ChemCatChem
The European Society Journal for Catalysis

Chemistry Europe
European Chemical Societies Publishing

Supported by GECATS German Catalysis Society

Accepted Article

Title: Polystyrene-Supported PPh3 in Macroporous Monolith: Effect of Cross-Linking Degree on Coordination Mode and Catalytic Activity in Pd-Catalyzed C-C Cross-Coupling of Aryl Chlorides

Authors: Hikaru Matsumoto, Yu Hoshino, Tomohiro Iwai, Masaya Sawamura, and yoshiko miura

To be cited as: *ChemCatChem* 10.1002/cctc.202000651

Link to VoR: https://doi.org/10.1002/cctc.202000651

WILEY-VCH

ChemCatChem 10.1002/cctc.202000651

WILEY-VCH

COMMUNICATION

Polystyrene-Supported PPh$_3$ in Monolithic Porous Material: Effect of Cross-Linking Degree on Coordination Mode and Catalytic Activity in Pd-Catalyzed C-C Cross-Coupling of Aryl Chlorides

Hikaru Matsumoto,[a] Yu Hoshino,[a] Tomohiro Iwai,[b] Masaya Sawamura,[b]* and Yoshiko Miura[a]**

Abstract: Hybridization of porous synthetic polymer and sophisticated ligand play important role in transition-metal catalysis for chemical transformations at laboratory and industrial level. A monolithic porous polymer, which is a single piece with continuous macropores, are desired for high permeability, fast mass transfer property, high stability, and easy modification. Herein, we first develop a monolithic porous polystyrene containing three-fold cross-linked PPh$_3$ (**M-PS-TPP**) for transition-metal catalysis. The monolithic and macroporous structure of **M-PS-TPP** was fabricated via polymerization-induced phase separation using porogenic solvent. Moreover, the **M-PS-TPP** was synthesized using different feed ratios of divinylbenzene (DVB) for site-isolation and mono-P-ligating behavior of PPh$_3$. ^{31}P CP/MAS NMR analysis revealed that the different selectivity of **M-PS-TPP**s was obtained in formation of mono-P-ligation toward Pd^{II}. The macroporous properties and controlled mono-P-ligating behavior of **M-PS-TPP** facilitated a challenging Pd-catalyzed Suzuki-Miyaura cross-coupling reactions of chloroarenes.

Porous materials have received much attention for their potential in applications such as catalysis and gas separation and storage because of their controllable pore size and large surface area.[1] In particular, porous synthetic polymers have straight-forward preparation, flexible chemical modification, high stability, and insolubility. This makes porous synthetic polymers attractive for energy efficient, cost-effective, and recyclable systems in laboratory and industrial processes.[2] During the past few decades, increasing demand for porous synthetic polymers have motivated the development of micro-,[3] meso-,[4] and macroporous[5] organic polymers. Among them, monolithic porous polymers, which consist of a single piece containing continuous macropores, have attracted much attention because of their high permeability, fast mass transfer properties, high stability, and ease of modification.[6,7] Monolithic porous polymers containing NHC,[8,10b] pyridine,[9] bipyridine,[10] pybox,[11] and phosphine[12] moieties have all been applied for transition-metal catalysis.

The combination of materials science and organic chemistry has led to innovative chemical transformations in science and industry. Recently, Sawamura and co-workers developed a cross-linked polystyrene(PS)-PPh$_3$ hybrid, where three-fold vinylated PPh$_3$ (TPP) was copolymerized (**PS-TPP**).[13] In the beaded **PS-TPP**, the PPh$_3$ unit was site-isolated and favored mono-P-ligation towards Pd^{II}. This resulted in excellent activity for Suzuki-Miyaura cross-coupling reactions of unactivated chloroarenes, which are typically challenging.[14] Further to the molecular design of the ligand, modulating the design of **PS-TPP** while maintaining the coordination behavior of the PPh$_3$ unit is essential. In this context, the monolithic and macroporous structure in **PS-TPP** could provide a catalytic system with fast mass transfer. For efficient and practical chemical transformations, the **PS-TPP** system has three requirements: 1) selective mono-P-ligation, 2) monolithic and macroporous structure, and 3) fast mass transfer. This has not yet been achieved experimentally.

Here, we report a monolithic porous **PS-TPP** (**M-PS-TPP**) where the PPh$_3$ unit is arranged for site-isolation and mono-P-ligation toward Pd^{II} (Figure 1). The monolithic and macroporous structure of **M-PS-TPP** was achieved via polymerization-induced phase separation using a porogenic solvent.[7] The PPh$_3$ unit was carefully arranged in **M-PS-TPP** by varying the feed ratio of divinylbenzene (DVB) as a cross-linker to favor mono-P-ligation, while maintaining the macroporous structure. Measurement of physical properties (macroporous structure or diffusivity of reactants) and ^{31}P CP/MAS NMR spectra were used to evaluate the molecular diffusion in the **M-PS-TPP**s and their mono-P-ligating behavior. The **M-PS-TPP**s were applied to Suzuki-Miyaura cross-coupling reactions of unactivated chloroarenes. The **M-PS-TPP**s showed excellent catalytic efficacy regulated by the macroporous structure and spatial density of PPh$_3$.

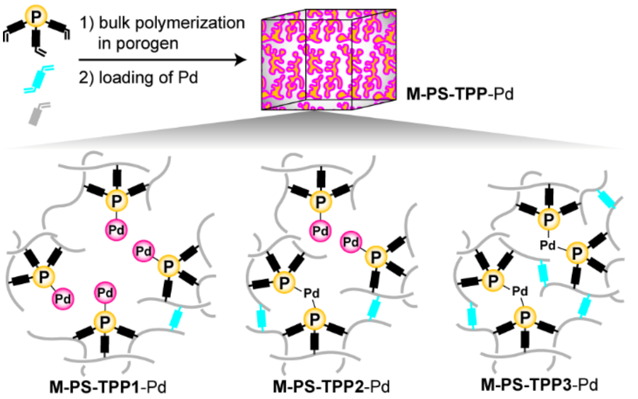


Figure 1. Schematic of the preparation of monolithic porous polystyrene(PS)-threefold vinylated PPh$_3$ hybrids (**M-PS-TPP1–3**) and controlled formation of

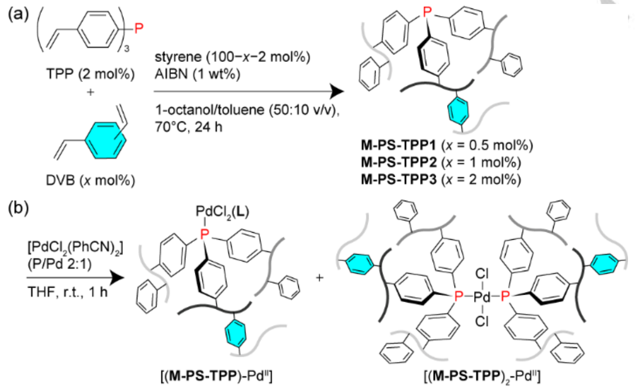
---

[a] H. Matsumoto, Assoc. Prof. Y. Hoshino, Prof. Y. Miura
Department of Chemical Engineering
Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
E-mail: miuray@chem-eng.kyushu-u.ac.jp
[b] T. Iwai, Prof. M. Sawamura
Department of Chemistry
Hokkaido University
Kita 10 Nishi 8, Kita-ku, Sapporo 060-0810, Japan
[c] Prof. M. Sawamura
Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University
Kita 21 Nishi 10, Kita-ku, Sapporo, 001-0021, Japan
E-mail: sawamura@sci.hokudai.ac.jp

mono-P-ligated Pd^{II} complex by divinylbenzene (DVB) contents. PPh$_3$ unit (set of yellow ball and three black nodes), mono-P-ligated Pd^{II} center (pink balls), DVB units (blue nodes), styrene (gray nodes), and PS chains (gray lines) are shown.

TPP (2 mol%), DVB (x mol%), and styrene (100−x−2 mol%) were copolymerized in 1-octanol/toluene (50:10 v/v) using 2,2'-azobis(isobutyronitrile) (AIBN, 1 wt.% with respect to total monomer) to give **M-PS-TPP**s.[7,13,15] The feed ratio of DVB was tuned to be x = 0.5, 1, and 2 mol% for preparing **M-PS-TPP1**, **M-PS-TPP2**, and **M-PS-TPP3**, respectively. The monomer solution was incubated in a glass vial at 70 °C for 24 h. The resulting solid was removed from the vial and washed with anhydrous THF to give a self-standing **M-PS-TPP** (Figure 2a). The **M-PS-TPP**s were dried in vacuo at room temperature overnight, to give **M-PS-TPP1**–**3** as a white solid (83–86% dry yield) (Scheme 1a, Table S1, Supporting Information (SI)). FE-SEM observations revealed that dried **M-PS-TPP**s consisted of an agglomerate of globules which formed interstitial macropores (Figures 2b and S1). The pore size distribution of the dried **M-PS-TPP**s was evaluated, and the median pore diameter ranged from 242 to 627 nm (Figure S2, Table S2). Increasing the DVB content of the **M-PS-TPP**s decreased the median pore diameter and increased the surface area. FT-IR (Figure S3) and ^{31}P CP/MAS NMR (Figures 3a and S6a,7a) spectra of the **M-PS-TPP**s confirmed the formation of the PS backbone (FT-IR peaks at 1600–1450, 1200–950, and 900–650 cm^{-1}) and coordinatively active PPh$_3$ (NMR peak at −6 ppm) in the cross-linked network, respectively. The amount of PPh$_3$ incorporated into **M-PS-TPP**s was 0.18 mmol g^{-1} based on the TPP feed ratio (Table S1).[16]

In anhydrous THF, **M-PS-TPP1**, **M-PS-TPP2**, and **M-PS-TPP3** had swelling volumes of 4.3, 3.7, and 3.6 cm^3 g^{-1}, respectively (Table S1). From compression tests, the fracture stresses of THF-swollen **M-PS-TPP1**, **M-PS-TPP2**, and **M-PS-TPP3** were 0.29 ± 0.01, 0.37 ± 0.03, and 0.40 ± 0.01 MPa, respectively (Figures S4a,5, open rectangles). The increasing DVB content of the **M-PS-TPP**s was reflected in the decreasing swelling volume and increasing compressive strength in THF.[17]



Scheme 1. (a) Synthesis of **M-PS-TPP**s and (b) loading of Pd (P/Pd 2:1; **L** = PhCN or solvent).

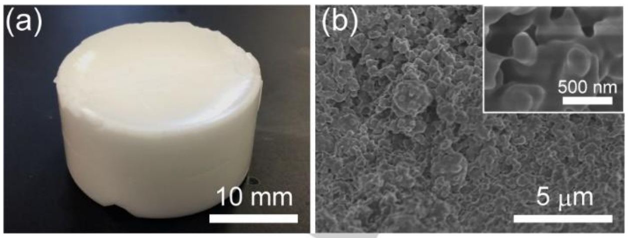


Figure 2. (a) Photograph of THF-swollen **M-PS-TPP1** and (b) FE-SEM image of internal structure of dried **M-PS-TPP1**.

The loading of Pd was performed by the reaction of **M-PS-TPP** with [PdCl$_2$(PhCN)$_2$] (P/Pd 2:1) (Scheme 1b). The amount of PPh$_3$-Pd complex in **M-PS-TPP**-Pd was ~47 mol% (molar ratio to total PPh$_3$) as determined using ICP-AES (Table 1, SI). In the ^{31}P CP/MAS NMR spectra of **M-PS-TPP**-Pd, new peaks attributable to the mono-P-ligated Pd^{II} complex [(**M-PS-TPP**)-Pd^{II}] (32–33 ppm) and bis-P-ligated Pd^{II} complex [(**M-PS-TPP**)$_2$-Pd^{II}] (24–25 ppm) were observed (Figures 3b and S6b,7b).[13a] Using the Gaussian peak fitting method, relative peak intensities were calculated to determine the selectivity of mono-P-ligation. **M-PS-TPP1**-Pd showed the highest relative peak intensity of the mono-P-ligated Pd^{II} complex (95%). Increasing the DVB content of **M-PS-TPP** decreased the relative peak intensities of the mono-P-ligated Pd^{II} complex (79 and 76% for **M-PS-TPP2**-Pd and **M-PS-TPP3**-Pd, respectively) (Table 1). The ^{31}P CP/MAS NMR analysis clearly indicated the formation of mono-P-ligated Pd^{II} complex regulated by the DVB content of **M-PS-TPP**s.

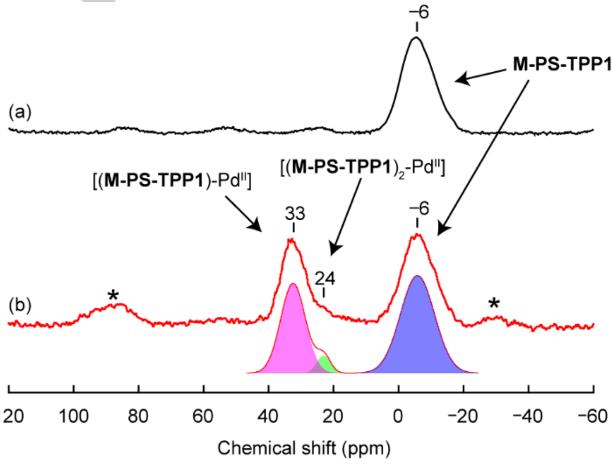


Figure 3. ^{31}P CP/MAS NMR spectra obtained from **M-PS-TPP1** (a) before and (b) after reaction with [PdCl$_2$(PhCN)$_2$] (P/Pd 2:1). The relative peak intensities of free **M-PS-TPP1**, mono-P-ligated Pd^{II} complex [(**M-PS-TPP1**)-Pd^{II}], and bis-P-ligated Pd^{II} complex [(**M-PS-TPP1**)$_2$-Pd^{II}] were estimated using Gaussian peak fitting method. Asterisks (*) indicate spinning side bands.

Table 1. The Pd Content and Relative Peak Intensity of ^{31}P CP/MAS NMR Spectra.

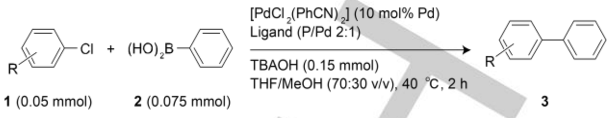
Ligand	Pd content (mol%)[a,b]	Relative peak intensity [(**M-PS-TPP**)-Pd^{II}]/[(**M-PS-TPP**)$_2$-Pd^{II}][c,d]
M-PS-TPP1	47	95:5
M-PS-TPP2	47	79:21
M-PS-TPP3	47	76:24

[a] Molar ratio to total PPh$_3$ of **M-PS-TPP** (0.18–0.19 mmol g^{-1}). [b] Determined using ICP-AES. [c] The peak intensity of bis-P-ligated Pd^{II} was divided by two. [d] Determined using ^{31}P CP/MAS NMR spectra.

The microenvironment of **M-PS-TPP1** favored mono-P-ligation toward Pd^{II} rather than bis-P-ligation. The molecular design of the incorporated PPh$_3$ was the same in all the **M-PS-TPP**s, so the mono-P-ligating behavior should be affected by different DVB contents of the **M-PS-TPP**s. In the present system, increasing the DVB content induced an increasing number of cross-linking points in the PS network, resulting in the **M-PS-TPP**s shrinking and stiffening (Table S1 and Figure S5). It has been reported that bis-P-ligation toward metal leads to additional cross-linking between polymer chains.[18] We confirmed the cross-linking effect via bis-P-ligation on the swelling volume of **M-PS-TPP**-Pd, however, no significant change was observed (± 3% change). **M-PS-TPP2**-Pd and **M-PS-TPP3**-Pd formed a certain amount of bis-P-ligated Pd^{II} complex (Table 1) and showed slightly higher compressive strengths (Figure S4b,5, filled rectangles). One explanation to the cross-linking via bis-P-ligation in the **M-PS-TPP**s is that the bis-P-ligated Pd^{II} complex formed in PPh$_3$-rich domains of the macroporous PS.[19,20] The formation of the cross-linking complex (bis-P-ligated Pd^{II} complex) hardened the **M-PS-TPP**s without causing them to shrink. In the **M-PS-TPP** system, tuning the DVB content controlled the **M-PS-TPP**s swelling and hence the spatial density of PPh$_3$ for selective mono-P-ligation toward Pd^{II}. This should lead to enhanced catalytic activity.

To assess the potential application of the **M-PS-TPP** system, [PdCl$_2$(PhCN)$_2$] (10 mol% Pd) and ligand (20 mol% P, P/Pd 2:1) complexes were employed for batch Suzuki-Miyaura cross-coupling reactions between 4-chlorotoluene (**1a**, 0.05 mmol) and phenylboronic acid (**2**, 0.075 mmol) in the presence of tetrabutylammonium hydroxide (TBAOH, 0.150 mmol) (Table 2).[21] Using **M-PS-TPP1**, **M-PS-TPP2**, and **M-PS-TPP3**, the yields of **3a** were 87, 68, and 56%, respectively (Table 2, entries 1, 2, and 3). The catalytic efficacy of the **M-PS-TPP**s-Pd could therefore be enhanced tuning the DVB content. Focusing on the morphological structure of **PS-TPP**, nonporous or beaded **PS-TPP**[13a] were also employed for cross-coupling reactions (Figures S9 and S10, SI), which gave yields of 56 and 90%, respectively (entries 4 and 5). Using homogeneous TPP solution or a ligand-free system, the production of **3a** was not observed (entries 6 and 7).[22,23]

Table 2. Pd-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions.[a]



Entry	Chloroarene **1**	Ligand	Product **3**	Yield (%)
1	**1a** (R = *p*-Me)	**M-PS-TPP1**	**3a**	87
2	**1a**	**M-PS-TPP2**	**3a**	68
3	**1a**	**M-PS-TPP3**	**3a**	56
4	**1a**	Nonporous **PS-TPP**	**3a**	56
5	**1a**	Beaded **PS-TPP**	**3a**	90
6	**1a**	TPP	**3a**	0
7	**1a**	none	**3a**	0
8	**1b** (R = *o*-NO$_2$)	**M-PS-TPP1**	**3b**	85
9	**1c** (R = *m*-NO$_2$)	**M-PS-TPP1**	**3c**	87
10	**1d** (R = *p*-NO$_2$)	**M-PS-TPP1**	**3d**	89
11	**1e** (R = *p*-COMe)	**M-PS-TPP1**	**3e**	82
12	**1f** (R = *p*-OMe)	**M-PS-TPP1**	**3f**	61

[a] Conditions: **1** (0.050 mmol), **2** (0.075 mmol), TBAOH (0.150 mmol), [PdCl$_2$(PhCN)$_2$] (0.005 mmol, 10 mol% Pd), Ligand (0.01 mmol, 20 mol% P), THF/MeOH (70:30 v/v, 1.45 mL), 40°C, 2 h.

M-PS-TPP1-Pd showed macroporous properties and selective mono-P-ligation and exhibited excellent activity (87%) in the batch Suzuki-Miyaura cross-coupling reaction, where the turnover frequency (TOF) of **M-PS-TPP1**-Pd was 23 h^{-1}.[23,24] The catalytic performance of **M-PS-TPP1**-Pd was comparable with that of beaded **PS-TPP**-Pd (90%), while the catalytic performance of nonporous **PS-TPP**-Pd was poor (56%). Diffusion experiments of reactants revealed that the apparent diffusion coefficients (*D*) of reactants were higher in all the **M-PS-TPP**s than in nonporous **PS-TPP** (Table 3 and Figure S12, SI). The macroporous structure of the **M-PS-TPP**s clearly enhanced the molecular diffusion of reactants in the catalytic system. The diffusivities in the **M-PS-TPP**s were not significantly different, despite the **M-PS-TPP**s-Pd showing different catalytic efficacies (Table 2, entries 1, 2, and 3). When using the **M-PS-TPP**s-Pd in the Suzuki-Miyaura cross-coupling reaction, the diffusivities of reactants were sufficiently fast, and selective mono-P-ligation was a more important factor affecting the catalytic efficacy. From these results, both the macroporous structure (Figures 2b and S1) and selective mono-P-ligation (Table 1) of **M-PS-TPP** were essential to efficiently facilitate this challenging chemical transformation via cross-coupling reaction.

Table 3. The Apparent Diffusion Coefficients (*D*) of Reactants in **M-PS-TPP**s and Nonporous **PS-TPP**.

Ligand	*D* ($\times 10^{-9}$ m^2 sec^{-1})		
	1a	**2**	**3a**
M-PS-TPP1	2.72	3.66	1.46
M-PS-TPP2	4.14	4.68	2.49
M-PS-TPP3	4.06	1.28	2.58
Nonporous **PS-TPP**	0.07	0.19	0.06

M-PS-TPP1-Pd was further examined in batch Suzuki-Miyaura cross-coupling reactions of various chloroarenes (Table 2). The **M-PS-TPP1**-Pd complex induced conversions for chloroarenes bearing electron-withdrawing groups, such as *o*, *m*, or *p*-substituted $-NO_2$ (85, 87, and 89% yields, entries 8, 9, and 10, respectively), and *p*-substituted –COMe (82% yield, entry 11). Moderate conversion of chloroarene bearing an electron-donating group, *p*-substituted –OMe (61% yield, entry 12), was observed. These results demonstrated the broad applicability of the **M-PS-TPP1** system for Pd-catalyzed Suzuki-Miyaura cross-coupling reactions.

In summary, a monolithic porous PS-three-fold crosslinked PPh_3 hybrid, **M-PS-TPP**, was synthesized via polymerization-induced phase separation using a porogenic solvent. Tuning the DVB content in the **M-PS-TPP** arranged the PPh_3 units for site-isolation and selective formation of the mono-P-ligated Pd^{II} complex. The **M-PS-TPP**-Pd complex exhibited good catalytic efficacy in Suzuki-Miyaura cross-coupling reactions of chloroarenes, which was enhanced by fast molecular diffusion and selective mono-P-ligation. These insights into monolithic porous polymers featuring macroporous structures, fast molecular diffusion, and controlled coordination mode of supported PPh_3 should be broadly extended to transition-metal catalysis.

Acknowledgements

This work was supported by a JSPS KAKENHI Grant Number JP16H01036, JP18J20345, 19H02766, 20H04825 and 20H05230.

Keywords: Cross-coupling • Porous material • Palladium • Phosphine • Polystyrene-supported catalyst

[1] a) N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675–683; b) A. Thomas, *Angew. Chem.* **2010**, *122*, 8506–8523; *Angew. Chem. Int. Edit.* **2010**, *49*, 8328–8344.

[2] a) J. Lu, P. H. Toy, *Chem. Rev.* **2009**, *109*, 815–838; b) M. R. Buchmeiser, *Chem. Rev.* **2008**, *109*, 303–321.

[3] a) B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, *Adv. Mater.* **2012**, *24*, 3390–3395; b) S. Ogasawara, S. Kato, *J. Am. Chem. Soc.* **2010**, *132*, 4608–4613. c) D. Mullangi, S. Nandi, S. Shalini, S. Sreedhala, C. P. Vinod, R. Vaidhyanathan, *Sci. Rep.* **2015**, *5*, 10876.

[4] a) R. Xing, Y. Liu, H. Wu, X. Li, M. He, P. Wu, *Chem. Commun.* **2008**, *47*, 6297–6299; b) P. Puthiaraj, K. Pitchumani, *Green Chem.* **2014**, *16*, 4223–4233.

[5] a) D. H. Lee, J. H. Kim, B. H. Jun, H. Kang, J. Park, Y. S. Lee, *Org.Lett.* **2008**, *10*, 1609–1612; b) A. M. Abu-Elfotoh, K. Phomkeona, K. Shibatomi, S. Iwasa, *Angew. Chem.* **2010**, *122*, 8617–8621; *Angew. Chem. Int. Ed.* **2010**, *49*, 8439–8443.

[6] A) K. Okada, M. Nandi, J. Maruyama, T. Oka, T. Tsujimoto, K. Kondoh, H. Uyama, *Chem. Commun.* **2011**, *47*, 7422–7424; b) M. Nandi, K. Okada, H. Uyama, *Funct. Mater. Lett.* **2011**, *4*, 407–410; c) G. Wang, D. Kundu, H. Uyama, *J. Colloid Interface Sci.* **2010**, *451*, 184–188; d) G. Wang, D. Kundu, H. Uyama, *J. Colloid Interf. Sci.* **2015**, *451*, 184–188.

[7] For reviews, see: a) F. Svec, J. M. J. Fréchet, *Ind. Eng. Chem. Res.* **1999**, *38*, 34–48; b) E. C. Peters, F. Svec, J. M. J. Fréchet, *Adv. Mater.* **1999**, *11*, 1169–1181; c) F. Svec, *J. Sep. Sci.* **2004**, *27*, 1419–1430; d) F. Svec, *J. Chromatogr. A* **2010**, *1217*, 902–924; e) E. B. Anderson, M. R. Buchmeiser, *ChemCatChem* **2012**, *4*, 30–44; f) D. Cantillo, C. O. Kappe, *ChemCatChem* **2014**, *6*, 3286–3305.

[8] a) M. Mayr, D. Wang, R. M. Kröll, N. Schuler, S. Pruhs, A. Furstner, M. R. Buchmeiser, *Adv. Synth. Catal.* **2005**, *347*, 484–492; b) N. Karbass, V. Sans, E. Garcia-Verdugo, M. I. Burguete, S. V. Luis, *Chem. Commun.* **2006**, *29*, 3095–3097; c) W. Gil, K. Boczoń, A. M. Trzeciak, J. J. Ziółkowski, E. Garcia-Verdugo, S. V. Luis, V. Sans, *J. Mol. Catal. A: Chem.* **2009**, *309*, 131–136.

[9] a) M. V. Rojo, L. Guetzoyan, I. R. Baxendale, *Org. Biomol. Chem.* **2015**, *13*, 1768–1777; b) F. G. Adly, A. Ghanem, *Tetrahedron Lett.* **2016**, *57*, 852–857.

[10] a) K. F. Bolton, A. J. Canty, J. A. Deverell, R. M. Guijt, E. F. Hilder, T. Rodemann, J. A. Smith, *Tetrahedron Lett.* **2006**, *47*, 9321–9324; b) A. Gömann, J. A. Deverell, K. F. Munting, R. C. Jones, T. Rodemann, A. J. Canty, J. A. Smith, R. M. Guijt, *Tetrahedron* **2009**, *65*, 1450–1454.

[11] a) M. I. Burguete, A. Cornejo, E. García-Verdugo, M. J. Gil, S. V. Luis, J. A. Mayoral, V. Martínez-Merino, M. Sokolova, *J. Org. Chem.* **2007**, *72*, 4344–4350; b) C. Aranda, A. Cornejo, J. M. Fraile, E. García-Verdugo, M. J. Gil, S. V. Luis, J. A. Mayoral, V. Martínez-Merino, Z. Ochoa, *Green Chemistry* **2011**, *13*, 983–990.

[12] Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F. S. Xiao, *J. Am. Chem. Soc.* **2015**, *137*, 5204−5209.

[13] a) T. Iwai, T. Harada, K. Hara, M. Sawamura, *Angew. Chem.* **2013**, *125*, 12548–12552; *Angew. Chem. Int. Ed.* **2013**, *52*, 12322–12326; b) T. Iwai, K. Asano, T. Harada, M, Sawamura, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 943–949.

[14] For reviews, see: a) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473; b) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555–1564; c) G. A. Molander, B. Canturk, *Angew. Chem.* **2009**, *121*, 9404–9425; *Angew. Chem. Int. Ed.* **2009**, *48*, 9240–9261; d) C. A. Fleckenstein, H. Plenio, *Chem. Soc. Rev.* **2010**, *39*, 694–711; e) R. J. Lundgren, M. Stradiotto, *Chem. Eur. J.* **2012**, *18*, 9758–9769.

[15] See the SI for the synthesis of TPP and **M-PS-TPP**s (Scheme S1,2).

[16] This assumption was verified through loading experiment of Pd^{II} (Figure S8, SI).

[17] J. He, Z. Zhang, H. Kristiansen, K. Redford, G. Fonnum, G. Modahl, *Express Polym Lett.* **2013**, *76*, 365–374.

[18] a) Y. M. A. Yamada, K. Takeda, H. Takahashi, S. Ikegami, *Org. Lett.* **2002**, *4*, 3371–3374; b) E. Lobry, A. F. Cardozo, L. Barthe, J. F. Blanco, H. Delmas, S. Chen, F. Gayet, X. Zhang, M. Lansalot, F. D'Agosto, R. Poli, E. Manoury, C. Julcour, *J. Catal*. **2016,** *342*, 164–172.

[19] K. J. Shea, G. J. Stoddard, *Macromolecules* **1991**, *24*, 1207–1209.

[20] Using the swelling volume and amount of PPh_3 incorporated, the average distance between each PPh_3 unit is estimated to be 3.2–3.4 nm, which is too far to formulate bis-P-ligated Pd^{II} complex. The X-ray crystal structure of *trans*-$[PdCl_2(PPh_3)_2]$ had a slightly distorted square-planar geometry with P-Pd bond length of 0.2355–0.2389 nm, see: A. Naghipour, A.

Ghorbani-Choghamarani, H. Babaee, M. Hashemi, B. Notash, *J. Organomet. Chem.* **2017**, *841*, 31–38.

[21] We attempted continuous-flow Suzuki-Miyaura cross-coupling reactions utilizing macroporous structure of **M-PS-TPP**s in a column format. Unfortunately, it failed due to **M-PS-TPP**s swelling and high pressure losses through columns.

[22] The ICP-AES measurement confirmed that Pd species did not dissolve into a reaction media (< 10 ppb).

[23] The **M-PS-TPP1**-Pd was recycled after use, showing activity decreasing (27% yield of **3a**) due to Pd aggregation (Figure S11).

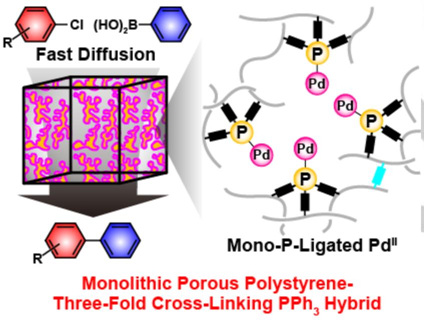
[24] See the SI for the time–yield profile for the kinetic study and hot filtration test in the catalytic system (Figure S13).

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Threefold vinylated PPh_3 (TPP) was copolymerized in monolithic porous polystyrene (PS) with different divinylbenzene (DVB) content. Optimizing the degree of crosslinking in the polystyrene, the catalytically active mono-P-ligated Pd complex was selectively formulated. This controlled mono-P-ligation of **M-PS-TPP**s facilitated a challenging Pd-catalyzed Suzuki-Miyaura cross-coupling reactions of chloroarenes.



Hikaru Matsumoto, Yu Hoshino, Tomohiro Iwai, Masaya Sawamura, and Yoshiko Miura***

Page No. – Page No.

Polystyrene-Supported PPh_3 in Monolithic Porous Material: Effect of Cross-Linking Degree on Coordination Mode and Catalytic Activity in Pd-Catalyzed C-C Cross-Coupling of Aryl Chlorides

Layout 2:

COMMUNICATION

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents