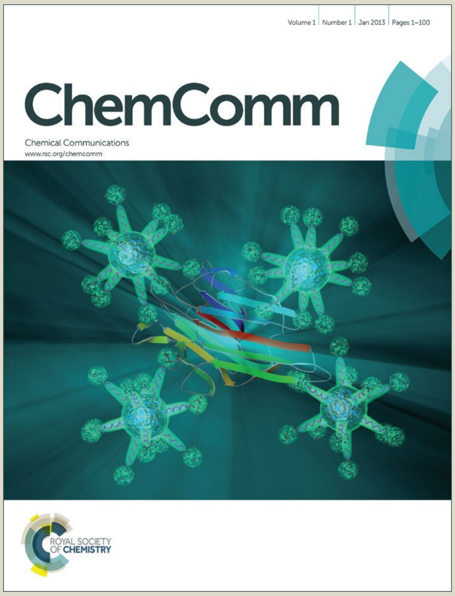


ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Chem. Commun.

COMMUNICATION

Accessing Conjugated Polymers with Precisely Controlled Heterobisfunctional Chain Ends via Post Polymerization Modification of OTf Group and Controlled Pd(0)/*t*-Bu$_3$P-Catalyzed Suzuki Cross-Coupling Polymerization

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

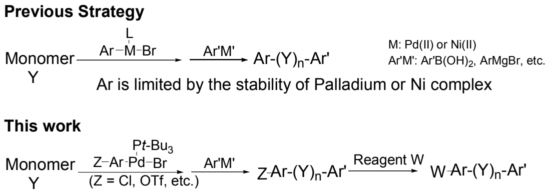
www.rsc.org/

Hog-Hai Zhang,[a†] Qiao-Sheng Hu,*[a] and Kunlun Hong*[b]

A general strategy toward the synthesis of well-defined conjugated polymers with controlled heterobisfunctional chain ends via combination of controlled Pd(0)/*t*-Bu$_3$P Suzuki cross-coupling polymerization with the post polymerization modification of triflate (OTf) group was disclosed.

Conjugated polymers have been intensively studied in the past two decades because they hold promising applications in many fields such as organic electronics.[1] Perfection of the primary structure of these polymers, including molecular weight, polydispersity, and chain end functionalities, is a prerequisite to obtain materials with reproducible performance.[2] Certain chain end functionality in conjugated polymers can play a major role in their electronic and photonic properties.[3] In addition, chain end functionalized polymers are used as macroinitiators for the synthesis of block copolymers, grafted copolymers, and others polymers with complex architectures.[4-6] Although the method for mono chain end functionalization of conjugated polymer is well-documented,[7] it still remains a challenge to achieve heterobis chain end functionalization with high fidelity. To date, the reported strategy for the synthesis of heterobisfunctionalized conjugated polymers is through the use of external initiator such as palladium(II) complexes or nickel(II) complexes, along with the *in-situ* capping process with various reagents (Scheme 1).[8] However, the scope of the functional end groups originating from external initiators is limited, due to the difficulty of isolation and purification of palladium(II) complex and nickel(II) complex.[9] In addition, it is still challenging to obtain conjugated polymers with narrow polydispersity (PDI<1.20) and high chain end group fidelity (>98%) for most of external initiators, because the polymerization process, especially in the initiation step, could be influenced by the characteristics of the initiators.[10] Therefore, a general method to introduce a variety of functional groups at both chain ends in conjugated polymers with high efficiency is highly needed.

We envisioned that in the controlled Pd(0)/*t*-Bu$_3$P-catalyzed cross-coupling polymerizations, if the initiator bears a dormant reactive site, different functional groups could be installed at the chain end of the polymer after the polymerization through the reaction of this dormant reactive site with various reagents (Scheme 1), and shortcomings associated with the reported strategy could thus be circumvented. The scope of the functional end groups would be controlled by the post polymerization modification reactions, such as the cross-coupling reactions, rather than the stability of external initiators, thus a broad spectrum of functional groups could be incorporated at the ends of a conjugated polymer.[11] By combining with the well-established termination reactions for the controlled Pd(0)/*t*-Bu$_3$P-catalyzed Suzuki cross-coupling polymerization,[8b,10c] conjugated polymers with precisely-controlled heterobisfunctional chain ends could be obtained. In addition, it would allow us to prepare conjugated polymers with the same molecular weight but different chain ends, which is important in revealing chain end functionalities dictating their optoelectronic and photonic properties. In this communication, we report our preliminary results on establishing such a strategy of combining the post polymerization modification of the OTf group with the controlled Pd(0)/*t*-Bu$_3$P-catalyzed Suzuki cross-coupling polymerization to precisely introduce a variety of functional end groups



Scheme 1. Heterobis chain end functionalization strategies.

---

[a] Department of Chemistry, College of Staten Island and the Graduate Center of the City University of New York, Staten Island, New York 10314.

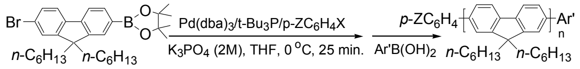
[b] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831.

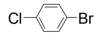
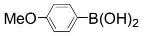
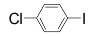
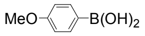
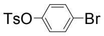
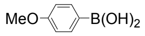
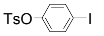
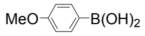
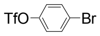
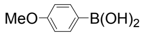
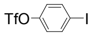
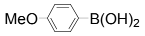
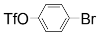
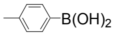
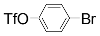
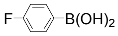
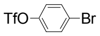
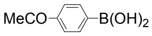
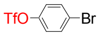
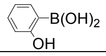
† Current address: Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831.

Electronic Supplementary Information (ESI) available: [Experimental procedure, characterization data and spectra copy]. See DOI: 10.1039/x0xx00000x

To be successful for the post polymerization modification-involved strategy, the key is to find the suitable initiator with a dormant reactive site, which would produce well-defined conjugated polymers with narrow polydispersities and meanwhile allow the reactive site to be easily converted to a variety of other functional structures via post polymerization modification reactions. Based on reported results and our own experience that Cl group and pseudo halo groups, *e. g.*, triflate (OTf), could be preserved under the cross-coupling polymerization condition with $Pd_2(dba)_3$/*t*-Bu_3P catalytic system and could be further converted to aryl groups through cross-coupling reactions with other catalyst systems,[12] we first examined $Pd_2(dba)_3$/*t*-Bu_3P/*p*-ZC_6H_4X (X =Br or I) as the initiators for controlled Suzuki cross-coupling polymerization using 2-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as monomer (Table 1). Narrowly distributed polymers (PDI as low as 1.15) with high chain end fidelity were achieved (Table 1, entries 1-6), particularly with $Pd_2(dba)_3$/*t*-Bu_3P/*p*-$TfOC_6H_4Br$ as the initiator system (Table 1, entry 5). The polymerization with $Pd_2(dba)_3$/*t*-Bu_3P/*p*-$TfOC_6H_4Br$ as initiator was also tested with other arylboronic acids as the quenching reagent (entry 7-10). We found that arylboronic acids with electron-withdrawing, electron-donating or *ortho*-position substitutions are all good quenching reagents, supported by forming the polymer with low polydispersities (PDI<1.20) and high chain end groups fidelity (>98%). The chain-growth nature of the $Pd_2(dba)_3$/*t*-Bu_3P/*p*-$TfOC_6H_4Br$-initiated polymerization process was supported by the linear relationship between the monomer conversion and the molecular weight of generated polymer (see Figure S4).

Table 1. Controlled Suzuki Cross-Coupling Polymerization with $Pd_2(dba)_3$/*t*-Bu_3P/ArX as Initiator



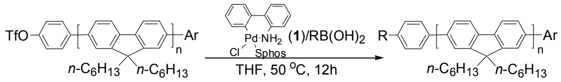
Entry[a]	ArX	$Ar^1B(OH)_2$	Yield[b]	M_n (PDI)[c]	fidelity[d]
1			87%	12 300 (1.18)	99.1%
2			87%	8 400 (1.26)	85.4%
3			83%	10 700 (1.17)	98.5%
4			80%	6 900 (1.21)	90.0%
5			87%	11 700 (1.15)	99.9%
6			87%	9 200 (1.22)	89.6%
7			87%	12 500 (1.17)	98.5%
8			80%	10 400 (1.16)	98.5%
9			73%	13 500 (1.16)	98.6%
10			80%	13 000 (1.17)	98.8%

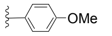
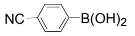
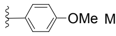
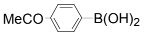
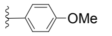
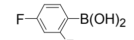
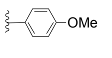
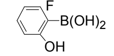
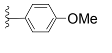
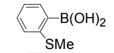
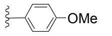
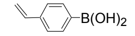
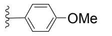
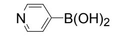
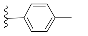
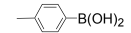
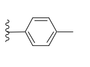
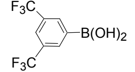
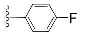
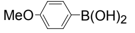
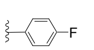
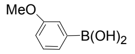
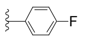
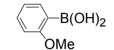
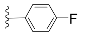
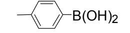
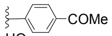
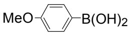
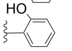
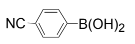
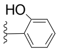
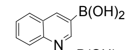
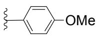
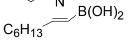
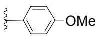
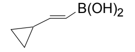
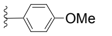
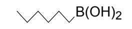
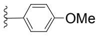
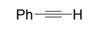
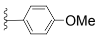
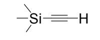
a. Polymerization condition: monomer (1 equiv.), $Pd_2(dba)_3$ (6 mol %)/*t*-Bu_3P (24 mol%)/ArX (20 mol %), K_3PO_4 (10 equiv), THF, 25 min. $Ar'B(OH)_2$ (1 equiv.). b. Isolated yield. c. As determined by GPC (PS standards, THF, 40 °C). d. One end of the polymer was capped with Ar, the other end was capped with Ar', as determined by Maldi-tof.

After identifying $Pd_2(dba)_3$/*t*-Bu_3P/*p*-$TfOC_6H_4Br$ as an appropriate initiator for controlled Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerization and the post polymerization modification strategy, we next turned our attention to introduce functional end groups via the post polymerization modification reactions. After screening the catalysts, we found S-Phos-coordinated 2-phenylaniline-based palladacycle complex **1** was an excellent catalyst for converting the OTf group to functionalized aryl groups via Suzuki cross-coupling reactions.[13] By using complex **1** as the catalyst, a number of arylboronic acids were examined for the post polymerization modification, and the results are summarized in Table 2 (entry 1-16). We found that arylboronic acids substituted by electron-withdrawing or -donating groups were suitable reagents for this post polymerization modification reaction, evidenced by low PDI and well-defined end groups being observed (Table 2, entries 1-16). This methodology is accessible to hetero bifunctional groups precisely installed at the ends of the polymer through post polymerization reactions. Moreover, the post polymerization modification reaction with arylboronic acids with functional groups, such as OH, $CH=CH_2$, were very efficient (Table 2, entries 2,4,6,7). Importantly, these functional groups could facilitate the preparation of block copolymers, grafted polymer via other controlled polymerization techniques.[14] To further expand the scope of the end groups, functionalized alkyl, alkenyl and alkynyl groups are also introduced at the end of the polymer via Suzuki or Sonagashira cross-coupling reaction (Table 2 entries 17-21). It is worthy to mention that the polymer with a terminal triple bond could be easily obtained by removing trimethylsilane group (entry 21), which is good precursor for alkynyl - azide click reaction to form a variety of block copolymers.[15] For application purpose, this terminal triple bond functionalized polymer has been prepared in a gram scale. These hetero bisfunctionalized conjugated polymers are of great interest, as they could potentially lead to the synthesis of novel copolymers with various complex architectures based on well-defined conjugated polymer structures.

The functional end groups of the polymers were confirmed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and ^1H-NMR spectrum. Taking the polymer shown at Entry 5 in Table 2 as an example, nearly only one series of peaks (>98%) were observed, which correspond to the polymer with a *para*-methoxylphenyl group at one end and an *ortho*-methylthiophenylphenyl group at the other end (designated as *p*-$MeOC_6H_4$/*o*-$MeSC_6H_4C_6H_4$) (Figure 1a). The ^1H NMR result further confirmed that the polymer chain exclusively bears the two desired end groups, evidenced by signals for -MeO group at 3.88 ppm and for -MeS group at 2.42 ppm in almost 1:1 ratio (Figure 1b).

Table 2. Post Polymerization Reaction between Polyfluorene and Different Boronic acids or Terminal Alkynes



Entry^a	Ar	RB(OH)$_2$	Yield^b	M_n (PDI)^c	Fidelity^d
1			85%	9 600 (1.16)	99.5%
2			95%	9 700 (1.15)	98.5%
3			95%	11 700 (1.14)	98.5%
4			95%	11 100 (1.15)	98.5%
5			95%	11 200 (1.16)	99.7%
6			95%	11 700 (1.14)	98.4%
7			95%	9 700 (1.17)	99.9%
8			90%	12 500 (1.17)	98.5%
9			95%	12 700 (1.17)	98.5%
10			95%	9 000 (1.16)	98.8%
11			95%	10 400 (1.18)	98.8%
12			95%	10 700 (1.16)	98.5%
13			95%	9 000 (1.17)	98.5%
14			95%	13 500 (1.16)	99.0%
15			90%	13 200 (1.18)	99.2%
16			90%	13 200 (1.17)	98.7%
17			88%	12 800 (1.18)	98.4%
18			94%	12 800 (1.17)	98.4%
19			90%	12 800 (1.17)	98.2%
20			90%	12 700 (1.18)	98.5%
21			92%	12 900 (1.17)	98.2%

a. Condition for entries 1-16: polymer (1 equiv.), arylboronic acid (20 equiv.), catalyst **1** (1 equiv. to polymer), THF, 50 °C, 12 h; for entries 17-18: polymer (1equiv.), alkenylboronic acid (20 equiv.), Pd(dppf)Cl_2 (1 equiv. to polymer), THF, 80 °C, 16 h; for entries 20-21: polymer (1 equiv.), alkyne (20 equiv.), $Pd(CH_3CN)_2Cl_2$ (1 equiv. to polymer), THF, 80 °C, 16 h. b. Isolated yields. c. As determined by GPC (PS standards, THF, 40°C).
d. The fedility of end groups was determined by Maldi-tof.

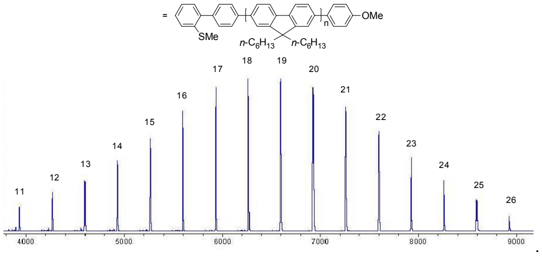
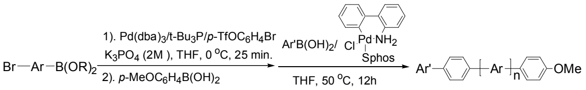


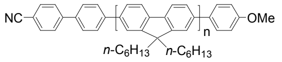
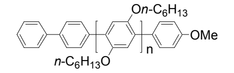
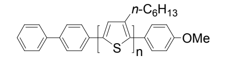
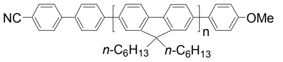
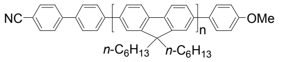
Figure 1a. Maldi-tof spectrum of polyfluorene with p-$MeOC_6H_4$/o-$MeSC_6H_4C_6H_4$ as two end groups.

Figure 1b. Portion of ^{1}H NMR spectrum of polyfluorene with p-$MeOC_6H_4$/o-$MeSC_6H_4C_6H_4$ as two end groups (3. 88 pm: OMe group; 2.42 ppm, SMe group).

Other AB-type monomers were also examined and excellent results were observed (Table 3, entries 1-3). We also observed that narrow PDI and high end group fidelity (>96%) were achieved for the polymers with higher molecular weight, which were prepared by using less amount of the initiator (SI, Figures S5 & S6). These results showed that controlled Suzuki cross-coupling polymerization with $Pd_2(dba)_3$/t-Bu_3P/p-$TfOC_6H_4Br$ as initiator coupled with the post polymerization modification of OTf group is a robust method for AB-type monomers to prepare conjugated polymer with controlled molecular weight and molecular weight distributions, and a variety of heterobis chain end groups.

Table 3. Controlled Suzuki Cross-Coupling Polymerization with Post Polymerization Modification



Entry^a	Polymer	Yield^b	M_n (PDI)^c	Fidelity
1		85%	9 600 (1.16)	99.5%
2		66%	4 400 (1.18)	98.2%
3		63%	8 700 (1.26)	96.3%
4		65%	19 400 (1.17)^d	98.2%
5		63%	30 000 (1.19)^e	98.0%

a. Polymerization condition: monomer (1 equiv.), 6 mol % $Pd_2(dba)_3$/24 mol%t-Bu_3P/10 mol% p-$TfOC_6H_4Br$, K_3PO_4 (10 equiv), THF, 30 min. b. Isolated yields. c. GPC analysis (polystyrene as standard, THF, 40 °C). d. 3 mol% $Pd_2(dba)_3$/12 mol %t-Bu_3P/5 mol% p-$TfOC_6H_4Br$ initiator loading was used. e. 2 mol % $Pd_2(dba)_3$/8 mol %t-Bu_3P/3 mol% p-$TfOC_6H_4Br$ initiator loading was used.

In summary, based on the consideration that conjugated polymers with a dormant reactive chain end could be functionalized by the reactions of such a dormant reactive site with different reagents, we demonstrated that $Pd_2(dba)_3$/t-Bu_3P/p-$TfOC_6H_4Br$ system was an efficient initiator to install OTf group at the chain end of the polymer with high fidelity (>98%) and narrow PDIs through controlled Pd(0)/t-Bu_3P-catalyzed Suzuki cross-coupling polymerization. The post polymerization modification reactions of the OTf group at the chain end via the Suzuki and Sonogashira cross-coupling reactions were performed to introduce a number of different groups including aryl, alkyl, alkenyl and alkynyl groups at the end of the polymer. Our results provided a general strategy for controlled Suzuki cross-coupling polymerization to precisely install a number of functional groups at the end of conjugated polymers with narrow PDI (PDI≤1.18). Our study also paved the road for us to explore the synthesis and characterization of block copolymers, brush polymer and other polymers with complex architectures containing conjugated blocks. Our future work in these directions will be reported in due course

Acknowledgements

We gratefully thank the NSF (CHE0911533) for funding. Part of synthesis and characterization of AB monomers was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Notes and references

1 (a) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897-1091. (b) Y. J. Cheng, S. H. Yang, C. S. Hsu, *Chem. Rev.* **2009**, *109*, 5863-5923. (c) A. Facchetti, *Chem. Mater.* **2011**, *23(3)*, 733-758. (d) X. Guo, M. Baumgarten, K. Mullen, *Prog. Polym. Sci.* **2013**, *38*, 1832-1908.
2 K. A. Mazzio, C. K. Luscombe, *Chem. Soc. Rev.* **2015**, *44*, 78-90.
3 (a) K. Palaniappan, J. W. Murphy, N. Khanam, J. Horvath, H. Alshareef, M. Q. Lopez, M. C. Biewer, S. Y. Park, M. J. Kim, B. E. Gnade, M. C. Stefan, *Macromolecules* **2009**, *42*, 3845-3848. (b) Q. Wang, B. Zhang, L. Liu, Y. Chen, Y. Qu, X. Zhang, J. Yang, Z. Xie, Y. Geng, L. Wang, F. Wang, *J. Phys. Chem. C* **2012**, *116*, 21727-21733. (c) Z. Mao, K. Vakhshouri, C. Jaye, D. A. Fischer, R. Fernando, D. M. DeLongchamp, E. D. Gomez, G. Sauve, *Macromolecules* **2013**, *46*, 103-112. (d) N. V. Handa, A. V. Serrano, M. J. Robb, C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 831-841.
4 (a) J. Liu, E. Sheina, T. Kowalewski, R. D. McCullough, *Angew. Chem. Int. Ed.* **2002**, *41*, 329-332. (b) C. A. Dai, W. C. Yen, Y. H. Lee, C. C. Ho, W. F. Su, *J. Am. Chem. Soc.* **2007**, *129*, 11036-11038. (c) H. C. Moon, A. Anthonysamy, Y. Lee, J. K. Kim, *Macromolecules* **2010**, *43*, 1747-1752. (d) R. H. Lohwasser, M. Thelakkat, *Macromolecules* **2010**, *43*, 7611-7616. (e) J. Brazard, R. J. Ono, C. W. Bielawski, P. F. Barbara, D. A. Vanden Bout, *J. Phys. Chem. B* **2013**, *117*, 4170-4176.
5 V. Senkovskyy, N. Khanduyeva, H. Komber, U. Oertel, M. Stamm, D. Kuckling, A. Kiriy, *J. Am. Chem. Soc.* **2007**, *129*, 6626-6632. (b) T. Beryozkina, K. Boyko, N. Khanduyeva, V. Senkovskyy, M. Horecha, U. Oertel, F. Simon, M. Stamm, A. Kiriy, *Angew. Chem. Int. Ed.* **2009**, *48*, 2695-2698. (c) S. J. Mougnier, C. Brochon, E. Cloutet, G. Fleury, H. Cramail, G. Hadziioannou, *Macromol. Rapid Commun.* **2012**, *33*, 703-709.
6 J. Xu, J. Wang, M. Mitchell, P. Mukherjee, M. Jeffries-EL, J. W. Petrich, Z. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 12828-12833. (b) R. A. Kruger, T. J. Gordon, T. Baumgartner, T. C. Sutherland, *ACS Appl. Mater. Interfaces* **2011**, *3*, 2031-2041. (c) M. Yuan, K. Okamoto, H. A. Bronstein, C. K. Luscombe, *ACS Macro. Lett.* **2012**, *1*, 392-395. (d) J. Park, H. C. Moon, J. K. Kim, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2225-2232. (e) B. Yameen, N. Zydziak, S. M. Weidner, M. Bruns, C. Barner-KoMllik, *Macromolecules* **2013**, *46*, 2606-2615. (f) C. S. Fischer, C. Jenewein, S. Mecking, *Macromolecules* **2015**, *48*, 483-491.
7 (a) Z. J. Bryan, A. J. McNeil, *Macromolecules* **2013**, *46*, 8395-8405. (b) T. Yokozawa, Y. Ohta, *Chem. Commun.* **2013**, *49*, 8281-8310.
8 (a) J. Lee, S. Ko, Z. Bao, *Macromol. Rapid Commun.* **2012**, *33*, 938-942. (b) E. Elmalem, F. Biedaermann, K. Johnson, R. H. Friend, W. T. S. Huck, *J. Am. Chem. Soc.* **2012**, *134*, 17769-17777. (c) C. S. Fischer, M. C. Baier, S. Mecking, *J. Am. Chem. Soc.* **2013**, *135*, 1148-1154.
9 (a) D. A. Culkin, J. F. Hartwig, *Organometallics* **2004**, *23*, 3398-3416. (b) A. Yokoyama, H. Suzuki, Y. Kubota, K. Ohuchi, H. Higashimura, T. Yokozawa, *J. Am. Chem. Soc.* **2007**, *129*, 7236-7237. (c) H. A. Bronstein, C. K. Luscombe, *J. Am. Chem. Soc.* **2009**, *131*, 12894-12895. (d) N. Doubina, S. A. Paniagua, A. V. Soldatova, A. K. Y. Jen, S. R. Marder, C. K. Luscombe, *Macromolecules* **2011**, *44*, 512-520.
10 (a) N. Doubina, A. Ho, A. K. Y. Jen, C. K. Luscombe, *Macromolecules* **2009**, *42*, 7670-7677. (b) A. Smeets, K. V. Bergh, J. D. Winter, P. Gerbaux, T. Verbiest, G. Koeckelberghs, *Macromolecules* **2009**, *42*, 7638-7641. (c) H.-H. Zhang, C.-H. Xing, Q.-S. Hu, *J. Am. Chem. Soc.* **2012**, *134*, 13156-13159. (d) H.-H. Zhang, C.-H. Xing, Q.-S. Hu, K. Hong, *Macromolecules* **2015**, *48*, 967-978.
11 (a) B. M. W. Langeveld-Voss, R. A. J. Janssen, A. J. H. Spiering, J. L. J. Van Dongen, E. C. Vonk, H. A. Claessen, *Chem. Commun.* **2000**, 81-82. (b) J. Liu, R. D. McCullough, *Macromolecules* **2002**, *35*, 9882-9889. (c) M. Jeffries-El, G. Sauve, R. D. McCullough, *Macromolecules* **2005**, *38*, 10346-10352.
12 A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020-4028.
13 (a) T. Kinzel, Y. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2010**, *132*, 14073-14075. (b) H.-H. Zhang, C.-H. Xing, G. B. Tsemo, Q.-S. Hu, *ACS Macro. Lett.* **2013**, *2*, 10-13. (c) H.-H. Zhang, J. Dong, Q.-S. Hu, *Eur. J. Org. Chem.* **2014**, 1327-1332.
14 (a) N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270-2299. (b) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2010**, *43*, 2093-2107.
15 Z. Li, R. J. Ono, Z. Q. Wu, C. W. Bielawski, *Chem. Commun.* **2011**, *47*, 197-199