

Supporting information to:

Pd Nanoparticles-loaded Vinyl Polymer Gels: Preparation, Structure and Catalysis

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Determination of monomeric unit ratio in poly(EDMA-co-MMA). Standard mixtures for IR spectral calibration were prepared as follows. Poly(MMA) (67.4 mg, 0.67 mmol per monomeric unit) was dissolved in CHCl₃ (10 mL). Four standard mixtures of poly(EDMA) and poly(MMA) were prepared by adding poly(EDMA) in the following amounts: (i) poly(EDMA) (9.15 mg, 0.046 mmol) to poly(MMA) solution (0.17 ml) ([EDMA]/([MMA]+[EDMA]) = 0.8); (ii) poly(EDMA) (10.84 mg, 0.054 mmol) to poly(MMA) solution (0.54 ml) ([EDMA]/([MMA]+[EDMA]) = 0.6); (iii) poly(EDMA) (11.67 mg, 0.058 mmol) to poly(MMA) solution (1.31 ml) ([EDMA]/([MMA]+[EDMA]) = 0.4); (iv) poly(EDMA) (9.86 mg, 0.049 mmol) to poly(MMA) solution (2.96 ml) ([EDMA]/([MMA]+[EDMA]) = 0.2). The volume of each solution was adjusted to 5 ml with CHCl₃ and homogenized by sonication for 10 min. Solvent was then removed, and the residue was dried under vacuum at 23 °C for 12 h. The samples were subjected to FTIR analysis (Figure S3) showing signals at 1637 cm⁻¹ (poly(EDMA)) and 755 cm⁻¹ (poly(EDMA) and poly(MMA)) whose ratios were plotted against ([EDMA]/([MMA]+[EDMA])) monomer unit ratio (Figure S4). The plot was well fitted to a linear equation, (EDMA signal intensity)/(EDMA signal intensity + MMA signal intensity) = 0.00727 x [EDMA unit]/[EDMA unit + MMA unit] – 0.19049, where R² value was 0.905.

Hot filtration test of Pd⁰/poly(DVB)-13% (leaching test). Benzyl alcohol (0.05 ml, 0.48 mmol), cyclohexene (0.1 ml, 0.98 mmol), nonane (0.025 ml, 0.14 mmol), cyclohexane (3 ml) and Pd⁰/poly(DVB)-13% (50 mg) were mixed in a 10-mL, two-necked flask and refluxed at 85 °C under N₂ atmosphere. After 2 min, about 1.5 mL from the reaction mixture was taken out with a syringe through a filter (Nylon, 13 mm f, 0.45 mm pore) to prevent the catalyst to enter the syringe, and the filtrated solution was transferred to another 10-mL, two-necked flask. The two reaction mixtures, the original one containing catalyst and the other from which the catalyst was filtrated out, were kept being heated at 85°C and were analyzed by ¹H NMR every 2 min.

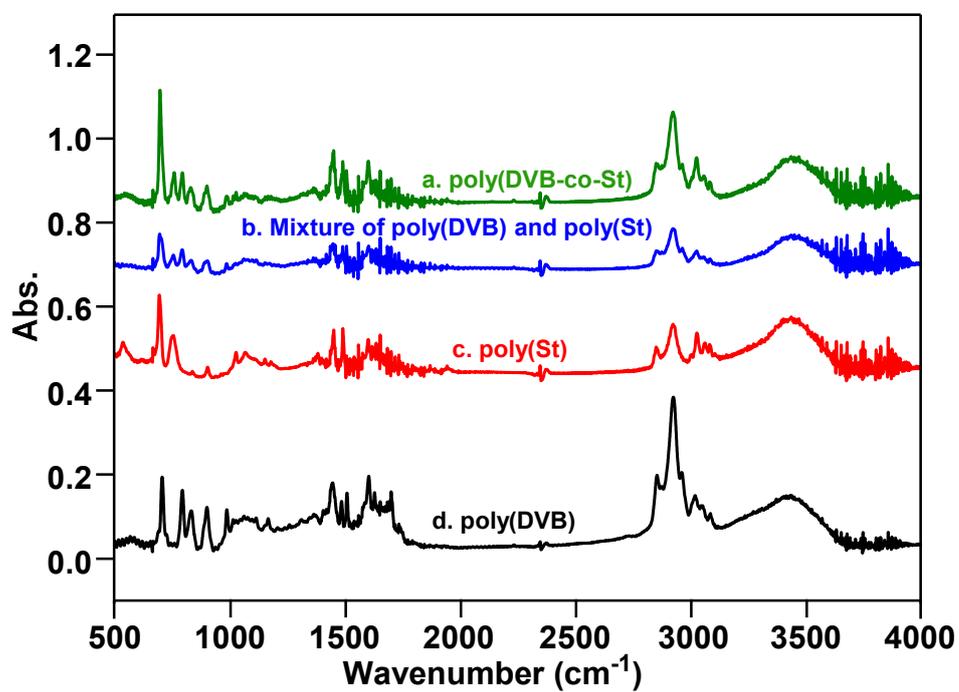


Figure S1. IR spectra of poly(DVB-co-St) (run 2 in table 1 in main text) (a), mixture of poly(DVB) (run 1 in table 1 in main text) and poly(St) at monomeric unit ratio 80/20 (b), poly(St) (c), and poly(DVB) (run 1 in table 1 in main text) (d).

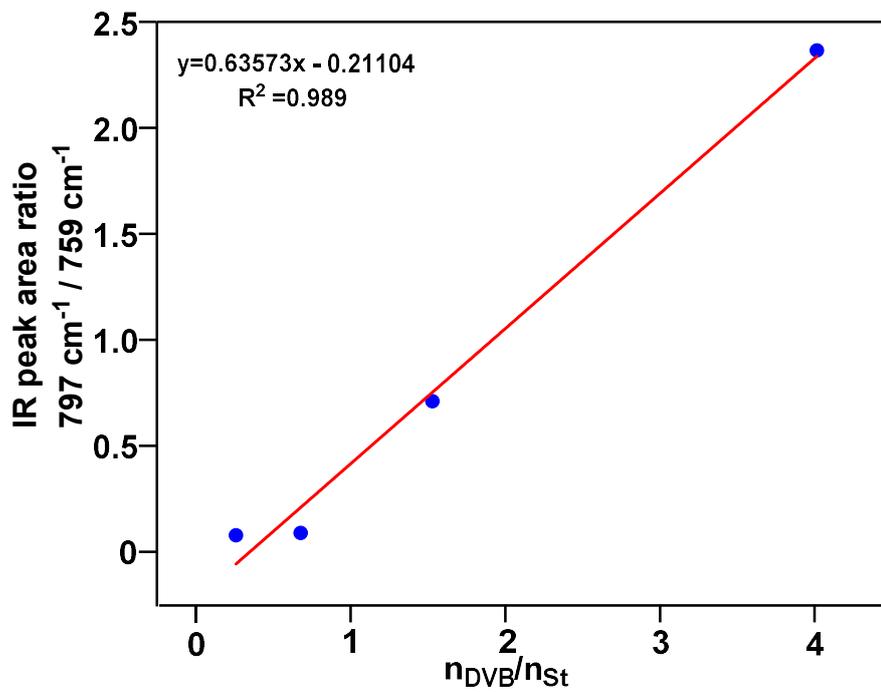


Figure S2. Calibration curve used for determination of the monomeric unit ratio of poly(DVB-co-St).

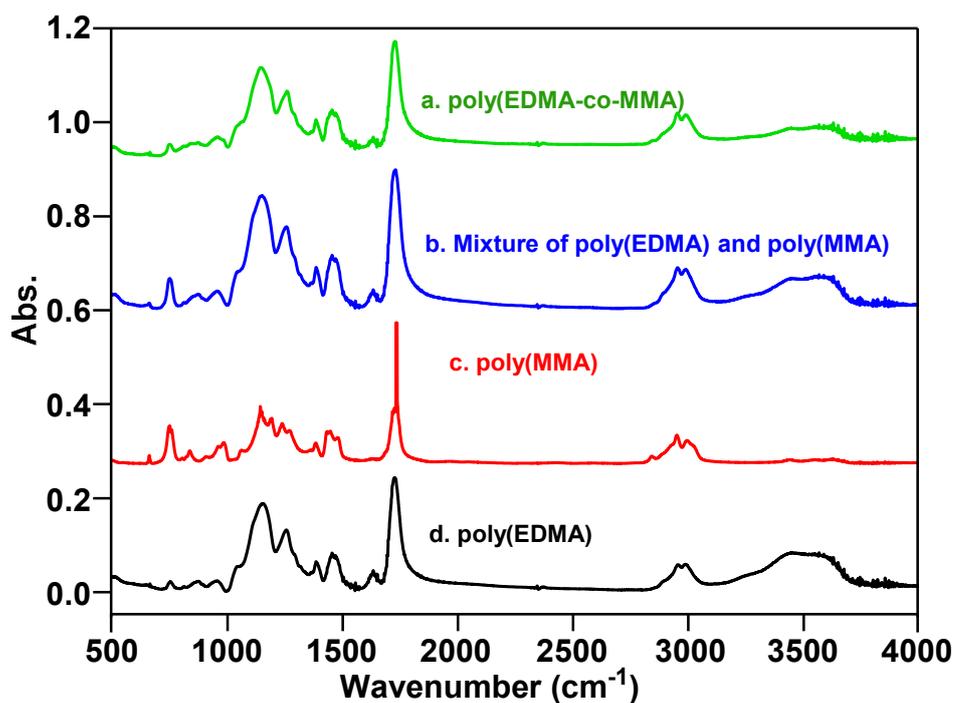


Figure S3. IR spectra of poly(EDMA-co-MMA) (run 4 in Table 1 in main text) (a), mixture of poly(EDMA) (run 3 in table 1 in main text) and poly(MMA) at monomeric unit ratio 60/40 (b), poly(MMA) (c), and poly(EDMA) (run 3 in Table 1 in main text) (d).

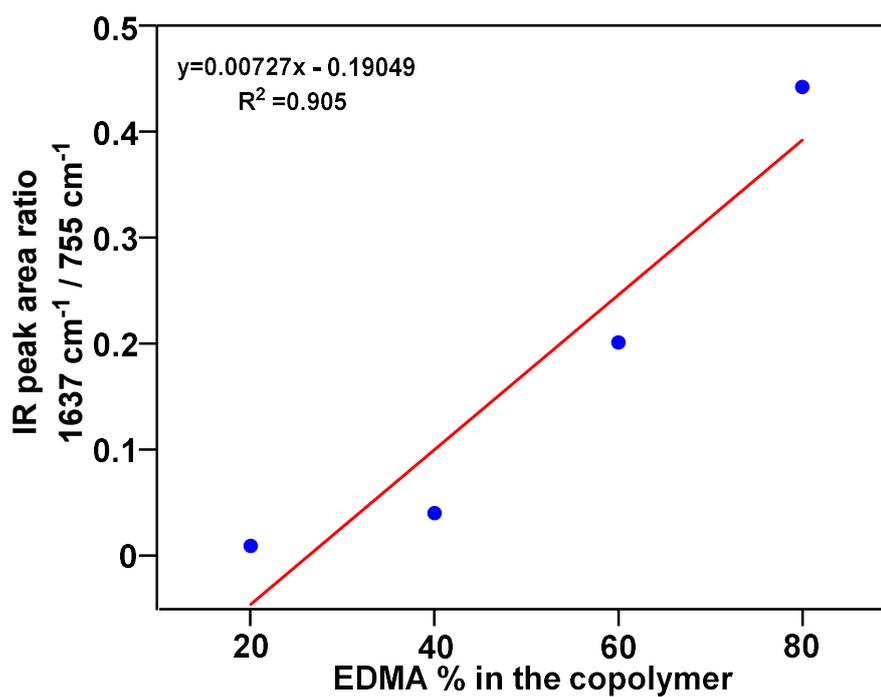


Figure S4. Calibration curve used for determination of the EDMA monomer unit percentage in poly(EDMA-co-MMA).

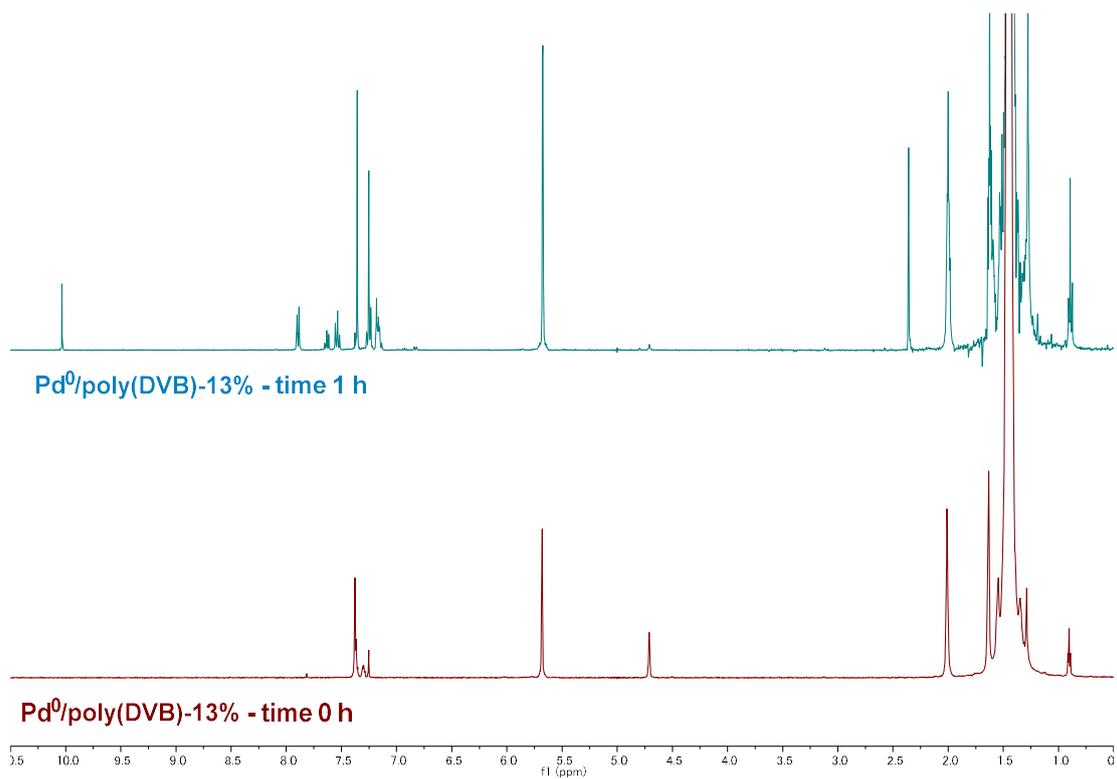


Figure S5. ¹H NMR spectra of reaction mixture before and after reaction by using Pd⁰/poly(DVB)-13%. Reaction conditions: benzyl alcohol (0.05 ml, 0.48 mmol); cyclohexene (0.1 ml, 0.98 mmol); cyclohexane (3 ml); Pd⁰/poly(DVB)-13% (50 mg, 0.029 mmol Pd); 85 °C and under N₂ atmosphere.

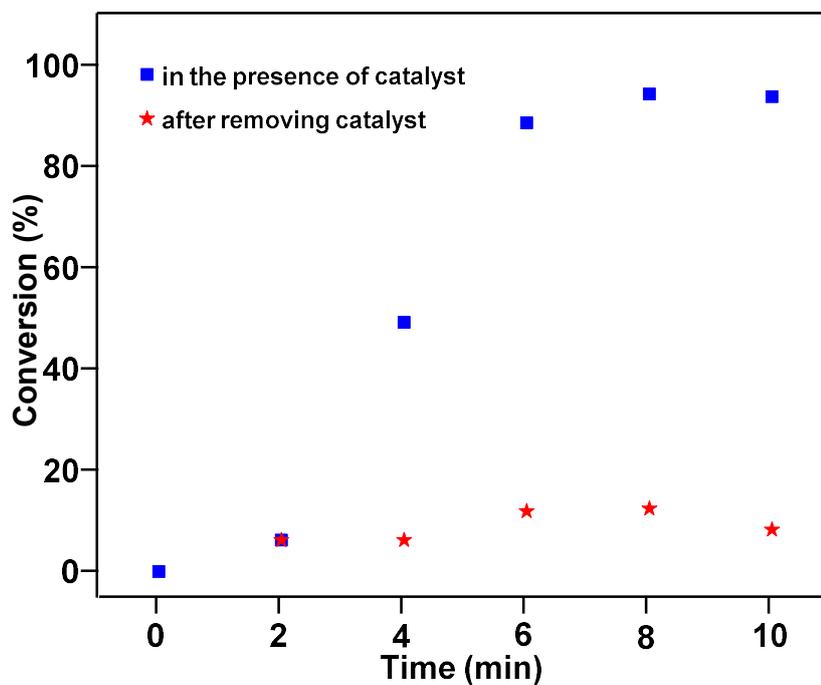


Figure S6. “Hot filtration” test of Pd⁰/poly(DVB)-13%. Reaction conditions: benzyl alcohol (0.05 ml, 0.48 mmol), cyclohexene (0.1 ml, 0.98 mmol), nonane (0.025 ml, 0.14 mmol), cyclohexane (3 ml), Pd⁰/poly(DVB)-13% (50 mg), 85 °C and under N₂ atmosphere.

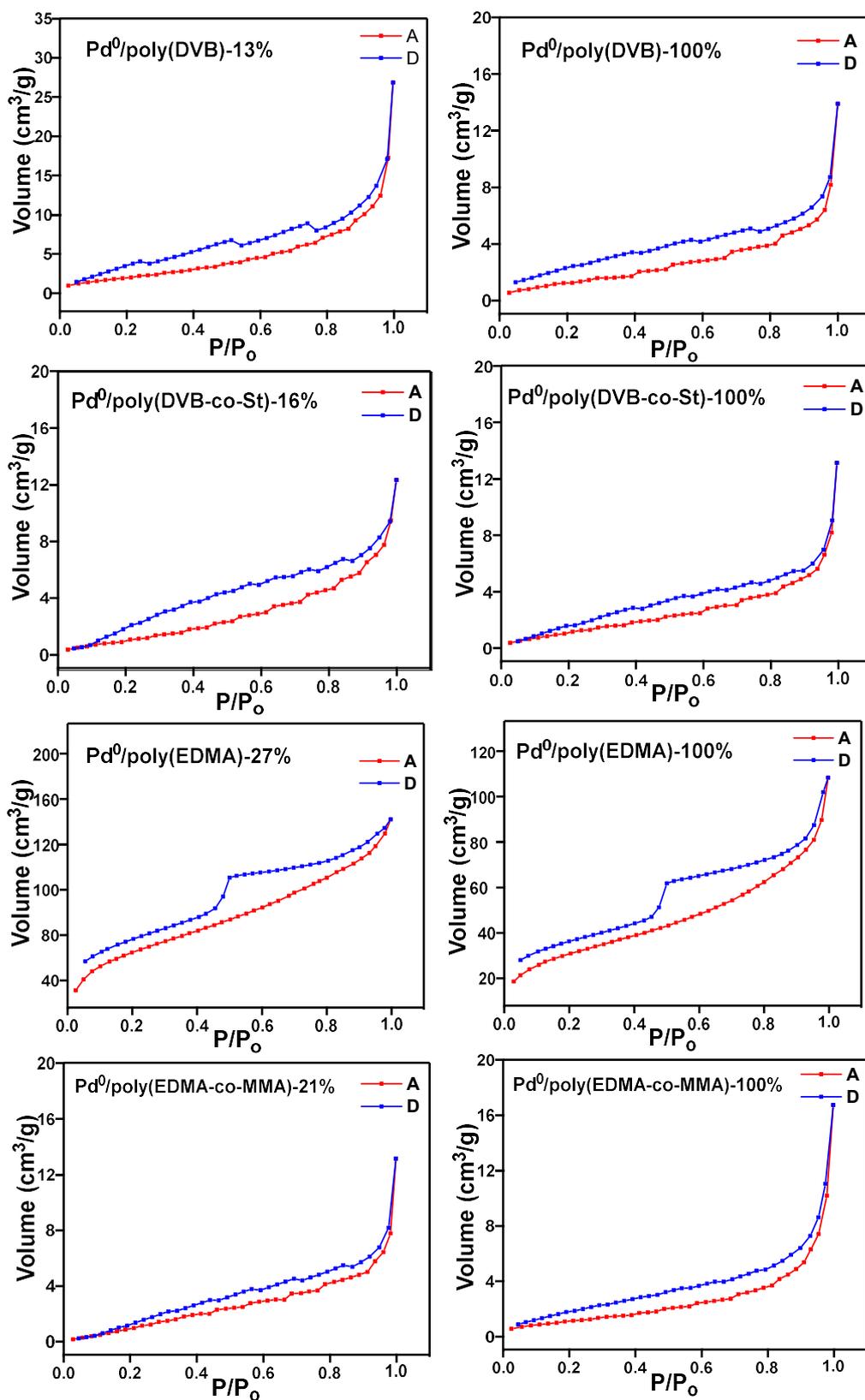


Figure S7. BET isotherm of Palladium nanoparticles supported on polymer gels.

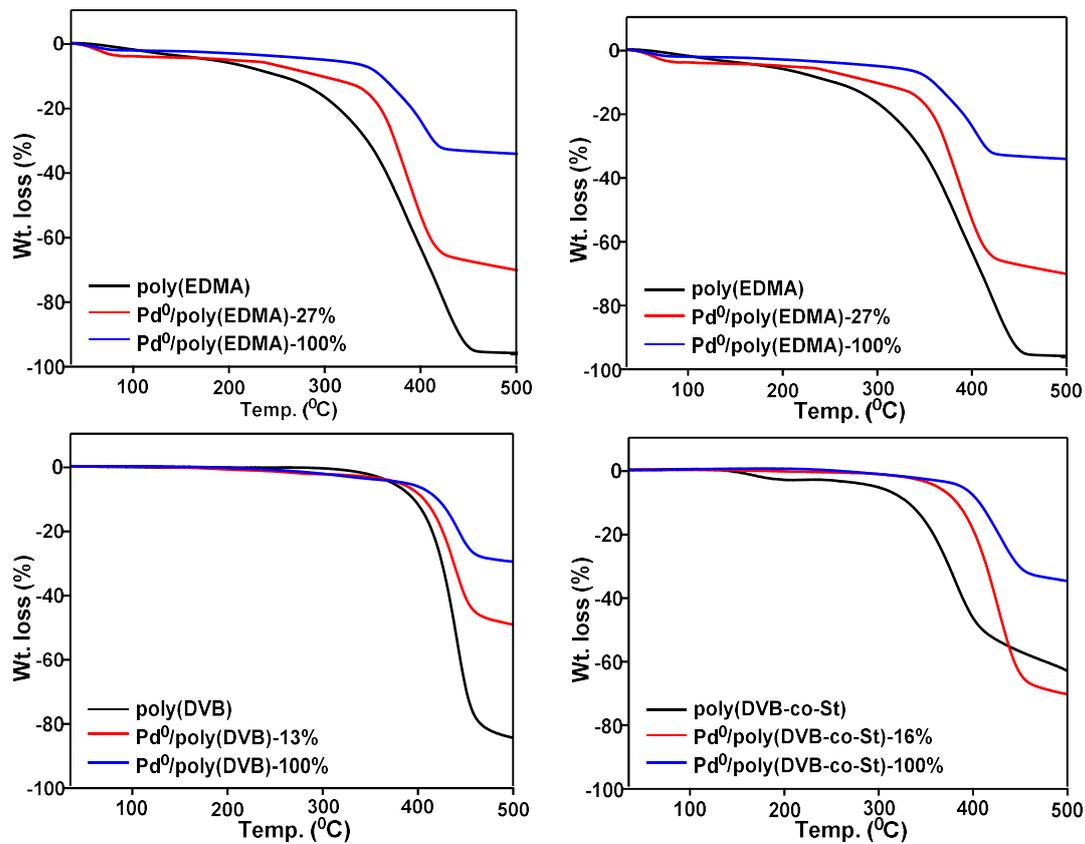


Figure S8. TGA of Palladium nanoparticles supported on polymer gels.

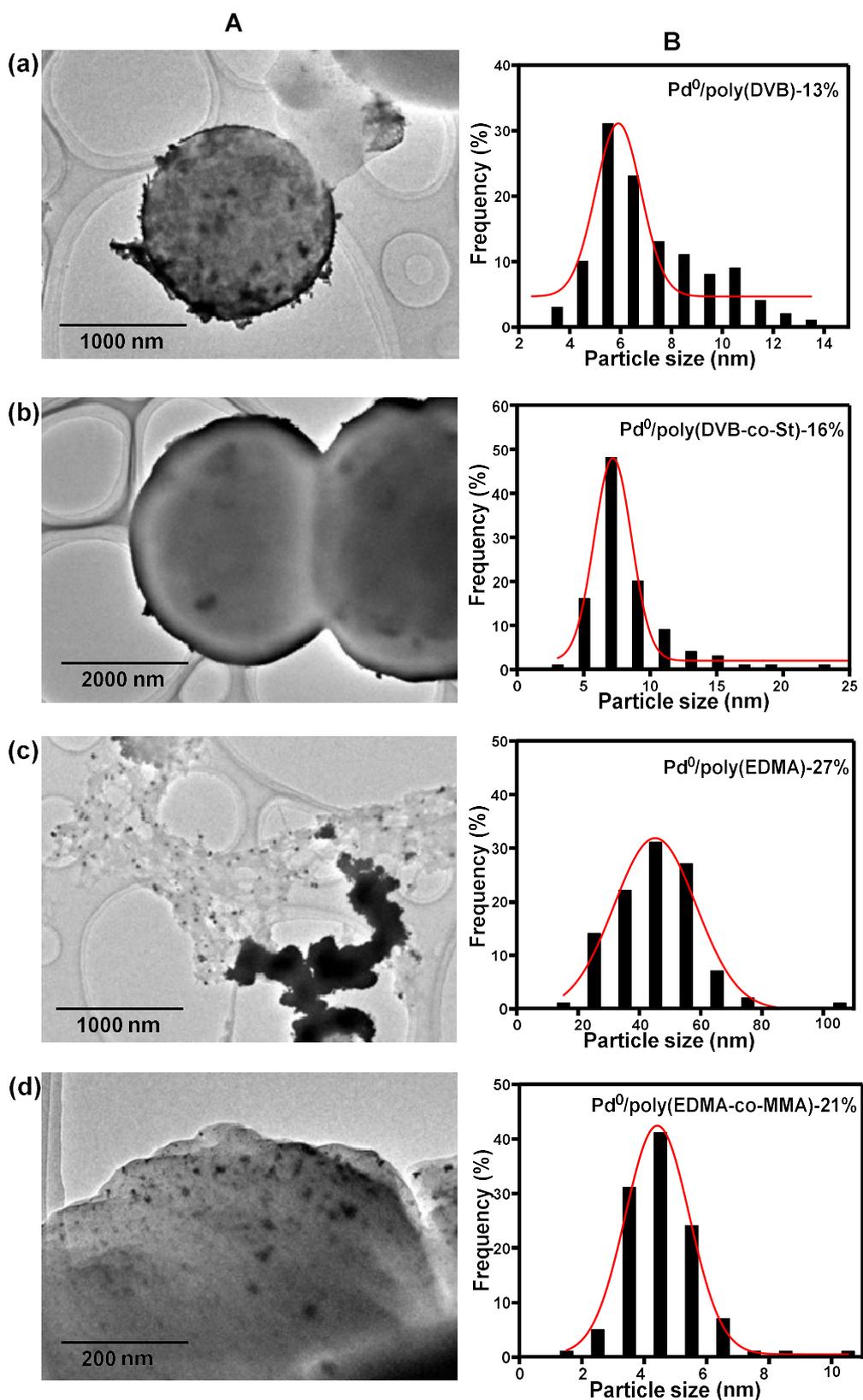


Figure S9. TEM images [A] and particle size distributions [B] of Pd⁰/poly(DVB)-13% (a), Pd⁰/poly(DVB-co-St)-16% (b), Pd⁰/poly(EDMA)-27% (c), Pd⁰/poly(EDMA-co-MMA)-21% (d).

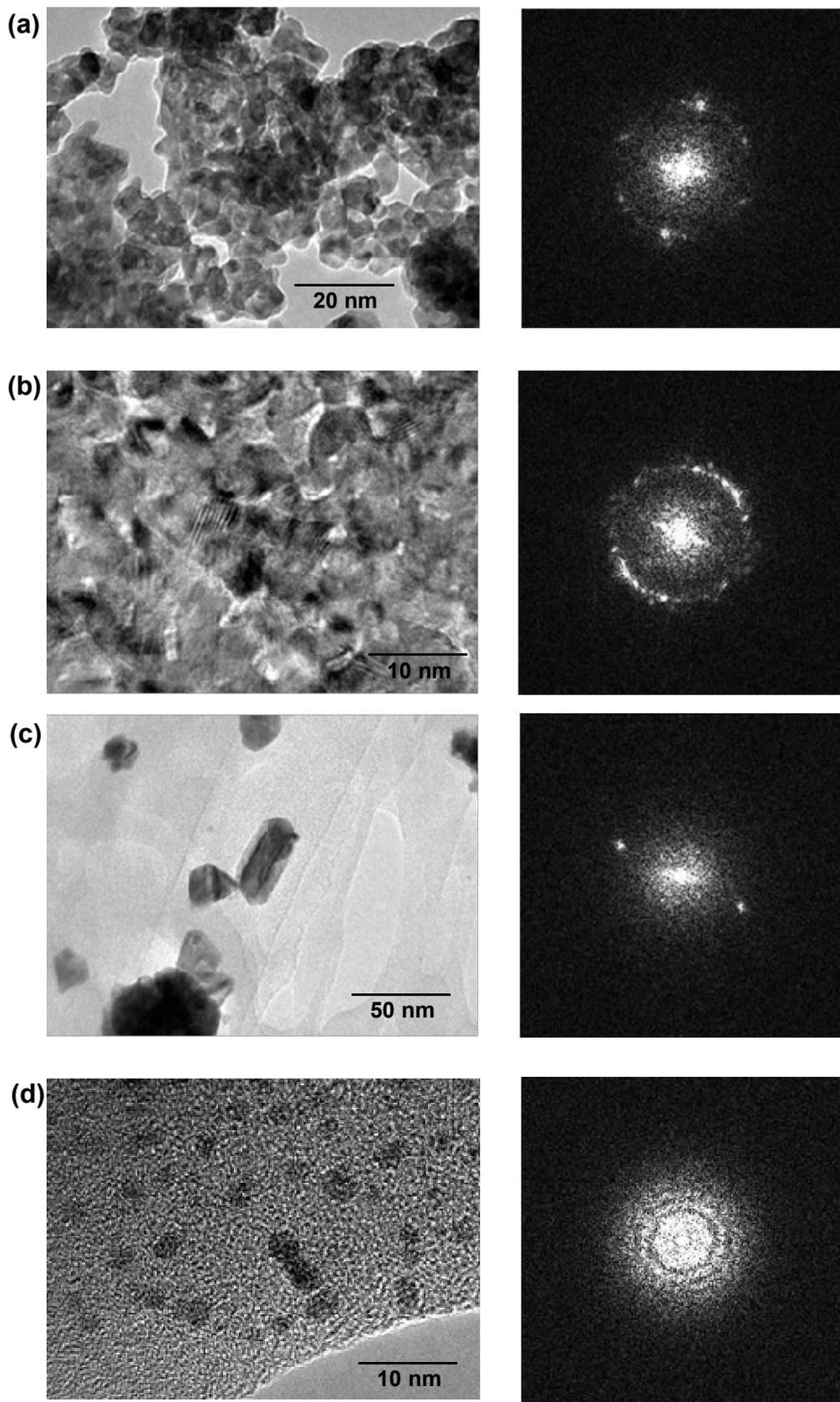


Figure S10. HRTEM images of Pd⁰/poly(DVB)-13% (a), Pd⁰/poly(DVB-co-St)-16% (b), Pd⁰/poly(EDMA)-27% (c), Pd⁰/poly(EGDMA-co-MMA)-21% (d).