Catalysts for Suzuki Polycondensation: Ionic and “Quasi-Ionic” Amphipathic Palladium Complexes with Self-Phase-Transfer Features

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Dedicated to Prof. Dr. Max Herberhold on the occasion of his 75th birthday

Suzuki polycondensation (SPC) is one of the most common ways to synthesize conjugated polarylenes polymers,[1] such as derivatives of poly(para-phenylene)[2] and poly(fluorene),[3] which are potentially active catalysts as active layers in light emitting diodes and photovoltaic devices.[4] Compared with many developments in the small molecule Suzuki coupling methodology,[5] the most recent SPC reactions still utilize only slight modifications of Schlüter’s original protocol,[6] which is based on the equally prolific small molecule Suzuki coupling reaction between an aryl halide and an aryl boronic acid,[7] often resulting in molecular weights limited to the 10^2 to 10^3 g mol⁻¹ range.[8]

Procedures used for these polymerization processes commonly employ biphasic reaction mixtures.[9] This is because the reactants and coupling products are always soluble in organic solvents, whereas inorganic bases are soluble in the water phase, which can facilitate the otherwise slow transmetalation of the boronic acid by replacing the halide in the coordination sphere of the palladium complex,[10] or by forming a more reactive boronate anion [ArB(OH)_3]⁻ with stronger nucleophilicity to the Pd center.[11] In this system, however, a chief obstacle is that the majority of organic solvents are immiscible with water, which is intensely unfavorable to the transmetalation step, because the step occurs at the interface of the two phases. The oxidative addition (O-A), usually the rate-controlling step, occurs smoothly in the organic phase, but the intermediate produced in the first step cannot contact well with the inorganic base or the boronate anion in the water phase because of its more favorable oil solubility. In particular, for the Pd^{II} intermediate contain-

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that using the hydrophilic system (or groups and phase-transfer agent) really was an effectual method to improve the polymerization as we had anticipated. However, in toluene/water systems, the molecular weight was still under 100000 g mol⁻¹ with PdCl₂(LSS-3), as the catalyst, and for Pd(LSS-3), it even showed no advantage (Table 1, entries 2 and 7).

It is speculated that the rather good hydrophilic property of the ionic sulfonated group (-SO₃Na) might contribute the water solubility of the complexes and the fact that they are hard to dissolve in weak polar organic solvents, which would inhibit the oxidative addition step and initiation of the catalytic cycle. Enlightened by the idea that the corresponding neutral acid ligands, with better lipophilicity and also good hydrophilicity, would result in the acidic hydrogen being deprotonated under the basic conditions of the polymerization,[18] we conceived that the process might be improved by replacing ionic ligands with such neutral acidic ones. Therefore, a single sulfonic acid group (-SO₃H) or carboxylic acid group (-COOH) was incorporated into the PPh₃ parent to form LS-3, LC-4, and LC-3 as amphipathic ligands. Because the neutral -SO₃H and -COOH would ionize during the polymerization, we called this type of ligands “quasi-ionic” ligands. Finally, we had a series of paired amphipathic catalysts, including Pd(II) and Pd(0) complexes, with ionic ligands: PdCl₂(LSS-3), and Pd(LSS-3)₂ and quasi-ionic ligands: PdCl₂(LS-3), and Pd(LS-3)₂, PdCl₂(LC-4)₂ and Pd(LC-4)₂, and PdCl₂(LC-3)₂ and Pd(LC-3)₂.

As shown in Table 1, the amphipathic Pd(II) complexes could be used as catalysts to obtain polymers with higher molecular weights than hydrophobic PdCl₂L₂ and PdL₄ in toluene/water systems. The Mn obtained from polymerizations with the Pd(II) quasi-ionic ligands (Table 1, entries 3–5 and Figure 1) increased even higher (Mn > 100 000 g mol⁻¹) than with the ionic ligand (Table 1, entry 2 and Figure 1) as we had speculated. The amphipathic Pd(0) complexes failed to promote polymerization in this system, presumably due to their extraordinarily good water solubility and no dissolubility in toluene, which hindered the O-A step due to the poor water compatibility of the PPh₃ parent to form LS-3, LC-4, and LC-3 as amphipathic ligands. Because the neutral -SO₃H and -COOH would ionize during the polymerization, we called this type of ligands “quasi-ionic” ligands. Finally, we had a series of paired amphipathic catalysts, including Pd(II) and Pd(0) complexes, with ionic ligands: PdCl₂(LSS-3), and Pd(LSS-3)₂ and quasi-ionic ligands: PdCl₂(LS-3), and Pd(LS-3)₂, PdCl₂(LC-4)₂ and Pd(LC-4)₂, and PdCl₂(LC-3)₂ and Pd(LC-3)₂.

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contact between the monomer and catalyst. With Pd(LC-4), a polymer product with a molecular weight of 500000 g mol\(^{-1}\) could be achieved probably due to its slight toluene solubility, which will be discussed and confirmed below.

When using these amphiphilic catalysts in the THF/water system, the best results were obtained with PdCl\(_2\)(LC-4), and Pd(LC-4), with which polymer products with molecular weights of nearly up to 600000 g mol\(^{-1}\) (Table 2, entries 4 and 9 and Figure 2) were obtained. For other amphiphilic ones, except Pd(LS-3), molecular weights were generally above 400000 g mol\(^{-1}\) (Table 2, entries 2, 3, 5, 7, and 10). Compared with only rare polymer precipitation in the toluene/water system, solid polymer product began to precipitate from the THF layer after 6 h, which might be due to the ultra-high molecular weight of the polymers and lower solubility in THF than in toluene. From the results, we presumed that the solubility of amphiphilic catalysts were improved in THF and the para-substituted hydrophilic group would further facilitate the transmetalation step. Here we also come to the conclusion that besides the rate-determining step (oxidative addition) of the catalytic cycle in the palladium-catalyzed SMC, the transmetalation step has a great influence on the process as well, which has, disappointingly, always been ignored.

We also tested this series of catalysts in homogeneous DMF/toluene systems with KF as a base (Table 3 in the Supporting Information). The new amphiphilic catalysts, with both Pd\(^{II}\) and Pd\(^0\), showed no advantage over traditional ones in the polymerization, which indicated that the achievement of high molecular weight was mainly from the dramatic improvement in the transmetalation step in micromeso- and also that these Pd complexes exhibited a special self-phase-transfer feature. The Pd\(^{II}\) intermediate produced in the oxidative addition can be anchored to the two-phase interface with the aid of the hydrophilic groups, which makes the components in the water phase react much more rapidly with it, resulting in efficient entry into the catalytic cycle.

The conclusion has been verified indirectly by the measurement of the UV/Vis spectrum in the same reactive systems as polymerization (including toluene, H\(_2\)O, K\(_2\)CO\(_3\) aq. (2m), THF, and DMF/toluene (2/1), see the Supporting Information). If there was no or very slight absorbance of some catalyst in the same solution/mixture, we could deduce that the catalyst hardly dissolved in this system. The amphiphilic catalysts had macroscopic insolubility in toluene, as shown in Figures S2a and S3a (in the Supporting Information). The Pd\(^0\) complexes except Pd(LC-4) did totally not dissolve in toluene, while all of the corresponding Pd\(^{II}\) ones could dissolve partly in it. Moreover, from the inset of Figure S2a (in the Supporting Information), the quasi-ionic Pd\(^{II}\) complexes, PdCl\(_2\)(LS-3), PdCl\(_2\)(LC-4), and PdCl\(_2\)(LC-3), showed a little better performance than the ionic PdCl\(_2\)-(LSS-3) as we had tentatively thought. PdCl\(_2\)(LSS-3) and PdCl\(_2\)(LS-3) were water soluble, and PdCl\(_2\)(LC-4) and PdCl\(_2\)(LC-3) turned out to be soluble in K\(_2\)CO\(_3\) aqueous solution (Figure S2b and c in the Supporting Information). All of the Pd\(^0\) amphiphilic complexes easily dissolved completely in water, not least in K\(_2\)CO\(_3\) aqueous solution (Figure S3b and c in the Supporting Information). It confirmed our speculation that the rather good water solubility and nearly no solubility in toluene was responsible for their disappointing activity in the toluene/water system. All amphiphilic Pd complexes showed better solubility properties in THF (Figures S2d and S3d in the Supporting Information), whereas Pd(LSS-3) was partly soluble in THF and Pd(LS-3) showed no solubility. The illustrations for solubility were consistent with the polymerization experimental results including the homogeneous DMF/toluene (2/1) system, in which all of the hydrophobic and amphiphilic catalysts dissolved completely (Figures S2e and S3e in the Supporting Information).

In summary, palladium(II) and palladium(0) complexes coordinated by phosphine ligands modified by introducing weak acidic groups on the phenyl ring are highly efficient and effective in promoting Suzuki polymerization. The amphiphilic nature of these complexes not only introduces self-phase-transfer features, but also to stabilizes low-valent metals. Ultra-high molecular weight polymers PFO (\(M_\text{n}\)) up to 600000 g mol\(^{-1}\) were achieved by using these amphiphilic palladium complexes as catalysts. Their dominant virtue relative to the classical Pd catalysts is that the complexes may accelerate the transmetalation step in the catalytic cycle, which is also the key step for synthesizing high molecular weight polymers. Considering the better solubility of the polymer product in toluene, studies concerning further improvement of the molecular weight in toluene/water systems are currently underway by introducing neutral hydrophilic groups for the balance of the water and oil solubility of the amphiphilic catalysts.
Experimental Section

Typical experimental procedure for the palladium-catalyzed Suzuki polycondensation: Toluene (8 mL) and a 2 M aqueous solution of K₂CO₃ (2 mL), or THF (8 mL) and a 2 M aqueous solution of K₂CO₃ (8 mL) were added to a mixture of monomers (1 mmol; purity > 99.7%) and catalyst (1.5 mol%) under an argon atmosphere. The reaction was stirred and refluxed for 12 h. After workup, the mixture was poured into methanol.

The resulting polymers obtained after vacuum drying were weighed as proximate volume and poured into methanol to obtain polymer fibers.

Keywords: amphiphiles · palladium · phase-transfer catalysis · polymers · Suzuki polycondensation

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Poly(9,9-dioctylfluorene) (PFO) with $M_n$ values above 100,000 g mol$^{-1}$ in a toluene/water system and $M_n$ values up to 600,000 g mol$^{-1}$ in a THF/water system has been obtained by improved Suzuki polycondensation using a new kind of amphipathic palladium catalyst with self-phase-transfer features, which could overcome the disadvantage caused by the immiscible biphasic mixture and accelerate the transmetalation step (see figure).
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