Supplementary Material (ESI) for Chemical Communications

Supporting Information

Solubility Adjustable Nanoparticles Stabilized by a Novel PVP Based Family: Synthesis, Characterization and Catalytic Properties

Ning Yan, Jiaguang Zhang, Yinyin Tong, Siyu Yao, Chaoxian Xiao, Zichen Li, Yuan Kou*

PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

1. Materials and Methods

Synthetic procedures of the Poly-3-alkyl-1-vinyl-2-pyrrolidone family were described in the "**Synthesis of Poly-3-alkyl-1-vinyl-2-pyrrolidone**" section. THF was refluxed under argon with Na wire and diphenylmethanone till the solution became dark blue in color. Then it was distilled under argon and kept with 4 A molecule sieves. Diisopropylamine was refluxed with NaH for three minutes and distilled into a dry receiver under argon. N-vinyl-2-pyrrolidone (NVP) was distilled under reduced pressure prior to use. CO (99.9%) was passed through activated 5 A molecular sieves prior to use. H_2 (99.999%), $RhCl_3 \cdot nH_2O$ (AR grade), H_2PtCl_6 (AR grade), $RuCl_3 \cdot nH_2O$ (AR grade), $PdCl_2$ (AR grade), $Co_2(CO)_8$ (AR grade), poly(N-vinyl-2-pyrrolidone) (PVP, K30) and other chemicals were commercial available and used without further purification. All organic synthesis was handled with standard schlenk techniques.

Molecular weights of polymers were measured with a gel permeation chromatography (GPC) system equipped with a Waters 2410 refractive index detector, a Waters 515 HPLC pump and two Waters styragel columns (HT 3 and HT 4) using THF as eluent at a flow rate of 1 ml/min at 35°C. The obtained data were processed against narrow polystyrenes as calibrations by professional software Millennium 32.

XPS spectra were collected on an Axis Ultra spectrometer (Kratos, UK). Elemental analyses were done on an Elementar Vario MICRO CUBE (Germany). NMR spectra were recorded at 20 °C either on a Bruker DMX 400 instrument or a Varian Gemini 300 MHz spectrometer with TMS as internal standard. The transmission electron microscopy (TEM) measurements were carried out on a Philips Tecnai F30 transmission electron microscope operating at 300 keV. TGA data were recorded on a Thermal Analysis SDT2960 simultaneous differential thermal analyzer with a heating rate of 10 $^{\circ}C\ min^{-1}$ under nitrogen or air. IR spectra were carried out on a Fourier transform infrared spectrophotometer (Tensor 27, Bruker) with a resolution of 1 cm^{-1}. GC analyses were carried out on an Agilent Chrompack HP-6820 equipped with an OV-101 capillary

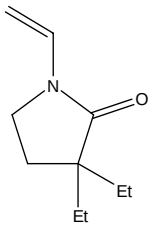
column (30 m × 0.25 mm, using nitrogen as carrier gas). ESI-MS data were obtained on a Thermo LCQ DECA XP Plus ESI Mass Spectrometer under positive mode.

2. Synthesis of Poly-3-alkyl-1-vinyl-2-pyrrolidone (C_n-PVP)

2.1 Synthesis of 3-ethyl-1-vinyl-2-pyrrolidone and 3,3-diethyl-1-vinyl-2-pyrrolidone

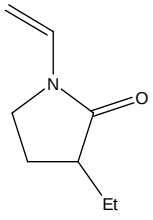
Diisopropylamine (7.4 ml, 52 mmol) was mixed with dry THF (70 ml). The mixture was cooled to -78 °C in an liquid nitrogen acetone bath. Then n-BuLi (29 ml, 1.6 M in hexane, 46 mmol) was dropwise added into the solution in 10 min. The mixture was warmed to 0 °C under stirring for 10 min and was cooled back to -78 °C. NVP (5 ml, 47 mmol) was then slowly added into the solution over 5 min and kept for another hour at -78 °C. Finally, ethylbromide (3.4 ml, 46 mmol) was added into the mixture over 5 min and the solution was slowly warmed to r.t. over a period of 10 h. The color of the solution changed from yellow to orange and then changed back to yellow. The reaction was quenched by adding deionized water (50 ml). The organic layer was separated and the aqueous layer was extracted by ether (20 ml × 3). The combined organic phase was dried over Na_2SO_4 and concentrated to get the raw product. After analysis by TLC (**two main products were detected**), the raw product was purified over LC by using ethyl acetate : hexane = 1 : 10 as eluent, giving the *3,3-Diethyl-1-vinyl-2-pyrrolidone* (Rf: 0.44, Yield: 1.92 g, 25%) and *3-Ethyl-1-vinyl-2-pyrrolidone* (Rf: 0.29, Yield: 4.12 g, 64%) as main products.

3,3-diethyl-1-vinyl-2-pyrrolidone



^{1}H NMR (400MHz, $CDCl_3$): 0.87 (t, 6 H, J = 7.0 Hz), 1.57 (m, 4 H), 1.96 (t, 2 H, J = 7.4 Hz), 3.39 (t, 2 H, J = 7.3 Hz), 4.37 (d, 1 H, J = 16.0 Hz), 4.42 (d, 1 H, J = 8.7 Hz), 7.12 (dd, 1 H, J_1 = 16.1 Hz, J_2 = 9.1 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 8.5, 26.8, 29.4, 41.9, 49.2, 93.8, 129.5, 176.8. ESI-MS (Methanol): 168.1 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2962, 2933, 2876, 1707, 1632, 1489, 1462, 1426, 1388, 1330, 1279, 1265, 1212, 1133, 1038, 982, 910, 843, 769, 722, 690, 613, 587.

3-ethyl-1-vinyl-2-pyrrolidone



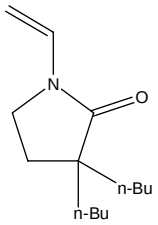
^{1}H NMR (400MHz, $CDCl_3$): 0.98 (t, 3H, J = 7.4 Hz), 1.47 (m, 1H), 1.75 (m, 1H), 1.89 (m, 1H),

2.28 (m, 1H), 2.47 (m, 1H), 3.47 (m, 1H), 3.50 (m, 1H), 4.38 (d, 1H, J = 16.0 Hz), 4.42 (d, 1H, J = 9.0 Hz), 7.10 (dd, 2H, J_1 = 16.0 Hz, J_2 = 9.1 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 11.2, 23.6, 23.9, 42.7, 43.5, 93.8, 129.3, 174.8. ESI-MS (Methanol): 140.1 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2964, 2926, 2880, 1705, 1633, 1492, 1461, 1424, 1389, 1329, 1278, 1262, 1037, 982, 909, 842, 724, 589.

2.2 Other 3-alkyl-1-vinyl-2-pyrrolidone and 3,3-dialkyl -1-vinyl-2-pyrrolidone

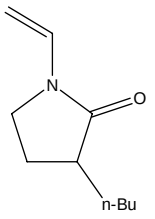
Other 3-alkyl-1-vinyl-2-pyrrolidone and 3,3-dialkyl-1-vinyl-2-pyrrolidone were prepared in a similar way except that corresponded alkyl bromide were used and the purifications were slightly different.

3,3-dibutyl-1-vinyl-2-pyrrolidone



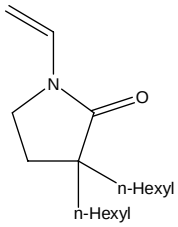
Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.49. Yield: 2.68 g, 26%. ^{1}H NMR (400MHz, $CDCl_3$): 0.89 (t, 6 H, J = 7.0 Hz), 1.26 (m, 8 H), 1.52 (t, 4 H, J = 7.8 Hz), 2.00 (t, 2 H, J = 7.5 Hz), 3.39 (t, 2 H, J = 7.2 Hz), 4.38 (d, 1 H, J = 16.0 Hz), 4.42 (d, 1 H, J = 9.1 Hz), 7.11 (dd, 1 H, J_1 = 16.0 Hz, J_2 = 9.0 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 11.9, 23.1, 26.3, 27.8, 37.0, 41.8, 48.3, 93.8, 129.5, 177.0. ESI-MS (Methanol): 224.2 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2957, 2931, 2872, 2860, 1705, 1632, 1491, 1466, 1458, 1424, 1389, 1330, 1279, 1260, 1152, 1038, 982, 842, 731, 691, 628, 589.

3-butyl-1-vinyl-2-pyrrolidone



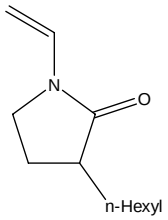
Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.23. Yield: 3.48 g, 45%. ^{1}H NMR (400MHz, $CDCl_3$): 0.91 (t, 3H, J = 7.3 Hz), 1.33 (m, 5H), 1.72 (m, 1H), 1.88 (m, 1H), 2.27 (m, 1H), 2.48 (m, 1H), 3.41 (m, 1H), 3.51 (m, 1H), 4.38 (d, 1H, J = 16.0 Hz), 4.42 (d, 1H, J = 9.1 Hz), 7.10 (dd, 2H, J_1 = 16.0 Hz, J_2 = 9.1 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 13.8, 22.5, 24.3, 29.2, 30.7, 42.3, 42.7, 93.8, 129.4, 175.1. ESI-MS (Methanol): 168.1 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2956, 2930, 2873, 1709, 1632, 1488, 1457, 1425, 1387, 1330, 1279, 1263, 1200, 1137, 1038, 982, 841, 721, 689, 595.

3,3-dihexyl-1-vinyl-2-pyrrolidone



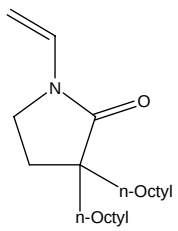
Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.50. Yield: 3.19 g, 25%. ^{1}H NMR (400MHz, $CDCl_3$) 0.87 (t, 6 H, J = 7.0 Hz), 1.27 (m, 16 H), 1.51 (m, 4 H), 1.97 (t, 2 H, J = 7.5 Hz), 3.39 (t, 2 H, J = 7.2 Hz), 4.37 (d, 1 H, J = 16.1 Hz), 4.42 (d, 1 H, J = 8.8 Hz), 7.11 (dd, 1 H, J_1 = 16.0 Hz, J_2 = 9.0 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$) 13.95, 22.52, 24.07, 27.85, 29.71, 31.62, 37.25, 41.88, 48.43, 93.77, 129.59, 177.00. ESI-MS (Methanol) 280.2 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2956, 2930, 2857, 1705, 1631, 1491, 1459, 1424, 1389, 1331, 1279, 1261, 1037, 982, 841, 724, 691, 589.

3-hexyl-1-vinyl-2-pyrrolidone



Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.25. Yield: 4.91 g, 55%. ^{1}H NMR (400MHz, $CDCl_3$): 0.88 (t, 3H, J = 6.6 Hz), 1.29 (m, 9H), 1.71 (m, 1H), 1.88 (m, 1H), 2.27 (m, 1H), 2.50 (m, 1H), 3.37 (m, 1H), 3.50 (m, 1H), 4.38 (d, 1H, J = 16.2 Hz), 4.42 (d, 1H, J = 9.1 Hz), 7.10 (dd, 2H, J_1 = 16.0 Hz, J_2 = 9.1 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 13.58, 22.44, 24.36, 26.94, 29.25, 31.02, 31.64, 41.87, 42.40, 92.45, 129.58, 174.16. ESI-MS (Methanol): 196.1 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2956, 2927, 2857, 1707, 1632, 1488, 1457, 1425, 1387, 1330, 1264, 1037, 982, 841, 723, 689, 599.

3,3-dioctyl-1-vinyl-2-pyrrolidone

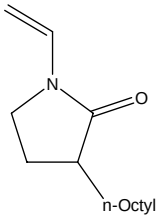


Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.63. By NMR analysis, the product obtained from LC is mixture of 3,3-dioctyl-1-vinyl-2-pyrrolidone and n-octyl bromide. The mixture was treated under vacuum at 140 °C for 4 h to remove n-octyl bromide completely.

Yield: 5.00 g, 32%.

^{1}H NMR (400MHz, $CDCl_3$) 0.89 (t, 6 H, J = 7.0 Hz), 1.26 (m, 24 H), 1.51 (m, 4 H), 1.97 (t, 2 H, J = 7.5 Hz), 3.39 (t, 2 H, J = 7.2 Hz), 4.37 (d, 1 H, J = 16.1 Hz), 4.42 (d, 1 H, J = 8.9 Hz), 7.11 (dd, 1 H, J_1 = 16.0 Hz, J_2 = 9.1 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$) 13.93, 22.51, 24.07, 27.81, 29.17, 29.35, 31.73, 37.18, 41.79, 48.32, 93.61, 129.51, 176.83. ESI-MS (Methanol) 336.4 ($M + H^+$). IR (KBr, cm^{-1}): 3109, 2956, 2926, 2855, 1708, 1631, 1491, 1459, 1424, 1388, 1331, 1278, 1265, 1038, 982, 841, 722, 691, 646, 589.

3-octyl-1-vinyl-2-pyrrolidone



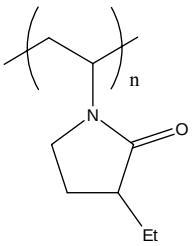
Purified over LC by using ethyl acetate : hexane = 1 : 20 as eluent. Rf: 0.27. Yield: 5.47 g, 53%.

^{1}H NMR (400MHz, $CDCl_3$): 0.89 (t, 3H, J = 6.6 Hz), 1.26 (m, 13H), 1.73 (m, 1H), 1.88 (m, 1H), 2.28 (m, 1H), 2.50 (m, 1H), 3.39 (m, 1H), 3.49 (m, 1H), 4.38 (d, 1H, J = 16.0 Hz), 4.42 (d, 1H, J = 9.1 Hz), 7.10 (dd, 2H, J_1 = 16.0 Hz, J_2 = 9.0 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$): 14.0, 22.5, 24.3, 27.0, 29.2, 29.3, 29.4, 31.1, 31.8, 42.3, 42.7, 93.7, 129.5, 175.0. ESI-MS (Methanol): 224.2 ($M + H^+$). IR (KBr, cm^{-1}): 3110, 2955, 2925, 2855, 1711, 1631, 1488, 1457, 1425, 1386, 1330, 1277, 1264, 1215, 1036, 982, 840, 722, 688, 589.

2.3 General procedure for the Polymerization of 3-alkyl-1-vinyl-2-pyrrolidone

3-alkyl-1-vinyl-2-pyrrolidone (15 mmol), AIBN (12 mg, 0.075 mmol) and 6 ml THF were first degassed by three freeze/thaw cycles and then placed in a preheated oil bath set at 60 °C with stirring. After 48 hours, the heating and stirring were stopped and the mixture was transferred to a chromatography column packed with silica. Ethyl acetate and hexane mixture (1:5) were used as eluent till no monomer was detected by TLC. Then the eluent was changed to methanol/dichloromethane mixtures (1:10) and monitored by TLC (C_n-PVP was not observable under UV light, so iodide was used to trace the presence of the polymer). The final product was first concentrated with a rotavapor and then dried under vacuum at 60 °C for 12 h.

Poly-3-ethyl-1-vinyl-2-pyrrolidone (C_2-PVP)

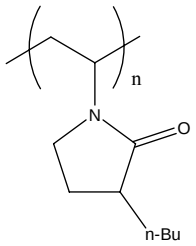


Yield: 1.55 g, 75%.

^{1}H NMR (400MHz, $CDCl_3$): 0.92 (s, br, 3H), 1.34 (s, br, 2H), 1.54-1.62 (br, 3H), 2.27 (br, 2H), 3.11 (s, br, 2H), 3.76 (br, 1H).

IR (KBr, cm^{-1}): 2959, 2933, 2873, 1682, 1492, 1456, 1426, 1377, 1310, 1276, 1132, 809, 798, 769, 718. Anal. Calc. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.86; H, 9.47; N, 9.89. GPC: M_w = 17 k/mol, M_w/M_n = 2.2.

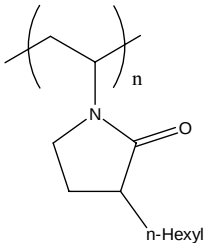
Poly-3-butyl-1-vinyl-2-pyrrolidone (C_4-PVP)



Yield: 1.90 g, 76%.

^{1}H NMR (400MHz, $CDCl_3$): 0.87 (s, br, 3H), 1.29 (s, br, 6H), 1.60-1.77 (br, 3H), 2.20 (br, 2H), 3.10 (s, br, 2H), 3.70 (br, 1H). IR (KBr, cm^{-1}): 2954, 2929, 2857, 1677, 1491, 1456, 1426, 1376, 1310, 1265, 1136, 1060, 917, 897, 731, 716, 650, 605. Anal. Calc. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.73; H, 10.04; N, 8.19. GPC: M_w = 16 k/mol, M_w/M_n = 2.1.

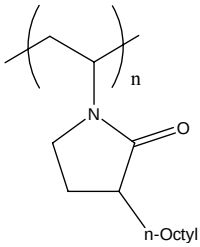
Poly-3-hexyl-1-vinyl-2-pyrrolidone (C_6-PVP)



Yield: 1.37 g, 47%.

^{1}H NMR (400MHz, $CDCl_3$): 0.86 (s, br, 3H), 1.25 (s, br, 10H), 1.61-1.78 (br, 3H), 2.24 (br, 2H), 3.10 (s, br, 2H), 3.73 (br, 1H). IR (KBr, cm^{-1}): 2954, 2923, 2854, 1684, 1491, 1456, 1426, 1376, 1269, 1183, 1129, 1071, 874, 717, 610. Anal. Calc. for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 73.94; H, 10.82; N, 7.06. GPC: M_w = 14 k/mol, M_w/M_n = 2.1.

Poly-3-octyl-1-vinyl-2-pyrrolidone (C_8-PVP)



Yield: 1.60 g, 48%.

^{1}H NMR (400MHz, $CDCl_3$): 0.86 (s, br, 3H), 1.26 (s, br, 14H), 1.60-1.78 (br, 3H), 2.09 (br, 2H), 3.10 (s, br, 2H), 3.70 (br, 1H).

IR (KBr, cm^{-1}): 2955, 2923, 2853, 1684, 1491, 1456, 1426, 1376, 1272, 1185, 1131, 1071, 874, 719, 607. Anal. Calc. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27. Found: C, 74.83; H, 10.98; N, 6.17. GPC: Mw = 19 k/mol, Mw/Mn = 2.1.

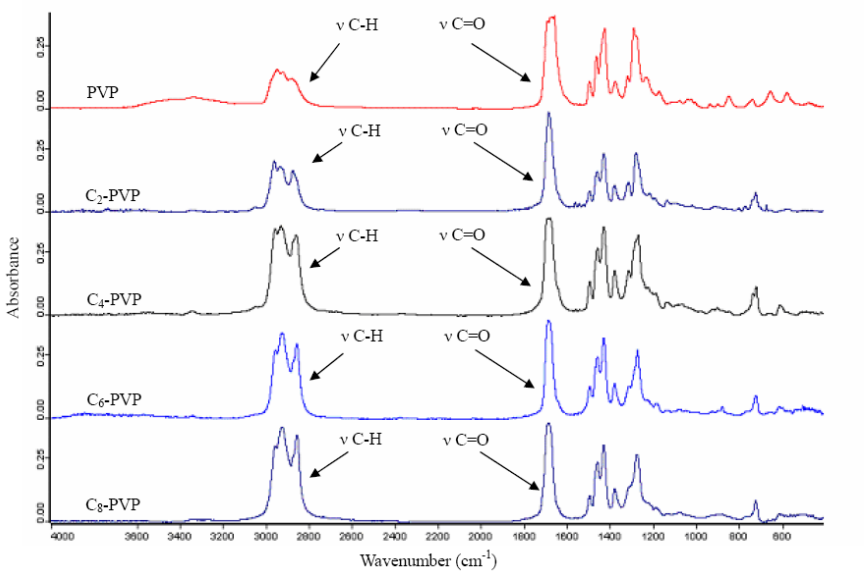


Figure S1, IR spectra of PVP, C_2-PVP, C_4-PVP, C_6-PVP and C_8-PVP.

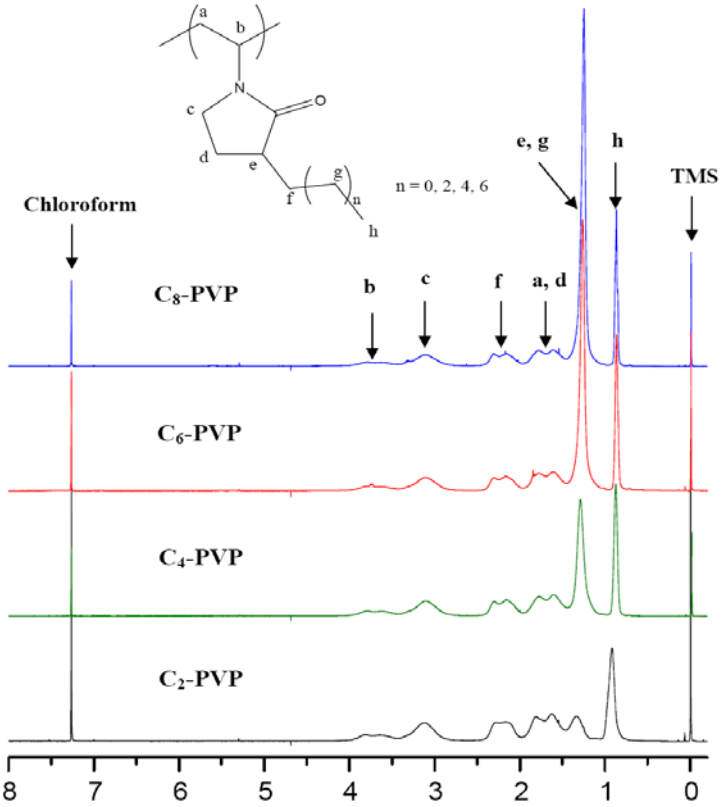


Figure S2. ^{1}H NMR of C_n-PVP in $CDCl_3$.

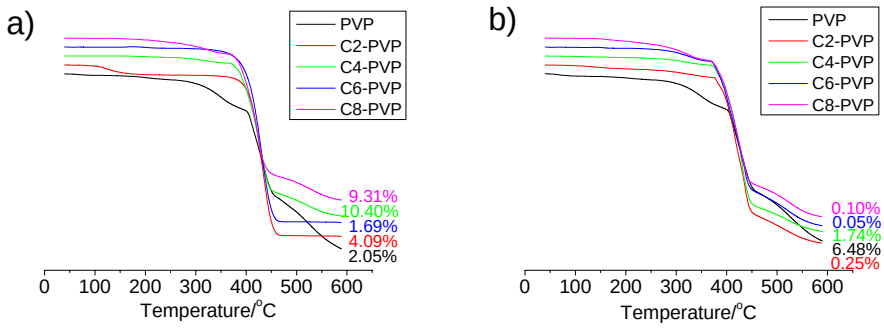


Figure S3. TGA Curves of C_n-PVP under different atmosphere: a) nitrogen; b) air.

2.4 General Procedure for the Polymerization of 3,3-dialkyl -1-vinyl-2-pyrrolidone

The polymerizations were conducted under exact the same procedures as described for 3-alkyl-1-vinyl-2-pyrrolidone, however, 3,3-dialkyl-1-vinyl-2-pyrrolidone were resistant to polymerization under applied conditions. The yields of the polymers were found to be lower than 5% for all the four substrates.

3. Synthesis, characterization and catalytic activity examination of Rh NPs Stabilized by C_n-PVP.

3.1 General Procedure for the Preparation of Rh NPs Stabilized by C_n-PVP.

$RhCl_3 \cdot xH_2O$(88 mg, 0.3 mmol) was dissolved in water (5 ml) and C_n-PVP (3 mmol based on monomer) was dissolved in ethanol (55 ml). Then the two solvents was mixed and transferred into a 100 ml autoclave. The autoclave was purged three times with N_2. Then 3MPa H_2 was introduced into the autoclave and the mixture was heated to 80 °C in half an hour and kept stirring at 800 rpm for another 1 hour. The color of the final solution changed from orange to dark after reduction. It was also worthy to note that C_6-PVP and C_8-PVP were not completely soluble in the ethanol-water mixture at room temperature. After cooling down, the mixture in the autoclave was concentrated with a rotavapor and re-dissolved in ethanol (60 ml). Na_2CO_3 (95 mg, 0.9 mmol) was then added and stirred with the solution for 1 hour at room temperature to remove acid generated during reductive process. Finally the mixture was filtrated and the NPs solution was stored at ambient conditions.

3.2 TEM and XPS Characterizations for Rh NPs.

For TEM analysis, the Rh NPs ethanol solution (1 ml) was treated by ultrasonication for 1 h, and then one drop of the solution was placed on a copper grid coated by a polymer or carbon film. The TEM measurements were carried out on a Philips Tecnai F30 transmission electron microscope operating at 300 keV. The size distributions of Rh NPs were determined from ~150 particles (For C_n-PVP-Rh (n = 0, 2, 4, 6, 8), 151, 153, 151, 151, 151 particles were counted, respectively). The

standard derivation was provided by OriginPro 8 software.

For XPS measurement, the Rh NPs ethanol solution (5 ml) was first concentrated with a rotavapor and then further dried under vacuum at 60 °C for 6 h. The black residue was sent to XPS measurements. XPS spectra were collected on an Axis Ultra spectrometer (Kratos, UK) using monochromatic Al KR (1486.71 eV) radiation at a source power of 225 W (15 mA, 15 kV).

3.3 Solubility Behaviors of the Rh NPs in Various Solvents.

Thirteen solvents, including water, ethanol, acetic acid, acetonitrile, acetone, ethyl acetate, THF, ethyl ether, dichloromethane, chloroform, toluene, cyclohexane and hexane, were selected to evaluate the solubility behaviors of Rh NPs protected by C_n-PVP. The Rh NPs ethanol solution (2 ml) was added to a 10 ml flask and dried under vacuum at 60 °C for 1 h. Then one of the selected solvents (2 ml) was added into the flask. If Rh NPs was dissolved in the solvent, the solution was directly transferred into a vial. If Rh NPs was insoluble/partial soluble in that solvent, the mixture was treated by ultrasonication to help removing the insoluble solid sticking to the inter surface of the flask. Then both the solvent and the remaining solid were transferred into a vial. In total, 65 samples were examined and their pictures are shown in Figure 3 (pictures taken after one month) and Figure S5 (pictures taken after one day). The dissolved Rh NPs are really stable in solvents; no precipitations occur in one month. The distributions of Rh-C_8-PVP and Rh-PVP between water and hexane are shown in Figure S4.

Figure S4. Distribution of Rh-C_8-PVP (left) and Rh-PVP (right) between water (bottom layer) and hexane (upper layer).

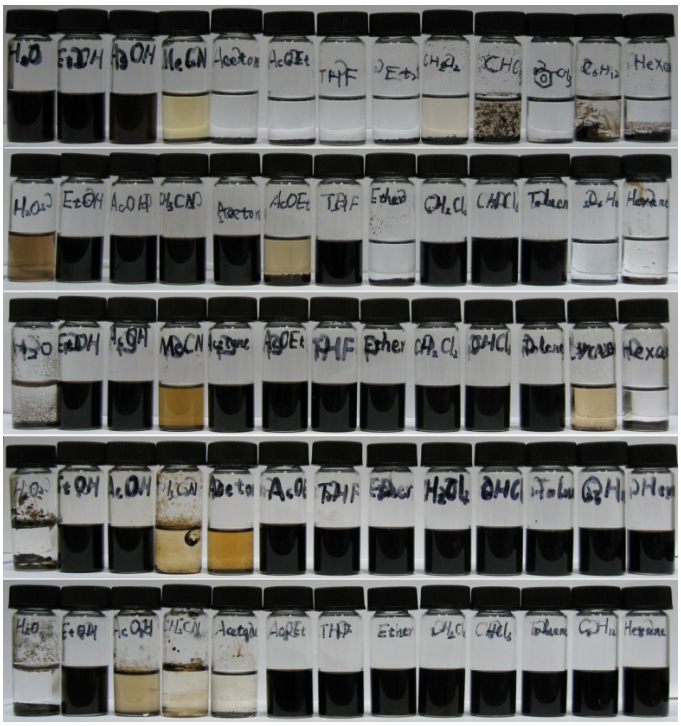


Figure S5. Solubility of Rh MNPs stabilized by PVP family in thirteen solvents (from top to bottom: Rh-PVP, Rh-C_2-PVP, Rh-C_4-PVP, Rh-C_6-PVP, Rh-C_8-PVP. C_{Rh} = 5 mM, Rh : Cn-PVP = 1 : 10, pictures taken after one day) The solvents used are, from left to right, H_2O, EtOH, AcOH, MeCN, Acetone, AcOEt, THF, diethyl ether, CH_2Cl_2, $CHCl_3$, toluene, cyclohexane and hexane.

3.4 IR analysis of CO adsorption on Rh nanoparticle surfaces

Rh-C_n-PVP ethanol solution (5 ml) as prepared in section *SI 3.1* was first concentrated to ca. 1 ml. Then the solution was transferred into a 10 ml autoclave. The autoclave was first purged with N_2 3 times and then filled with 1 MPa CO. The autoclave was kept stirring at 800 rpm for 2 hours. Then one drop of the solution was put on KBr plate for IR analysis. The infrared spectrum of CO adsorbed on Rh-C_n-PVP were illustrated in Figure S6.

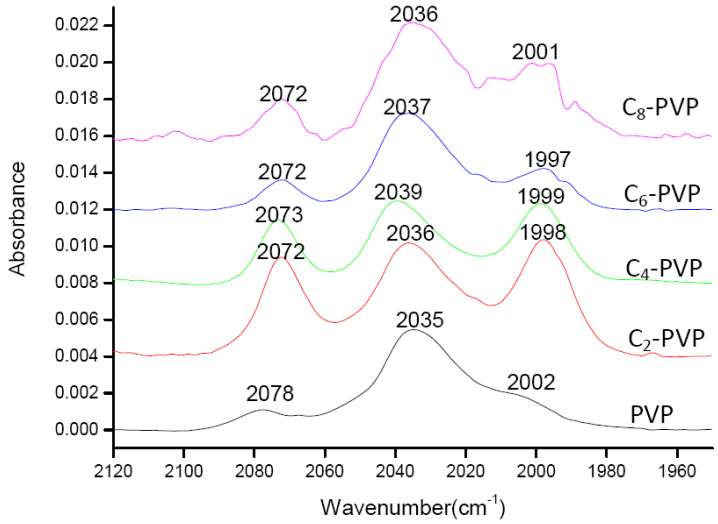


Figure S6. The infrared spectrum of CO adsorbed on Rh-C_n-PVP.

3.5 Catalytic Activity Test for the Rh NPs Using Toluene Hydrogenation as Model Reaction.

Rh-C_n-PVP ethanol solution as prepared in *section 3.1* (5 ml, Rh content: 0.025 mmol) was diluted by absolute ethanol into 10 ml and transferred into a 100 ml autoclave. Then toluene (2 ml, 19 mmol) was added into the autoclave. After purged with nitrogen (5 bar) three times, the autoclave was sealed (with 5 bar nitrogen inside) and heated to 80 °C with a stirring speed of 800 rpm. The autoclave was kept at this temperature for another hour to ensure the temperature was stable. Then hydrogen (40 bar) was introduced into the autoclave. After 10 min, the stirring was stopped and the autoclave was put immediately into iced water. The hydrogen was released after another minute and the liquid sample was sent for GC analysis.

4. Synthesis, Characterization of Other Metal NPs Stabilized by C_n-PVP and F-T Reaction over Co NPs.

4.1 Synthesis (Ethanol as the Reducing Agent) and Characterization of Pd NPs.

$PdCl_2$ (11 mg, 0.06 mmol) was dissolved in 10 ml hot acetonitrile. Then the solution was evaporated to dryness under vacuum at 60 °C. The residue ($Pd(CH_3CN)_2Cl_2$) was redissolved in ethanol (10 ml) and water (1 ml) solution containing C_4-PVP (0.10 g, 0.6 mmol). The mixture was gently refluxed for 1 h during which the color of the solution gradually changed from orange to dark. Finally the solution was cooled down to room temperature and stored without any other precautions. The homogenous, clear solution was kept for months without forming any precipitations. The Pd NPs were characterized by TEM and EDX analysis (Figure S7, a).

4.2 Synthesis ($NaBH_4$ as the Reducing Agent) and Characterization of Pt and Ru NPs.

$H_2PtCl_6 \cdot 6H_2O$ (32 mg, 0.06 mmol) and C_4-PVP (0.10 g, 0.6 mmol) were dissolved in ethanol (10 ml) with vigorous stirring. Then $NaBH_4$ aqueous solution (140 mg, 5wt%, 0.18 mmol) was added into the solution in one portion. The color of the solution changed immediately from orange to dark and the bubbles came out of the solution. After stirring for another half an hour, the stirring was stopped. The dark brown solution of Pt NPs can be stored under ambient conditions for months without forming any precipitations.

Ru NPs were prepared under similar conditions except that $RuCl_3 \cdot XH_2O$ was used as the precursor and C_2-PVP was used as the stabilizer. The Pt and Ru NPs were characterized by TEM and EDX analysis (Figure S7, b-c).

4.3 Synthesis ($LiAlH_4$ as the Reducing Agent) and Characterization of Ag NPs.

AgAc (9 mg, 0.06 mmol), C_6-PVP (0.12 g, 0.6 mmol) and $LiAlH_4$ (43 mg, 1.2 mmol) were added into THF (10 ml). Then the mixture was treated with sonication at 40 °C for 2 h. The color of the mixture gradually became brown and formed a homogenous, clear solution finally. The solution

was kept under nitrogen for several weeks without forming any precipitates. The Ag NPs were characterized by TEM and EDX analysis (Figure S7, d).

4.4 Synthesis (Thermal Decomposition of Metal Carbonyls) and Characterization of Fe, and Co NPs.

For Co NPs, $Co_2(CO)_8$ (17 mg, 0.05 mmol) and C_8-PVP (220 mg, 1.0 mmol) was transferred into degassed Toluene (2 ml) under argon. Then the mixture was heated at 110 $^{\circ}$C monitored by IR. After half an hour, the reaction mixture was cooled to RT. the resulting dark brown, clear, homogenous solution was kept under argon after cooling down and analyzed by TEM and EDX techniques (Figure S7, e).

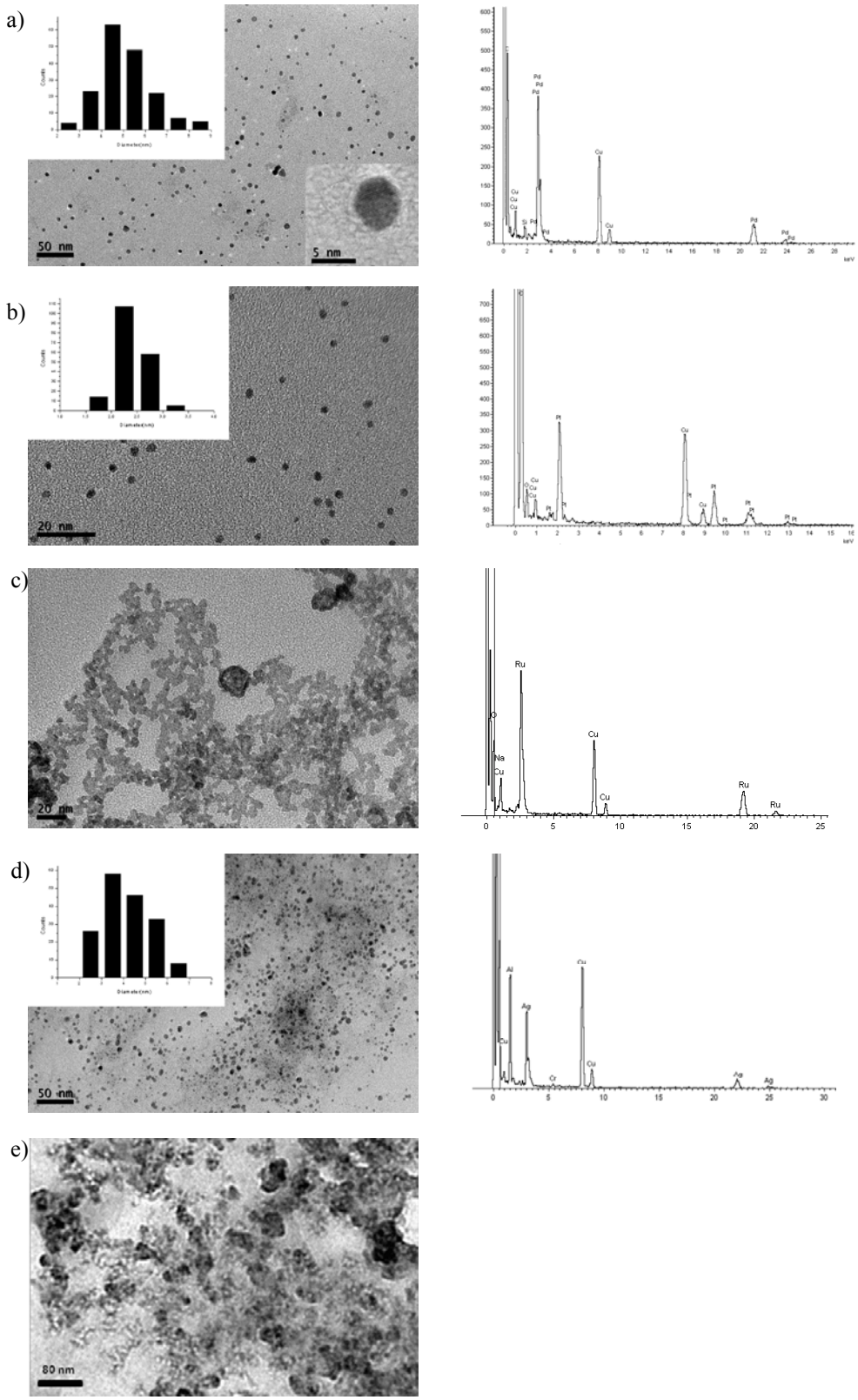


Figure S7, TEM micrographs, size distributions and EDX of different metal NPs: a) Pd NPs reduced by ethanol and stabilized by C_4-PVP; b) Pt NPs reduced by $NaBH_4$ and stabilized by C_4-PVP; c) Ru NPs reduced by $NaBH_4$ and stabilized by C_2-PVP; d) Ag NPs reduced by $LiAlH_4$ and stabilized by C_6-PVP; e) Co NPs prepared by thermal decomposition of $Co_2(CO)_8$ by C_8-PVP.

4.5 F-T synthesis over Co NPs stabilized by C_8-PVP in squalane.

In a typical experiment, the freshly prepared Co NPs (0.1 mmol of Co) in 20 ml squalane were placed in a 90-ml stainless steel autoclave. Decahydronaphthalene (10 μl) was injected as the internal standard. Then the reactor was purged three times with CO (99.9%, purified by 5A molecular sieves) and was then sealed at a CO pressure of 1.0 MPa. Additional 2.0 MPa H_2 (99.999 %) was added (H_2/CO mole ratio equal to 2). The autoclave was kept at different temperatures (150-200 °C), 800 rpm until the total pressure decreased to ~2 MPa, except for the cases of very slow reaction rates. The reaction time is about 12-36 h. After reaction, the autoclave was cooled to room temperature. Then, the gas and liquid phase were collected and analyzed immediately by GC, GC-MS and IR. The catalytic activity was monitored by the pressure drop and also confirmed by the conversion of carbon monoxide. In the gas phase, the major products were found to be CO_2 and C_1-C_5 alkanes (alkenes were also detected in much smaller amount). The amounts of CO and CO_2 were determined by FTIR spectroscopy (Bruker Vector 22 spectrometer) using appropriate calibration curves. C_1–C_5 products were measured by GC (Fuli 9790, Porapak Q, FID). In the liquid phase, the main products are C_{3+} alkane products. Their amounts were determined by GC (Fuli 9790, 30 m*0.25 mm i.d OV-101, FID).

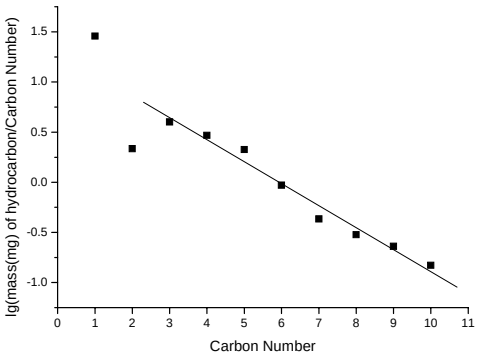


Figure S8, Anderson-Schulz-Flory distribution of products.

Table S1. The catalytic activity of some Co catalysts reported in literature and in our study for the F-T synthesis

T [°C]	Catalyst	Activity [mol_{CO} mol_{metal}^{-1} h^{-1}]	Reference
220	Co/Carbon nanofiber	1.4–7.4	[1]
190	Co/Al_2O_3	3.3	[2]
190	Co/silica	0.45–0.96	[3]
180-190	Co/Al_2O_3	0.8(180°C),1.6(190°C)	[4]
200	Co/SiO_2	2.75	[5]
210	Co NPs in IL	0.04	[6]
150	Co NPs - C_8-PVP	Not observed	In this study
170	Co NPs - C_8-PVP	0.2	In this study
185	Co NPs - C_8-PVP	0.7	In this study
200	Co NPs - C_8-PVP	1.3	In this study

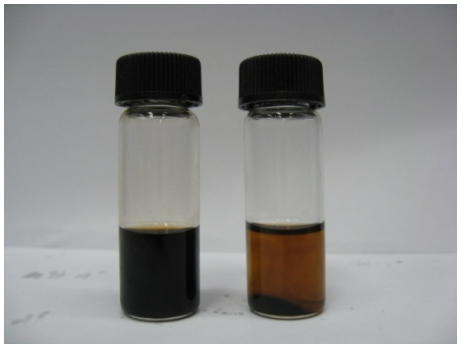


Figure S9. Co- squalane solutions from thermal decomposition of $Co_2(CO)_8$ in the presence (left) and absence (right) of C_8-PVP (C_{Co} = 5 mM, Co : C_8-PVP = 1 : 10) Pictures taken after one day.

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