

Recovery of Palladium in Highly-Viscous Polymer Solution Using Precipitation of Water-Soluble Polymer

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To recovery palladium (mean size 6 nm) in acrylonitrile butadiene rubber (NBR) acetone solution, the solution of poly 2-(dimethylamino)ethyl methacrylate (poly(DMAEMA)) (molecular weight 700,000) dissolved in water was added. Poly(DMAEMA) added to acetone solution captured palladium with amino group, then forming precipitation via dehydration by acetone. This technique using precipitation would possess a high-speed recovery of palladium in a high-viscous polymer solution.

1. Introduction

Palladium has been used as a catalyst for organic chemistry and polymer chemistry. Palladium is immobilized on the support such as silica particle and activated carbon. During the catalytic reaction, however, some of palladium immobilized is leaked to the reaction media [1]. After the reaction, leaked palladium needs to be recovered based on the economical view.

To recovery palladium, many researchers have studied the recovery of palladium in water media using solvent extraction [2], adsorption [3], and membrane [4] techniques. However, palladium in high-viscous solution, for instance in polymer solution, does not transfer; that is, there is a difficulty to recovery palladium in polymer solution because of the low mass transfer in viscous media. Thus, the high-speed recovery method of palladium in high-viscous solution have to be created.

Acrylonitrile butadiene rubber (NBR) is used for the polymer of automotive and aerospace industries [5]. Palladium is a catalyst for the change of double bond to single bond of NBR via hydrogenation reaction in organic media [6]. In this study, palladium in NBR dissolved in acetone was recovered using the precipitation of poly 2-(dimethylamino)ethyl methacrylate (poly(DMAEMA)) in water. By addition of poly(DMAEMA) solution to palladium solution, amino group in poly(DMAEMA) captures palladium via dehydration with acetone, forming precipitation. This technique has the easiness of solid and liquid separation because of the formation of precipitation as well as the potential for the recovery of palladium at high speed.

2. Experimental

2.1 Reagents

Poly(acrylonitrile-butadiene) (average molecular weight 40,000, acrylonitrile composition: 37 – 39 wt%, NBR) was obtained from Sigma-Aldrich Co., MO, U. S. A. 2-(Dimethylamino) ethyl methacrylate (DMAEMA), activated alumina, ammonium persulfate (APS), and palladium(II) acetate

were purchased from Wako Pure Chemical Industries, Ltd., Japan. Polyvinyl pyrrolidone (average molecular mass: 40,000) was obtained from Tokyo Chemical Industry Co., Ltd., Japan. WA30 (porous spherical resin, functional group: tertiary amine) and HP20 (porous spherical resin, poly(styrene-divinylbenzene)) was purchased from Mitsubishi Chemical Corporation, Japan. Other chemicals were of analytical grade or higher.

2.2 Polymerization of poly(DMAEMA)

Nitrogen-bubbled DMAEMA (9.30 g), ammonium persulfate (APS, 0.33 g), and pure water (34.4 g) was mixed at 303 K with the rotation of 360 rpm for 24 h. The obtained polymer solution was added to acetone to obtained white gel-like precipitation. The purification of the obtained polymer was twice performed. The polymer weight was characterized using size-exclusion chromatography. The molecular weight of the obtained poly(DMAEMA) was approximately at 700,000.

2.3 Recovery of palladium particle by precipitation of poly(DMAEMA)

Palladium acetate (0.224 g), polyvinyl pyrrolidone (0.539 g) and ethanol (25 mL) were refluxed at 343 K for 2.0 h [7]. One mL of the synthesized palladium dispersed solution was diluted with acetone to 100 mL. The size of palladium was observed using transmission electron microscopy (JEOL-2100, JEOL Ltd., Japan). The mean size of the palladium particle was measured to be about 6 nm.

Palladium and NBR-containing-acetone solution were mixed in the glass vial (diameter: 2.2 cm, height 4.0 cm). Poly(DMAEMA) solution dissolved in pure water was dropped to the palladium solution at 303 K and 150 rpm. The concentration of palladium and NBR was changed. After the filtration to remove the precipitant of poly(DMAEMA), the concentration of palladium was determined by absorption spectroscopy (AA-6800, Shimadzu Corporation, Japan). For comparison, the commercially-available resins, HP20 and WA30, were used for palladium adsorption in batch mode. The amount of precipitation was determined in mass. The characterization of the precipitant was performed using ATR method of infrared spectroscopy (IRAffinity-1, Shimadzu Corporation, Japan). The recovery percentage of palladium particle was calculated using the following equation,

$$\text{Recovery percentage of palladium recovery [\%]} = 100 (C_0 - C) / C_0 \quad (1)$$

where C_0 and C are the concentration of palladium before recovery and the concentration of palladium after recovery, respectively. The remained solution after the precipitation was dried and re-dissolved to acetone-D6 to analyze the interaction of NBR and poly(DMAEMA) by nuclear magnetic resonance (JEOL JNM-GX300).

3. Results and Discussion

3.1 Recovery of palladium by the precipitation of poly(DMAEMA)

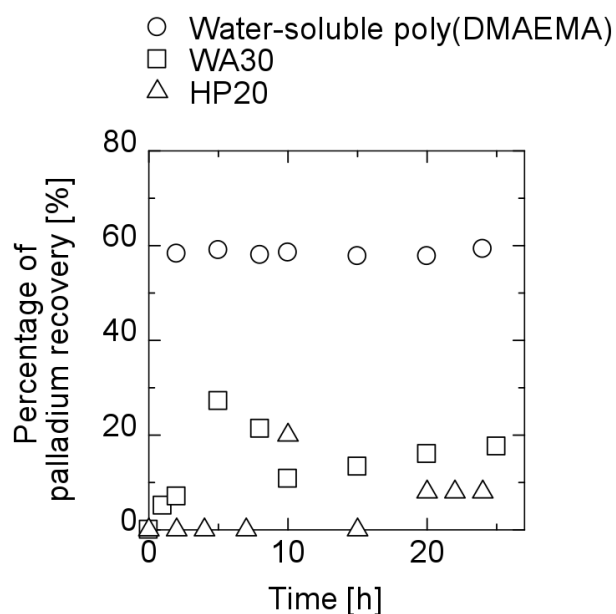


Figure 1. Time course curves of palladium recovery using adsorption and precipitation methods. Palladium solution (5 mL, 20 mg/L), concentration of NBR 22,000 mg/L, poly(DMAEMA) solution (0.1 mL, 0.1 g/mL), WA30 and HP20 100 mg.

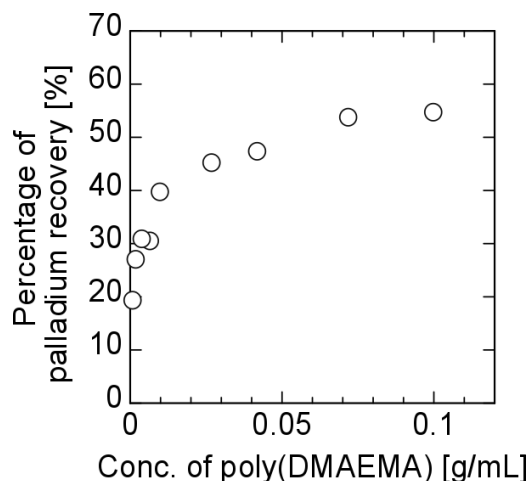


Figure 2. Effect of concentration of poly(DMAEMA) on recovery of palladium percentage. Palladium solution (5 mL, 20 mg/L), concentration of NBR 22,000 mg/L, poly(DMAEMA) solution (0.1 mL, 0.1 g/mL).

Palladium was dispersed in high viscous solution of NBR-acetone solution. Due to the high viscosity, palladium has the difficulty to move to the adsorbent. Figure 1 shows the time course curve of palladium recovery percentage using the commercially-available resins, WA30 and HP20, along with that of the proposed method in this study. In conventional adsorption, HP20 composed of poly(styrene divinylbenzene) had no ability to adsorb palladium. While WA30 with tertiary amino group had the adsorption percentage of 18% after 20 h. This indicated that amine group had the affinity to palladium. However, the conventional resin represented the slower speed of adsorption because NBR-containing-acetone solution had the high viscosity and palladium did not move to the resin faster. On the other hand, in the case of the addition poly(DMAEMA) solution, proposed in this study, the recovery percentage of palladium reached at 60% only for one hour. This technique includes the complexation with palladium in water-soluble poly(DMAEMA) and the dehydration of palladium-complexed polymer resulting in the precipitation formation. During this process, palladium could be captured quickly because of the faster binding with the amino group in poly(DMAEMA) as well as precipitation due to dehydration by acetone.

3.2 Concentration dependence of poly(DMAEMA) on recovery percentage of palladium

Poly(DMAEMA) in water has the hydrated structure with water. In palladium-acetone solution, hydrated water in poly(DMAEMA) moves to acetone forming a precipitation of poly(DMAEMA) binding with palladium. During capturing palladium, water has a critical role to change the phase transition of poly(DMAEMA) from soluble to insoluble states in acetone. Figure 2

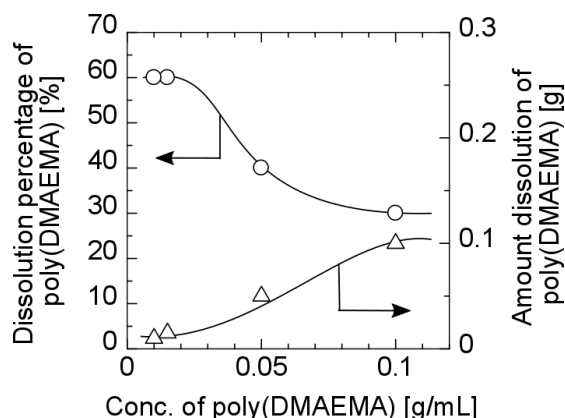


Figure 3. Effect of concentration of poly(DMAEMA) on dissolution of poly(DMAEMA) in NBR-acetone solution. Palladium solution (5 mL, 20 mg/L), concentration of NBR 22,000 mg/L, poly(DMAEMA) solution (0.1 mL, 0.1 g/mL).

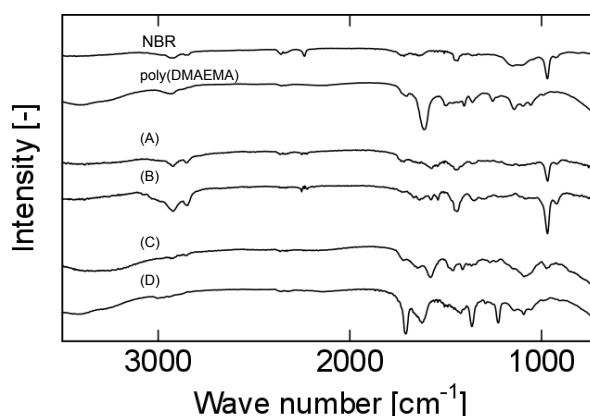


Figure 4. Infrared spectrograms of precipitants by adding poly(DMAEMA) solution. (A) 0.010 g/mL, (B) 0.015 g/mL, (C) 0.050 g/mL, (D) 0.10 g/mL.

shows the dependence of concentration of poly(DMAEMA) on the recovery percentage of palladium. With increasing the concentration of poly(DMAEMA) in water, the recovery percentage gradually increased and reached the percentage of 55%.

The dissolved poly(DMAEMA) added in NBR-acetone solution at the different concentrations of poly(DMAEMA) is shown in Figure 3. With increasing the concentration of poly(DMAEMA), the dissolution percentage of poly(DMAEMA) decreased. At lower concentration of poly(DMAEMA), there were much hydrated water around poly(DMAEMA) to make difficult form the precipitation. At higher poly(DMAEMA) concentration, the less water to hydrate, the less dissolution percentage in acetone.

To analyze the precipitant of mainly poly(DMAEMA), the precipitant was analyzed by infrared spectroscopy, as shown in Figure 4. NBR had peaks of 991 cm^{-1} and 2237 cm^{-1} assigned to C=C and C≡N groups, respectively [8]. At low concentration of poly(DMAEMA) as Figure 4 (A) and (B), the peaks at 991 cm^{-1} were clearly observed demonstrating that NBR would be co-precipitated with poly(DMAEMA). At higher concentration of poly(DMAEMA), the peaks of NBR disappeared because the more poly(DMAEMA) was precipitated by dehydration in acetone.

3.3 Interaction of poly(DMAEMA) and NBR with palladium

Water-soluble poly(DMAEMA) was not perfectly precipitated via dehydration as shown in Figure 3. The recovery percentage of palladium was 60%, shown in Figure 2, meaning that 40% of palladium was still dissolved in NBR-acetone solution. To enhance the recovery percentage of palladium, the interaction of poly(DMAEMA) with NBR or palladium need to be considered. The remained solution after the recovery of palladium was dried and re-dissolved in deuterated acetone to analyze them using nuclear magnetic resonance, as shown in Figure 5 (a) along with the assignments

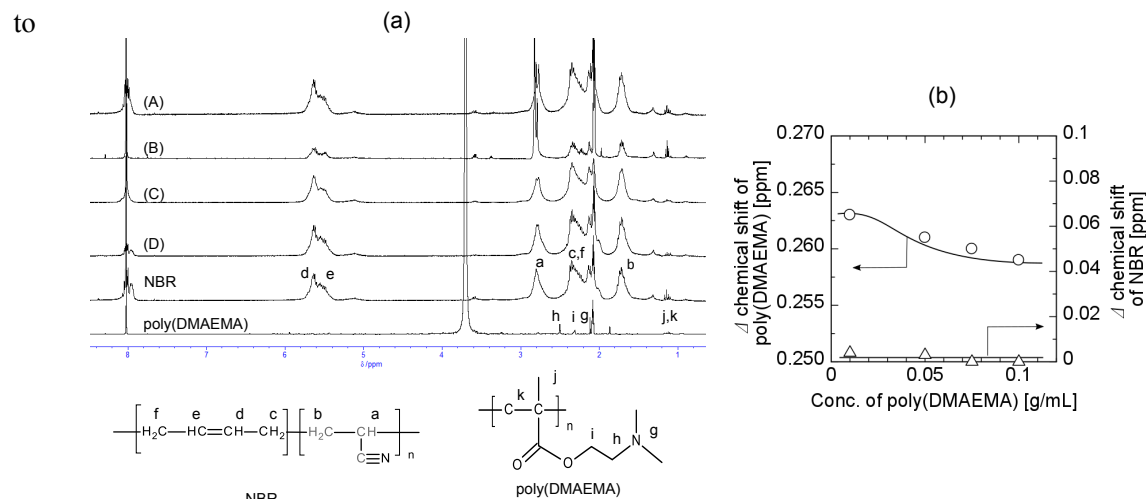


Figure 5. Interaction of polymers and palladium. (a) Spectra of nuclear magnetic resonance of remained NBR and poly(DMAEMA) solution after forming precipitation. (A) 0.1 g/mL poly(DMAEMA) added, (B) 0.075 g/mL poly(DMAEMA) added, (C) 0.050 g/mL poly(DMAEMA) added, (D) 0.010 g/mL poly(DMAEMA) added. Chemical shift standard used was CHCl_3 . (b) Change of chemical shift of *h* in poly(DMAEMA) and *a* in NBR.

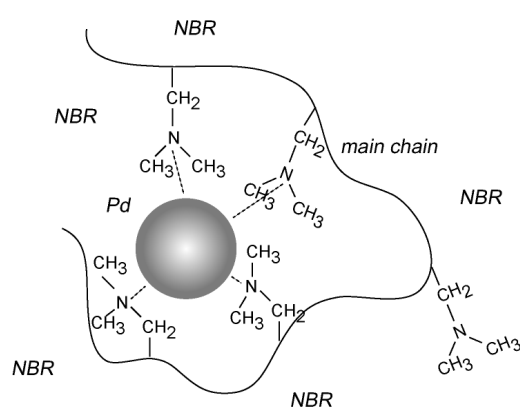


Figure 6. Pd complexation with poly(DMAEMA) in the presence of NBR.

The appropriate design of the functional group in monomer as well as the macroscopic structure of the polymer would be crucial for the sophisticated recovery of palladium in high-viscous solution using the precipitation method.

4. Conclusions

Palladium has been used as a catalysis for organic and polymer chemistry. During reaction, a part of palladium immobilized on the support is leaked to the media. In this study, palladium in high-viscous polymer acetone solution, acrylonitrile butadiene rubber, was recovered using the

precipitation of poly 2-(dimethylamino)ethyl methacrylate (poly(DMAEMA)). Compared with the conventional adsorption of palladium with the resin, this precipitation technique possessed the high-speed recovery of palladium. From the analysis of nuclear magnetic resonance, the amino group in poly(DMAEMA) would bind palladium.

References

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