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Controlled Pd(0)/*t*-Bu_3P-Catalyzed Suzuki Cross-Coupling Polymerization of AB-Type Monomers with PhPd(*t*-Bu_3P)I or $Pd_2(dba)_3$/*t*-Bu_3P/ArI as the Initiator

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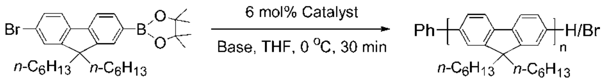
Supporting Information

ABSTRACT: Controlled Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerizations of AB-type monomers via the chain-growth mechanism with an ArPd(*t*-Bu_3P)I complex as the initiator are described. ArPd(*t*-Bu_3P)I complexes, either prepurified or generated in situ from $Pd_2(dba)_3$/*t*-Bu_3P/ArI (dba = dibenzylideneacetone) without separation/purification, were found to be efficient initiators in general for the controlled Suzuki cross-coupling polymerization, with narrow polydispersity indexes (PDIs) of 1.13−1.35 being observed. The $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4I combination was identified as a highly robust initiator system, with PDIs of ≤1.20 in general and as low as 1.13 being obtained. Higher number-average molecular weights (M_n) were achieved without a significant increase in the PDI (from 1.14 for a polymer with a M_n = 9500 to 1.20 for a polymer with M_n = 31 400) by using a smaller amount of the $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4I initiator in the polymerization.

Although Pd(0)-catalyzed Suzuki cross-coupling polymerizations via the step-growth mechanism have been established as powerful tools for the synthesis of a wide range of conjugated polymers over the past decades,[1,2] controlled Pd(0)-catalyzed Suzuki cross-coupling polymerizations via the chain-growth mechanism can only be regarded to be in an infant stage to date.[3−7] In 2005, we hypothesized that the key to achieving Pd(0)-catalyzed Suzuki cross-coupling polymerization in a controlled fashion would be to achieve the preferential oxidative addition of the regenerated Pd(0) catalyst with the newly formed coupling product from the same catalytic cycle, a concept that was essential for changing the Pd(0)-catalyzed Suzuki cross-coupling polymerization from a step-growth process into a chain-growth process.[3] We established that Pd(0)/*t*-Bu_3P is an efficient catalyst to achieve such a preferential oxidative addition,[3] paving the road for the development of controlled Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling reactions.[4] Since the disclosure of our results, Yokozawa reported Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerizations of AB-type monomers with PhPd(*t*-Bu_3P)Br as the initiator,[5,6] in which a polydispersity index (PDI = M_w/M_n) of ≥1.33 was observed with aqueous Na_2CO_3 as the base[5a] and a narrower PDI (≥1.18) but lower number-average molecular weight (M_n = 6400) were observed with CsF/18-crown-6 as the base.[5b,c] Huck has reported Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerizations of *n*-type fluorene-containing AB-type monomers with ArPd(*t*-Bu_3P)Br as the initiator,[7] with narrow PDIs (1.15−1.16) at low

Table 1. Pd(0)/*t*-Bu_3P-Catalyzed Suzuki Cross-Coupling Polymerization of 7-Bromo-9,9-dihexylfluoren-2-ylboronic Acid Pinacol Ester[a]



Entry	Catalyst	Base	Yield (%)[b]	M_n (PDI)[c]
1	PhPd(*t*-Bu_3P)I	K_3PO_4(s)	–[d,e]	900 (1.32)
2	PhPd(*t*-Bu_3P)I	K_3PO_4(s)	83[f]	8600 (1.82)
3	PhPd(*t*-Bu_3P)I	K_3PO_4(aq)[g]	76	14800 (1.33)
4	$Pd_2(dba)_3$/*t*-Bu_3P	K_3PO_4(aq)[g]	80	47300 (1.95)
5	PhPd(*t*-Bu_3P)Br	K_3PO_4(aq)[g]	76	14500 (1.35)

[a] Polymerization conditions: monomer (1 equiv), Pd catalyst (6 mol %), base (10 equiv), THF, 0 °C, 30 min. [b] Isolated yields. [c] Determined by gel-permeation chromatography (GPC) [polystyrene (PS) standards, THF, 40 °C]. [d] Reaction time 6 h. [e] No precipitation was observed upon the addition of MeOH. [f] Reaction time 36 h. [g] 2 M concentration.

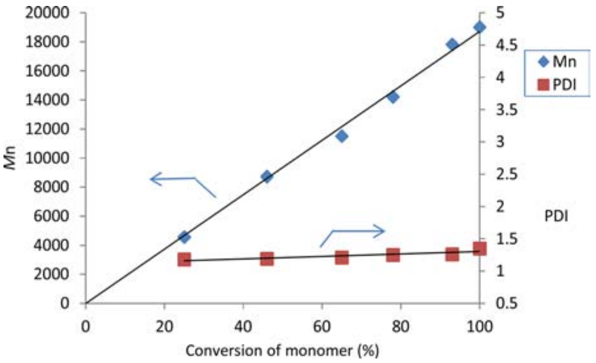


Figure 1. Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerization of 7-bromo-9,9-dihexylfluoren-2-ylboronic acid ester with PhPd(*t*-Bu_3P)I as the initiator ($[\text{monomer}]_0$ = 15.4 mmol/L, $[\text{PhPd}(t\text{-Bu}_3\text{P})\text{I}]_0$ = 0.46 mmol/L, 2 M K_3PO_4(aq), THF, 0 °C; see the SI for details).

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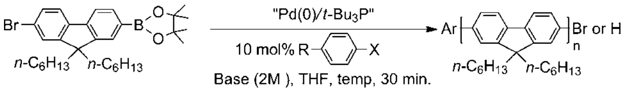
Table 2. Pd(0)/*t*-Bu_3P-Catalyzed Suzuki Cross-Coupling Polymerization with $Pd_2(dba)_3$/*t*-Bu_3P/ArI as the Initiator[a]



Entry	Pd(0)/*t*-Bu_3P	R	X	Base	*T* (°C)	Yield (%)[b]	M_n (PDI)[c]
1	Pd(*t*-$Bu_3P)_2$	H	I	K_3PO_4	0	55	23500 (1.60)
2	$Pd_2(dba)_3$/*t*-Bu_3P	H	I	K_3PO_4	0	70	9700 (1.29)
3	$Pd_2(dba)_3$/*t*-Bu_3P	H	Br	K_3PO_4	0	87	25900 (1.42)
4	$Pd_2(dba)_3$/*t*-Bu_3P	Cl	I	K_3PO_4	0	80	9100 (1.25)
5	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_3PO_4	0	80	9500 (1.14)
6	$Pd_2(dba)_3$/*t*-Bu_3P	F	I	K_3PO_4	0	77	11200 (1.21)
7	$Pd_2(dba)_3$/*t*-Bu_3P	I	I	K_3PO_4	0	70	7700 (1.25)
8	$Pd_2(dba)_3$/*t*-Bu_3P	OMe	I	K_3PO_4	0	60	9500 (1.35)
9	$Pd_2(dba)_3$/*t*-Bu_3P	CO_2Et	I	K_3PO_4	0	80	7800 (1.26)
10	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_3PO_4	0	83	10400 (1.20)[d]
11	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_3PO_4	0	70	10300 (1.17)[e]
12	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_3PO_4	rt	87	9100 (1.17)
13	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_2HPO_4	rt	99	4700 (1.24)
14	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	Na_2CO_3	rt	90	5300 (1.30)
15	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_2CO_3	rt	18	2500 (1.78)
16	$Pd_2(dba)_3$/*t*-Bu_3P	Br	I	K_3PO_4	−10	70	11100 (1.20)

[a] Polymerization conditions: monomer (1 equiv), "Pd(0)/*t*-Bu_3P" [either Pd(*t*-$Bu_3P)_2$ (6 mol %) or $Pd_2(dba)_3$ (6 mol %)/*t*-Bu_3P (24 mol %)], *p*-RC_6H_4X (10 mol %), base (10 equiv), THF, rt, 0.5 h. [b] Isolated yields. [c] As determined by GPC (PS standards, THF, 40 °C). [d] 18 mol % *t*-Bu_3P was used. [e] 30 mol % *t*-Bu_3P was used.

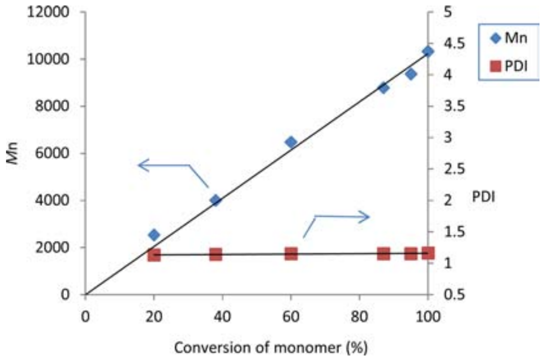


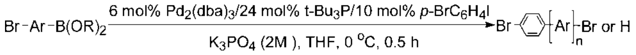
Figure 2. Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerization of 7-bromo-9,9-dihexylfluoren-2-ylboronic acid pinacol ester with $Pd_2(dba)_3$/*t*-Bu_3P/*p*-BrC_6H_4I as the initiator ($[\text{monomer}]_0$ = 15.6 mmol/L, $[Pd_2(dba)_3]_0$ = 0.95 mmol/L, $[p\text{-}BrC_6H_4I]_0$ = 1.6 mmol/L, 2 M K_3PO_4(aq), THF, 0 °C; see the SI for details).

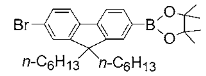
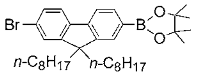
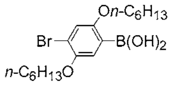
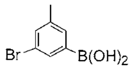
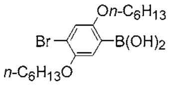
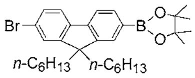
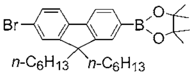
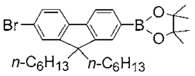
molecular weights (M_n = 3300) and increased PDIs (1.27–1.29) at slightly higher molecular weights (M_n = 7700) being observed.[6] In addition, the use of AB_2-type monomers for the preparation of hyperbranched polymers with $Pd_2(dba)_3$/*t*-Bu_3P (dba = dibenzylideneacetone) as the catalyst was reported by Bo.[8]

In our laboratory, after establishing the preferential oxidative addition concept,[3] we naturally turned our attention to the controlled Suzuki cross-coupling polymerization of AB-type monomers, as hypothesized in our previous report.[3] Because our study of the preferential oxidative addition addressed the propagation step for the polymerization via a chain-growth mechanism, we reasoned that the identification of appropriate initiators for an efficient initiation process could likely be the last obstacle for us to achieve controlled Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerizations with narrow PDIs (≤1.20). On the basis of the considerations that the decomposition of even a very small amount of the initiator ArPd(L)X would significantly increase the PDI and that PhPd(*t*-Bu_3P)I has been demonstrated to undergo reductive elimination more reluctantly than PhPd(*t*-Bu_3P)Br,[9] we envisioned that ArPd(*t*-Bu_3P)I complexes could be efficient initiators for controlled Suzuki cross-coupling polymerization. In addition, because it has been established that aryl iodides readily undergo oxidative addition with Pd(0)/*t*-Bu_3P to form ArPd(*t*-Bu_3P)I complexes,[10] we further envisioned that a combination of Pd(0)/*t*-Bu_3P and ArI, which could generate an ArPd(*t*-Bu_3P)I complex in situ, might be used as an initiator system for the controlled polymerization. Importantly, the direct use of Pd(0)/*t*-Bu_3P and ArI as the initiator system, which would eliminate the isolation and purification steps for the ArPd(*t*-Bu_3P)I complex and thus could minimize the decomposition of the ArPd(*t*-Bu_3P)I complex due to the handling process, might further narrow the PDI for the controlled polymerization. In this communication, we report our results on establishing such possibilities, specifically, the use of ArPd(*t*-Bu_3P)I complexes, including ones generated in situ from $Pd_2(dba)_3$/*t*-Bu_3P/ArI, as a class of highly efficient initiators for controlled Pd(0)/*t*-Bu_3P-catalyzed Suzuki cross-coupling polymerization of AB-type monomers, with PDIs of ≤1.20 in general and as low as 1.13 being achieved.

Our study began with the polymerization of 7-bromo-9,9-dihexylfluoren-2-ylboronic acid pinacol ester using PhPd(*t*-Bu_3P)I[10a] as the initiator. We found that with solid K_3PO_4 as the base,[3] the polymerization occurred very slowly, affording a polymer with a PDI of 1.82 after 36 h (Table 1, entries 1 and 2). The slow polymerization likely was due to the insolubility of K_3PO_4 in tetrahydrofuran (THF), which resulted in slow transmetalation processes, including the initiation step, and thus slow polymerization and a high PDI for the generated polymer. Such speculation was confirmed by the use of aqueous K_3PO_4 as the base,[1] with which the polymerization occurred significantly faster and, more importantly, afforded the polymer with narrower PDI of 1.33 (Table 1, entry 3). For comparison purposes, the polymerization with $Pd_2(dba)_3$/*t*-Bu_3P as the

Table 3. Pd(0)/t-Bu$_3$P-Catalyzed Suzuki Cross-Coupling Polymerization with Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I as the Initiator[a]



Entry	Br−Ar−B(OR)$_2$	Yield(%)[b]	M$_n$ (PDI)[c,d]
1		80	9 500 (1.14)
2		80	14 600 (1.19)
3		67	4 100 (1.13)
4		99	4 100 (1.14) [e]
5		70	7 100 (1.17)[f]
6		83	15 300 (1.15)[g]
7		76	21 200 (1.20)[f]
8		73	31 400 (1.20)[h]

[a] Polymerization conditions: monomer (1 equiv), initiator [6 mol % Pd$_2$(dba)$_3$ + 24 mol % t-Bu$_3$P + 10 mol % p-BrC$_6$H$_4$I], K$_3$PO$_4$ (10 equiv), THF, 0 °C, 30 min. [b] Isolated yields. [c] Determined by GPC (PS standards, THF, 40 °C). [d] Formation of the minor isomers having Br−Ar−p-C$_6$H$_4$−[Ar−]$_n$Br or H termini was also observed. [e] Initiator loading: 1.5 mol % Pd$_2$(dba)$_3$/6 mol % t-Bu$_3$P/2.5 mol % p-BrC$_6$H$_4$I. [f] Initiator loading: 3 mol % Pd$_2$(dba)$_3$/12 mol % t-Bu$_3$P/5 mol % p-BrC$_6$H$_4$I. [g] Initiator loading: 4 mol % Pd$_2$(dba)$_3$/16 mol % t-Bu$_3$P/6.7 mol % p-BrC$_6$H$_4$I. [h] Initiator loading: 2 mol % Pd2(dba)3/8 mol % t-Bu3P/3.3 mol % p-BrC6H4I.

catalyst system was also carried out and yielded a polymer with a PDI of 1.95 (Table 1, entry 4), a typical PDI for a polymer generated via the step-growth polymerization mechanism. The much narrower PDI (1.33) for PhPd(t-Bu$_3$P)I-initiated polymerization suggested that PhPd(t-Bu$_3$P)I-initiated polymerizations likely did not occur via step-growth polymerization but rather proceeded via the chain-growth polymerization mechanism. This chain-growth nature was confirmed by the linear relationship between the monomer conversion and the molecular weight of the generated polymer (Figure 1).[11] We also employed PhPd(t-Bu$_3$P)Br[10a] as the initiator for the polymerization, and a slightly higher PDI of 1.35 was observed for the generated polymer (Table 1, entry 5). These results showed that PhPd(t-Bu$_3$P)I complex is an efficient initiator for Suzuki cross-coupling polymerization via a chain-growth mechanism.

We next turned our attention to the use of in situ-generated ArPd(t-Bu$_3$P)I complexes for the controlled polymerization. We first employed Pd(t-Bu$_3$P)$_2$ and PhI to generate the initiator, and the polymerization afforded a polymer with M_n = 23 500 and PDI = 1.60 (Table 2, entry 1). We speculated that the increased PDI might be due to slow oxidative addition of Pd(t-Bu$_3$P)$_2$ with PhI, which might leave some Pd(t-Bu$_3$P)$_2$ in the initiator system. On the basis of Fu's results that Pd(0)/t-Bu$_3$P species generated from Pd$_2$(dba)$_3$/t-Bu$_3$P are more active than those from Pd(t-Bu$_3$P)$_2$,[10c] we examined the combination of Pd$_2$(dba)$_3$/t-Bu$_3$P and PhI for the in situ generation of PhPd(t-Bu$_3$P)I and found it to be an efficient initiator for the controlled polymerization, affording the polymer with a PDI of 1.29 (Table 2, entry 2). For comparison purposes, we also examined the combination of Pd$_2$(dba)$_3$/t-Bu$_3$P with PhBr for in situ generation of the initiator and found this system to be a less efficient initiator for the controlled polymerization, as evidenced by the PDI of 1.42 for the generated polymer (Table 2, entry 3). Because the oxidative addition reactivity of iodobenzenes would be influenced by the substitutent on the phenyl ring, we thus examined several para-substituted iodobenzenes in the Pd$_2$(dba)$_3$/t-Bu$_3$P/ArI initiator system. We found these Pd$_2$(dba)$_3$/t-Bu$_3$P/ArI combinations in general to be efficient initiators that gave narrow PDIs (1.14−1.35) (Table 2, entries 4−9). The Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I combination was found to be the best initiator for the controlled polymerization, affording a polymer with a PDI of 1.14 (Table 2, entry 5). Further studies showed that a 2:1 ratio of t-Bu$_3$P to Pd yielded the best initiator system (Table 2, entries 5, 10, and 11). A brief screen of the base and temperature showed K$_3$PO$_4$ to be the best base and 0 °C to be the best temperature for the controlled polymerization (Table 2, entries 5 and 12−16).[11]

To support the chain-growth nature of the Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I-initiated polymerization process, we examined the relationship between the monomer conversion and the molecular weight of the generated polymer. We found a linear relationship between them, with almost no change in PDI (1.13−1.16) for polymers obtained at different conversions (Figure 2), a characteristic of chain-growth polymerization. These results suggested that the polymerization with Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I as the initiator likely occurs via a chain-growth process.[12]

With Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I as the initiator, several bromoarylboronic acids/acid esters were examined for the controlled polymerization (Table 3). We found the Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I system to be an excellent initiator for these AB-type monomers, with very narrow PDIs (1.13−1.19) being obtained for the generated polymers (Table 3, entries 1−4). We further examined the polymerization using different amounts of the initiator. We found higher molecular weights could be achieved by using smaller amounts of the initiator, and importantly, the PDIs increased only slightly [Table 3, entry 3 vs 5 and entry 1 vs 6−8; also see the Supporting Information (SI)]. These results compared favorably with those for controlled polymerizations using ArPd(t-Bu$_3$P)Br complexes as the initiators, in which the PDI increased from 1.33 to 1.51 as M_n increased from 17 700 to 20 700 with Na$_2$CO$_3$(aq) as the base[5a] and from 1.15 to 1.27 as M_n increased from 3300 to 7700.[6] Our results show that the Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I combination is a highly robust initiator for controlled Suzuki cross-coupling polymerization of AB-type monomers.[13]

In summary, we have demonstrated for the first time that ArPd(t-Bu$_3$P)I complexes are a class of efficient initiators for the controlled Suzuki cross-coupling polymerization of bromoarylboronic acids/acid esters (AB-type monomers) via the chain-growth mechanism. ArPd(t-Bu$_3$P)I complexes, either prepurified or generated in situ from Pd$_2$(dba)$_3$/t-Bu$_3$P/ArI without separation/purification, were found to be efficient initiators in general, with narrow PDIs being observed (1.13−1.35). The Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I combination was found to be a highly robust initiator for the controlled Suzuki cross-coupling polymerization, with PDIs of ≤1.20 in general and as low as 1.13 being observed. Importantly, higher molecular weights could be achieved by using smaller amounts of the Pd$_2$(dba)$_3$/*t*-Bu$_3$P/*p*-BrC$_6$H$_4$I initiator with only a slight increase in the PDI (from 1.14 for the polymer with M_n = 9500 to 1.20 for the polymer with M_n = 31400). Our study has provided a class of readily available, robust initiators and a general initiator generation strategy for the controlled Pd(0)/*t*-Bu$_3$P-catalyzed Suzuki cross-coupling polymerization of AB-type monomers. The Pd$_2$(dba)$_3$/*t*-Bu$_3$P/*p*-BrC$_6$H$_4$I initiator system may find application in other controlled Pd(0)-catalyzed cross-coupling reactions.[14] The in situ initiator generation strategy described herein has also paved the road for us to explore the use of other Pd(0) sources and other ArX (X = Br, OTf, etc.) for the in situ generation of initiators for controlled cross-coupling polymerizations, including Suzuki cross-coupling polymerization. Our future work in these directions will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. 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) For recent reviews on Suzuki cross-coupling reactions, see: (a) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11−59. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147−168. (c) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4211. (d) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (e) Darses, S.; Genet, J.-P. *Chem. Rev.* **2008**, *108*, 288−325. (f) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133−173.

(2) (a) Hu, Q.-S.; Pu, L. In *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*; Itsuno, S., Ed.; Wiley: Hoboken, NJ, 2011; pp 323−364. (b) Hu, Q.-S. In *Synthetic Methods for Step-Growth Polymers*; Rogers, M., Long, T., Eds.; Wiley: Hoboken, NJ, 2003; pp 467−526.

(3) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006−10007.

(4) For recent reviews, see: (a) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595−5619. (b) Yokoyama, A.; Yokozawa, T. *Macromolecules* **2007**, *40*, 4093−4101. (c) Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlueter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653−687.

(5) For examples of Pd(0)/*t*-Bu$_3$P-catalyzed controlled Suzuki cross-coupling polymerizations, see: (a) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236−7237. (b) Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010**, *43*, 7095−7100. (c) Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. *Macromol. Rapid Commun.* **2011**, *32*, 801−806.

(6) Also see: Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695−2698.

(7) Elmalem, E.; Kiriy, A.; Huck, W. T. S. *Macromolecules* **2011**, *44*, 9057−9061.

(8) Huang, W.; Su, L.; Bo, Z. *J. Am. Chem. Soc.* **2009**, *131*, 10348−10349.

(9) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944−13945.

(10) (a) Stambuli, J. P.; Incarvito, C. D.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184−1194. (b) Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346−9347. (c) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020−4028.

(11) The end groups of the polyfluorene polymer, as analyzed by matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) mass spectrometry, were found to be mainly Br/Br and Br/H (see the SI for details).

(12) To understand the polymerization propagation direction after the initial reductive elimination, which would generate a product with two Br groups as possible propagation sites, the reaction of 7-bromo-9,9-dihexylfluoren-2-ylboronic acid pinacol ester with the Pd$_2$(dba)$_3$/*t*-Bu$_3$P/*p*-BrC$_6$H$_4$I initiator system in a 1:1 ratio was carried out. GC−MS analysis showed that 2-(4-bromophenyl)-9,9-dihexylfluorene and 2-bromo-7-phenyl-9,9-dihexylfluorene were formed in a 3:1 ratio, suggesting that either Br group could serve as the polymerization propagation site (see the SI for details).

(13) Other bromoiodoarenes instead of 1-bromo-4-iodobenzene could be used in the initiator system. For example, the use of Pd$_2$(dba)$_3$/*t*-Bu$_3$P/2-bromo-9,9-dihexyl-7-iodofluorene as the initiator for the polymerization of 7-bromo-9,9-dihexylfluoren-2-ylboronic acid pinacol ester, which could avoid the structural defect caused by the use of 1-bromo-4-iodobenzene in the initiator system, yielded a polyfluorene polymer in 80% yield with M_n = 15 300 and PDI = 1.19 as determined by GPC with PS standards (see the SI for details).

(14) Examples of other cross-coupling polymerizations: (a) Suzuki−Heck polymerization: Grisorio, R.; Suranna, G. P.; Mastrorilli, P. *Chem.—Eur. J.* **2010**, *16*, 8054−8061. (b) Negishi coupling polymerization: Verswyvel, M.; Verstappen, P.; De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 5339−5349.