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AB- Versus AA+BB-Suzuki Polycondensation: A Palladium/Tris(*tert*-butyl)phosphine Catalyst Can Outperform Conventional Catalysts

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A Pd/P*t*-Bu$_3$ catalyst having bulky, electron-rich ligands significantly outperforms conventional "step-growth catalysts" Pd(PPh$_3$)$_4$ and Pd(P*o*-Tol$_3$)$_3$ in the Suzuki polycondensation of the AB-type arylene-based monomers, such as some of the substituted fluorenes, carbazoles, and phenylenes. In the AA+BB polycondensation, Pd/P*t*-Bu$_3$ also performs better under homogeneous reaction conditions, in combination with the organic base Et$_4$NOH. The superior performance of Pd/P*t*-Bu$_3$ is discussed in terms of its higher reactivity in the oxidative addition step and inherent advantages of the intramolecular catalyst transfer, which is a key step joining catalytic cycles of the AB-polycondensation. These findings are applied to the synthesis of a carbazole-based copolymer designed for the use as a hole conductor in solution-processed organic light-emitting diodes.

π-Conjugated (semiconducting) polymers (CPs) are an important class of materials for organic electronics and other applications.[1] Nowadays, polycondensations based on transition metal-catalyzed cross-coupling are the most powerful tools for preparation of CPs.[2] Among the cross-coupling methods, Suzuki polycondensation (SPC)[3] of boron-organic monomers attracts researchers, because it tolerates the presence of many useful functional groups and does not involve big amounts of toxic heavy metals, like Stille or Yamamoto coupling. In most cases, SPC is performed in a step-growth AA+BB approach, which involves reaction of two types of monomers having complimentary leaving groups (where A is, e.g., an electrophilic C-Br group and B is a nucleophilic group, e.g., metalorganics or organoboron derivatives, **Scheme 1**.[3] An alternative approach involves reaction of AB-monomers in which leaving groups of both types are placed in the same molecule.[4] Each approach has its own advantages and disadvantages. The AA+BB method benefits from its simplicity and versatility because incorporation of two identical leaving groups into the molecule is technically simpler than the introduction of two dissimilar leaving groups. An important restriction of the AB-approach is the difficulty of the monomer preparation in cases when electrophilic functional groups (e.g., carbonyl of ester groups) are present in the monomer precursor because the incorporation of boronic leaving group involves strong nucleophilic metalorganic reagents, incompatible with the electrophilic groups. In such cases, preparation of AB-monomers requires additional protection steps. In this regard, the AA+BB approach is more flexible because it allows placing of more demanding functional groups into bis-halogenated monomers. Achieving of ultra-high molecular weight polymers is possible within the AA+BB SCP, although it requires tedious optimizations of reaction conditions.[5–7] In general, the step-growth mechanism inherent to the AA+BB polycondensation method suffers from a poor control over molecular weight (MW), dispersity ($Đ$) and end groups identity, which leads to undesirable batch-to-batch variations of properties.[8] In contrast, AB-monomers in the presence of Pd catalysts having bulky electron rich ligands may polymerize in a chain-growth manner, due to realization of an intramolecular catalyst-transfer mechanism.[4] This polymerization type is advantageous because it allows preparation of well-defined conjugated homo-, gradient-, and block-copolymers having controlled MW and narrow $Đ$.[9]

Besides the choice of the coupling method (AA+BB or AB), the ligand kind has significant impact on the polycondensation performance. Traditionally, palladium catalysts having triphenyl phosphine or tri-tolyl phosphine ligands are used in SPCs.[3,5,6] Meanwhile, related Suzuki cross-coupling of small-molecules underwent impressive progress in the last decade and new, more efficient Pd catalysts were developed.[10] In particular, the use of

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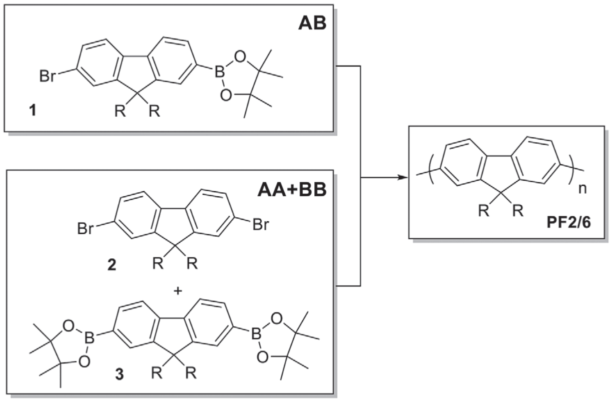


Scheme 1. The AB- and AA+BB Suzuki polycondensation routes to polyfluorenes.

bulky and electron-rich ligands enables, in many cases, cross-couplings to proceed under mild conditions, with low catalyst loadings and involving otherwise inactive electrophiles.[7,8] One of such “modern” catalysts, Pd/P*t*-Bu$_3$, comprehensively studied by Gregory Fu,[11] supports the chain-growth polycondensation of AB-monomers.[4] Similarly, Buchwald’s type Pd/SPhos, catalyst outperforms “classical” catalysts in SPC of m-phenylene monomer.[12] However, in the case of AA+BB SPC, no clear-cut advantages of the “new generation” ligands were identified.[13] At the same time, greatly increased interest on semiconducting polymers drives the research in this field from purely polymer chemistry into multidisciplinary studies for device application, which requires more and more universal methods for preparation of polymers avoiding tedious optimizations.[14] In this regard, the Stille polymerization, despite its toxicity to health and environment, is often the method of choice, as it is the most universal and robust synthetic tool.[2] Hence, a face-to-face comparison of AB- versus AA+BB SPC protocols is a pressing task in order to provide guidance facilitating optimization efforts.

Our previous work compared AB and AA+BB methods on example of Negishi polycondensation of fluorene-based zinc-organic-monomers.[15] It was found that polymerization of AB-monomers proceeds two orders of magnitude faster and requires much lower catalyst loadings than the respective AA+BB-polycondensation. These results were attributed to a faster and safer intramolecular (versus intermolecular) catalyst-transfer process underlying the chain-growth mechanism inherent to only the AB-monomers.

Herein, in the first step, we compare Pd/P*t*Bu$_3$-catalyzed SPC of model fluorene-based AB- and AA+BB-types of monomers. Knowledge obtained with the model monomers is applied to the preparation of a practically important carbazole-based copolymer designed for the use as hole conductor in solution-processed organic light emitting diodes (OLEDs).

The chain-growth behavior of the polymerization of the fluorene-based AB-type monomer 1 in the presence of Pd/P*t*-Bu$_3$ was previously established; however, the polymerization of the related AA+BB system under otherwise identical reaction conditions was not studied.[4] To compare AB- and AA+BB SPC toward PF2/6 of model fluorene-based monomers, we first tested the most frequently utilized reaction conditions, which include the use of Na$_2$CO$_3$ as a base and THF/water as the solvents mixture. In this work, a strong attention was paid to purity of utilized monomers, as it greatly influences polymerization behavior. Particularly, the AA+BB polycondensation is notoriously sensitive to monomer purity even if impurities do not directly interfere with the growth process,[16] since impurities cause a stoichiometric imbalance, which in turn limits the molar mass of the product.[16] In contrast to the AA+BB polycondensation, the AB-polycondensation is generally less demanding on monomer purity and degrades mostly in the presence of metalorganic impurities, such as BuLi, Grignard reagents, and so forth.[9] To avoid the above-mentioned impact of impurities, all monomers were carefully purified by column chromatography and their quality was verified by 1H and 13C NMR spectroscopy (see Figures S6–S10, Supporting Information). Typically, we utilized monomer batches with purity higher than 98%, in many cases, better than 99%. To ensure a fair comparison of polymerization conditions and to avoid possible imbalances caused by handling of small quantities, all experiments listed in **Table 1** were conducted by using appreciable amounts of monomers (≈0.5 g of each monomer for experiments shown in entries 1–6, and ≈2 g in entries 17–20).

In the first series of experiments, monomer 1 was polymerized at room temperature (RT) in the presence of different concentrations of an in situ-forming Pd/P*t*Bu$_3$ catalyst (2) prepared by mixing of Pd(CH$_3$CN)$_2$Cl$_2$ and P*t*Bu$_3$ (1 equiv. of each). At the catalyst loading of 5 mol%, the polymerization follows almost linear M_n/p dependence (M_n = number-average MW; p = monomer conversion, **Figure 1**). Relatively high molecular weight PF2/6 is formed early in the polymerization (e.g., M_n = 4.8 kg mol^{-1}, P_{1a} = 42%), indicating a chain-growth mechanism (Figure 1a). The deviation of the observed polymerization degree DP from the theoretical value given by the monomer to catalyst ratio (24 instead of 20) is due to a tendency of GPC, based on polystyrene standards, to overestimate MW for rigid-rod polymers.[3] Relatively large dispersity shows that the polymerization is not perfect (Table 1, entry 1). At 100/1 monomer/initiator ratio, the polymerization levels at p = 84% and PF2/6 with M_n = 42.3 kg mol^{-1} is forming (Table 1, entries 2), which again, due to the GPC overestimation, is larger than the expected theoretical value for 84-mer (32.2 g mol^{-1}). The polymerization performance degrades at lower catalyst loadings and at a catalyst concentration of 0.02 mol% the monomer conversion does not exceed 50%. In this case, the M_n versus p dependence is not linear and M_n of the resulting polymer of 76 kg mol^{-1}, which is corresponding to a DP of 200 (Table 1, entry 3), does not reach the theoretical value DP of 500. The limited molecular weight and its broad $Đ$ (2.0) suggests that chain termination take place, which can be explained by a polymer solubility limit. The incomplete monomer conversion suggests that the catalyst species, released after the chain-termination, are not able to re-initiate new chains, in contrast to the Negishi polymerization of a fluorene-based monomer studied earlier.

To assess the AA+BB route, the Suzuki polycondensation of a mixture of monomers 2 and 3 at exactly 1/1 ratio was attempted at the same conditions, that is, at RT, in the presence of Pd/P*t*Bu$_3$, Na$_2$CO$_3$, in a THF-water mixture. To eliminate a negative impact of impurities on the polymerization process, all polymerization experiments were conducted with the same batches of the monomers 2 and 3, both having purity higher than 99% (Figures S7 and S8, Supporting Information).

Table 1. Polymerization results for polyfluorenes PF2/6 and carbazole-based copolymers.

Entry	Monomer	Catalyst, [mol%]	Base/solvent	T [°C]	t [h]	p [%][a)]	M_n[b)] [kg mol^{-1}]	$Đ$
1	1	Pd/Pt-Bu$_3$, 5%	Na$_2$CO$_3$/THF	RT	4	95	9.2	1.3
2	1	Pd/Pt-Bu$_3$, 1%	Na$_2$CO$_3$/THF	RT	5	79	42.3	1.4
3	1	Pd/Pt-Bu$_3$, 0.2%	Na$_2$CO$_3$/THF	RT	24	47	76.4	2.0
4	2 + 3	Pd/Pt-Bu$_3$, 5%	Na$_2$CO$_3$/THF	RT	24	93	9.2	2.1
5	2 + 3	Pd/Pt-Bu$_3$, 1%	Na$_2$CO$_3$/THF	RT	24	41	2.7	-
6	1	Pd/Pt-Bu$_3$, 1%	Na$_2$CO$_3$/THF	70	10	71	19.1	1.8
7	2 + 3	Pd/Pt-Bu$_3$, 1%	Na$_2$CO$_3$/THF	70	10	55	<2	–
8	1	Pd/Pt-Bu$_3$, 1%	Na$_2$CO$_3$/Tol/aliquat336	RT-110	24	0	no polymer	–
9	2 + 3	Pd(PPh$_3$)$_4$, 1%	Na$_2$CO$_3$/Tol/aliquat336	RT	10	85	0.8	–
10	2 + 3	Pd(PPh$_3$)$_4$, 1%	Na$_2$CO$_3$/Tol/aliquat336	110	10	40	3.8	2.2
11	1	Pd(PPh$_3$)$_4$, 1%	Et$_4$NOH/THF	70	10	85	4.9	1.9
12	2 + 3	Pd(PPh$_3$)$_4$, 1%	Et$_4$NOH/THF	70	1	80	5.8	2.2
13	1	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	70	1	85	23.5	1.7
14	2 + 3	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	70	1	65	3.6	2.1
15	1	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	RT	1	>95	34.8	1.2
16	2 + 3	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	RT	2	>95	25.9	2.1
17	4 + 5	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	RT	1	>95	11.0	1.2
18	6 + 7	Pd/Pt-Bu$_3$, 1%	Et$_4$NOH/THF	RT	1	>95	20.8	2.05
19	6 + 7	Pd(PPh$_3$)$_4$, 1%	Na$_2$CO$_3$/THF	70	24	>50	<2	–
20	6 + 7	Pd(Po-Tol$_3$)$_3$,1%	Et$_4$NOH/THF	70	24	>50	<1.8	–

[a)]After washing of the reaction product with methanol; [b)]GPC, polystyrene calibration.

As seen from Table 1, only at the highest used catalyst loading of 5 mol% (entry 4), a polymer with a reasonable molecular weight of about 9000 g mol^{-1} was formed, whereas the formation of short oligomers with $M_n < 3000$ g mol^{-1} and monomer conversion below 40% was observed at more practical catalyst loadings, such as in the presence of 1 mol% of Pd/PtBu$_3$ (entry 5). Increase of the polymerization temperature up to the boiling point of THF not only did not improve the polymerization performance, but led to its degradation. For the AB-route, it caused a twofold decrease of the molecular weight (entry 6), whereas the degradation is more pronounced for the AA+BB route and only oligomers with $M_n < 3000$ g mol^{-1} were obtained at elevated temperature (entry 7). Comparison of the kinetics of Pd/Pt-Bu$_3$-catalyzed AB- and AA+BB-Suzuki polycondensations (Turnover frequency (TOF) = 0.27 and 0.01 s^{-1}, respectively) shows that AB-route proceeds an order of magnitude faster than the AA+BB-route (**Figure 2**).

Since the use of Pd/Pt-Bu$_3$ as the catalyst in a combination with Na$_2$CO$_3$ and THF/water as base and solvent mixture, respectively, worked improperly at practical catalyst loadings for AA+BB polycondensation, other conditions were studied. First, we studied the polymerization carried out at “typical” step-growth SPC conditions, which is the use of Pd(PPh$_3$)$_4$ and Aliquat 336 as the coupling and phase-transfer catalyst, respectively, Na$_2$CO$_3$ as the base, in toluene/water mixture. These conditions turned out to be ineffective to produce any polymer from the AB monomer in a broad temperature range (Table 1, entry 8). For the AA+BB monomers, the polymerization at RT

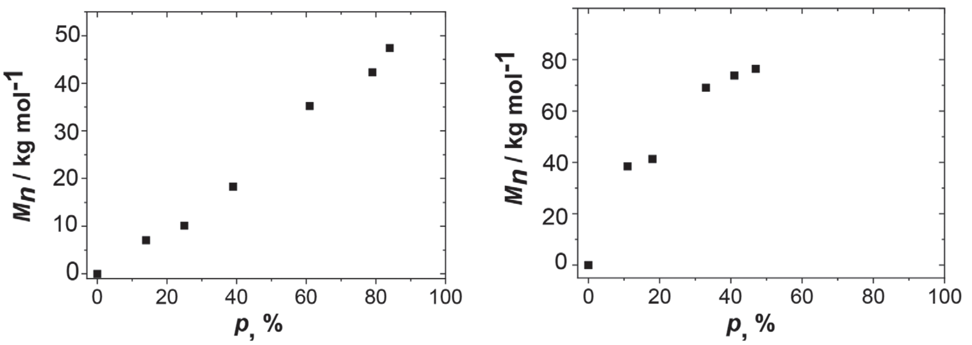


Figure 1. Number average molecular weight versus monomer conversion p plot for the AB-type Suzuki polycondensation performed at room temperature with [**1**]/[Pd/Pt-Bu$_3$] ratio of a) 100 and b) 500 (for ratio 20, see Figure S1, Supporting Information).

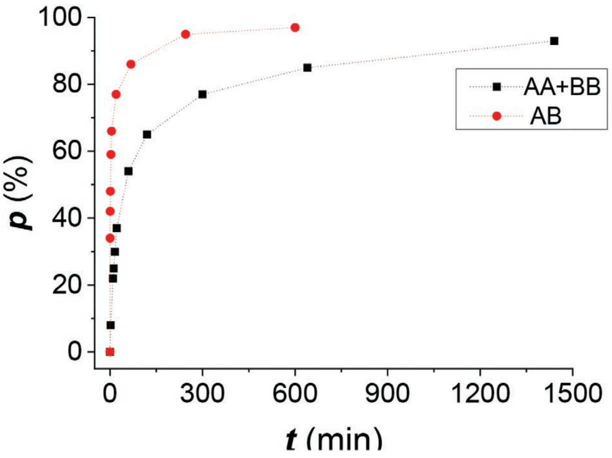


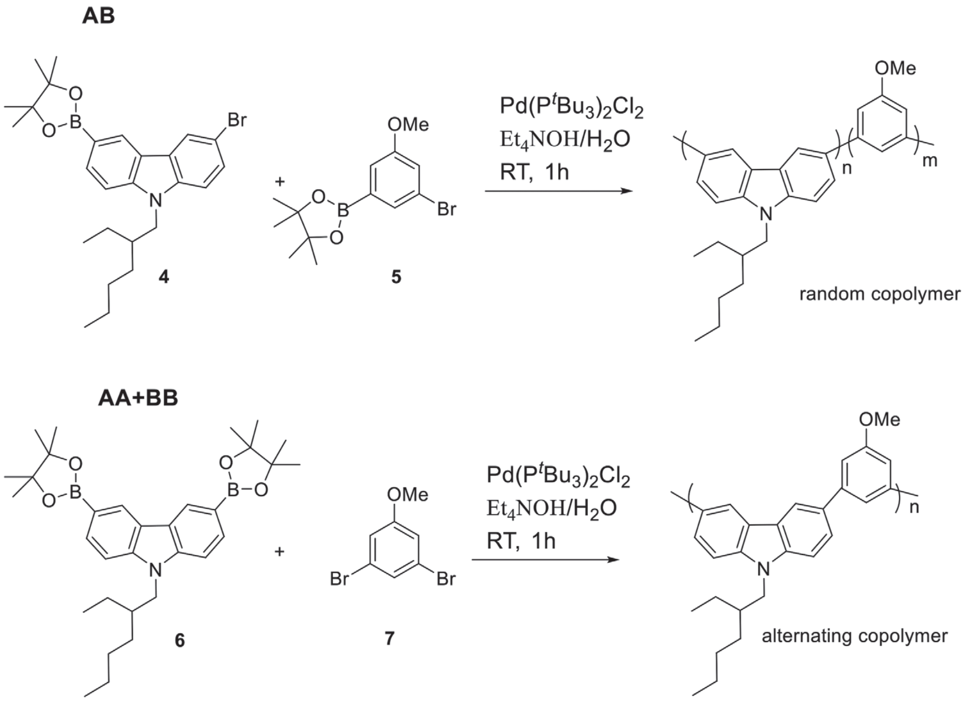
Figure 2. Comparison of the kinetics (monomer conversion on polymerization time) for AA+BB (black line) versus AB (red line) Suzuki polycondensation routes performed at the same [monomer] = 0.03 M and [Pd] = 1.5×10^{-3} M (feed ratio 20/1): $\mathrm{TOF}_{\mathrm{initial\_AB}}/\mathrm{TOF}_{\mathrm{initial\_AA+BB}} = 27$ (for other feed ratios see Figures S2 and S3, Supporting Information).

also failed, but moderate molecular weight PF2/6 in a 3–8 kg mol^{-1} range was obtained at reflux (Table 1, entries 9 and 10).

In the next step, we verified the use of an organic base, tetraethylammonium hydroxide (Et_4NOH), which allows to carry out the polymerization at homogeneous conditions.[17] Previously, the use of Et_4NOH in combination with $Pd[P(p\text{-Tol})_3]_3$ allowed a slight improvement of MW of poly(m-phenylene)s.[12]

As seen from Table 1 (entries 11 and 12), only moderate molecular weight polymers were obtained when AB and AA+BB monomers were polymerized in the presence of $Pd(PPh_3)_4$ and Et_4NOH at 110 °C (M_n = 4.9 and 5.8 kg mol^{-1}, respectively). In contrast, the use of a typical chain-growth catalyst Pd/P*t*-Bu$_3$ in combination with Et_4NOH was remarkably successful for both types of polymerizations. Particularly, PF2/6 with M_n close to theoretical value, was obtained fast (in 1 h) and in a high yield by polymerization of the AB monomer. This is a better performance than the one obtained with the use of Na_2CO_3 under biphasic conditions (Table 1, entry 2). Furthermore, while the biphasic conditions failed to polymerize AA+BB monomers, the use of catalyst Pd/P*t*-Bu$_3$ and Et_4NOH under homogeneous conditions at room temperature resulted in a relatively high MW PF2/6 with M_n = 25.9 kg mol^{-1} (Table 1, entry 16). It is noteworthy that these conditions work especially well at room temperature, whereas elevation of the temperature has a detrimental effect, especially in the case of AA+BB polycondensation (entry 14). These experiments highlight a difference in the temperature behavior of the two catalysts: the only case when SPC benefits from the temperature increase is the AA+BB polycondensation in the presence of "step-growth" catalysts, such as $Pd(PPh_3)_4$. In other cases (in all cases with Pd/P*t*-Bu$_3$ and the AB-monomer, with $Pd(PPh_3)_4$), the temperature increase is not favorable for the polymerization performance.

The knowledge obtained with model monomers was applied to the synthesis of a carbazole-based copolymer (**Scheme 2**), designed for the use as a hole conductor in solution-processed organic light emitting diodes (OLEDs). Regarding the polymer design, multiple kinks were introduced into the copolymer structure by copolymerizing 3,6-substituted carbazole-based monomer and meta-substituted benzene to enable high energy triplet states,[18] which is a necessary prerequisite for hole conductors to be suitable for applications in OLEDs. An iso-octyl side group in the carbazole imparts the polymer solubility, whereas labile ether groups in benzene rings provide the possibility for introduction of other functionalities



Scheme 2. Preparation of carbazole-based copolymers.

(e.g., cross-linkable, light-emitting, or electron-conducting groups). These design features make the polymer a versatile material for solution-processable devices.

The AB and AA+BB monomers (Scheme 2) were prepared as shown in Supporting Information. As the synthesis of the monomer having two boronic leaving groups involves a bis-lithiation step and because the corresponding bis-lithiated intermediate turned to be unstable, these leaving groups were introduced into the carbazole structure. Correspondingly, the anisole derivative acted as the dibromo-monomer. The corresponding monomers were purified by column chromatography to get 99% purities (NMR spectra of the monomers are exemplified in Figures S9 and S10, Supporting Information). Polymerizations were performed at best conditions, that is, by using Pd/P*t*-Bu$_3$ as the catalyst (1 mol%), Et$_4$NOH as the base in toluene, at RT for 1 h. A random copolymer with $M_n = 11.1$ kg mol^{-1} and PDI = 1.2 (after washing with acetone) was obtained upon copolymerization of the two AB-monomers 4 and 5. Even higher molecular weight polymer ($M_n = 20.8$ kg mol^{-1}, PDI = 2.05) was obtained in the case of the AA+BB copolymerization of 6 and 7. As expected, the latter method resulted in a copolymer with a perfectly alternating structure, as it follows from the relatively simple and easily interpretable NMR spectrum (Figure S4, Supporting Information). In contrast, the AB-copolymerization route, $A_1B_1+A_2B_2$, to mark it more precisely, gave a random copolymer, which is consistent with more broadened and complex NMR spectrum, due to the presence of **44** and **55** monomer diades (Figure S5, Supporting Information). In fact, the obtained random and alternating copolymers are different materials with respect to their structure, which might have effects on their optoelectronic properties.

For comparison, "standard" step-growth Suzuki polymerization conditions[3] were also tested. As seen from Table 1, entries 17 and 18, only low molecular products were obtained in these cases, similarly as in the model experiments discussed above. It is important to emphasize that all copolymerizations were conducted with relatively large quantities of monomers **4–7** (≈2 g) having high enough purity (>99%). Furthermore, the same monomer batches were utilized in all experiments so that the low molar masses in polymerizations shown in Table 1, entries 17 and 18, can be attributed solely to inferior polymerization conditions.

Further derivatization of the polymers 15 and 16 into cross-linkable hole transporting materials was already accomplished in our lab. Their properties and application in optoelectronic devices will be published elsewhere.

The conducted experiments can be summed up as follows.

1) Under Pd/P*t*-Bu$_3$ catalyst condition, the AB-route compared to the AA+BB ones proceeds an order of magnitude faster, which can be explained in terms of a faster *intra*molecular versus *inter*molecular catalyst transfer process. Indeed, it is reasonable to assume that 1D-restricted "sliding" of the catalyst along a few double bonds of the fluorene monomer upon the *intra*molecular transfer is an entropically more favored process than the transfer of the catalyst from one molecule to another through solution. Hence, as the AB-polymerization involves only *intra*molecular catalyst transfers, whereas the AA+BB one involves equal amounts of intra- and intermolecular steps (Schemes S1 and S2, Supporting Information), the AB-polymerization proceeds faster than the AA+BB one.
2) The lower turnover number for the AA+BB polycondensation compared to AB can be explained in terms of deactivation of the catalyst, occurring predominantly upon the *inter*molecular transfer. Indeed, as Pd(0) catalysts formed after the RE step are highly reactive due to their unsaturated coordination, they are prone to undergo deactivation reactions with various chemicals (base, water, reaction by-products, impurities) present in the reaction mixture. In contrast, the *intra*molecular transfer seems to be a "safer" way for the catalyst transfer because in this case Pd(0) species are coordinated with polymer chains and in such a way sterically protected from potential catalyst poisons.
3) In contrast to a previously studied AB-Negishi polycondensation, where each Pd/P*t*-Bu$_3$ catalyst molecule was able to polymerize many thousands of chains, in the AB-Suzuki polycondensation, each catalyst species polymerizes only a single chain, which accounts to the controlled character of the latter polymerization. We again attribute this phenomenon to the more "hazardous" conditions of the Suzuki polycondensation, that is, to the presence of water and bases, which deactivate the catalysts soon after they are released from a grown chain. Thus, in general undesirable catalyst deactivation reactions play here a positive role, enabling control over the polymer molecular weight.
4) The typical "chain-growth catalyst" Pd/P*t*-Bu$_3$ significantly outperforms conventional "step-growth catalysts" such as Pd(PPh$_3$)$_4$ and Pd(P*o*-Tol$_3$)$_3$, in Suzuki polycondensation of AB-monomers. Furthermore, Pd/P*t*-Bu$_3$ in a combination with Et$_4$NOH, works better than conventional catalysts in the polymerization of AA+BB monomers, although in this case its advantage is less pronounced. The difference in the catalysts performance is explained by the in general higher reactivity of Pd/P*t*-Bu$_3$ in the Suzuki catalytic cycle, which has no drawbacks for the AB-route, where a rapid and safe intramolecular catalyst transfer is involved. In contrast, the high reactivity of Pd/P*t*-Bu$_3$ may be disadvantage for the AA+BB route, because the relatively unstable Pd/P*t*-Bu$_3$ eliminated at the inter-molecular catalyst transfer is exposed to a reactive heterogeneous environment, containing water and Na$_2$CO$_3$, or similar bases. However, this drawback can be overcame for the reaction under homogeneous conditions in the presence of an organic base such as Et$_4$NOH, which favors efficient operation of the Pd/P*t*-Bu$_3$ catalyst. This conclusion is valid for, at least, some of the substituted arylenes (e.g., 2,7-fluorenes, 3,6-carbazoles and meta-phenylenes); however, it is likely to have a broader applicability. The advantage of Pd/P*t*-Bu$_3$ compared to other catalysts were exemplified in the synthesis of practically important copolymers designed for use in solution-processed OLEDs.

Experimental Section

General Procedure for AB-Type Suzuki Polymerization: In a two-neck round-bottom flask, 1 (595 mg, 1 mmol) was placed and vacuum was applied, which was then canceled with argon. THF (stabilizer free, 25 mL) and 20% aqueous solution of Et$_4$NOH (2 mL) were added, and the mixture was stirred at room temperature. The polymerization was initiated by adding a solution of Pd(CH$_3$CN)$_2$Cl$_2$ and PtBu$_3$ (0.1 mol% based on Pd) in THF (4 mL). After overnight stirring, the organic phase was separated and poured into a mixture of 2 mol L^{-1} hydrochloric acid (10 mL) and methanol (80 mL) with stirring. The precipitate was collected by filtration, washed with water and methanol, and dried under reduced pressure overnight to give PF2/6 as a yellow powder.

General Procedure for AA+BB-Type Suzuki Polymerization: In a two-neck round-bottom flask, monomers 2 (595 mg, 1 mmol) and 3 were placed and vacuum was applied, which was then canceled with argon. THF (stabilizer free, 25 mL) and 20% aqueous solution of Et_4NOH (2 mL) were added, and the mixture was stirred at room temperature. The polymerization was initiated by adding a solution of $Pd(CH_3CN)_2Cl_2$ and P*t*Bu$_3$ (0.1 mol% based on Pd) in THF (4 mL). After overnight stirring, the organic phase was separated and poured into a mixture of 2 mol L^{-1} hydrochloric acid (10 mL) and methanol (80 mL) with stirring. The precipitate was collected by filtration, washed with water and methanol, and dried under reduced pressure overnight to give PF2/6 as a yellow powder.

Polymerization Behavior: In order to monitor the polymerization behavior, the polymerization was performed similarly to the above-described general procedure. To analyze the conversion of the monomers and M_n and M_w/M_n values, small aliquots (300 µL) of reaction mixtures were sampled at different polymerization times (Table S1, Supporting Information). The aliquots were quenched with 2 mol L^{-1} hydrochloric acid solution in methanol, diluted by water, extracted with CH_2Cl_2 and analyzed by GPC and ^{1}H NMR.

Further experimental details on instrumentation, monomer, and polymer synthesis and their characterization can be found in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

conjugated polymers, palladium catalysts, Suzuki polycondensation

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[1] P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009.
[2] B. Carsten, F. He, H. J. Son, Tao Xu, L. Yu, *Chem. Rev.* **2011**, *111*, 1493.
[3] a) J. Sakamoto, M. Rehahn, G. Wegner, A. D. Schlüter. *Macromol. Rapid Commun.* **2009**, *30*, 653; b) R.-D. Rusu, A. D. Schlüter. *RSC Adv.* **2014**, *4*, 57026; c) J. Liu, Q. Pei. *Macromolecules* **2010**, *43*, 9608; d) X. Li, J. Guo, L. Yang, M. Chao, L. Zheng, Z. Ma, Y. Hu, Y. Zhao, H. Chen, Y. Liu. *Front. Chem.* **2019**, *7*, 362. e) Y.-H. Lin, K. A. Smith, C. N. Kempfa, R. Verduzco. *Polym. Chem.* **2013**, *4*, 229.
[4] a) A. Yokoyama, H. Suzuki, Y. Kubota, K. Ohuchi, H. Higashimura, T. Yokozawa. *J. Am. Chem. Soc.* **2007**, *129*, 7236. b) E. Elmalem, A. Kiriy, W. T. S. Huck. *Macromolecules* **2011**, *44*, 9057.
[5] R. Kandre, K. Feldman, H. E. H. Meijer, P. Smith, A. D. Schlüter. *Angew. Chem., Int. Ed.* **2007**, *46*, 4956.
[6] J. Murage, J. W. Eddy, J. R. Zimbalist, T. B. McIntyre, Z. R. Wagner, F. E. Goodson. *Macromolecules* **2008**, *41*, 7330.
[7] B. Hohl, L. Bertschi, X. Zhang, A. D. Schlüter, J. Sakamoto. *Macromolecules* **2012**, *45*, 5418.
[8] a) H. K. H. Lee, Z. Li, I. Constantinou, F. So, S. W. Tsang, S. K. So. *Adv. Energy Mater.* **2014**, *4*, 1400768; b) J. Li, Y. Zhao, H. S. Tan, Y. L. Guo, C. A. Di, G. Yu, Y. Q. Liu, M. Lin, S. H. Lim, Y. Zhou, H. Su, B. S. Ong. *Sci. Rep.* **2012**, *2*, 754; c) H. N. Tsao, D. M. Cho, I. Park, M. R. Hansen, A. Mavrinskiy, D. Y. Yoon, R. Graf, W. Pisula, H. W. Spiess, K. Müllen, *J. Am. Chem. Soc.* **2011**, *133*, 2605.
[9] a) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202; b) T. Yokozawa, A. Yokoyama. *Chem. Rev.* **2009**, *109*, 5595; c) V. Senkovskyy, M. Sommer. *Macromol. Rapid Commun.* **2011**, *32*, 1503; d) K. Okamoto, C. K. Luscombe, *Polym. Chem.* **2011**, *2*, 2424; e) E. L. Lanni, A. McNeil, *J. Am. Chem. Soc.* **2009**, *131*, 16573.
[10] R. Martin, S. L. Buchwald. *Acc. Chem. Res.* **2008**, *41*, 1461.
[11] a) A. F. Littke, G. C. Fu. *Angew. Chem.* **1998**, *110*, 3586; b) *Angew. Chem., Int. Ed.* **1998**, *37*, 3387; c) M. R. Netherton, G. C. Fu, *Org. Lett.* **2001**, *3*, 4295; d) N. Kudo, M. Perseghini, G. C. Fu, *Angew. Chem.* **2006**, *118*, 1304; e) *Angew. Chem., Int. Ed.* **2006**, *45*, 1282; f) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555.
[12] B. Hohl, L. Bertschi, X. Zhang, A. D. Schlüter, J. Sakamoto. *Macromolecules* **2012**, *45*, 5418.
[13] N. E. Huddleston, S. K. Sontag, J. Bilbrey, G. Sheppard, J. Locklin. *Macromol. Rapid Commun.* **2012**, *33*, 2115.
[14] As an example of a simple and convenient protocol, which became a popular polymerization method “for everyone,” read: K. Matyjaszewski, H. Dong, W. Jakubowski, J. Pietrasik, A. Kusumo, *Langmuir* **2007**, *23*, 4528.
[15] R. Tkachov, V. Senkovskyy, T. Beryozkina, K. Boyko, V. Bakulev, A. Lederer, Karin Sahre, B. Voit, A. Kiriy. *Angew. Chem., Int. Ed.* **2014**, *53*, 2402.
[16] B. Deffner, A. D. Schlüter. *Polym. Chem.* **2015**, *6*, 7833.
[17] a) B. Zhang, X. Hu, M. Wang, H. Xiao, X. Gong, W. Yang, Y. Cao. *New J. Chem.* **2012**, *36*, 2042. b) J. Bouffard, T. M. Swager. *Macromolecules* **2008**, *41*, 5559.
[18] A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel, K. Brunner. *J. Am. Chem. Soc.* **2004**, *126*, 7718.