of the resulting polymer poly-**a2a**$_{100}$ (the footnote indicates the initial feed ratio of the monomer to initiator) confirmed the polymerization was succeeded. As shown in Figure 1a, a single modal elution peak appeared at high-molecular weight
25 region was observed. The M_n and M_w/M_n were estimated to be 3.1×10^4 and 1.10, respectively.

To examine whether the polymerization was proceeded in a living/controlled manner, a series polymerizations of **2a** with **1a** as initiator in different initial feed ratios was conducted.
30 As shown in Fig. 1a, all the resulting polymers exhibited single-modal elution peak on SEC chromatograms. The M_ns of obtained polymers increased linearly and in proportion to the initial feed ratios of **2a** to **1a**, and all the isolated polymers exhibited narrow M_w/M_n (< 1.20) (Fig. 1b). These results
35 confirmed the polymerization did proceeded in living/controlled chain-growth fashion. Therefore, a series of poly-**a2a**$_m$ with different M_n and narrow M_w/M_n was readily prepared by just varying the initial feed ratio of **2a** to **1a** (Table 1). FT-IR spectrum of isolated poly-**a2a**$_m$ showed an
40 characteristic absorption band at 1599 cm^{-1} due to $\upsilon_{(C=N)}$, no absorption of the monomer around 2260 cm^{-1} was observed (Figure S2, ESI). The absolute M_n value was determined from ^{1}H NMR spectrum through integral ratio of the methyl signal of the polymer end to the signal of the OCH_2 group derived
45 from the repeat units of **2a** (Fig. S3, ESI). The M_n (NMR) was consistent with the SEC data and also in good agreement with the ideal M_n estimated from the initial feed ratio of the polymerization reaction. ^{13}C NMR spectrum showed a relatively sharp resonance corresponding to the imino carbons
50 of the polymer backbone at δ 162.70 ppm with a half-bandwidth of 28 Hz (Fig. S4, ESI), suggesting the

polyisocyanide prepared by this new polymerization method has high stereoregularity of the imino groups. This is much better than the poly(aryl isocyanide)s prepared by a nickel
55 catalyst, which have low stereoregularity of the imino groups.[10] Furthermore, ^{31}P NMR spectrum of **1a** showed an resonance at 17.9 ppm, while it was disappeared after the polymerization with **2a**, and a new miltiple peaks at 14.4 ppm was observed (Fig. S5, ESI).

60 **Table 1** Polymeriztion results of isocyanide **2a** with **1a** as initiator in different solvents at 55 °C^a

run	ratio^b	solvent	polymer	M_n^c (kDa)	PDI^c	DP^d	Yield^e
1	55	THF	poly-**a2a**$_{55}$	15.9	1.13	52	95%
2	85	THF	poly-**a2a**$_{85}$	25.1	1.08	82	96%
3	100	THF	poly-**a2a**$_{100}$	31.0	1.10	100	91%
4	200	THF	poly-**a2a**$_{200}$	61.0	1.11	--^{f}	94%
5	75	Toluene	poly-**a2a**$_{75}$	22.2	1.20	72	96%
6	100	Toluene	poly-**a2a**$_{100}$	29.1	1.22	95	95%
7	50	CHCl$_3$	poly-**a2a**$_{50}$	16.2	1.11	50	93%
8	80	CHCl$_3$	poly-**a2a**$_{80}$	23.0	1.12	76	87%
9	50	DMF	poly-**a2a**$_{50}$	15.2	1.17	50	92%
10	80	DMF	poly-**a2a**$_{80}$	23.1	1.22	75	85%
11	50	Acetone	poly-**a2a**$_{50}$	13.4	1.21	45	89%
12	80	Hexane	poly-**a2a**$_{80}$	23.8	1.40	80	85%

^{a}The polymers were synthesized according to Scheme 1. ^{b}The initial feed ratio of **2a** to **1a**. ^{c}The M_n and PDI were determined by SEC and reported as equivalent to standard PSt. ^{d}The degree of polymerization (DP) was
65 estimated from the integral analysis of ^{1}H NMR spectra. ^{e}Isolated yield. ^{f}Too large to be estimated from ^{1}H NMR.
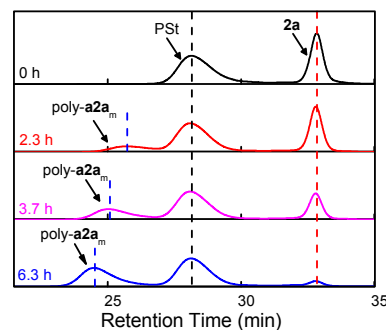

Fig. 2 Time-dependent size exclusion chromatograms for the polymerization of **2a** with **1a** as initiator in THF at 55 °C with PSt as
70 internal standard ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1a**]$_0$ = 60).

The polymerization of **2a** with **1a** as initiator can be carried out in various organic solvents with different polarity such as CHCl$_3$, toluene, hexane, DMF and acetone (Table 1, and Fig. S7-S10, ESI). However, owning to the poor solubility of the
75 afforded polymers, the polymerization of **2a** was failed in methanol and water. To get great insight into the polymerization, we performed the trace experiment of the polymerization of **2a** with **1a** in THF at 55 °C with the presence of standard PSt (M_n = 2630, M_w/M_n = 1.06) as
80 internal standard ([**2a**]$_0$ = 0.2 M, [**2b**]$_0$/[**1a**]$_0$ = 60). Time-dependent SEC chromatograms for the polymerization were shown in Fig. 2. It can be found that more than 88% of **2a** was consumed within 6.3 h. The SEC trace was shifting to higher-molecular weight region with the increase of monomer
85 conversion. Both M_n-conversion and M_w/M_n-conversion

relationships are plotted in Figure 3a, the M_n(SEC) values of the isolated polymers at different polymerization stage are linearly correlated with the conversion of **2a** and kept a narrow distribution, suggesting that the present polymerization had a living nature. Kinetic studies revealed that the polymerization obeyed the first-order rate law because a linear correlation could be observed between the – Ln([**2a**]/[**2a**]$_0$) and polymerization time. The rate constant was estimated to be ~8.87 × 10^{-5} s^{-1} according to kinetic plot.
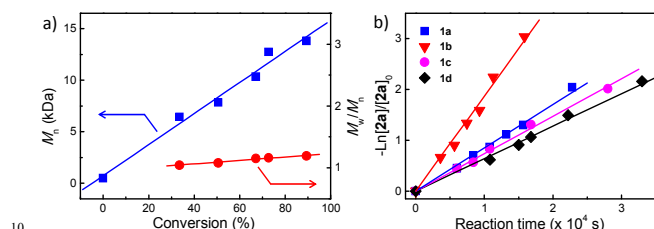

Fig. 3 (a) Plots of M_n and M_w/M_n values as a function of **1a**-initiated conversion of **2a** in THF at 55 °C ([**2a**]$_0$ = 0.2 M, [**2a**]$_0$/[**1a**]$_0$ = 60). (b) First-order kinetics plots for polymerization of **2a** initiated by **1a**, **1b**, **1c**, and **1d**.

Similarly, polymerizations of **2a** with Pd(II) complexes **1b-d** were also investigated in THF at 55 °C. It was found that all these complexes exhibited high polymerization activity to lead to the formation of expected polyisocyanide in living/controlled chain growth manner (Fig. S11-22, ESI). The polymerizations initiated by **1b-d** were also obeyed the first-order rate law and the rate constants for **1b**, **1c** and **1d** were estimated to be 1.87 × 10^{-4}, 7.37 × 10^{-5}, and 6.39 × 10^{-5} s^{-1}, respectively (Fig. 3b). These data indicated the incorporation of an electron-donating group to the benzene ring of the phenylethynyl Pd(II) complex improved the polymerization activity. The polymerization of **2a** 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 and (phenylbuta-1,3-diynyl)palladium(II) complexes. It is worthy to note that the polymerizations were all carried out in open reaction systems due the high stability of the Pd(II) complexes to air, the inert atmosphere protection and schlenk technique are not required.

Since **1b** is the most active, polymerization behaviors of isocyanide **2b-f** were then examined with **1b** as initiator. The polymerization of **2b** was continuously failed in THF at 55 °C and in toluene at 90 °C because insoluable solid was precipitated during the polymerization. Due to the poor solubility of the afforded materials, further characterization of the isolated polymer was not possible. The polymerization of **2c** with **1b** was also failed in THF at 55 °C owning to the low reactivity of **2c**, however, it was succeeded in toluene at 90 °C. The polymerization was also proceed in a living/controlled chain-growth manner because the M_n can be easily controlled by the variation on the initial feed ratio of monomer to catalyst although the M_w/M_n values were broader than that of **2a**. These results support the fact that the activity of phenyl isocyanide decreased with incorporation of electron-donating group on the phenyl ring. Isocyanide **2d** and **2e** can be easily polymerized with **1b** in THF at 55 °C in living/controlled

manners (Table S1, ESI). The poly-**b2e**$_{50}$ exhibited a positive Cotton effects at 364 nm with $\Delta\varepsilon_{364}$ = +11.6, indicates the formation of a single-handed helical polyisocyanide. However, unlike the polymerization behavior of **2b** and **2c**, polymerization of isocyanide **2f** bearing methyl group on the ortho position of the benzene ring was failed even in toluene at 100°C and the monomer was recovered. Considering the similar electronic character of **2b**, **2c** and **2f**, this failure may ascribed to the steric hindrance of **2f**. Due to the poor reactivity of alkyl isocyanide, 1-isocyanohexadecane **2g** couldn't be polymerized by **1b** even the reaction was performed in toluene at 100 °C.

In summary, the facile prepared phenylethynyl Pd(II) complexes were unexpectedly found to promote the polymerization of phenyl isocyanide in living/controlled manner. The afforded well-defined poly(phenyl isocyanide)s possess controlled M_n, narrow M_w/M_n and high stereoregularity, which is important for maintaining the helical sense of the polymer main chain. We believe our finding will provide a useful method for preparation of various polyisocyanides with controlled structures, specific chain terminus and novel functions.

Notes and references

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei 230009, China. E-mail: zqwu@hfut.edu.cn

†Electronic Supplementary Information (ESI) available: additional experimental procedures and spectroscopic data. See DOI: 10.1039/b000000x/

1   (a) J. J. Cornelissen, M. Fischer, N. A. Sommerdijk and R. J. Nolte, *Science*, 1998, **280**, 1427; (b) J. Kumaki, S.-i. Sakurai and E. Yashima, *Chem. Soc. Rev.*, 2009, **38**, 737; (c) E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.*, 2009, **109**, 6102; (d) E. Schwartz, M. Koepf, H. J. Kitto, R. J. M. Nolte and A. E. Rowan, *Polym. Chem.*, 2011, **2**, 33.

2   (a) S. Foster, C. E. Finlayson, P. E. Keivanidis, Y.-S. Huang, I. Hwang, R. H. Friend, M. B. J. Otten, L.-P. Lu, E. Schwartz, R. J. M. Nolte and A. E. Rowan, *Macromolecules*, 2009, **42**, 2023; (b) K. Tamura, T. Miyabe, H. Iida and E. Yashima, *Polym. Chem.,* 2011, **2**, 91; (c) T. Miyabe, H. Iida, M. Banno, T. Yamaguchi and E. Yashima, *Macromolecules*, 2011, **44**, 8687; (d) M. Dama and S. Berger, *Org. Lett.,* 2011, **14**, 241; (e) T. Miyabe, H. Iida, A. Ohnishi and E. Yashima, *Chem. Sci.,* 2012, **3**, 863; (f) G. Hu, W. Li, Y. Hu, A. Xu, J. Yan, L. Liu, X. Zhang, K. Liu and A. Zhang, *Macromolecules*, 2013, **46**, 1124.

3   (a) Deming, T. J. and Novak, B. M. *Macromolecules,* 1991, **24**, 6043; (b) Deming, T. J. and Novak, B. M. *J. Am. Chem. Soc.*, 1993, **115**, 9101.

4   S. Asaoka, A. Joza, S. Minagawa, L. Song, Y. Suzuki and T. Iyoda, *ACS Macro Lett.,* 2013, **2**, 906.

5   (a) Z.-Q. Wu, R. J. Ono, Z. Chen and C. W. Bielawski, *J. Am. Chem. Soc.,* 2010, **132**, 14000; (b) Z.-Q. Wu, J. D. Radcliffe, R. J. Ono, Z. Chen, Z. Li and C. W. Bielawski, *Polym. Chem.,* 2012, **3**, 874; (c) N. Liu, C.-G. Qi, Y. Wang, D.-F. Liu, J. Yin, Y.-Y. Zhu and Z.-Q. Wu, *Macromolecules*, 2013, **46**, 7753; (d) Z.-Q. Wu, C.-G. Qi, N. Liu, Y.

Wang, J. Yin, Y.-Y. Zhu, L.-Z. Qiu and H.-B Lu, *J. Polym. Sci., Part A: Polym. Chem.,* 2013, **51**, 2939.

6 (a) K. Onitsuka, T. Mori, M. Yamamoto, F. Takei and S. Takahashi, *Macromolecules*, 2006, **39**, 7224; (b) K. Onitsuka, M. Yamamoto, T.
5   Mori, F. Takei and S. Takahashi, *Organometallics*, 2006, **25**, 1270.

7 (a) K. Onitsuka, T. Joh and S. Takahashi, *Angew. Chem. Int. Ed.*, 1992, **31**, 851; (b) K. Onitsuka, K. Yanai, F. Takei, T. Joh and S. Takahashi, *Organometallics*, 1994, **13**, 3862; (c) Z.-Q. Wu, K. Nagai, M. Banno, K. Okoshi, K. Onitsuka and E. Yashima, *J. Am. Chem.*
10 *Soc.*, 2009, **131**, 6708.

8 Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding, H. Zhou and Z.-Q. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 4706.

9 (a) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 1974, **13**, 438; (b)
15 T. Yamada and M. Suginome, *Macromolecules*, 2010, **43**, 3999.

10 F. Takei, K. Onitsuka and S. Takahashi, *Macromolecules*, 2005, **38**, 1513.

Polymer Chemistry Accepted Manuscript