

Supporting Information

Polyelectrolyte as solvent and reaction media

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Experimental section

Materials

3-Sulfopropyl acrylate potassium salt, chloroplatinic acid hexahydrate, β -cyclodextrin ($\geq 97\%$), iodine ($\geq 99.8\%$), bromine ($\geq 99.5\%$), selenium (99.99%), phosphorus ($\geq 97\%$), sulfur ($\geq 99.5\%$), D-(+)-mannose ($\geq 99\%$), neutral red ($\geq 90\%$), 4,4'-bipyridine (98%), Nile red (technical grade), indigo (synthetic, 95%), single-walled carbon nanotubes, Amber Jet 1200 hydrogen form, poly(ethylene glycol) methyl ether ($M_n = 750$ g/mol), poly(sodium 4-styrenesulfonate) ($M_w \sim 70,000$ g/mol) and poly(acrylic acid) ($M_w \sim 2000$ g/mol) were obtained from Sigma-Aldrich and used without further purification. 2,2'-Azobis(2-methylpropionitrile) (98%, Aldrich) was recrystallized from methanol. Styrene ($\geq 99\%$, Aldrich) was freshly distilled before use. Tris(2-(2-methoxyethoxy)ethyl)amine (95%) was obtained from Alfa Aesar and freshly distilled before use. The solvents and other materials were used as received.

Preparation of AAPS-IL monomer

33.31 g (0.143 mol) of 3-sulfopropyl acrylate potassium salt was firstly given over the ion-exchange resin Amber Jet 1200 (hydrogen form) for the cation exchange. The formed 3-(acryloyloxy)-1-propanesulfonic acid in 30 mL of H₂O and 48.69 g (0.151 mol) of the freshly distilled tris(2-(2-methoxyethoxy)ethyl)amine were given into an argon purged 500 mL schlenk flask equipped with a

magnetic stir bar. The mixture was stirred at ambient temperature for 10 h. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) characterization indicated that the acid-base neutralization reaction proceeded rapidly at ambient temperature and ended up with full conversion within 10 h. After the reaction was finished the water was removed by high vacuum (1×10^{-3} mbar). A transparent light amber oil was obtained with a yield of 99%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 9.14 (br s, 1H), 6.34-6.29 (dd, 1H, $J = 17.3$ Hz), 6.21-6.14 (dd, 1H, $J = 17.3$ Hz), 5.95-5.92 (dd, 1H, $J = 10.3$ Hz), 4.17 (t, 2H, $J = 6.68$ Hz), (t, 6H, $J = 4.68$ Hz), 3.59-3.56 (m, 6H), 3.48-3.46 (m, 6H), 3.39 (br s, 2H), 3.50 (br s, 9H), 2.49-2.43 (m, 6H), 1.94-1.87 (m, 2H).

Preparation of PAAPS-PIL

To the prepared AAPS-IL was added 500 mg (3.04 mmol) of 2,2'-azobis(2-methylpropionitrile) (AIBN) under argon purge. The sealed reaction flask was allowed to vent to a blubber, and heated to 100°C for 12 h. A quantitative monomer conversion was observed, and eventually no vinyl residue peak was detected in the $^1\text{H-NMR}$ spectrum of the reaction mixture. Upon cooling to ambient temperature, the transparent brown-orange amber mixture was cleaned by dialysis using a dialysis tube with a molecular weight cutoff (MWCO) of 3500 Da for 72 h with constant changing of MilliQ water (every 2 h in daytime). Yield: 50 %. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 9.28 (br s, 1H), 4.05 (br s, 2H), 3.78 (m, 6H), 3.59-3.57 (m, 6H), 3.49-3.46 (m, 6H), 3.43-3.40 (m, 9H), 3.34 (br s, 2H), 2.45-2.42 (m, 6H), 1.85 (br s, 2H), 1.74-1.69 (m, 2H), 1.44 (s, 1H).

Pt nanoparticle synthesis

5 mg (0.012 mmol) of chloroplatinic acid hexahydrate and 15 mg (0.242 mmol) of ethylene glycol were given to 2 g (3.864 mmol) of PAAPS-PIL in a glass reactor in a glove box equipped with argon supply. After sealing the flask the reaction mixture was heated at 150°C for 1 h. For characterization of the particle size by TEM, the Pt nanoparticle dispersion in bulk PAAPS was dialysed in water using a dialysis membrane with a MWCO of 100 KDa. For the catalytic tests, the reaction mixture was dialysed in water (MWCO \sim 3.5 KDa) and then dried at 100°C under high vacuum.

PS latex synthesis

In a 50 mL schlenk tube 2 g (3.864 mmol) of PAAPS-PIL, 10 mg (0.061 mmol) of AIBN and 200 mg (1.920 mmol) of freshly distilled styrene were weighted. Then three freeze-pump-thaw-cycles were carried out. The reaction was conducted under argon atmosphere, equipped with a KPG-stirrer, and kept at 100 °C for 2 h. The purification was done by ultrafiltration with a membrane with a pore size of 50 nm.

Dye absorption

Dye solutions were prepared in heptane: 1) Nile red 3.3×10^{-5} mg/mL, 2) Indigo 0.33mg/mL. 2 mL of each solution was placed into a 5 mL vial together with 1g (1.932 mmol) of dried PAAPS-PIL. The vials were heated to 90 °C and shaken by a vortex-shaker at 3000 rpm. The decoloring was proven by naked eyes as well as UV/VIS-measurments of the dye solutions in heptane before and after treatment with the PIL.

Stabilization of CNTs

5 g (9.66 mmol) of dry AAPS-IL was placed in a 25 mL schlenk tube equipped with a magnetic stir bar. 5 mg of SWCNTs were first sonicated in 5 ml of DMF for 15 min, before it was added in the schlenk tube. The mixture was treated again by sonication for 5 min before AIBN (83 mg, 0.506 mmol) was added. The reaction mixture was degassed and purged with argon for three times. Finally, the schlenk tube was placed in a preheated oil bath (90°C) for 12 h for the polymerization. After polymerization, DMF was removed by high vacuum (1×10^{-3} mbar) at 100 °C, and a homogeneous CNT dispersion in bulk PIL was obtained.

Catalytic reactions

1 g of the as-prepared Pt nanoparticle dispersion in bulk PIL and 0.5 mmol substrate (Table S2) were placed in a 10 mL schlenk tube equipped with a magnetic stir bar. The tube was placed in a preheated oil bath (130 °C) for 4 h under 2 bar initial hydrogen pressure by using a ballon. After

extraction of the products by heptane and drying the system under high vacuum, it was directly used for recycle experiment, and the yield was determined by GC-MS (Table S2).

Characterization Methods

TGA experiments were accomplished on a Netzsch TG209-F1 apparatus at a heating rate of 10 K min⁻¹ under nitrogen.

Differential scanning calorimetry (DSC) measurements were performed under nitrogen flow on a Perkin-Elmer DSC-1 instrument. The heating/cooling rate was adjusted to 10 K/min. The melting points were determined from the heating curve.

FT-IR spectra were performed on a BioRad 6000 FT-IR spectrometer; samples were measured in solid state using a Single Reflection Diamond ATR.

NMR measurements were carried out at room temperature using a Bruker DPX-400 spectrometer. Deuterated solvents were used.

Particle sizes were determined on a Submicron Particle Sizer NICOMP 380.

Bright field TEM specimens were prepared by putting approximately 5 μ l of a 0.2 wt% solution on a TEM copper grid with carbon support film (200 mesh, Science Services, Munich, Germany). The carbon coated copper grids have been pretreated by 20 seconds of glow discharge. The excess of liquid was blotted with a filter paper after 2 minutes. The remaining liquid film on the TEM grid was dried at room temperature for at least one hour. The specimen was inserted into sample holder (EM21010, JEOL GmbH, Eching, Germany) and transferred to a JEOL JEM2100 with a LaB₆ cathode (JEOL GmbH, Eching, Germany). The TEM was operated at an acceleration voltage of 200 kV. All images were recorded digitally by a bottom-mounted 4k*4k CMOS camera system (TemCam-F416, TVIPS, Gauting, Germany) and processed with a digital imaging processing system (EM-Menu 4.0, TVIPS, Gauting, Germany).

As for the cryogenic TEM measurements, the specimens were vitrified by plunging the samples into liquid ethane using an automated plunge freezer (Vitrobot Mark IV, FEI Deutschland GmbH, Frankfurt a. M., Germany). The lacey carbon grids have been pretreated for 20 seconds with glow discharge. Approximately 5 μ l of a 0.2 wt% solution on a TEM copper grid with lacey carbon

support film (200 mesh, Science Services, Munich, Germany). The liquid was blotted with a filter paper applying a blot force of 0 for 1 second. No wait time or drain time have been used. The specimen was inserted into a pre-cooled high-tilt cryo transfer sample holder (Gatan 914, Gatan, Eching, Germany) and transferred into a JEOL JEM 2100 (JEOL GmbH, Eching, Germany). TEM investigations were carried out at temperature around 90 K. The TEM was operated at an acceleration voltage of 200 kV.

HRTEM investigations were carried using a JEOL JEM2200FS under zero-loss conditions using a 10 eV energy slit. All images were recorded digitally using a 1k slow-scan CCD camera (Gatan GmbH, Munich, Germany).

Rheology tests were done under dry air on a MCR301 by Anton Paar. The used cone-plate had a diameter of 50 mm and a cone angle of 0.017 rad. The flow curves of the PIL were measured from 0.01s^{-1} to 1000s^{-1} with a time ramp of 300s to 20s, whereas the viscosity of the monomer was measured from 1000s^{-1} down to 0.01s^{-1} with a time ramp of 20s to 100s.

Analytical ultracentrifugation (AUC) measurements were performed on a XL-I (Beckman-Coulter, Palo Alto, CA, USA) ultracentrifuge with Rayleigh interference and UV/visible absorption optics at 25 °C. Sedimentation-velocity experiment was done with a 1.5 mg/mL polymer solution in 0.1 M aqueous NaCl at a rotational speed of 60K rpm. Sedimentation coefficient distributions $g^*(s)$ were evaluated with the direct boundary modelling included in the software package SEDFIT (version 13.0b beta P. Schuck 2012) (Schuck, P. *Biophys. J.* **2000**, 78, 1606). For equilibrium experiments, seven polymer solutions (0.4-4.0 mg/mL polymer in 0.1 M aq. NaCl) were analyzed at different speeds starting from 3K rpm up to 25K rpm. Data were evaluated with the program MSTAR (Kristian Schilling, Nanolytics, Germany) (Cölfen, H.; Harding, S. E. *Eur. Biophys. J.* **1997**, 25, 333).

Determination of the molecular weight distribution and the absolute weight-averaged molecular weight of PAAPS

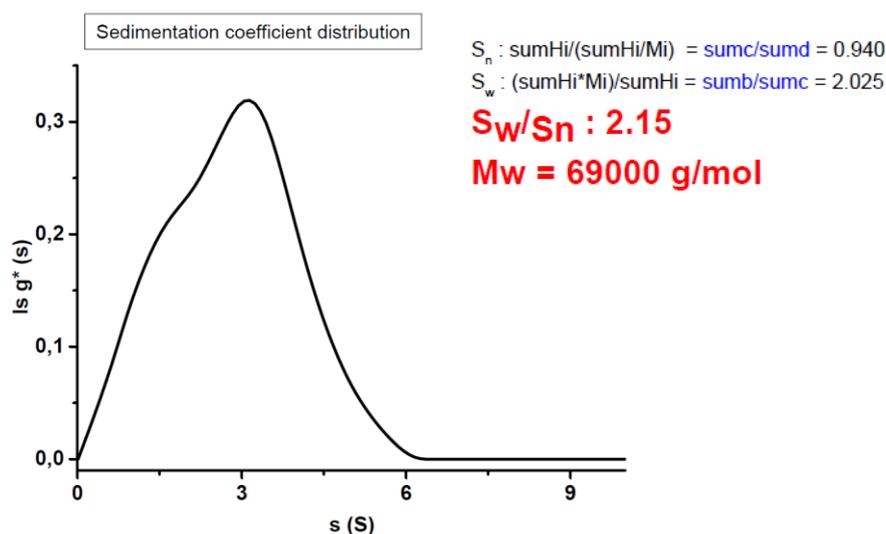


Figure S1. Sedimentation coefficient distributions obtained from AUC measurements of PAAPS.

Table S1. Solubility test of various chemicals in PAAPS at 5 wt% at different temperatures.

Soluble temperature	Substance
Insoluble (even after heating)	Br ₂ , I ₂ , Se, P(red), S, β-cyclodextrine, neutral red, cellulose, PEI, poly(3-butyl-1-vinylimidazolium bromide), n-hexane, n-heptane, diethyl ether
Soluble at 25 °C	H ₂ O, MeOH, EtOH, DMSO, CHCl ₃ , CH ₂ Cl ₂ , acetone benzontirle, THF, DMF, acetontrile
Soluble only above 50 °C	benzene, toluene
Soluble only above 100 °C	4,4-bipyridine, triethylene glycol, glucose, PAA (2000 g/mol), poly(HEMA) (20000), PVP (40000), naphthalene
Soluble only above 150 °C	PNIPAM, PAANa (5100 g/mol), mannose
Soluble only above 200 °C	PEG (750 g/mol)
Soluble assisted by solvent addition and evaporation	PEG (1900 or 500 g/mol) ^a

^aPEG with high molecular weight can be homogeneously dissolved in the PIL when added as a solution in chloroform and followed by removing chloroform at 100 °C under high vacuum (1×10^{-3} mbar).

$^1\text{H-NMR}$ spectra of IL monomer AAPS and PIL PAAPS

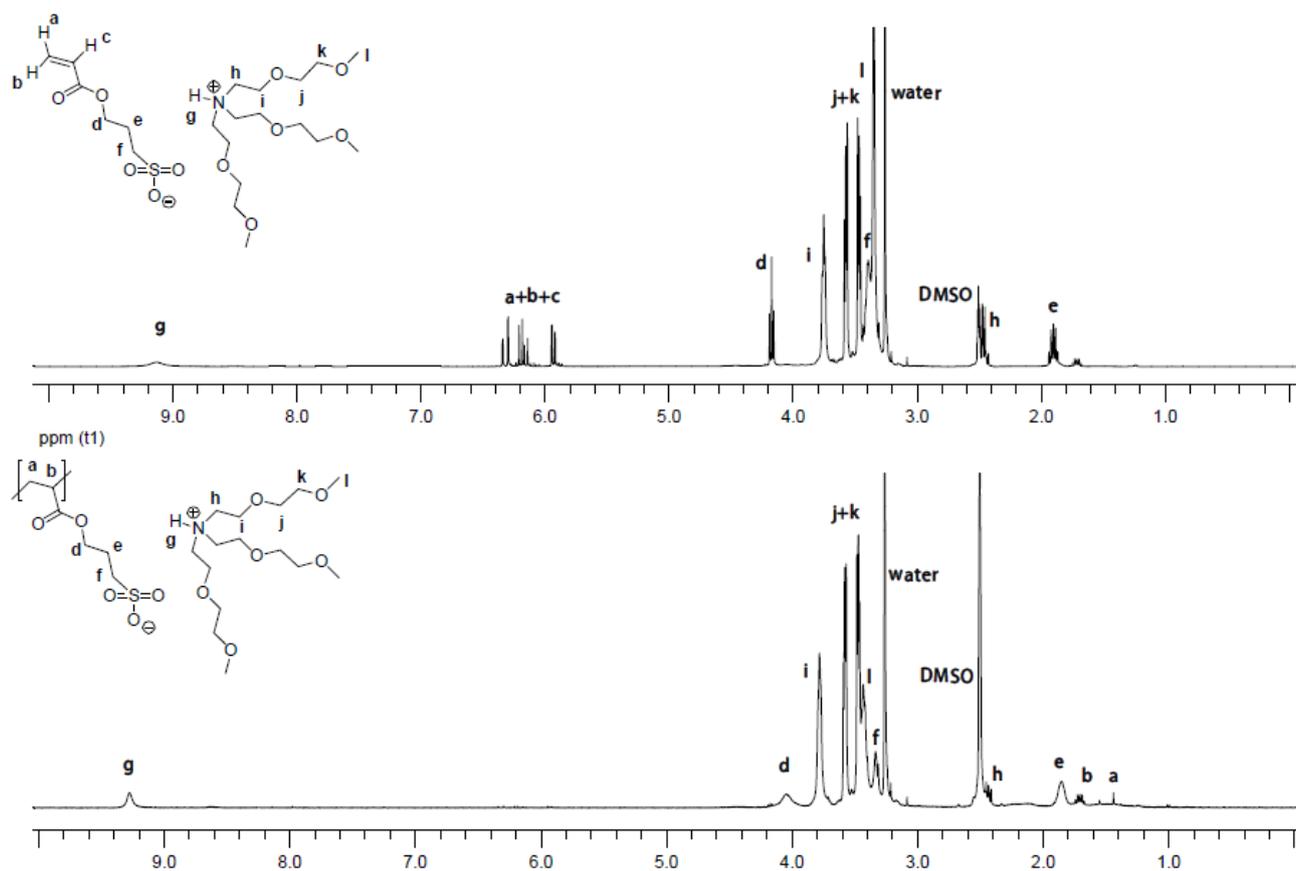


Figure S2. $^1\text{H-NMR}$ spectra of IL monomer AAPS and PIL PAAPS in $\text{DMSO-}d_6$.

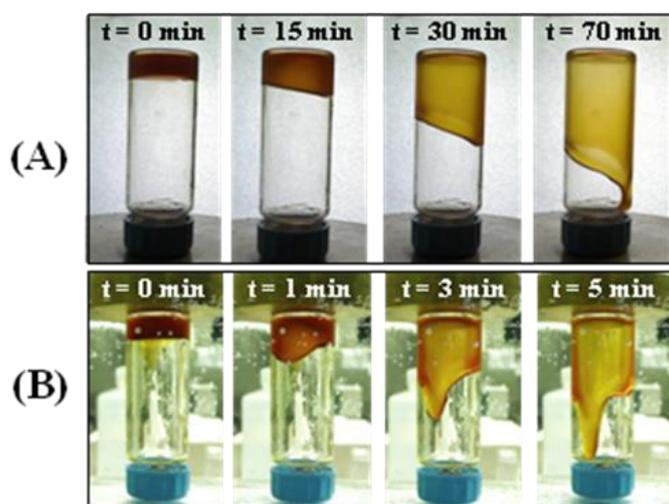


Figure S3. Photographs recording the flow of PAAPS in a sealed upside-down glass at 25 °C (A) and 60 °C (B). For this experiment, 5 g of dry PAAPS was loaded and tightly sealed in a round bottom glass under argon. The setup was initially thermostated for 15 min at each temperature to accomplish the thermal equilibrium. By quickly turning the glass bottle upside down, the polymer started to drop due to the gravity.

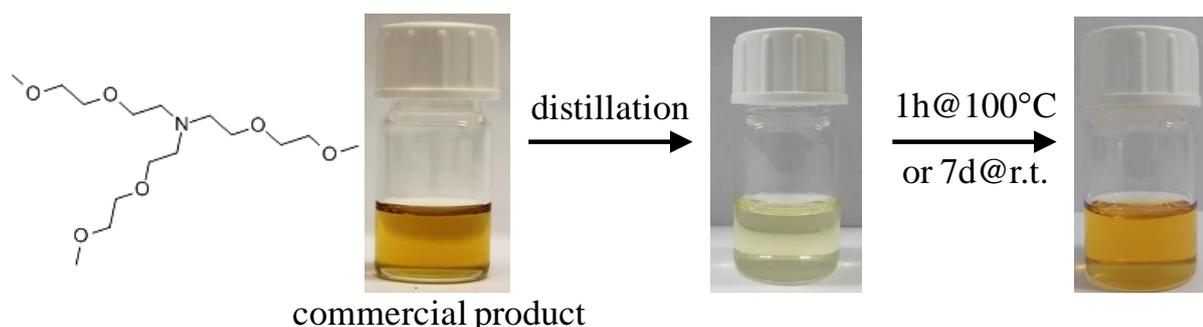


Figure S4. Photographs of commercial tris(2-(2-methoxyethoxy)ethyl)amine from Alfa Aesar (left), after distillation (middle), and after heated at 100 °C for 1 h or stored at rt for 7 d. This amine functionality is responsible for the colorization of PAAPS, prepared at 100 °C for 12 h.

Table S2. Hydrogenation of nitroaromatics catalysed by Pt nanoparticles dispersed in bulk PAAPS^a

Entry	Substrate	Product	Yield (%) ^b
1			> 99
2			90
3			> 99
4			> 99

^a At 130 °C for 4 h under 2 bar initial hydrogen pressure by using a balloon. ^b GC-MS yield. Entry 3 and 4 are the cycling reaction of Entry 1 for 6 h.

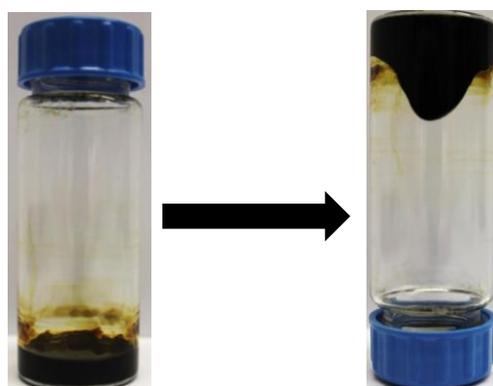


Figure S5. A stable dispersion of SWCNTs (0.1 wt %) in bulk PAAPS. By turning the vial upside down, the dispersion flowed slowly ($T \sim 80^\circ\text{C}$). The dispersion state was confirmed by dilution with water into a stable homogeneous aqueous dispersion.

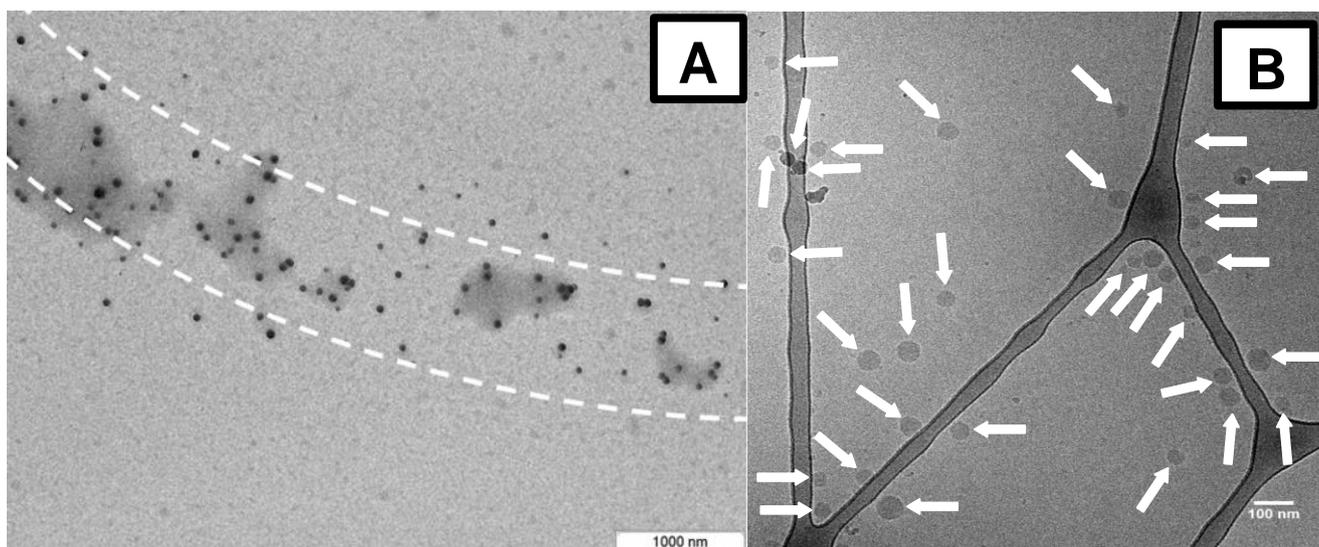


Figure S6. (A)TEM image of PS latex prepared in bulk PAAPS, which show the “coffee ring” phenomenon. The dashed lines point out the up and bottom rim of the “coffee-ring”. (B) Cryo-TEM image of the PS latex in aqueous solution, revealing the individual PS latex (indicated by white arrows). The Cryo-TEM characterization confirmed that the “coffee ring” structure (agglomerated PS latex) was due to the drying effect and not the real solution state.

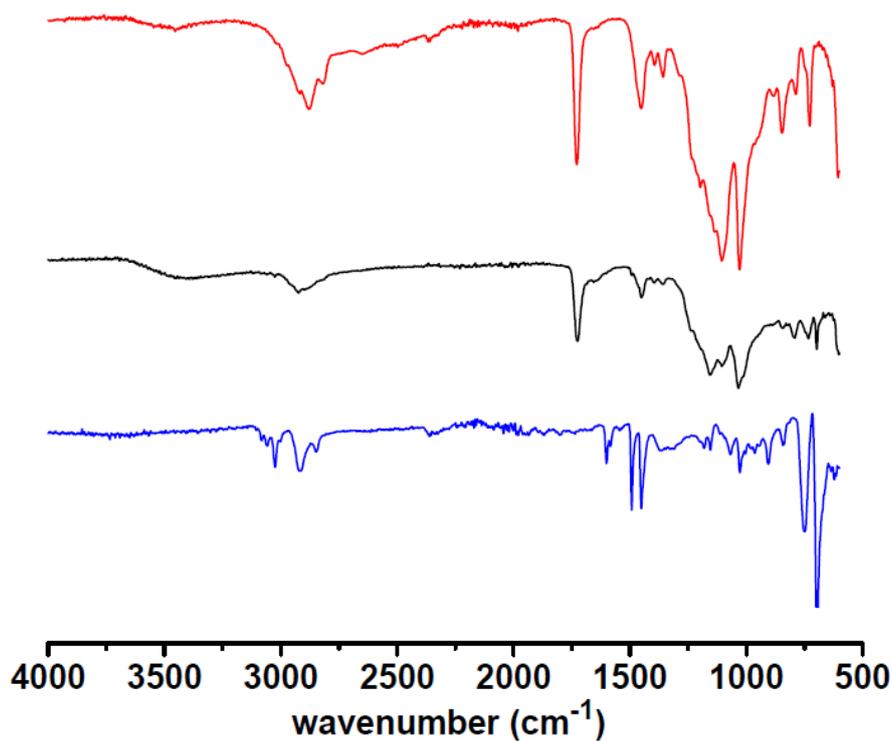


Figure S7. FTIR-ATR spectra of PAAPS PIL (top), PS latex prepared in PIL (middle), and pure PS polymer (bottom).

Standard size distribution of Pt-nanoparticles

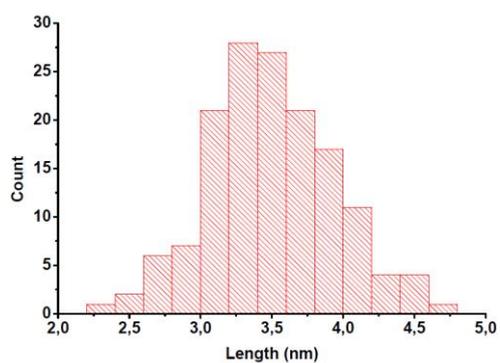


Figure S8. Standard size distribution plot of platinum nanoparticles (3.5 ± 0.4 nm) characterized by TEM. Averaged by 150 counts.

Standard size distribution of PS-nanoparticles

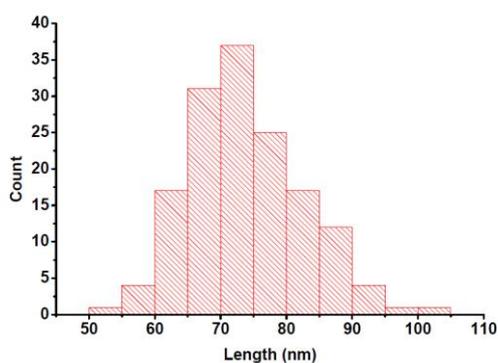


Figure S9. Standard size distribution plot of polystyrene nanoparticles (75 ± 10 nm) characterized by TEM. Averaged by 150 counts.

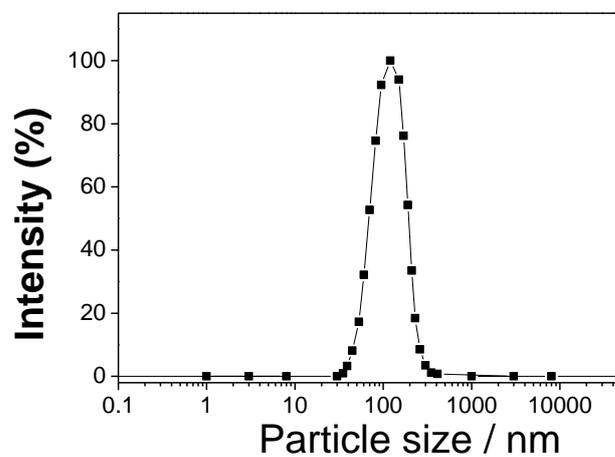


Figure S10. Size distribution curve of PS latex by DLS measurements.