Catalyst-Transfer Polycondensation

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Palladium-Catalyzed Chain-Growth Polycondensation of AB-type Monomers: High Catalyst Turnover and Polymerization Rates**

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Abstract: *Chain-growth catalyst-transfer polycondensations of AB-type monomers is a new and rapidly developing tool for the preparation of well-defined π-conjugated (semiconducting) polymers for various optoelectronic applications. Herein, we report the Pd/PtBu$_3$-catalyzed Negishi chain-growth polycondensation of AB-type monomers, which proceeds with unprecedented TONs of above 100000 and TOFs of up to 280 s^{-1}. In contrast, related AA/BB-type step-growth polycondensation proceeds with two orders of magnitude lower TONs and TOFs. A similar trend was observed in Suzuki-type polycondensation. The key impact of the intramolecular (vs. intermolecular) catalyst-transfer process on both polymerization kinetics and catalyst lifetime has been revealed.*

π-Conjugated (semiconducting) polymers have become an important class of materials for applications in polymer solar cells, field-effect transistors, and light emitting diodes.[1] π-Conjugated polymers are generally produced by step-growth polymerizations, most often by Pd-catalyzed Stille[2] and Suzuki[3] polycondensations with the so-called AA/BB approach.[4] π-Conjugated polymers synthesized in such a way frequently suffer from a low degree of control over molecular weight (MW) which is undesirable for optoelectronic applications. Another drawback of step-growth Stille and Suzuki polycondensations is that they are relatively slow processes because of the moderate nucleophilicity of tin- and boron-organics. With these methods, synthesis of high MW polymers (which are especially attractive for applications)[5] usually requires long reaction times, high temperatures, and high loadings of expensive Pd catalysts.[2] The formation of toxic byproducts is another drawback inherent to Stille polycondensation. On the other hand, Negishi type polycondensation, which utilizes non-toxic and strongly nucleophilic zinc-organic-based monomers, is a promising technique for industrial-scale production.[6] Impressive progress was achieved in the last decade in the development of new, more efficient Pd catalysts for cross-couplings of small molecules.[6] Particularly, it was demonstrated that the use of 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] Turnover numbers (TONs)[8] above 100000 where demonstrated in Suzuki, Negishi, and Heck cross-couplings, making them attractive for commercial applications.[9] Surprisingly, mechanistically related polycondensations underwent little improvement since their discovery.[2,3]

Chain-growth catalyst-transfer polycondensations of AB-type monomers is a new and rapidly developing alternative for the preparation of well-defined conjugated homo-, gradient-, and block-copolymers.[10] Unlike the situation with step-growth polycondensations, promising results were achieved in chain-growth polycondensations initiated by new-generation catalysts.[10–12] Particularly, it was shown that Pd/P*t*Bu$_3$ is an efficient initiator for chain-growth Suzuki polycondensation.[11] Very recently, Pd/P*t*Bu$_3$-based catalysts were utilized in Kumada[12] and Stille[13] surface-initiated polymerizations, both reactions involved AB-type monomers polymerized in a chain-growth manner. On the other hand, previous work that compared performances of different catalysts in the step-growth Suzuki polycondensation of AA/BB monomers did not identify the clear advantages of new-generation ligands compared to traditional ones.[14] Hence, a comparison of AB- versus AA/BB-polycondensations with the same catalyst was an actual task. Herein we compare the performances of AB- and AA/BB-type polycondensations of zinc-organic- and boron-organic-based monomers (Negishi and Suzuki cross-coupling polycondensations, respectively). We found that, for both polycondensation types, the AB-approach is much more efficient in terms of the polymerization rate and catalyst lifetime, due to a fundamental difference in the polymerization mechanisms.

Fluorene-based AB-type monomers **1a** and **1b** were prepared by selective monolithiation of dibromo-fluorene **2** followed by exchange of Li onto ZnCl or MgCl counterions, respectively (Scheme S1). The monolithiation was performed under cryogenic conditions and with some excess of **2** to minimize the amount of the bismetalated product **3**.[15] For most polymerizations, catalyst **4**, prepared by mixing Pd(CH$_3$CN)$_2$Cl$_2$ and P*t*Bu$_3$ (1 equiv each) was used. [Pd]/

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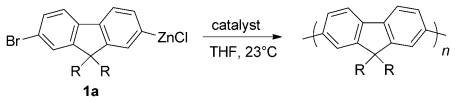
Table 1: Results of AB-type polymerization of **1a**[a]



Entry	[**1a**]/[**cat**]	*t*	*P*[g] [%]	M_n[h] [kgmol^{-1}]	*TON*[j]
1[b]	1×10^3	20 s	89	48.3	897
2[b]	1×10^4	1 h	90	26.3	9133
3[b]	2×10^4	1 h	90	25.8	18300
4[b]	1×10^5	20 h	70	22.3	71270
5[b]	5×10^5	20 h	40	12.5	206200
6[b]	1×10^4	7 s	18	5.3	1930
7[b]	1×10^4	30 s	42	7.8	4410
8[b]	1×10^4	100 s	69	11.2	7140
9[b]	1×10^4	680 s	87	24.8	8600
10[b]	1×10^4	2 h	90	49.8	9000
11[c]	2×10^4	20 h	88	28.0	17850
12[d]	2×10^4	20 h	89	24.1	18100
13[e]	2×10^4	20 h	59	4.6	12800
14[f]	2×10^4	20 h	4	0.85	2500

[a] Initial [**1a**] = 0.1 M; see Table S1 for all polymerization results. [b] Catalyst = $Pd(CH_3CN)_2Cl_2/PtBu_3$ (**4**). [c] Catalyst = $[Pd(PtBu_3)_2]$. [d] Catalyst = [Ph-Pd($PtBu_3$)-Br]. [e] Catalyst = $[Pd(PPh_3)_4]$. [f] Catalyst = $[Ni(dppp)Cl_2]$. [g] *P* = monomer conversion as determined by GPC. [h] M_w values are about twice larger, See Table S1. [j] For a definition of TON see Refs. [7] and [8].

$[PtBu_3] = 1{:}1$ was intuitively chosen to facilitate the formation of coordination-unsaturated Pd/$PtBu_3$ species, as they were demonstrated to have the highest catalytic activity.[16] For a comparison, other Pd and Ni catalysts were also tested. As it follows from the literature, typical loadings of Pd catalysts in Suzuki and Stille polymerizations lie in the 2–0.5 mol% range.[2,3] We found that room temperature polymerization of **1a** proceeds almost immediately, even with much lower amounts of **4**. Particularly, in the polymerization of a solution of **1a** (0.1M) with **4** (0.1 mol%), the conversion of the monomer **1a** (P_{1a}) reached ca. 90% already in 20 seconds (that is, within the time during which it was technically possible to withdraw and quench the first sample; Table 1, entry 1). Notably, the monomer conversion and MW[17] of the formed poly[2,7-(9,9-bis(2-ethylhexyl)fluorene], PF2/6, ($M_n \approx 48$, $M_w \approx 96$ kg mol^{-1}), were virtually independent of polymerization time, suggesting that the polymerization was completed in 20 seconds (Supporting Information, Table S1, entry 2). Reduction of the polymerization temperature down to −40 °C using **4** (0.5 mol%) did not lead to measurable reduction of the polymerization rate (Table S1, entry 3).

To further explore the efficiency of catalyst **4**, two series of polymerization experiments were performed with different catalyst concentrations using two independently prepared monomer batches (Tables 1 and S1). In the first series, polymerizations were performed at [**1a**]/[**4**] ratios of 1000:1, 2000:1, 5000:1, 10000:1 and 20000:1. For experimental simplicity, all polymerizations were conducted at the exceedingly large reaction time of one hour to ensure reaction completeness. All polymerizations within this series provided nearly the same P_{1a} (ca. 90%) and similar MWs of the resulting PF2/6 (Table S1, entries 4–8). From the result obtained at the 20000:1 ratio, a TON of ca. 18300 can be estimated (Table 1, entry 3). Because the first series did not show any signs of degradation of the polymerization behavior upon decrease of the catalyst concentration, the second series was performed at even lower [**1a**]/[**4**], and varied from 20000:1 to 1000000:1 (Table S1, entries 9–12). For such low catalyst loadings, MWs and P_{1a} were dependent on the [**1a**]/[**4**] ratio. The highest MW ($M_n = 53.06$, $M_w = 123.1$ kg mol^{-1}) was obtained at the 20000:1 ratio (Table S1, 9). PF2/6 with somewhat lower MW and conversion of **1a** were obtained at the 100000:1 ratio ($M_n = 22.7$, $M_w = 54.2$ kg mol^{-1}, $P_{1a} \approx 70\%$; Table 1, entry 4). This indicates that PF2/6 with satisfactory quality for optoelectronic applications can be obtained in polymerizations with down to $\delta = 10$ ppm catalyst loadings. Further decrease of the catalyst concentration down to 500000:1 and 1000000:1 led to significant degradation of the polymerization performance: low P_{1a} values of 40% and 15%, respectively, were observed and oligomeric products were formed. From the result at $\delta = 10$ ppm of **4**, the maximum achievable TON was calculated to be ca. 71270. To the best of our knowledge, such high TONs have not been previously reported in cross-coupling polycondensations.

Polymerization kinetics were monitored at [**1a**]/[**4**] = 10000:1 (Table 1 and Figure 1; see also Table S1). Even with such a low catalyst loading, the polymerization proceeded extremely fast, and P_{1a} reached 69% in 100 seconds. The monomer conversion curve was saturated at a value of 80–90% within 4–11 min (Figure 2). Relatively high MW PF2/6 was formed early in the polymerization (e.g., $M_n = 7.8$ kg mol^{-1}, $P_{1a} = 42\%$). This result demonstrates that the chain-growth mechanism (i.e., one-by-one addition of mono-

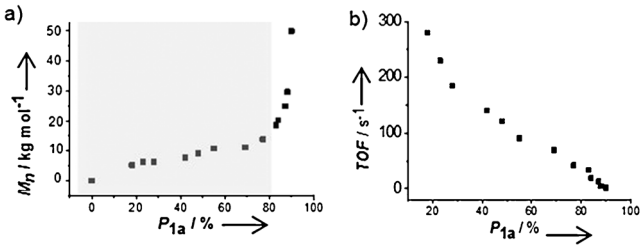


Figure 1. (a) M_n versus P_{1a} plot for Pd/$PtBu_3$-catalyzed polycondensation of **1a** ([**1a**]/[**4**] = 10000:1; [**1a**]$_0$ = 0.1 M); chain-growth stage (grey zone), step-growth stage (colorless zone). (b) TOF versus P_{1a} plot.

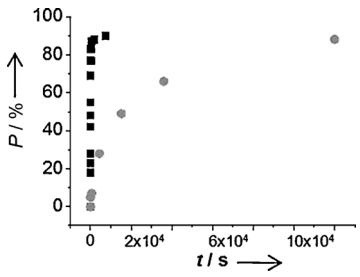


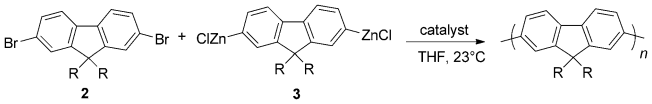
Figure 2. Monomer conversion versus time plot for: **1a** polymerized at [**1a**]/[**4**] = 10000:1 (■) and **2** + **3** monomers polymerized at [**2+3**]/[**4**] = 1000:1 (●).

mers to the initiator) is the dominating pathway at the initial polymerization stage. However, the performance is not a living polymerization, because 1) the DP of resulting PF2/6 cannot be predicted from the [**1a**]/[**4**] ratio and 2) polydispersities indexes (PDI = M_w/M_n) are rather high (>2). In living processes, every initiator species derives only a single chain. However, here every Pd/P*t*Bu$_3$ species polymerizes many PF2/6 chains (e.g., <1000 chains in the experiment at the $\delta = 10$ ppm of **4**). It is noteworthy that the MW of PF2/6 continued to grow when **1a** was fully consumed (Table 1, entry 9 vs. 10, and Figure 1a). This suggests that shorter chains formed in the chain-growth process with $M_n \approx 10\ kg\,mol^{-1}$ underwent further step-growth coupling up to $M_n \approx 50\ kg\,mol^{-1}$. The turnover frequency (TOF), defined as the number of catalyst turnovers per unit of time, is an important characteristic of the catalytic activity. In this work, TOFs were estimated for different polymerization times in reactions conducted at a 10000:1 ratio. TOFs in the 280–90 s^{-1} range were observed for $P_{\mathbf{1a}}$ values in the 18–48% range (Figure 1b). These are the highest TOFs reported for transition-metal-catalyzed cross-coupling polycondesations.

We wanted to understand whether or not the observed extremely high catalytic activity is a unique feature of the particular catalyst used (mixture of Pd(CH$_3$CN)$_2$Cl$_2$ and P*t*Bu$_3$). To address this question, polymerizations were conducted in the presence of $\delta = 50$ ppm of 1) **4**, 2) [Pd$_2$dba$_3$]/P*t*Bu$_3$ (1:2), 3) [Pd(P*t*Bu$_3$)$_2$], 4) [Ph-Pd(P*t*Bu$_3$)-Br], 5) [Pd(PPh$_3$)$_4$], 6) [Ni(dppp)Cl$_2$], and 7) [Ni(dppe)Cl$_2$] with overnight stirring using the same batch of **1a** (Table 1, entries 11–14; see also Table S1, 28–34). All Pd catalyst precursors ligated by P*t*Bu$_3$ behaved similarly, providing $P_{\mathbf{1a}} \approx 85\%$ and PF2/6 with M_n in the 22–24 $kg\,mol^{-1}$ range. Such insensitivity of the polymerization result to the nuances of the Pd catalyst precursor structure (unless they were ligated by P*t*Bu$_3$) is not very surprising in light of the extremely high TONs observed. Indeed, variation in the catalyst precursor structure may be important only for the very first catalytic cycle, the contribution of which to the overage kinetics is negligibly small, if TONs are large values. The Mg-containing monomer **1b** polymerized gave worse results than its Zn-counterpart in the presence of $\delta = 50$ ppm of **4** (Table S1, 26). In this experiment, PF2/6 with much lower $M_n = 8.3\ kg\,mol^{-1}$ was formed along with a modest $P_{\mathbf{1a}} = 57\%$. Hence, the Zn–organic monomer appears to be more suitable for polymerization catalyzed by Pd/P*t*Bu$_3$, although Mg–organic monomers display higher reactivity in Ni-catalyzed polycondesations.[18] Other tested catalysts show clearly worse performance. Only short oligomers were formed with the conventional [Pd(PPh$_3$)$_4$] catalyst, along with a moderate $P_{\mathbf{1a}}$ (Table 1, entry 13). Interestingly, Ni catalysts [Ni(dppp)Cl$_2$ and Ni(dppe)Cl$_2$] were completely inactive at $\delta = 50$ ppm. At normal concentrations of Ni(dppp)Cl$_2$ (1%) polymerization proceeded, but relatively slowly ($M_n < 8\ kg\,mol^{-1}$ was reached in 15 min).[19]

It is now interesting to compare performances of polycondensations of AB- versus AA/BB-type monomers having the same functionality. This study should reveal an origin of the high AB-type polymerization efficiency observed in this work: whether it comes solely from the high catalytic activity of Pd/P*t*Bu$_3$ (in this case, similar efficiencies of the two polymerizations are expected), or it originates from efficiency of the catalyst-transfer process inherent only to the chain-growth polycondensation of AB-monomers. To this end, bismetalated AA-type monomer **3** was cleanly prepared by the treatment of **2** with 2 equivalents of BuLi followed by addition of ZnCl$_2$. NMR and GC analysis of the mixture quenched with water reveal the formation of the corresponding alkyl fluorene as a single product. Thus-prepared AA-type monomer **3** was combined with dibromide **2** (here acting as the BB-monomer) and polymerized at room temperature for 20 h at different [**2+3**]/[Pd/P*t*Bu$_3$] ratios (Tables 2 and S1).

Table 2: Results of AA/BB-polymerization of **2** + **3**; initial [**2+3**] = 0.1 M.[a]



2 **3**

Entry	[**2+3**]/[**4**]	*t*	*P*[g] [%]	M_n [kg mol^{-1}]	*TON*[j]
1	1×10^2	20 h	89	7.4	850
2	2×10^3	20 h	89	8.1	1700
3	5×10^3	20 h	65	2.4	2600
4	1×10^3	30 s	5	0.95	40
5	1×10^3	1 h	28	1.1	200
6	1×10^3	4 h	49	7.3	500
7	1×10^3	32 h	88	8.5	800

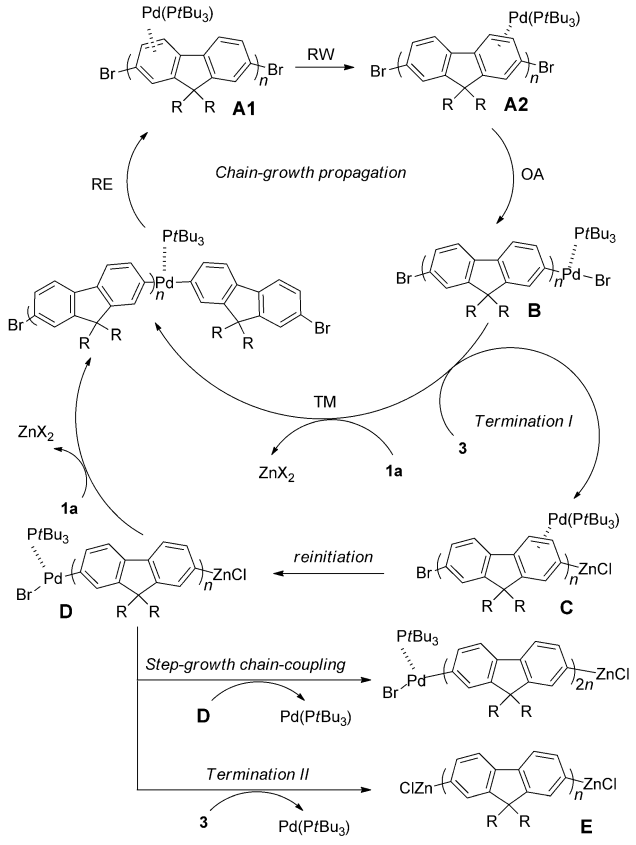
[a] See Table S1 for all polymerization results.

Experiments with ratios of 100:1, 500:1, 1000:1, and 2000:1 gave PF2/6 with similar MW ($M_n \approx 8$, $M_w \approx 16\ kg\,mol^{-1}$) and **2** + **3** conversion (P_{2+3}) of ca. 90% (Table S1, 35–38). In experiments at higher ratios, only short oligomers (if any) were formed along with low P_{2+3}. For example, polymerization at a 5000:1 ratio resulted into oligomers with $M_n = 2.4\ kg\,mol^{-1}$ and $P_{2+3} = 65\%$ (Table 2, entry 3). The maximum achievable TON was estimated from experiments with incomplete monomer consumption. Particularly, we found that the Pd catalyst makes ca. 2600 turnovers in the polymerization at a 5000:1 ratio. Although this TON is relatively high, it is two orders of magnitude smaller than TONs observed in the chain-growth polymerization of **1a**. Polymerization kinetics were monitored at [**2+3**]/[**4**] = 1000:1 (Table 2, entries 4–7, and Figures 2 and S3). Despite of the fact that catalyst concentration was ten times higher than in kinetic experiments with **1a**, the polymerization rate was much lower: only 28% of **2** + **3** was consumed in one hour, and short oligomers were formed at this point (Table 1, entries 6–8). A moderate P_{2+3} was reached in 32 h, which resulted in PF2/6 with $M_n = 8.5\ kg\,mol^{-1}$. The highest TOF = $1.6\ s^{-1}$ was observed at the initial polymerization stage and it rapidly decreased to TOF $\approx 10^{-2}\ s^{-1}$ toward the polymerization end, owing to catalyst deactivation (Figure S4). Importantly, these TOFs are more than two orders of magnitude lower than TOFs observed in the polycondensation of **1a**.

From first sight, it may seem somewhat surprising that polymerizations of related monomers (**1a** vs. **2** + **3**) in the presence of the same catalyst under otherwise the same conditions display markedly different kinetics (TOFs) and catalyst stability (TONs). Indeed, as the monomers in the two

polymerizations have the same nucleophilic and electrophilic functions, similar polymerization mechanisms might be expected. It is believed that catalytic cycles of cross-coupling polycondensations involve consecutive transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) steps. The major difference in the structure of the monomers (**1a** versus **2**+**3**) lies in the positioning of the functional groups (nucleophilic and electrophilic functions in **1a** are located in the same molecule, whereas in **2**+**3**, the functions are in different molecules). This structural difference is clearly of high importance to the polymerization mechanism, because it defines the way the eliminated Pd^0 species in the two cases transfers to the next electrophilic (C–Br) group. It is generally accepted for chain-growth polymerizations of AB-type monomers that undercoordinated metal (0) species formed in the RE step, remain associated with their own polymer chains and slide along the chains in a catalyst ring-walking (RW)[20] process until they reach terminal C–Br bonds to undergo OA (an intramolecular catalyst-transfer process). We assume that this mechanism is realized in the polymerization of **1a** (Scheme 1).

For efficient cross-couplings, the high reactivity of Pd^0 is required to provide fast OA. At the same time, too high reactivity of free Pd^0 species may facilitate their deactivation. The catalyst reactivity is clearly fortuitously balanced in the Pd/P*t*Bu$_3$-catalyzed polymerization of **1a** to provide high cross-coupling efficiency without a significant catalyst deactivation. Particularly, we suggest that the observed high catalyst stability (i.e., high TONs) is due to the intramolecular character of the catalyst transfer, which occurs through the intermediate Pd^0 π-complexes **A1**–**A2** (Scheme 1). In these complexes, Pd^0 is coordinated with the phosphine ligand and the PF2/6 chain serving as the second, temporary ligand, which suppresses catalyst deactivation.[21] During the clean chain-growth stage, each Pd/P*t*Bu$_3$ species undergoes 25–50 intramolecular catalyst-transfer steps before chain termination, which is believed to occur when the growing chain reacts with the bismetalated monomer **3** that is present in the reaction mixture as an undesirable impurity (Scheme 1).[15] In the absence of C–Br groups at the growing chain end (which is the case after the chain reacts with **3**) Pd/P*t*Bu$_3$ species are forced to transfer intermolecularly onto an appropriate arylbromide. This leads to reinitiation and growth of a new chain. The chain-termination mechanism was confirmed experimentally by performing polymerization of **1a** prepared from **2** at different [**2**]/[BuLi] ratios. We found that the polymerization proceeds even more efficiently with a large excess of dibromide **2** than at equimolar amounts of **2** and BuLi. Thus, the polymerization at a 2:1 [**2**]/[BuLi] ratio reproducibly results in PF2/6 with $M_n = 63\ kg\,mol^{-1}$, which was hardly possible in polymerizations at a 1:1 [**2**]/[BuLi] ratio (Table S1, entry 48). The lowest PDI (1.7) were obtained in experiments with a two-fold excess of **2** relative to **1a**, whereas PDIs of >2 were observed in polymerizations without a significant excess of **2**. At the same time, even a small excess of BuLi drastically decreases the MW of the resulting polymer. Thus, oligomers with DP ≈ 10 and DP ≈ 5 were formed at [**2**]/[BuLi] = 0.9 and 0.8, respectively (Table S1, entries 49 and 50), as can be expected if the chain termination and reinitiation occur after the coupling of the growing chain with **3**. To shed more light on the chain-termination mechanism, polymers obtained at different polymerization times were analyzed by MALDI-TOF. Two major types of endgroups, H/H and H/Br, were identified in PF2/6 samples; the abundance of Br/Br-PF2/6 was low in all samples. As seen from Figure S6a, H/Br-PF2/6 is the major product (62% abundance), and is formed at an early polymerization stage (Table 1, entry 7), that is, at incomplete conversion of **1a** (42%). Increase of the polymerization time led to the accumulation of H/H-PF2/6 at the expense of the H/Br-terminated product (Figure S6b,c). The high MW PF2/6 formed at long polymerization times (i.e., in 2 h, Table 1, entry 10) is mostly H/H-PF2/6 (Figure S6d). The obtained data can be rationalized as follows: The absence of Br/Br-PF2/6 suggests that the chain termination neither occurs owing to intermolecular diffusion of Pd^0 nor through the disproportionation of the propagating Br-PF2/6-Pd(P*t*Bu$_3$)-Br chains (Scheme S2), as frequently happens in Ni-catalyzed chain-growth polycondensations.[10] H/Br-terminated PF2/6 may, in principle, be formed upon hydrolysis of Br-PF2/6-Pd(P*t*Bu$_3$)-Br, which is formed in a clean chain-growth process, however its contribution is negligibly small because of extremely low Pd catalyst loadings (0.01%). Instead, H/Br-PF2/6 reflects the primary chain-termination product Br-PF2/6-ZnCl formed through the coupling of Br-PF2/6-Pd(P*t*Bu$_3$)-Br (**B**) with bismetalated monomer **3**. The thus-formed Br-



Scheme 1. Mechanism of the chain-growth intramolecular catalyst-transfer polycondensation of AB-type monomer **1a**.

PF2/6-ZnCl (**C**) can further participate in the chain-growth polymerization, after Pd^0 species eliminated in the chain-termination step oxidatively add to the C–Br present at the end opposite to the ZnCl end (in the same or a different chain) to form **D**. Intermediates **D** can couple with each other, which corresponds to the second polymerization stage when the increase of the polymer molar mass occurs after the full monomer consumption (white zone in Figure 1 a). The chain growth proceeds until **D** meets the second bismetalated monomer **3**, which results in **E** having ZnCl-groups from both sides. Hydrolysis of **E** gives H/H-PF2/6, which was fully supported by MALDI-TOF data.

The numbers of the intramolecular versus intermolecular catalyst-transfer steps in the polymerization of **1a** can be estimated as follows: In the polymerization conducted, for example, at a 100000:1 ratio, PF2/6 with $M_n = 22\ kg\,mol^{-1}$ (corresponding to a DP on the order of 50)[17] was formed at 70% monomer conversion. These data suggest that each Pd species generated $0.7 \times 100000/50 = 1400$ chains and hence, underwent 1400 intermolecular catalyst transfers, whereas the number of intramolecular transfers was 70000 (1400×50). In contrast, the number of intermolecular and intramolecular catalyst-transfer processes is equal in the step-growth polycondensation of **2** + **3** (Scheme S2). In this case, the catalytic cycle starts from the intermolecular OA of [Pd$P t$Bu$_3$] to one of the two C–Br bonds of **2**; further TM and RE steps lead to [Pd$P t$Bu$_3$] associated with the fluorene having the second C–Br bond (Scheme S3). In the next step, Pd/$P t$Bu$_3$ undergoes intramolecular OA (as it is more favored than intermolecular OA) followed by coupling with the next monomer **3**.[22,11a] According to this assumption, terfluorene (and pentafluorene) should be preferentially formed over difluorene (and tetrafluorene), which is clearly seen in GPC curves for polymerizations with low conversions of **2** + **3** (Figure S7). As such, the highest achievable TON in the step-growth polycondensation of **2** + **3** of 2600 is provided by 1300 intermolecular and 1300 intramolecular catalyst-transfer processes before catalyst deactivation. Remarkably, very rough estimations gave similar maximum numbers of the intermolecular Pd transfers for the AB- and AA + BB-polycondensations (1400 and 1300, respectively). This coincidence, together with the fact that the maximum TON in the chain-growth process is much higher than the maximum number of intermolecular transfers (70000 versus 1400) suggest that, in polycondensations (chain-growth and the step-growth), the catalyst degradation occurs predominantly during the intermolecular transfer process. This assumption does not seem surprising, as Pd/$P t$Bu$_3$ species are potentially more vulnerable to various side reactions in their free state during the intermolecular transfer than in the state in which they are protected by the conjugated chain upon intramolecular transfer.[21] On the other hand, the chain-growth polycondensation of **1a** proceeds much faster (with higher TOFs) than the step-growth polycondensation of **2** + **3**, because the intramolecular transfer (ring-walking along π-conjugated chains) proceeds much faster than the intermolecular transfer of the catalyst through the solvent. Entropy arguments may play a role here (during the intramolecular transfer, [$Pd^0 P t$Bu$_3$] is restricted by the one-dimensional conjugated chain whereas in the intermolecular process, the species diffuse in a three-dimensional space).

To verify whether or not the higher efficiency of the AB- than AA/BB-polycondensations is a general phenomenon, Pd/$P t$Bu$_3$-catalyzed Suzuki-type polycondensation of fluorene-based monomers was also studied. We found that, similar to the Negishi polycondensation case, AB-type Suzuki polycondensation proceeds about two order of magnitude faster and requires much less catalyst than the AA + BB-Suzuki polycondensation (see the Supporting Information, pages S14–S18).

In conclusion, we have found that Negishi chain-growth polycondensation of the Zn–organic AB-type monomer **1a** catalyzed by Pd complexes ligated by bulky electron-rich $P t$Bu$_3$ occurs rapidly under mild conditions at extremely low catalyst loadings (down to ppm concentrations), and leads to high molecular weight PF2/6 with MWs of up to 120 $kg\,mol^{-1}$. Such low catalyst loadings are attractive for the preparation of electronic-grade materials free from metal impurities. Unprecedentedly high turnover numbers (above 70000) and turnover frequencies of up to 280 s^{-1} were observed, which are the highest values reported in the literature for transition-metal-catalyzed cross-coupling polycondensations.[23] In contrast, the corresponding step-growth polycondensation of functionally-related AA/BB-type monomers **2** + **3** provided two orders of magnitude lower TONs and TOFs. Similar trends were observed in AB- versus AA + BB-Suzuki polycondensations. The much higher polymerization rate and longer catalyst lifetime are due to a faster and safer intramolecular (vs. intermolecular) catalyst-transfer process underlying the chain-growth mechanism. These findings are important for the design of the next generation of polycondensation catalysts.

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