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Preferential Oxidative Addition in Suzuki Cross-Coupling Reactions Across One Fluorene Unit

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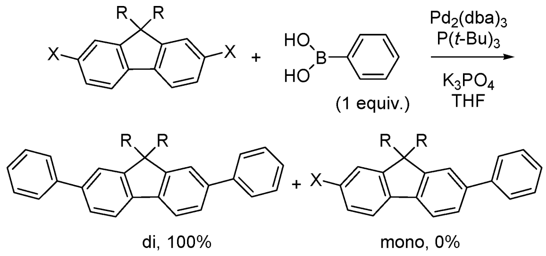
ABSTRACT



The Suzuki-type cross-coupling reaction of 2,7-dihalofluorenes with 1 equiv of arylboronic acid and $Pd_2(dba)_3$/P(*t*-Bu_3) as a catalyst system is investigated. The exclusive formation of the diarylated coupling product demonstrates that "preferential oxidative addition" is also applicable to fluorene monomers due to a controlled intramolecular motion of the regenerated Pd(0) catalyst across the "large" distance between the 2- and the 7-position of one fluorene monomer.

9,9′-Dialkyl-substituted polyfluorenes (PFs) have emerged as important semiconducting organic materials incorporated in polymer light-emitting diodes (PLEDs) over the last 25 years because of their exceptional efficiencies as blue light emitters.[1−3]

The generation of PF and related polymers in a controllable fashion continues to be one of the great challenges in the field of semiconducting polymer synthesis and has not been reported yet. Controlled "chain-growth polymerizations" leading to narrowly distributed polymer samples are well-known for cationic,[4−6] anionic,[7−9] and living radical polymerizations[10−13] (see the widely applied atom transfer radical polymerization, ATRP[14−17]), but not for palladium-assisted cross-coupling polymerizations. In palladium-assisted cross-coupling polymerizations, the oxidative addition−transmetalation−reductive elimination sequence is repeated multiple times as shown in Scheme 1 for AB-type bifunctional monomers. In the second catalytic cycle, the reductively regenerated Pd(0) catalyst (**3**) has two possibilities to insert into an aryl−halogen bond in the next oxidative addition step: One possibility is the reaction with the initial monomer **1**; the second possibility is the intramolecular reaction with the newly generated oligomer **2**. Such arbitrary

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(1) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.
(2) Scherf, U.; List, E. *Adv. Mater.* **2002**, *14*, 477.
(3) Leclerc, M. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 2867.
(4) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317.
(5) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* **1985**, *18*, 611.
(6) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.
(7) Morton, M. *Anionic Polymerization, Principles and Practice*; Academic Press: New York, 1983,
(8) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 994.
(9) Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87.
(10) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638.
(11) Hawker, C. *Trends Polym. Sci.* **1996**, *4*, 183.
(12) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371.
(13) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(14) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.
(15) Hawker, C.; Bosman, A.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(16) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.
(17) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.

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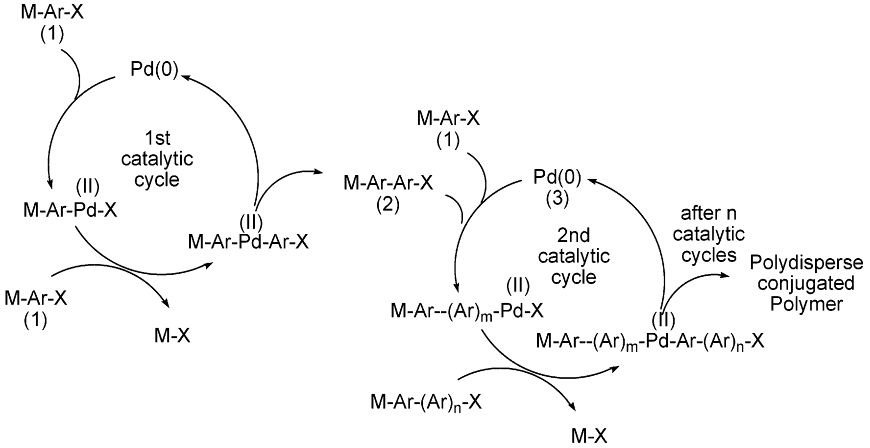
Scheme 1. Catalytic Cycle of Pd(0)-Catalyzed Cross-Coupling Polycondensations (AB Approach)



X = Br, I; M = $B(OH)_2$; m,n = 0 or 1.

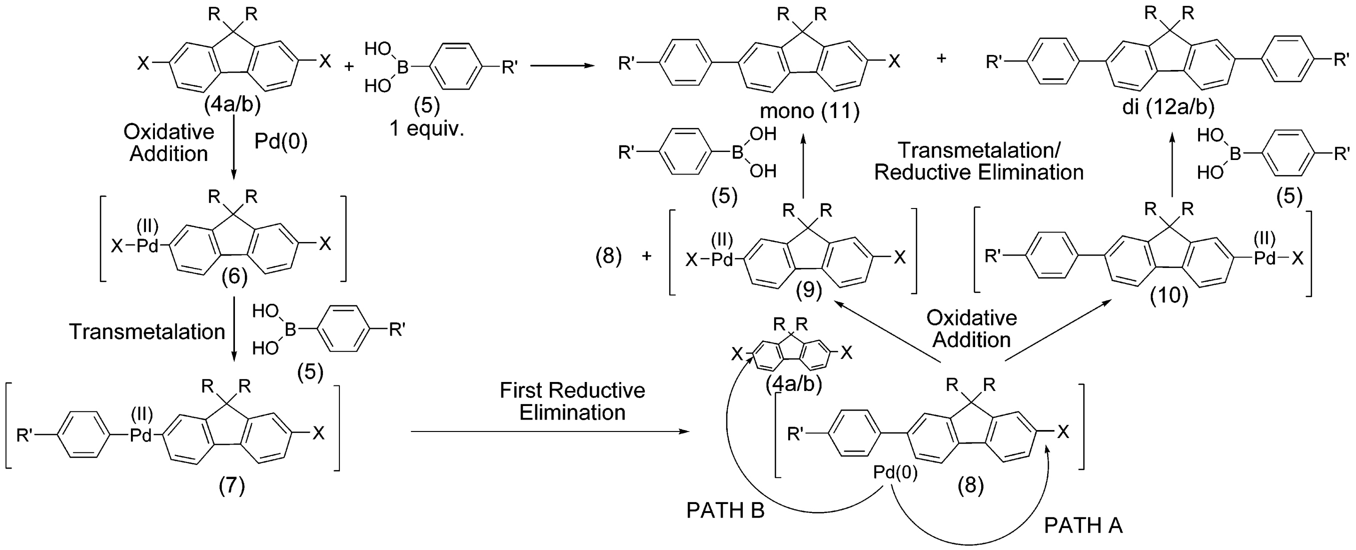
oxidative addition allows multiple species of the reaction mixture to participate in the transmetalation and thus leads to a nonselective reaction. To obtain a “chain-growth polymerization”, the oxidative addition process has to occur selectively between the regenerated Pd(0) catalyst and the just formed coupling product. With such a so-called “preferential oxidative addition”,[18] the polymerization proceeds via a “chain-growth-mechanism”. In the resulting “chain-growth polymerization”, the monomer units are added sequentially to the growing polymer chain. Hereby, the intramolecular oxidative addition of the regenerated Pd(0) catalyst has to be much faster than the diffusion of the palladium to another aryl halide.

Hu et al. published a study on the cross-coupling of dihalobenzenes with 1 equiv of arylboronic acid as a model reaction for a “preferential oxidative addition”.[18] They demonstrated that the regenerated Pd(0) catalyst in the cross-coupling of dihaloarenes with arylboronic acids could undergo oxidative addition preferentially with the already formed coupling product. Pd(0)/*t*-Bu_3P was identified as a powerful catalyst system to achieve efficient “preferential oxidative addition”.[18] The weak tris(*tert*-butyl)phosphane ligands reduce the mobility of the Pd catalyst.

The use of 1 equiv or less of boronic acid as reported by Hu and Dong[18] and Sherburn and Sinclair[19] is necessary to differentiate the products obtained via the “preferential oxidative addition pathway” (Scheme 2, path A) and the “nonpreferential oxidative addition pathway” (Scheme 2, path B).

First, the dihaloarene (in Scheme 2 shown for 2,7-dihalofluorene **4**) undergoes oxidative addition with the Pd-

Scheme 2. Suzuki-Type Cross-Coupling of 2,7-Dihalofluorene with 1 equiv of Benzeneboronic Acid as a Model Reaction for a “Preferential Oxidative Addition”



X = Br, I; R’ = H, *t*-Bu; 4a = 2,7-dibromo-9,9’-*bis*(2-ethylhexyl)fluorene; 4b = 2,7-diiodo-9,9’-*bis*(2-ethylhexyl)fluorene; 12a = 2,7-diphenyl-9,9’-bis(2-ethylhexyl)fluorene; 12b = 2,7-bis(4-*tert*-butylphenyl)-9,9’-bis(2-ethylhexyl)fluorene.

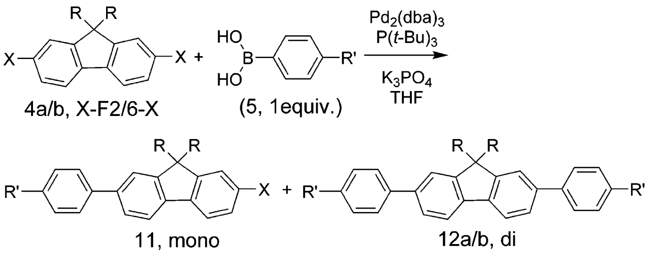
(0) catalyst leading to metalated intermediate **6**. In the next step, the arylboronic acid **5** undergoes the transmetalation step with **6** to obtain intermediate **7**. The Pd(II) species **7** is then reduced in the first reductive elimination step leading to the monoarylated product **8** and Pd(0). If the diffusion process of the Pd(0) core away from the coupling product **8** is faster than the oxidative addition step, the regenerated Pd(0) catalyst is expected to undergo oxidative addition mainly with another molecule of the more reactive 2,7-dihalofluorene **4** starting material, leading to a second molecule of the monoarylated coupling product **11** (path B, hereafter referred to as **mono**) as the major coupling product. If the oxidation addition process occurs faster than the diffusion process, the regenerated Pd(0) catalyst will undergo oxidative addition preferably with the monosubstituted fluorene **8**, leading to the disubstituted product **12** (path A, hereafter referred to as **di**). Therefore, this specific reaction represents a very suitable model for the mechanism of the coupling reaction.

Moreover, it was observed that in controlled Suzuki-type cross-couplings with "preferential oxidative addition" 1,4-dihalobenzenes underwent a much slower coupling than their 1,2- and 1,3-analogues.[18] These results indicate that the oxidative addition of the regenerated Pd(0) into the para-carbon−halogen bond, although faster than the diffusion of the Pd(0) to another monomer, occurs more slowly than the similar oxidative addition for the 1,2- and 1,3-disubstituted analogues and represents the rate-limiting step. For complete conversions, systems with spatially more separated reactive sites need longer reaction times and higher temperatures.[18] Comparing the distance of the two reactive sites of 1,2-dihalobenzenes (about 3.6 Å) and 2,7-dihalofluorene **4** (about 11.2 Å), the regenerated Pd(0) has to migrate over a much longer distance for a "preferential oxidative addition" step for fluorene monomers.

Therefore, an investigation of the above outlined model reaction for 9,9′-disubstituted fluorenes, which represent well-suited monomers toward semiconducting polyfluorenes, seems to be very attractive. If the Pd(0) species can preferentially "migrate" also over the "large" distance of approximately two benzene rings, a controlled chain-growth polymerization of fluorene monomers should be possible. With the already reported $Pd_2(dba)_3/P(t\text{-}Bu)_3$[20] as the catalyst system, K_3PO_4 as the base, and THF as solvent, cross-coupling reactions of 2,7-dihalofluorenes **4** with 1 equiv of either benzeneboronic acid ($C_6H_5B(OH)_2$) or 4-*tert*-butylbenzeneboronic acid ($4\text{-}t\text{-}BuC_6H_4B(OH)_2$) have been carried out (Table 1).

Excellent ratios of diarylfluorenes **12a** to monoarylfluorenes (**11**, R′ = H) in good overall yields of ca. 90% were observed for couplings both of 2,7-dibromo-9,9′-bis(2-ethylhexyl)fluorene **4a** with X = Br, Br-F2/6-Br, Table 1, entry 1, and 2,7-diiodo-9,9′-bis(2-ethylhexyl)fluorene **4b** with X = I, I-F2/6-I, Table 1, entry 3, and benzeneboronic acid.

Table 1. Suzuki-Type Cross-Couplings of Dihalofluorenes and Benzeneboronic Acids[a]



X = Br, I; R = 2-ethylhexyl; R' = H, *t*-Bu.

entry	dihalide	boronic acid	sm[b,e] (%)	mono[c,e] (%)	di[d,e] (%)	mono/di
1	Br-F2/6-Br[f]	$C_6H_5B(OH)_2$[h]	52.0		48.0	0:100
2	Br-F2/6-Br	$4\text{-}t\text{-}BuC_6H_4B(OH)_2$[i]	99.3		0.7	
3	I-F2/6-I[g]	$C_6H_5B(OH)_2$	46.5		53.5	0:100
4	I-F2/6-I	$4\text{-}t\text{-}BuC_6H_4B(OH)_2$	100.0		0.0	

[a] Reaction conditions (not optimized): dihalide (1 equiv), boronic acid (1 equiv), $Pd_2(dba)_3$ (1.5%), $P(t\text{-}Bu)_3$ (6%), K_3PO_4 (3 equiv), THF (5 mL), 80 °C, 5 days. [b] Starting material. [c] Monosubstituted product. [d] Disubstituted product. [e] Detected by GC−MS. [f] 2,7-Dibromo-9,9′-bis(2-ethylhexyl)fluorene (**4a**, X = Br). [g] 2,7-Diiodo-9,9′-bis(2-ethylhexyl)fluorene (**4b**, X = I). [h] Benzeneboronic acid. [i] 4-*tert*-Butylbenzeneboronic acid.

An approximate 1:1 ratio of disubstituted product and remaining starting material (because only 1 equiv of arylboronic acid is used) indicates that the reaction proceeds exclusively via the "preferential oxidative addition pathway" (path A). Obviously, the reaction of 2,7-dihalofluorenes **4** with 1 equiv of 4-*tert*-butylbenzeneboronic acid (Table 1, entries 2 and 4) leads to almost no conversion of the dihalofluorenes. This should result from the "deactivating", electron-donating character of the *tert*-butyl substitutent (for synthesis and characterization of **4a/b** with X = Br/I and **12a/b** with R′ = H, *t*-Bu, see the Supporting Information).

To summarize, this work demonstrates that a "preferential oxidative addition" via a strictly intramolecular motion of the regenerated Pd(0) catalyst is observed for extended 2,7-substituted fluorene monomers. In such a process, 2,7-diarylfluorene and 2,7-dihalofluorene as starting materials are the exclusive reaction products of a coupling of 1 equiv of 2,7-dihalofluorene and 1 equiv of arylboronic acid. These results show that a controlled, intramolecular Pd insertion in Suzuki-type cross-coupling reactions is also possible across the "large" distance of the fluorene monomer.

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Supporting Information Available: Representative procedures and characterization data of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006.
(19) Sinclair, D. J.; Sherburn, M. S. *J. Org. Chem.* **2005**, *70*, 3730.
(20) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.