Suzuki Polycondensation toward High Molecular Weight Poly(*m*-phenylene)s: Mechanistic Insights and End-Functionalization

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Supporting Information



Open-chain poly(m-phenylene) with defined end groups

ABSTRACT: Synthesis of a poly(m-phenylene) by Suzuki polycondensation (SPC) using an AB-type *m*-phenylene monomer is reported (A and B refer to bromo and boron functional groups, respectively). Despite the attempted high molecular weight products, SPC under the conventional conditions using $Pd[P(p-Tol)_3]_3$ as catalyst gave rise to oligomeric products only. They comprise cycles and several series of open-chain poly(m-phenylene)s with various end group patterns. These patterns were caused by side reactions such as ligand scrambling. Buchwald's SPhos ligand was therefore alternatively employed for high turnover catalysis to accelerate SPC over such detrimental side reactions. This modification indeed led to the formation of high molecular weight products ~40 kDa (DP ~ 210), while oligomeric cyclic products still remained prominent. Cycle formation could, however, drastically be reduced by slow monomer addition. SPC was also performed in the presence of an excess monofunctional compound, R–A or R–B. The molecular weights of the products were found to be sensitive to the presence of R–B but not so much to R–A. This suggests a chain-growth-like mechanism as previously reported by Yokozawa et al. The modified SPC protocol was also used to demonstrate an efficient end-functionalization of the SPC products at both A and B termini with distinct chemical moieties. This revealed that the chain directionality expected from the AB monomer was largely retained when $Pd(dba)_2$ was used as palladium source for the SPC catalyst but not as for $Pd(OAc)_2$. This is presumably due to involvement of the homocoupling between phenyl boronates leading to reduction of Pd(II).

■ INTRODUCTION

Suzuki–Miyaura cross-coupling is one of the most prominent tools for aryl–aryl or aryl–vinyl bond formation in organic synthesis.^{1,2} It has also been utilized for the synthesis of polymers then being referred to as Suzuki polycondensation (SPC).^{3,4} A great variety of polyphenylenes and related polymers have been prepared by SPC in both academia and industry often aiming at applications in electroluminescent devices.⁵ In contrast to poly(*p*-phenylene) (PPP) and its derivatives, poly(*m*-phenylene) (PMP) has been much less explored. While the kinked *m*-phenylene unit disrupts the conjugation along the polymer chain,⁶ it enables the polymer to adopt numerous possible conformations ranging from the most extended zigzag to a compact helix (Figure 1). Consequently, improved solubility and processability are expected for PMP in addition to the opportunities for chain entanglement⁷ and "foldamer" formation.^{8–10} PMP can therefore be considered as promising candidate for high-performance polymeric materials with intriguing properties in addition to the expected thermal, chemical, and mechanical stabilities. For example, a high molecular weight poly(m,p-phenylene) (PMPP) was previously reported to form a tough, amorphous self-supporting film,¹¹ where effective chain entanglement is crucial.⁷ PMP is isomeric to PMPP but comprises *m*-phenylene units only. At a given molecular weight, these two polymer types can be compared in order to gain insights into how properties depend on kink density.

In the present study, we explored SPC to a PMP with high molecular weights by using an AB-type *m*-phenylene monomer

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Figure 1. Chemical structures of poly(p-phenylene) (PPP), poly(m,p-phenylene) (PMPP), and poly(m-phenylene) (PMP). In contrast to the "shape-persistent" PPP (a), rotation of the internal bonds allows PMPP (b) and PMP (c) to adopt numerous conformations including the extended zigzag (left) and a compact helix (right). Note that solubilizing side chains are omitted for clarity.

Scheme 1. SPC of AB-Type m-Phenylene Monomers 1a-c with Three Different Side Groups



(Scheme 1).¹²⁻¹⁴ SPC reported in the literature is often conducted under poorly optimized conditions. Consequently, the full potential of the method was not exploited and products are often oligomeric. Oligomer formation may sometimes be caused by poor solubility of the growing species, resulting in an early precipitation. This problem, however, has been circumvented by introducing proper side chains to confer sufficient solubility throughout polymerization.¹⁵ There is another critical issue which arises from side reactions during SPC. In organic synthesis, side reactions of Suzuki-Miyaura cross-coupling² are often considered negligible because a "small" amount of side products can easily be removed. However, in polymer synthesis, side reactions cannot be tolerated because they may create irremovable defects in the polymer and also can cause loss of end-functional groups essential for further growth. We therefore carried out an in-depth structure analysis of the products from the present SPC synthesis by matrix-assisted laser desorptionionization time-of-flight mass spectrometry (MALDI-TOF MS) in order to elucidate the nature of side reactions and to possibly suppress them by changing conditions. This changing of conditions eventually not only led to a drastic improvement of the average molecular weight of the products but also provided interesting mechanistic insights. Under the improved conditions, efficient end-capping of both bromo and boron termini of PMP

could be demonstrated, which also allowed for an inspection of the chain directionality expected from an AB monomer.¹⁶

RESULTS AND DISCUSSION

Monomer Design and SPC under Conventional Conditions. AB-type monomer 1a possesses a benzyl hydroxide protected with a tetrahydro-2*H*-pyranyl (THP) group. The reasons for selection of this particular side group are as follows: (i) mediation of good solubility of the growing species during SPC and also of the eventual products for subsequent analyses, (ii) feasibility of quantitative deprotection of the polymers for future studies, and (iii) easy detection of the individual SPC products as Na⁺ adducts by matrix-assisted laser desorptionionization time-of-flight mass spectrometry (MALDI-TOF MS) which turned out to be so powerful for identification of the product structures.

For the synthesis of monomer 1a (Scheme 2), the hydroxyl group of 3,5-dibromobenzyl alcohol (3)¹⁷ was THP-protected, followed by borylation at one of the bromo carbons via lithiation with 1 equiv of BuLi to furnish 1a. The overall yield of 1a was 67% (16 g) after recrystallization. The purity was estimated to be higher than 99.5% by high-resolution ¹H NMR (700 MHz) spectroscopy where ¹³C satellite peaks were used as internal reference.^{4c,d} Other monomers 1b and 1c (Scheme 1) were also synthesized according to similar procedures for the use in control experiments (see Supporting Information). Their structures are analogous to 1a but carry linear alkyl side groups with different chain lengths (C₄ and C₁₂).

AB monomer 1a (Scheme 1) was first subjected to SPC under the conditions previously reported: (a) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), NaHCO₃ (8 equiv) in THF-water 3:1, 70 °C for 3 days under nitrogen.¹⁸ We started with these conditions because they led to the formation of high molecular weight PMPPs in previous studies using AA/BB monomers.^{11,19} The products 2a were analyzed by gel permeation chromatography (GPC) and resulted in a bimodal elution curve positioned in a disappointingly low molar mass regime. The peak of lower molar mass (P_L) was more intense than that of the higher molar mass (P_H) . The peak maxima of P_L and P_H correspond to 1.5 and 8 kDa on polystyrene standards, respectively (Figure 2a). When the other monomers 1b and 1c were separately subjected to SPCs under similar conditions, the products (2b and 2c, respectively) likewise gave bimodal GPC curves. These results suggest that the bimodal distribution of the products is common among the three *m*-phenylene monomers irrespective of the side group difference (see Supporting Information).²⁰

Next, the conditions were modified in order to inspect any eventual impact on the molecular weight distribution of the SPC products. We first changed the base and the amount of water in order to promote the transmetalation in the catalytic cycle.² The same monomer la was thus subjected to the new SPC conditions: (b) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), CsCO₃ (1.5 equiv), water (5 equiv) in THF, and (c) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), Bu₄NOH·30H₂O (1.6 equiv) in THF. Similarly with the previous conditions, $Pd[P(p-Tol)_3]_3$ and THF were chosen as catalyst and solvent, respectively, whereas new bases which are supposed to be better soluble in THF were employed with a reduced amount of water.^{2,21} The new SPCs also gave bimodal products (Figure 2b,c) with P_H evidently larger for conditions (b) and (c) than in the previous SPC (a) and even shifted to higher molecular weights for (c), while P_{L} remained around 1.5 kDa. These results exemplify that the molecular weights can be improved by modifying conditions.

Scheme 2. Synthesis of Monomer 1a (a) and Its Purity Inspected by ¹H NMR (700 MHz) Spectroscopy (b)^a



^{*a*}The inset shows a magnified aromatic region where 13 C satellite peaks are marked (*).



Figure 2. GPC elution curves obtained from SPCs of monomer **1a** under various reaction conditions as follows: (a) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), NaHCO₃ (8 equiv) in THF–water 3:1; (b) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), CsCO₃ (1.5 equiv), water (5 equiv) in THF; and (c) $Pd[P(p-Tol)_3]_3$ (0.01 equiv), Bu₄NOH·30H₂O (1.6 equiv) in THF. The SPCs were performed at 70 °C for 3 days under nitrogen. The curves were recorded with a RI detector.

Structural Analysis of the SPC Products. The products obtained under conditions (b) were subjected to preparative

GPC to separate into two fractions I and II at the saddle point between P_H and P_L , respectively. They were then analyzed by MALDI-TOF MS, showing that P_H and P_L consist of open linear and cyclic products, respectively (see below). The mass spectrum recorded of fraction I exhibits several series of signals (Figure 3a). The signals of cyclic products are found only in the lower mass region, where P_H partially overlaps with P_L. Open linear species with various end groups are thus the predominant constituents of P_H. Notably, neither bromo nor boron end groups can be seen. They were lost during SPC due to cyclization, ligand scrambling,^{22,23} hydration,²⁴ or hydroxylation^{25,26} to give rise to the products with the end-group patterns as shown in Figure 3b. Occurrence of such reactions by necessity causes the growth to come to a halt and can account for the low molar masses resulted in. Note that the spectrum does not show any sign of P-incorporation in the middle of the chains. The fact that all detected products except cycles suffer from ligand scrambling at least at one of the two chain ends indicates that this is a major side reaction which needs to be addressed in order to achieve the high molecular weight products aimed at (see below).

The mass spectrum of fraction II confirms formation of cyclic products with various ring sizes (n = 6-25) (Figure 4a). Cycle formation is preferred in the lower mass region, which reflects the probability for intramolecular chain-end collision in dependence of chain length.²⁷ Fraction II was resubjected to preparative GPC to separate the individual components as far as possible. Thereby, the cycles (n = 6-14) could be isolated in pure or semipure form (see Supporting Information). The cyclic hexamer not only was the smallest ring found but also the one formed in highest yield presumably due to its least ring strain expected. In fact, a comparison of the ¹H NMR spectra of the various cycles

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Figure 3. MALDI-TOF mass spectrum of the higher mass fraction I (a). The inset shows a magnification of the region which contains all detected end-group patterns (b). All assigned signals have mass values corresponding to $[M + Na]^+$. X/Y (X, Y = H, OH, Tol, P(Tol)₂ or PO(Tol)₂) represent the end-group situation of the obtained PMP species.²³

shows that the aromatic protons of the cyclic hexamer are remarkably deshielded (Figure 4b). This can reasonably be explained by its overall planar conformation. As the ring size increases, the deshielding effect decreases to be minimal around the cyclic nonamer and thereafter increases asymptotically to the level of open-chain products. This tendency may be associated with an increase and a decrease, respectively, of the average dihedral angle between consecutive phenylene units of the cycles and thus their overall strains.

Further Modifications of Conditions toward High Molecular Weights. In order to prevent an early halt of the growth due to ligand scrambling, Buchwald's SPhos,²⁸ an active ligand for high-turnover catalysis, was considered.^{13,29,30} Monomer 1a was subjected to a SPC under new conditions: Pd(dba)₂ (0.01 equiv),³¹ SPhos (0.02 equiv), NaHCO₃ (8 equiv) in THF–water 3:1, 70 °C under N₂. As expected, the reaction was accelerated and completed within 24 h. Similarly with the previous SPCs, the GPC curve also shows open-chain (P_H) and cyclic products (P_L), respectively (Figure 5a). Although P_L remained around 1.5 kDa, the peak maximum of P_H was drastically shifted to a higher molecular weight ~40 kDa (DP ~ 210).

Next, the other side reactions were targeted. Specifically, it was an initial thought that those associated with the C–B bond of the monomer which is prone to undergo hydration (protodeboronation)³² and hydroxylation^{2,33} under the aqueous basic SPC conditions could be suppressed. Accordingly, the monomer was slowly added over 10 h to reduce its exposure to the reaction medium to a minimum. Figure Sb shows the GPC

profile obtained from this experiment with slow monomer addition. Surprisingly, P_L was diminished while the proportion of P_H was drastically increased with the high molecular weight being kept ($M_w = 45$ kDa, $M_n = 26$ kDa, $M_w/M_n = 1.7$).³⁴ This finding indicates that slow addition favors linear growth over cyclization, the reason for which remains yet to be clarified.

Since the use of $Bu_4NOH\cdot 30H_2O$ instead of $NaHCO_3$ resulted in the formation of higher molecular weight products when $Pd[P(p-Tol)_3]_3$ was employed as catalyst (Figure 2), the same organic base was also tested with $Pd(dba)_2/SPhos$ under comparable conditions. In contrast to the previous results, this new base–catalyst combination, however, did not lead to higher molecular weight products (see Supporting Information). This exemplifies that the choices of base, catalyst and other conditions are crucial but not independent of each other for the SPC conditions to be optimized.³⁵

Mechanistic Insights and End-Functionalization. Using SPhos ligand also provided interesting insights into the polymerization mechanism. The appearance of P_H around 40 kDa was observed from a very early stage of the polymerization when the conversion was still only a few percent. This is incompatible with step-growth polymerization and therefore suggests involvement of a chain-growth-like mechanism.^{13,36,37} Such a mechanism could possibly be brought about by intramolecular "catalyst transfer"³⁸ along the growing chain toward its bromo terminus, whereby the bromo end is always kept activated by the remaining catalyst ready to extend the chain



Figure 4. MALDI-TOF mass spectrum of the lower mass fraction II (a). The cycles with n = 6-14 could be isolated or semi-isolated from the others and analyzed by ¹H NMR in *d*-chloroform (b). Because of the partial overlap of P_L with P_H, the larger cycles 8–14 could not be fully isolated from the linear species by GPC.

further. This view was indeed confirmed by the following experiments.

If SPC proceeds based on a step-growth mechanism represented by the Carothers equation, the stoichiometric misbalance between A and B functional groups should cause a decrease in the average molecular weight of the eventual products.³⁹ The AB structure of monomer 1a presets the mole ratio to be exact 1:1. We therefore intentionally disturbed this mole ratio by adding monofunctional compounds to the polymerization solution as follows: 10% of the monomer was first added slowly to the polymerization solution, an excess amount of either 4-fluorophenyl bromide (5: R¹-A) or 4-fluorophenylboronic acid (6a: R¹-B) was added at once, and thereafter the slow monomer addition was continued to complete (Figure 6). Consequently, two GPC profiles were obtained which are sharply contrasted with each other (Figure 7). While the addition of R¹-B caused the subsequent SPC to give only short oligomeric products ($M_{\rm p}$ < 1 kDa), the presence of a large excess R¹-A did not lead to any such drastic decrease in the



Figure 5. GPC elution curves obtained from new SPCs with $Pd(dba)_2$ (0.01 equiv), SPhos (0.02 equiv), NaHCO₃ (8 equiv) in THF–water 3:1. The monomer was present in the polymerization solution from the beginning (a) or slowly added over 10 h (b). The curves were recorded with a UV detector.



Figure 6. Chemical structures of Buchwald's SPhos ligand and the monofunctional compounds 5, 6a, and 6b. Cy: cyclohexyl.

molecular weight ($M_n \sim 20$ kDa). The latter result clearly contradicts the Carothers equation.

A similar SPC was also performed with the setup in which the polymerization solution already contained 5 prior to the slow addition of monomer 1a. In comparison with the SPC without 5 (Figure 8a), the resultant GPC profile (Figure 8b) shows complete suppression of cycle formation (P_L) and a decrease in overall molecular weight ($M_w = 20$ kDa, $M_n = 13$ kDa, $M_w/M_n =$ 1.5).⁴⁰ In addition, the MALDI-TOF MS analysis of the products indicates that the boron termini are largely capped with 5, while the bromo groups at the other ends are lost by ligand scrambling (Figure 9). This suggests that the chain growth is initiated from 5 and terminated by ligand scrambling. Assuming that the ligand scrambling took place after monomer addition, the GPC results can be accounted for by the end-capped boron termini on the growing species which prevents the chains from cyclization or coupling with each other. The growing species can therefore only grow further at the bromo ends by reaction with monomers. Note that if the monomer was added at once instead of by slow addition, significant formation of cycles (P_L) and slight shift of P_H to higher molecular weights were observed. This indicates that the polymerization can partially be initiated by the monomer itself if the monomer concentration is high relative to that of the initiator.

If the side reactions occur only when there is no more monomer to react with the activated bromo ends, there may



Figure 7. GPC traces from SPCs of 1a with disturbed stoichiometry using monofunctional compounds 5 (a) and 6a (b). After 10% of monomer 1a was slowly added to the polymerization solution over 1 h, either 5 (5 equiv for 1a) or 6a (1 equiv for 1a) was added at once and thereafter monomer addition was continued. Note that vacuum drying of the samples prior to the GPC analysis largely removed the excess amount of 5 (bp ~155 °C), while 6a should remain and equilibrate with its condensates including cyclic trimer (boroxine) whose molecular weight is 366 Da. The curves were recorded with a UV detector.

still be a chance to end-cap the bromo termini right after completion of monomer addition. 4-Methoxyphenylboronic pinacolate (**6b**: \mathbb{R}^2 -B) was thus used for this purpose. Consequently, while the GPC curves remained similar before and after the addition of **6b** (1 equiv), MALDI-TOF MS analysis unequivocally showed that the products are indeed largely end-capped with **6b** at the bromo ends (Figure 10). Thus, the chain growth was initiated from **5** and terminated by **6b** in an efficient manner. This key experiment demonstrates the feasibility of efficient end-functionalization to the SPC



Figure 8. GPC elution curves obtained from SPCs (a) without the presence of 5 prior to the slow addition of monomer 1a and (b) with it. The average molecular weights are estimated by a relative method using polystyrene standards and refer to the main peaks to be $M_w = 45$ kDa and $M_n = 26$ kDa for (a)³⁴ and $M_w = 20$ kDa and $M_n = 13$ kDa for (b).⁴⁰ The curves were recorded with a UV detector.

products both at the boron and bromo termini with independent functional moieties.

Both bromo and boron termini can in principle undergo similar side reactions such as ligand scrambling,^{4c,d} hydra-tion,^{24,26} and hydroxylation.⁴¹ It is therefore often hard to distinguish the original chemical nature of the chain termini once they suffer from such side reactions. By taking advantage of the efficient end-capping method we have developed, the original bromo and boron ends can now easily be identified by marking them with 6b and 5, respectively. This also allows for inspection whether the chain directionality is retained, as expected from the AB monomer structure employed for the SPC. The MALDI-TOF mass spectrum shows that the chain directionality is largely retained when Pd(dba)₂/SPhos was used as catalyst. However, if the catalyst was replaced with Pd(OAc)₂/SPhos, the mass signals attributed to the products with bromo groups at both ends became prominent (Figure 11). An increased amount of $Pd(OAc)_2/SPhos$ enhanced these signals significantly. This is a clear indication of the involvement of the homocoupling between the boron ends presumably due to the action of Pd(II).42,43 This result indicates that the boronic ester reduces the Pd(II) to the active Pd(0) catalyst for the SPC.44

CONCLUSIONS

In summary, SPC synthesis of a high molecular weight PMP using an AB-type *m*-phenylene monomer has been investigated. The previous conditions using a conventional catalyst, Pd[P(*p*-Tol)₃]₃, renders cyclization favorable over linear growth. In addition, linear products remain in the oligomeric regime because of loss of the end-functional groups caused by side reactions during SPC. MALDI-TOF MS analysis indicates that ligand scrambling is such a detrimental side reaction. Indeed, when Buchwald's SPhos ligand was used with Pd(dba)₂ as palladium source, the linear species could grow further to high molecular weight products. Cycle formation could be suppressed when the SPC was combined with a slow monomer addition protocol. Thus, the preparation of linear PMP with high molecular weights ($M_w = 45$ kDa, $M_n = 26$ kDa, $M_w/M_n = 1.7$)³⁴ could be achieved. SPCs were also performed in the presence of



Figure 9. MALDI-TOF mass spectrum obtained from the SPC with the slow addition of monomer **1a**. Monofunctional compound **5** (0.25 equiv) was present in the polymerization solution prior to the monomer slow addition. The SPC was expected to proceed as described in the scheme shown below the spectrum.



Figure 10. MALDI-TOF mass spectrum obtained from the SPC with the slow addition of monomer 1a. Monofunctional compounds 5 (0.25 equiv) and 6b (1 equiv) were added to the polymerization solution before and right after the monomer addition, respectively. The SPC was expected to proceed as described in the scheme shown below the spectrum.

monofunctional compounds which suggest the polymerization mechanism to be not step-growth but rather chain-growthlike. The drastically lessened side reactions' involvement and the suggested chain-growth mechanism have enabled efficient end-capping of the SPC products at both bromo and boron chain ends with independent functional moieties. This also allowed for proving that the chain directionality is largely retained when Pd(0) was used as palladium source but partially lost when Pd(II) was in use. We intend to use the obtained PMP to prepare films and fibers for which higher molecular weights in the 100 kDa range could be desirable. Therefore, the SPC conditions are being further optimized for even better control over polymerization in view of the synthesis of high molecular weight block copolymers by SPC as well.



Figure 11. MALDI-TOF mass spectra obtained from SPCs using (a) $Pd(dba)_2$ (0.01 equiv for 1a), (b) $Pd(OAc)_2$ (0.01 equiv), and (c) $Pd(OAc)_2$ (0.1 equiv) as palladium source for catalyst. The signals marked with arrows are the SPC products indicative of the occurrence of the homocoupling presumably caused by the action of Pd(II).

ASSOCIATED CONTENT

S Supporting Information

All experimental procedures including NMR and HR-MS data, GPC elution curves, and a MALDI-TOF mass spectrum of SPC using $Pd(OAc)_2$ (0.1 equiv) as palladium source. 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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