Preparation and Catalytic Function of Substituted Polyacetylenes Coordinated to Palladium Nanoclusters

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ABSTRACT: Poly(4-ethynylaniline) [poly(**1**)] coordinated to palladium nanoclusters (Pd NCs) were prepared. The coordination of Pd NCs was confirmed by X-ray photoelectron spectroscopy and scanning transmission electron microscopy. Pd NCs were coordinated with the benzene rings as well as amino groups of poly(**1**). Pd NCs were partly coordinated with the polymers, maintaining their original size, and formed aggregates with sizes of several tens–hundreds nanometers. Poly(**1**) coordinated to Pd NCs efficiently served as catalysts for the Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions.

1. Introduction

Metal nanoclusters (NCs) with sizes less than 2 nm feature high surface area and proportion of surface-exposed metal atoms. Metal NCs exhibit excellent catalytic activity for various reactions, including addition, condensation, hydrogenation, oxidation and coupling reactions. The preparation of well-dispersed metal NCs is the key factor in achieving efficient catalytic reactions, because metal NCs tend to precipitate or aggregate into bulk metals, resulting in loss of catalytic activity. Various attempts have been made to stabilize metal NCs with diatomaceous earth,[1] carbon nanotubes,[2] amino phosphines,[3] and ionic liquid micro emulsions.[4,5]

Palladium (Pd) NCs have been extensively studied because Pd catalyzes industrially important reactions such as hydrogenation and cross-coupling reactions.[6,7] It is desirable to develop a preparation method for surfactant-free and stable metal nanoclusters with minimum surface deactivation in order to develop highly active catalysts. We have established a method for preparing *N,N*-dimethylformamide (DMF)-protected surfactant-free Pd NCs with particle sizes of 1–1.5 nm.[8] DMF-protected Pd NCs efficiently catalyze Suzuki-Miyaura, Mizoroki-Heck and Migita-Kosugi-Stille cross-coupling reactions, as well as hydrosilylation of aryl halides,[8–10] wherein the catalyst turnover numbers are extremely high compared with those of

conventional Pd catalysts. DMF-protected Pd NCs are recyclable more than five times, thus leading to reduction of Pd consumption for catalytic purposes. We have recently succeeded in Sonogashira-Hagihara and Mizoroki-Heck coupling polymerizations catalyzed with DMF-protected Pd NCs to obtain poly(phenyleneethynylene) and poly(phenylenevinylene) derivatives with moderate molecular weights.[11] Thus, Pd NCs are promising for synthesis of π-conjugated polymers by coupling polymerizations.

Several attempts have been made to stabilize Pd NCs with polymers having aromatic rings and/or heteroatoms, including poly(styrene) derivatives,[12] poly(methylphenylsilane),[13] diamine-functionalized mesoporous polymers with a phenolic resin framework,[14] phenylene-branched dendrimers,[15–17] and poly(vinylimidazolium)-based ionic liquids.[18] Polymer-supported Pd NCs are readily separated and recovered from reaction mixtures, leading to easy recycling and reuse of precious transition metal catalysts. Meanwhile, π-conjugated polymers such as polyacetylene, poly(p-phenylene) and poly(p-phenylenevinylene) have attracted considerable attention due to their useful photoelectric properties. They have been extensively researched in the fields of organic conductors, nonlinear optics, electric luminescent materials, solar cells, high energy-density batteries, and modified electrodes.[19,20] If we employ π-

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conjugated polymers such as polyacetylene as matrices for Pd NCs, we may expect that Pd NCs are significantly stabilized by coordination of π-electrons to Pd.

We have synthesized a series of polyacetylenes substituted with various functional groups, and have examined their secondary structures, liquid crystallinity, stimulus response, photoelectricity, and gas permeability/separation.[21–32] Early second- and third-row transition metals, including niobium, tantalum, molybdenum, and tungsten, catalyze polymerization of hydrocarbon-based acetylene monomers through a metathesis mechanism to give high-molecular-weight polymers with uncontrolled *cis*/*trans* geometries of the main chains. On the other hand, later members of these transition series, including rhodium and iridium polymerize acetylene monomers through a coordination-insertion mechanism to give *cis*-stereoregulated substituted acetylene polymers. Some of these form chirally ordered helices and/or aggregates stabilized by intra-/intermolecular hydrogen bonding, π–π and van der Waals interactions between the side chains. The rigid π-conjugated main chain also plays a crucial role in facilitating substituted acetylene polymers to adopt such higher order structures. For example, a ruthenium-coordinated helical polyacetylene catalyzes asymmetric hydrogen-transfer reaction;[33] while L-valine- and L-proline-carrying polyacetylenes catalyze asymmetric reduction of aromatic ketimines[34] and aldol reactions,[35] respectively. Substituted acetylene

polymer microporous networks with terminal ethynyl groups act as effective heterogeneous polymeric catalysts for acetylization of aldehydes and ketones.[36] Such polyacetylene catalysts exhibit recyclability, easy separation, and recovery from reaction mixtures, and their catalytic activity can be tuned by the presence of functional centers.

In the course of our study on substituted acetylene polymers, we have designed novel polymer complexes consisting of poly(phenylacetylene) [poly(PA)] and DMF-protected Pd NCs. It is expected that poly(PA) can coordinate to Pd NCs, and stabilize Pd NCs, keeping catalytic activity in a manner similar to polystyrene derivatives.[37] The present study deals with the preparation of complexes of DMF-stabilized Pd NCs with poly(4-ethynylaniline) [poly(1)], and examination of their catalytic activities in Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions. We employed amino-substituted poly(PA), because amine is widely used as a ligand for Pd complexes.

2. Results and Discussion

2.1 Preparation of Poly(1) Coordinated to Pd NCs-A, B, C [Poly(1)⊃Pd NCs-A, B, C]

Three kinds of poly(1)⊃Pd NCs samples were prepared using three different routes, as illustrated in Scheme 1. Route A involves the coordination of Pd NCs with 1, followed by

acetylene polymerization; in Route B, acetylene polymerization of *N-tert*-butoxycarbonyl

(Boc)-protected 4-ethynylaniline (**1a**) is followed by deprotection and coordination; and Route

C consists of the acetylene polymerization of *N*-fluorenylmethyloxycarbonyl (Fmoc)-protected

4-ethynylaniline (**1b**), followed by deprotection and coordination. The samples were analyzed

by IR spectroscopy to confirm the acetylene polymerization and coordination of Pd NCs.

Monomer **1** exhibited an IR absorption peak around 2100 cm^{-1} corresponding to the ethynyl

C≡C stretching vibration, while poly(**1**)⊃Pd NCs-A obtained in Route A did not exhibit the

peak, as shown in Figures 1, supporting the occurrence of acetylene polymerization. **1**⊃Pd

NCs(DMF) exhibited an ethynyl C≡C IR absorption peak smaller than that of **1**, indicating the

coordination of Pd NCs with the ethynyl group of **1**, which explains the low number-average-

molecular weight (M_n = 640) of poly(**1**) ⊃ Pd NCs-A(DMF). The polymerization of **1** is

unsuccessful without protection of the amino group due to coordination of the amino group to

Rh, resulting in deactivation.[38] Poly(**1**)⊃Pd NCs-A(CHCl$_2$CHCl$_2$) was insoluble in THF,

CHCl$_3$ and DMF, suggesting that the M_n was much higher than that of poly(**1**)⊃Pd NCs-

A(DMF). It is therefore considered that the ethynyl group of **1** coordinates to Pd NCs in

CHCl$_2$CHCl$_2$ but does not so strongly than in DMF, presumably due to interaction between

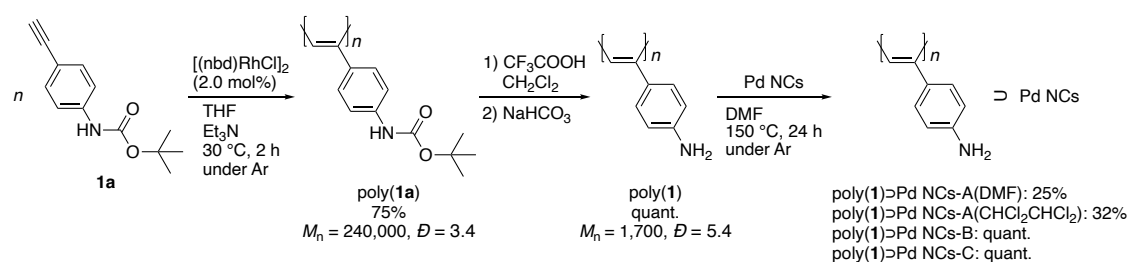lone-pair electrons of Cl with Pd, leading to more favorable polymerizability of **1**⊃Pd NCs

(CHCl$_2$CHCl$_2$) compared to **1**⊃Pd NCs (DMF).

Scheme 1. Preparation of Poly(1)⊃Pd NCs [a]
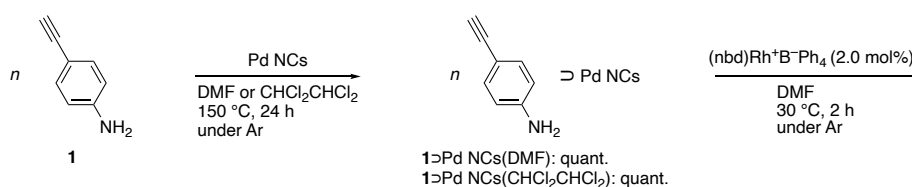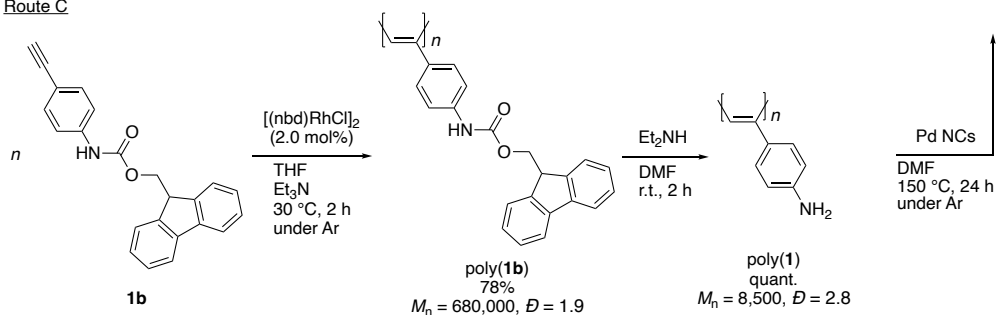
[a] **1**⊃Pd NCs(DMF) and **1**⊃Pd NCs(CHCl$_2$CHCl$_2$) were prepared by the coordination of **1** to Pd NCs in DMF and CHCl$_2$CHCl$_2$; poly(**1**)⊃Pd NCs-A(DMF) and poly(**1**)⊃Pd NCs(CHCl$_2$CHCl$_2$) were prepared by the polymerization of **1**⊃Pd NCs(DMF) and **1**⊃Pd NCs(CHCl$_2$CHCl$_2$) in Route A; poly(**1**)⊃Pd NCs-B and poly(**1**)⊃Pd NCs-C were prepared by the coordination of poly(**1**)s to Pd NCs in Routes B and C, respectively.
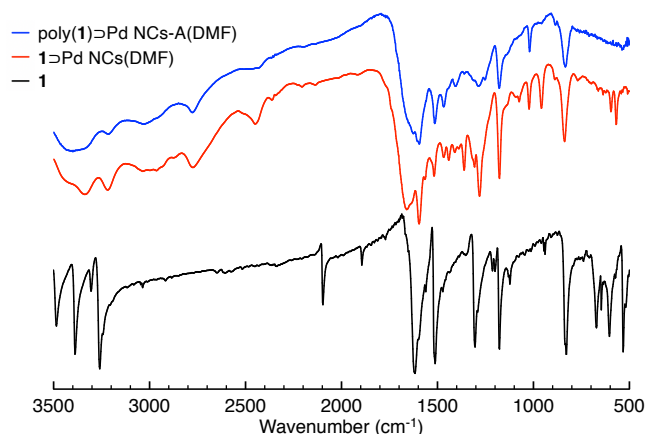
Figure 1. IR spectra (KBr pellet) of **1**, **1**⊃Pd NCs(DMF) and poly(**1**)⊃Pd NCs-A(DMF) prepared via Route A in Scheme 1.

Poly(**1a**) and poly(**1b**) were successfully obtained by the polymerization of *N*-Boc- and *N*-Fmoc-protected monomers **1a** and **1b** (Routes B and C in Scheme 1), whose structures were confirmed by ^{1}H NMR spectroscopy. Judging from the integration ratios between the *cis*-vinylene proton signal in the main chain around 5.7 ppm and the aromatic proton signals, the *cis*-geometry is dominant in the present polymers similar to polyacetylenes obtained by Rh-catalyzed acetylene polymerization. The M_n's of poly(**1a**) and poly(**1b**) were as high as 240,000 and 680,000, respectively, confirming the effectiveness of *N*-protection of **1** for enhancement of polymerizability. The M_n of poly(**1**), obtained by removing the Boc group of poly(**1a**) with trifluoroacetic acid (TFA) treatment followed by neutralization, was as low as 1,700. The M_n of poly(PA) remarkably decreased from 6,500 to 670 accompanied by the increase of dispersity (*Đ*) from 2.2 to 6.2 upon TFA treatment for 2 h. The main chain would be partially cloven due

to cyclic trimerization,[39] but the detail is unclear. On the other hand, the M_n of poly(**1**), obtained

by removing the Fmoc group of poly(**1b**) with Et$_2$NH treatment, was 8,500.

Another control experiment was carried out to check the effect of Et$_2$NH on the decrease

of M_n. Poly(PA) was dissolved in DMF/Et$_2$NH = 6/1 (volume ratio) mixed solvent, and the

resultant solution (c = 0.5 M) was stirred at room temperature for 2 h. The polymer was

recovered from the solution by precipitation with Et$_2$O followed by filtration, and the molecular

weight was measured. The M_n and $Đ$ (6,500 and 2.2) of the recovered poly(PA) sample were

almost the same as those of the pristine sample (6,300 and 2.2). It is accordingly considered

that two factors caused the decrease of M_n of poly(**1**) after deprotection. One is the deprotection

of Fmoc groups, and the other is underestimation of M_n due to the interaction between the amino

groups in the side chain of poly(**1**) and the poly(styrene) gel of size exclusion chromatography

(SEC) columns, resulting in extension of elution time. Poly(styrene) gels commonly contain

polar groups such as carbonyl, carboxy and peroxy groups formed during usage and aging. This

is especially true when tetrahydrofuran (THF) is used as an eluent, because peroxides and

oxygen are present even if the solvent is degassed.[40] Poly(**1**)s obtained by the polymerization

of *N*-Boc- and *N*-Fmoc-protected monomers **1a** and **1b** followed by deprotection exhibited no

ethynyl C≡C peak. The M_n's of poly(**1**)⊃Pd NCs-B and poly(**1**)⊃Pd NCs-C could not be measured due to insolubility in DMF, THF or CHCl$_3$ available for use as SEC eluents.

Figure 2 (a) shows the UV-vis absorption spectra of poly(**1**)⊃Pd NCs-A(DMF), together with those of **1**, Pd NCs and **1**⊃Pd NCs(DMF). Polymer complex **1**⊃Pd NCs(DMF) exhibited a shoulder peak at 300–350 nm, while **1** and Pd NCs did not exhibit a shoulder in this wavelength range, indicating the formation of **1**⊃Pd NCs. The absorbance of poly(**1**)⊃Pd NCs-A(DMF) around 350–600 nm was larger than that of **1**⊃Pd NCs(DMF), indicating the formation of a conjugated polyacetylene backbone.

Figure 2 (b) shows the photoluminescence spectrum of poly(**1**)⊃Pd NCs-A(DMF) together with those of **1**, Pd NCs and **1**⊃Pd NCs(DMF). Complexes **1**⊃Pd NCs(DMF) and poly(**1**)⊃Pd-A(DMF) luminesced in a wavelength region ca. 20 nm longer than Pd NCs, indicating the exchange of the DMF ligand of Pd NCs with **1** and poly(**1**).[41] The relative emission intensity of **1**⊃Pd NCs(DMF) around 350 nm was smaller than that of **1**. On the other hand, poly(**1**)⊃Pd NCs-A(DMF) did not luminesce at 300–400 nm. These data, including the bathochromic shift of photoluminescence, support the coordination of **1** and poly(**1**) to Pd NCs, and the occurrence of acetylene polymerization. The photoluminescence spectra of poly(**1**)⊃Pd NCs-B and C could not be measured due to insolubility in the solvent.
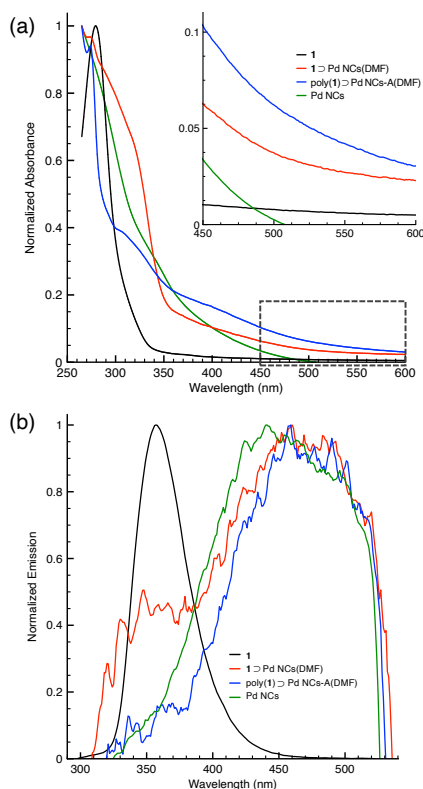
Figure 2. (a) UV-vis absorption and (b) emission spectra of **1**, Pd NCs, **1**⊃Pd NCs(DMF) and poly(**1**)⊃Pd NCs-A(DMF) measured in DMSO (c = 0.01 mM); inset shows the expansion of the area surrounded with broken lines. The absorbances were normalized at 269 nm except **1** (λ_{max} = 285 nm). Excitation wavelength = 270 nm. The samples were prepared *via* Route A in Scheme 1.

XPS measurements were performed to obtain information on the coordination site of the polymer complexes. Pd NCs exhibited Pd 3d peaks attributable to Pd^0 around 335 and 340 eV, as shown in Figure 3 (a). On the other hand, poly(**1**)⊃Pd NCs-A(DMF), -A(CHCl$_2$CHCl$_2$), -B and -C exhibited Pd 3d peaks attributable to Pd^{2+} around 337 and 342 eV. It is suggested that the Pd species of Pd NCs were oxidized during the preparation of the polymer complexes. Apparently surface of Pd NCs is more easily oxidized compared to core.[42,43] Further

investigation is desirable such as XAFS measurement to clarify the valency of surface and core of Pd NCs. It seems that the amino group of **1** coordinates to Pd NCs, judging from the N 1s XPS peaks in poly(**1**)⊃Pd NCs-A(DMF), -A(CHCl$_2$CHCl$_2$), -B and -C, which are observed at the higher binding energy region than that of poly(**1**) as shown in Figure 3 (b). There was no remarkable difference of the N 1s peaks among the samples, indicating the contribution of amino groups to coordination is similar irrespective of the preparation method. Poly(**1**)⊃Pd NCs-B and poly(**1**)⊃Pd NCs-C exhibited C 1s XPS in a fashion similar to poly(**1**), as shown in Figure 3 (c), while poly(**1**)⊃Pd NCs-A(DMF) and -A(CHCl$_2$CHCl$_2$) exhibited a shoulder around 284.5 eV. It is therefore suggested that the phenyl groups as well as amino groups of poly(**1**) coordinate to Pd NCs in Route A.
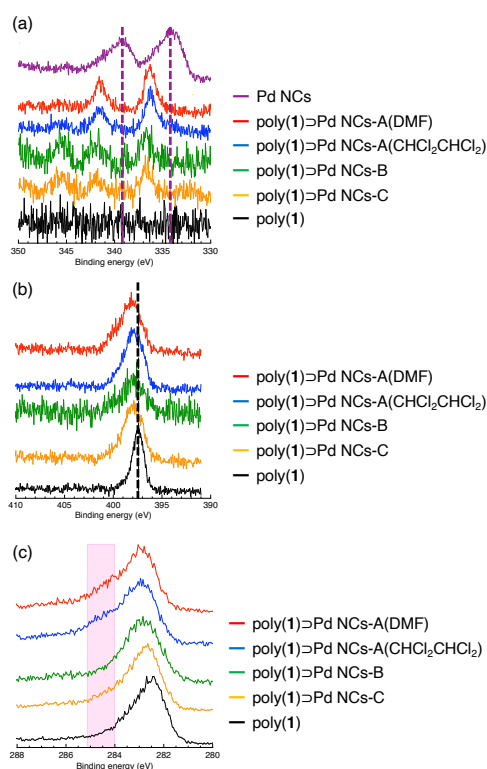
Figure 3. XPS profiles of (a) Pd 3d, (b) N 1s and (c) C 1s of Pd NCs, poly(**1**)⊃Pd NCs prepared *via* the four routes illustrated in Scheme 1, as well as poly(**1**) prepared *via* Route C in Scheme1.

Figures 4–6 show the results of scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) measurements of poly(**1**)⊃Pd NCs-A(DMF), -A($CHCl_2CHCl_2$), -B, -C. Pd NCs with a diameter of 1–2 nm were observed in the STEM images of poly(**1**)⊃Pd NCs-A(DMF) and -A($CHCl_2CHCl_2$) samples, as shown in Figure 4. No particle with a diameter larger than several nm was observed. Because the size was the same as that of Pd NCs before coordination,[43] this result confirmed that the Pd NCs were coordinated with poly(**1**) without further aggregation. On the other hand, aggregates of Pd NCs with diameters of 30–200 nm were observed in the STEM images of poly(**1**)⊃Pd NCs-B and -C samples, as shown in Figures 5 (a) and 6 (a), and the corresponding elemental mapping images shown in Figures 5 (b) and 6 (b). It should be noted that the energy dispersive X-ray spectroscopy (EDS) measurement of poly(**1**)⊃Pd NCs-B and -C samples [Figures 5 (d) and 6 (d)] confirmed the presence of Pd in the area [blue square and circle in Figures 5 (c) and 6 (c)] where no aggregate was observed in poly(**1**)⊃Pd NCs-B and -C. It is therefore concluded that Pd NCs are partially coordinated with the polymer, maintaining their original size (several nm), while the other Pd NCs are aggregated with sizes of several tens–hundreds nm. Consequently, the Pd NCs kept

their original size upon polymerization of **1**⊃Pd NCs (Route A in Scheme 1), while coordination of poly(**1**) to Pd NCs resulted in aggregation (Routes B and C in Scheme 1). It is considered that molecules of **1** are small, and therefore they coordinate to Pd NCs efficiently, leading to the homogenous growth of polymer chain upon polymerization of **1**⊃Pd NCs, and resulting in no aggregation of Pd NCs. On the contrary, molecules of poly(**1**) are large, and they coordinate to Pd NCs less efficiently, resulting in aggregation of Pd NCs.
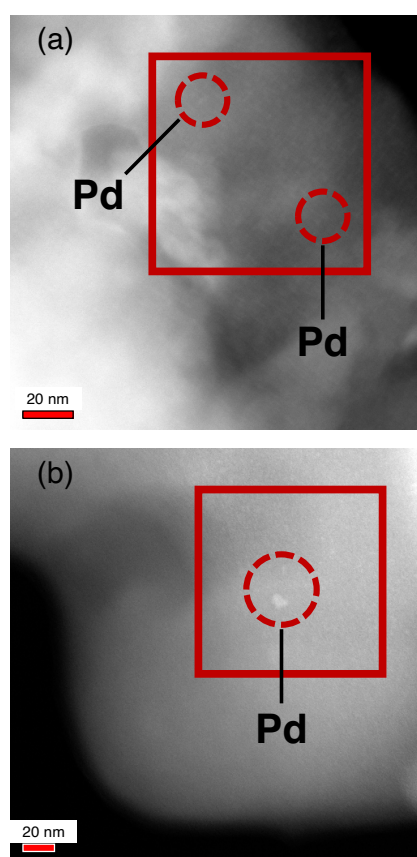

Figure 4. STEM images of (a) poly(**1**)⊃Pd NCs-A(DMF) and (b) poly(**1**)⊃Pd NCs-A(CHCl$_2$CHCl$_2$). The samples were prepared *via* Route A in Scheme 1.
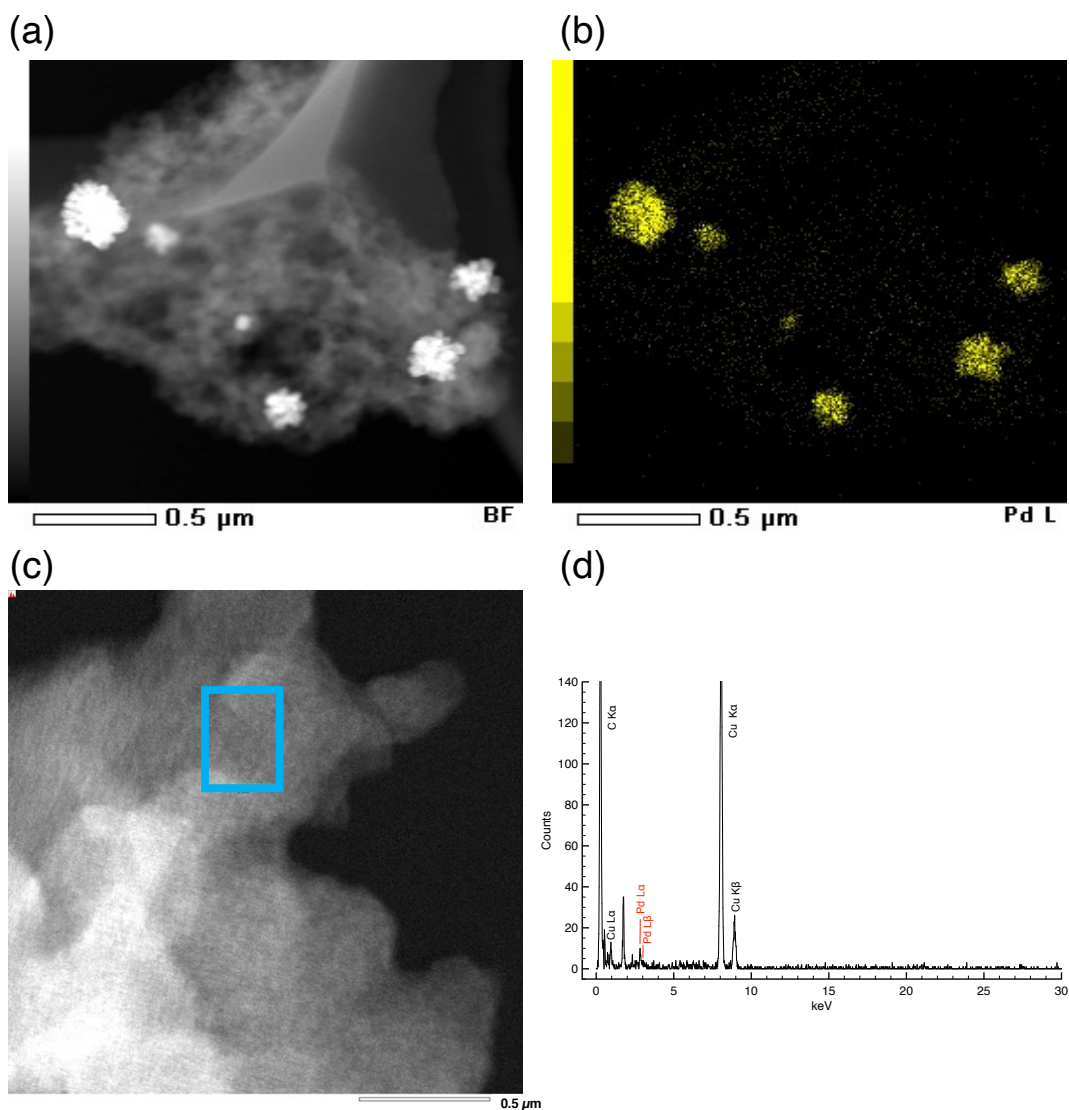
Figure 5. Sample: poly(**1**)⊃Pd NCs-B prepared *via* Route B in Scheme 1. (a) STEM image. (b) STEM elemental mapping image of Pd. (c) SEM image in which the blue square indicates the area irradiated with X-rays in EDS coupled measurements. (d) EDS plot.

Figure 6. Sample: poly(**1**)⊃Pd NCs-C prepared *via* Route C in Scheme 1. (a) STEM image. (b) STEM elemental mapping image of Pd. (c) SEM image in which the blue circle indicates the area irradiated with X-rays in EDS-coupled measurements. (d) EDS plot.
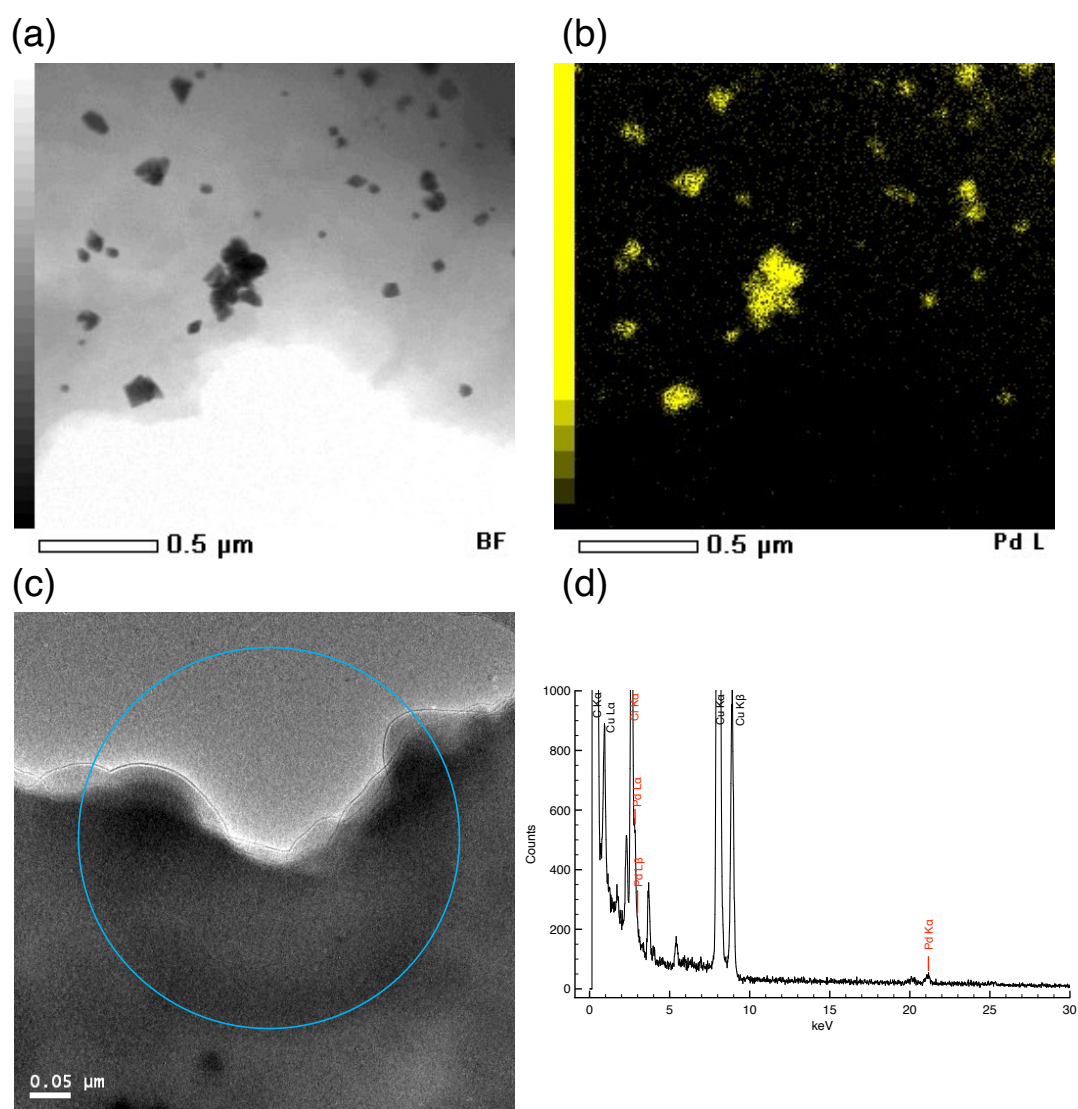
2.2. Catalytic Function

The Mizoroki-Heck coupling reaction of iodobenzene (**2**) and styrene (**3**) was first carried out using the polymer-coordinated Pd NCs to obtain stilbene (**4**) and 1,1-diphenylethylene (**5**), as illustrated in Scheme 2. The reaction mixtures containing polymer-coordinated Pd NCs were

turbid due to insolubility in the solvent. Table 1 lists the product yields determined by gas

chromatography (GC) using tridecane as a standard, together with the results using Pd NCs as

a catalyst for comparison. Poly(**1**)⊃Pd NCs-B gave the products with the highest yields (run 6)

among the catalysts examined. On the other hand, the other polymer–Pd NCs gave the products

with yields lower than those of Pd NCs (runs 1 and 2). It is considered that the difference in the

synthetic routes leads to the difference in the aggregation of Pd NCs and coordination with the

polymer. There was no clear tendency in the selectivity between **4** and **5**.
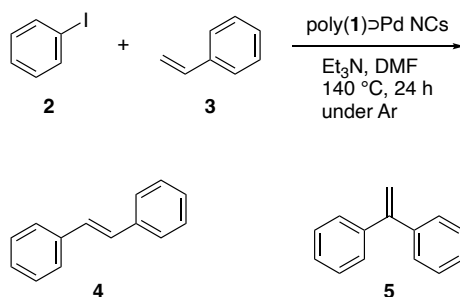
Scheme 2. Mizoroki-Heck Coupling Reaction of 2 and 3

Table 1. Yields of 4 and 5 Obtained by the Mizoroki-Heck Coupling Reaction of 2 with 3 [a]

run	catalyst	[Et$_3$N]/[2]	yield [b] (%)	
			4	5
1	Pd NCs	1	33	4
2	Pd NCs	2	60	8
3	poly(**1**)⊃Pd NCs-A(DMF)	1	24	3
4	poly(**1**)⊃Pd NCs-A(DMF)	2	57	12
5	poly(**1**)⊃Pd NCs-A(CHCl$_2$CHCl$_2$)	2	39	11
6	poly(**1**)⊃Pd NCs-B	2	82	18
7	poly(**1**)⊃Pd NCs-C	2	48	14

[a] Conditions: [**2**]$_0$ = 1.0 M, [**3**]$_0$ = 1.2 M, [Pd] = 50 μM in DMF at 140 °C for 24 h under Ar. [b] Determined by GC using tridecane as a standard.

The Suzuki-Miyaura coupling reaction of 4-iodotoluene (**6**) and phenylboronic acid (**7**) was next carried out using the polymer-coordinated Pd NCs to obtain 4-methylbiphenyl (**8**), as illustrated in Scheme 3. Table 2 lists the product yields determined by GC using tridecane as a standard, together with the result using Pd NCs as a catalyst for comparison. Poly(**1**)⊃Pd NCs-A(DMF), -A(CHCl$_2$CHCl$_2$) and -B gave **8** in 70–92% yields, which were almost the same as the yields using Pd NCs. On the other hand, poly(**1**)⊃Pd NCs-C gave **8** in 46% yield, lower than those of the other samples. Trace amounts (2.2% and less) of 4,4′-dimethylbiphenyl (**9**) were produced as a byproduct. There was no evidence for the occurrence of hydrolytic deboronation.[44] The molecular weight of poly(**1**) (M_n = 8,500) of poly(**1**)⊃Pd NCs-C is higher than that of poly(**1**) (M_n = 1,700) of poly(**1**)⊃Pd NCs-B, and presumably higher than that of poly(**1**)⊃Pd NCs-A(DMF) (M_n including Pd NCs = 640). It is therefore assumed that the mobility of polymer complexes decreases as the molecular weight of poly(**1**) moiety increases, leading to a decrease in the frequency of contact between the active Pd species and substrates. Thus the trend of molecular weights of poly(**1**) moieties and the catalytic activity were different for Suzuki-Miyaura coupling and Mizoroki-Heck coupling reactions. It is likely that solvent (DMF and MeOH) and temperature (140 and 100 °C) also affect the active site around the Pd

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metals in conjunction with the mobility and swelling degree of the polymer ligand, but the

concrete reason is unclear at the moment.

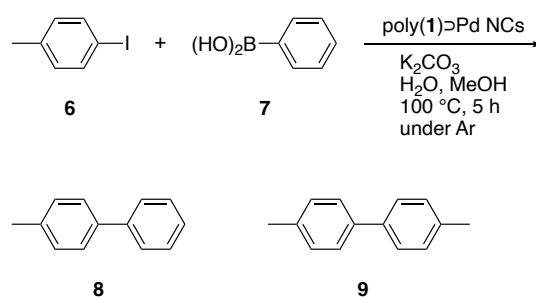**Scheme 3. Suzuki-Miyaura Coupling Reaction of 7 and 8**

Table 2. Yields of 8 and 9 Obtained by the Suzuki-Miyaura Coupling of 6 with 7[a]

run	catalyst	yield[b] (%)	
		8	9
1	Pd NCs	94	0.9
2	poly(**1**)⊃Pd NCs-A(DMF)	85	0.7
3	poly(**1**)⊃Pd NCs-A(CHCl$_2$CHCl$_2$)	70	0.5
4	poly(**1**)⊃Pd NCs-B	79	2.2
5	poly(**1**)⊃Pd NCs-C	46	n.d.[c]

[a] Conditions: [**6**]$_0$ = 0.250 M, [**7**]$_0$ = 0.375 M, [Pd] = 25 μM in MeOH at 100 °C for 5 h under Ar. [b] Determined by GC using *n*-tridecane as internal standard. [c] Not detected by GC.

3. Conclusion

In this article, we have demonstrated the preparation of polyacetylenes poly(**1**)s

coordinated to PdNCs. The XPS measurements revealed that the phenyl groups as well as amino

groups of poly(**1**) coordinated to Pd NCs. Pd NCs around 1 nm were observed in the STEM

image of poly(**1**)⊃Pd NCs prepared by the acetylene polymerization of 4-ethynylaniline

(compound **1**)⊃Pd NCs, while aggregates of Pd NCs with sizes of 10–100 nm were observed

in the STEM of poly(**1**)⊃Pd NCs prepared by the coordination of poly(**1**) with Pd NCs. It is

considered that Pd NCs with sizes of several nm were partially coordinated with the polymers,

thus maintaining the original size, while the other Pd NCs were aggregated with sizes of several

tens–hundreds nm. The Pd NCs-coordinated to polyacetylenes efficiently catalyzed the

Mizoroki-Heck and Suzuki-Miyaura coupling reactions. Thus, we have successfully developed

novel polymer-supported Pd NCs applicable as catalysts for coupling reactions. Polymer-

supported catalysts are promising for development of highly efficient, selective and recyclable

catalytic technology.[45–47] We believe that the present study provides a new methodology for

designing polymer catalysts as well as metal nanocluster catalysts. Further studies on versatility,

enhancement of catalytic activity, and use in recycling are now in progress.

4. Experimental Section

4.1. Measurements

^{1}H (400 MHz) NMR spectra were recorded on JEOL ECZ-400 and ECS-400 spectrometers. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Number-average molecular weight (M_n) and dispersity ($Đ$) values of polymers were determined by an SEC system consisting of JASCO RI-930, UV-4570, PU-4580, DG-2080-53 and CO-965 equipped with Shodex KF-805L×3, TSK gel α-M and GMHXL columns eluted with a solution of LiBr (10 mM) in N,N-dimethylformamide (DMF) at 40 °C and calibrated with polystyrene standards. UV-vis absorption spectra were measured on a JASCO V-550 spectrophotometer. Photoluminescence spectra were measured on a SHIMADZU RF-6000 spectrofluorophotometer. Gas chromatography was performed on a SHIMADZU GC-2010 equipped with a Trajan Scientific BP5 capillary column (length: 25 m, internal diameter: 0.22 mm, film thickness: 0.25 µm) and flame ionization detector (FID). The injector and FID were kept at 280 and 300 °C, respectively. The samples were injected with a column temperature at 40 °C and held for 4 min, then heated to 280 °C with a heating rate of 15 °C/min, and held at 280 °C for 10 min. X-ray photoelectron spectroscopy (XPS) was performed on a ULBAC-PHI PHI 5000 Versa Probe III and the X-ray source with an Al Kα (1400 eV) X-ray source. Scanning transmission electron microscopy (STEM) measurements were performed on a JEOL JEM-ARM 200F with a copper grid and 200 kV accelerating voltage. SEM-EDS measurements

were performed on a JEOL JSM-6500F coupled with a JEOL dry silicon drift detector JED-2300.

4.2. Reagents

N-(*tert*-Butoxycarbonyl)-4-ethynylaniline (**1a**),[48] *N*-(9-fluorenylmethyloxycarbonyl)-4-ethynylaniline (**1b**),[49] (nbd)Rh$^+$B$^-$PPh$_4$[50] and Pd NCs (1 mM in DMF)[8] were prepared according to the literature. All the other reagents were purchased and used without purification. Solvents used for polymerization that were dried over molecular sieves 4A 1/16, and degassed by Ar bubbling.

4.3 Preparation of 1⊃Pd NCs(DMF)

A mixture of **1** (117 mg, 1.0 mmol) and Pd NCs in DMF (1.0 mM, 50.0 mL) was stirred at 150 °C for 24 h under Ar. The resulting solution was concentrated on a rotary evaporator. The residual mass was washed with MeOH to obtain **1**⊃Pd NCs as a black solid (330 mg, yield = quant.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.41 (s, 1H, $^-$C≡CH), 6.07 (br, 1H, –NH$_2$), 6.59 (d, 2H, J = 8.0 Hz, Ar), 7.76 (d, 2H, J = 8.0 Hz, Ar).

4.4 Polymerization of 1⊃Pd NCs(DMF)

(nbd)Rh$^+$B$^-$PPh$_4$ (27.0 mg, 0.053 mmol) was dissolved in DMF (2.6 mL) in a Schlenk tube filled with Ar. Then a solution of **1**⊃Pd NCs (323 mg, 2.65 mmol) in DMF (4.0 mL) was fed into the tube, and the resulting solution was stirred at 30 °C for 2 h ([**1**⊃Pd NCs(DMF)]$_0$/[Rh] = 50, [**1**⊃Pd NCs(DMF)]$_0$ = 0.88 mol/L). CH$_3$COOH (0.46 mL, 8.00 mmol) was added to the reaction mixture, and the resulting mixture was poured into Et$_2$O (100 mL) to precipitate a solid mass. It was separated from the solution by filtration with a membrane (ADVANTEC H100A047A), and dried *in vacuo* to obtain poly(**1**)⊃Pd NCs-A(DMF) as a black solid (329 mg, yield = quant.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.11–7.87 (m, Ar), 8.55 (br, –NH$_2$). M_n = 640, $Đ$ = 2.0.

4.5. Poly(1)⊃Pd NCs-A(CHCl$_2$CHCl$_2$)

The title complex was prepared by complexation of **1** and Pd NCs in CHCl$_2$CHCl$_2$, followed by polymerization in a manner similar to the procedure for the preparation of poly(**1**)⊃Pd NCs-A(DMF). **1**⊃Pd NCs-A(CHCl$_2$CHCl$_2$) was a black solid (236 mg, yield = quant.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 1H, –C≡CH), 6.61 (d, 2H, J = 8.0 Hz, Ar), 7.70 (d, 2H, J = 8.0 Hz, Ar), 8.77 (br, 1H, –NH$_2$). Poly(**1**) ⊃ Pd NCs-A(CHCl$_2$CHCl$_2$) was obtained as a

brownish solid (88.1 mg, yield = 32%). The ^{1}H NMR spectrum of poly(**1**) ⊃ Pd NCs-

A(CHCl$_2$CHCl$_2$) could not be measured due to insolubility in common organic solvents.

4.6. Polymerization of 1a and 1b

[(nbd)RhCl]$_2$ (13.8 mg, 0.03 mmol) was dissolved in THF (2.5 mL) in a Schlenk tube filled

with Ar. Then a solution of **1b** (509 mg, 1.50 mmol) in THF (1.2 mL) and Et$_3$N (42 μL, 0.3

mmol) were fed into the tube, and the resulting solution was stirred at 30 °C for 2 h ([**1b**]$_0$/[Rh]

= 50, [**1b**]$_0$ = 0.40 mol/L, [Et$_3$N]/[Rh] = 10). CH$_3$COOH (0.15 mL, 2.62 mmol) was added to

the reaction mixture, and the resulting mixture was poured into Et$_2$O (100 mL) to precipitate a

solid mass. It was separated from the solution by filtration with a membrane (ADVANTEC

H100A047A), and dried *in vacuo* to obtain a polymer [poly(**1b**)] as a yellow solid (396 mg,

yield = 78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.07 (br, –CH$_2$–CH<), 5.90 (br, –CH=C<),

7.00–7.87 (m, Ar), 9.66 (br, –NH–). M_n = 680,000, $Đ$ = 1.9. Poly(**1a**) was synthesized in a

manner similar to the polymerization of **1b**. A yellow solid (324.4 mg, yield = 75%). ^{1}H NMR

(400 MHz, CDCl$_3$): δ 1.48 (br, –C(CH$_3$)$_3$), 5.72 (br, –CH=C<), 6.55–6.84 (m, Ar). M_n =

240,000, $Đ$ = 3.4.

4.7. Poly(1)⊃Pd NCs-B

Poly(**1a**) (170 mg, 0.78 mmol) was dissolved in CH_2Cl_2 (6.0 mL) in a flask. Then trifluoroacetic acid (3.0 mL) was fed into the flask, and the resulting solution was stirred at room temperature for 2 h. The resulting mixture was concentrated on a rotary evaporator, and the residual mass was dissolved in H_2O (6.0 mL). The reaction mixture was neutralized with saturated $NaHCO_3$, and concentrated on a rotary evaporator to obtain a black solid. It was dissolved in MeOH (5 mL), and the solution was poured into Et_2O (150 mL) to precipitate a solid mass. It was separated by filtration with a membrane (ADVANTEC H100A047A) and dried *in vacuo* to obtain a polymer [poly(**1**)] as a black solid (100 mg, yield = quant.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.00–5.31 (br, $-NH_2$), 5.50–7.41 (br, Ar and $-CH=C<$). M_n =1,700, $Đ$ = 5.4. Then poly(**1**)⊃Pd NCs-B was prepared by complexation of poly(**1**) and Pd NCs in DMF in a manner similar to the procedure for the preparation of **1**⊃Pd NCs(DMF). A black solid (72.8 mg, yield = quant.)

4.8. Poly(1)⊃Pd NCs-C

Poly(**1b**) (305 mg, 0.90 mmol) was dissolved in DMF (7.0 mL) in a flask. Then Et_2NH (1.2 mL) was fed into the flask, and the resulting solution was stirred at room temperature for 2 h.

The reaction mixture was poured into Et$_2$O (100 mL) to precipitate a solid mass. It was separated by filtration with a membrane (ADVANTEC H100A047A) and dried *in vacuo* to obtain a polymer [poly(**1**)] as a dark green solid (107 mg, yield = quant.). ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ 4.79 (br, –NH$_2$), 5.42–7.48 (m, Ar and –CH=C<). M_n =8,500, $Đ$ = 2.8. Then poly(**1**)$\supset$Pd NCs-C was prepared by complexation of poly(**1**) and Pd NCs in DMF in a manner similar to the procedure for the preparation of **1**$\supset$Pd NCs(DMF) to yield a black solid (130 mg, yield = quant.)

Acknowledgements

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