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Preparation of Pd-PS, Pd-PSB and Pd-PSC nanoparticles by γ-irradiation and their catalytic efficiency in Sonogashira coupling reaction

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Abstract

The poly(styrene), PS, of 450 nm diameter, poly(styrene-*co*-4-vinylphenylboronic acid), PSB, nanoparticles of 220–400 nm diameter, and poly(styrene-*co*-4-vinylbenzoic acid), PSC, nanoparticles of 240–305 nm were prepared by emulsifier-free emulsion polymerization. The surface of PS, PSB, and PSC nanoparticles were loaded with Pd nanoparticles by reduction of Pd ions using γ-irradiation in order to apply catalyst in Sonogashira coupling reaction. The Pd-PS, Pd-PSB and Pd-PSC were characterized by High-Resolution Transmittance Electron Microscopy (HR-TEM), Field-Emission Scanning Electron Microscopy (FE-SEM), and Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), respectively. The HR-TEM, XRD and ICP-AES data show that the Pd nanoparticles were loaded on the surface of PS, PSB, and PSC nanoparticles, respectively. Catalytic efficiency of the Pd-PS, Pd-PSB and Pd-PSC nanoparticles was tested in Sonogashira coupling reaction. The catalytic efficiency of the Pd-PS, Pd-PSB, and Pd-PSC nanoparticles was increased with increasing Pd nanoparticle contents.

Keywords: Emulsifier-free emulsion polymerization; Poly(styrene-*co*-4-vinylphenylboronic acid); PSB; Nanoparticles; Poly(styrene-*co*-4-vinylbenzoic acid); PSC; Nanoparticles ;γ-Irradiation; Catalysts; Sonogashira reaction

1. Introduction

The conventional emulsion polymerization has been widely applied in polymer materials preparation. Many biomedicine materials can also be prepared through this method [1]. However, the residuary of emulsifier in materials will greatly influence the purification and performance of the products. Moreover, the environmental pollution coming from the usage of emulsifier is also more severity. So the emulsifier-free emulsion polymerization has been more attentions in recent years. Compared to the conventional emulsion polymerization, it provides one or more of the following advantages: no emulsifier migration during film formation, mono-disperse particle size distribution, and excellent shear stability [2,3]. It is also used for some medical and biochemical purposes because of cleanness of the disperse medium and functionality due to the on-surface groups.

In a previous paper [4], the Ag and Ag-SiO_2 nanoparticles were synthesized by γ-irradiation, and tested their antibacterial and antifungal efficiency against *Salmonella enterica* serovar Typhimurium and *Botrytis cinerea*. Test results showed the Ag-SiO_2 nanoparticles have strong potential as an antifungal as well as an antibacterial agent. At the presence of 50 ppm of the Ag-SiO_2 particles, the *S. enterica* serovar Typhimurium grew much slower, and at 100 ppm, they did not grow fully even after 58 h. The antifungal efficiency of the Ag-SiO_2 nanoparticles against *B. cinerea* was about 65.0, 99.9, and 99.9% at the concentration of the Ag-SiO_2 particles of 10, 50, and 100 ppm, respectively.

On the other hand, Ag-PS and Ag-PSS nanoparticles were also prepared by γ-irradiation by reduction of silver ions in PS and PSS colloids prepared by emulsifier-free emulsion polymerization in order to apply antimicrobial agents to coating cloth

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antimicrobial activity of the Ag-PS and Ag-PSS nanoparticles (0.4 g) with ca. 100 ppm Ag, which is coated onto yarn (KS K 0905-1996 rule), was tested against *Staphylococcus aureus* ATCC 6538 and *Klebsiella pneumoniase* ATCC 4352 after 100 cycles washing (KS K 0432-1999 rule). The antimicrobial activity of the Ag-PS nanoparticles against *S. aureus* ATCC 6538 and *K. pneumoniase* ATCC 4352 was 99.9% after 100 cycles washing [5].

In this study, the Pd-PS, Pd-PSB and Pd-PSC were prepared by γ-irradiation, and characterized by High-Resolution Transmittance Electron Microscopy (HR-TEM), Field-Emission Scanning Electron Microscopy (FE-SEM), X-ray Diffraction (XRD), and Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), respectively. Furthermore, the catalytic efficiency of the Pd-PS, Pd-PSB and Pd-PSC nanoparticles, was tested in Sonogashira coupling reaction.

2. Experiment

2.1. Chemicals

Styrene (99%), 2-iodothiophene, phenylacetylene, iodobenzene and potassium persulfate ($K_2S_2O_8$) were obtained from Sigma–Aldrich Co. 4-Vinylphenylboronic acid and 4-vinylbenzoic acid were purchased from Tokyo-Kasei (Japan). Palladium nitrate ($PdNO_3$) was obtained from Kojima Chemicals Co. Ltd. (Japan). All other chemicals were in reagent grade, and were used without further purification.

2.2. Synthesis of PS, PSB and PSC nanoparticles by emulsifier-free emulsion polymerization

The PS nanoparticles were prepared as follows: at first, potassium persulfate (KPS) was dissolved completely in deionized water (800 mL). A styrene was added KPS solution, and polymerized at 75 °C for 24 h by stirring of 350 rpm under nitrogen atmosphere.

The PSB nanoparticles were prepared as following manner: the potassium hydroxide (0.1 g) and KPS was dissolved completely in deionized water (800 mL). A styrene and 4-vinylphenylboronic acid (0.5, 1.0, and 2.0 g, respectively) was added KPS solution, and polymerized at 75 °C for 24 h by stirring of 350 rpm. The reaction condition was described as shown in Table 1. The PSC nanoparticles were also prepared as same method as the preparation of PSB method.

2.3. Synthesis of Pd-PS, Pd-PSB and Pd-PSC nanoparticles by γ-irradiation

Briefly, the $PdNO_3$ of 3.0×10^{-4} M was prepared in PS, PSB or PSC colloids of 150 mL. Nitrogen gas was bubbled through the solution for 30 min to remove oxygen, and the solution was irradiated by γ-ray from Co-60 source. The Pd-PS, Pd-PSB, and Pd-PSC were obtained by filter paper with 2.0 μm pore (Advantec, Tokyo, Japan). The formation Pd nanoparticles from the metal ions can be explained by the following mechanism. In an aqueous solution, hydrated electrons are generated by γ-irradiation (see Eq. (1)).

$$H_2O \rightarrow e_{aq}^-, H_3O^+, H^\bullet, H_2, OH^\bullet, H_2O_2 \quad (1)$$

The Pd ions are reduced by the hydrated electrons to form metallic Pd (Pd^0) (see Eq. (2)), which are aggregated to form more stable Pd particles (Pd_{agg}) (see Eq. (3)).

$$e_{aq}^- + Pd^{2+} \rightarrow Pd^0 \quad (2)$$

$$nPd_0 \rightarrow Pd_2 \rightarrow Pd_n \rightarrow Pd_{agg} \quad (3)$$

In Eq. (3), n is the number of aggregated Pd_0 and Pd_{agg} is the aggregate in the final stable state.

2.4. Catalytic efficiency examination of Pd-PS, Pd-PSB and Pd-PSC nanoparticles in Sonogashira coupling reaction [6–8]

The catalytic efficiency examination was performed according to the reported paper [9]. Briefly, the Pd-PS catalyst (43 mg), aryl halide (1.0 mmol), terminal alkyne (1.5 mmol), and K_2CO_3 (2.0 mmol), were added in EtOH (20 mL), and then the mixture was refluxed under nitrogen atmosphere for 6 h. The resulting brown liquid was filtered by membrane filter with 0.45 pore (MFS-25 PVDF, ADVANTEC MFS, Inc., Japan). The resulting yields were determined HPLC.

2.5. Characterization

Particle size and morphology of Pd-PS, Pd-PSB and Pd-PSC nanoparticles were investigated by a FE-SEM (Hitachi, S-4700, Japan), and HR-TEM (JEOL, JEM-2010, USA). The contents of Pd were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Jobin-Yvon, Ultima-C, USA).

Table 1
Size effects of comonomer in emulsifier-free emulsion polymerization[a]

No.	St (g)	4-VBA (g)	Size[b] (nm)	No.	Styrene (g)	4-VPB (g)	Size[b] (nm)
1	45.3	0	450	–	–	–	–
2	45.3	0.5	400	5	45.3	0.5	305
3	45.3	1	280	6	45.3	1	260
4	45.3	2	220	7	45.3	2	240

St, styrene; 4-VBA, 4-vinylphenylboronic acid; 4-VPB, 4-vinylbenzoic acid.
[a] Reaction condition: KPS (0.08 g) as initiator KOH (0.08 g); KH_2PO_4 (0.05 g) as pH controller; in water (775 mL); at 75 °C; with stirring of 350 rpm; for 24 h.
[b] Determined by FE-SEM.