# **Electronic Supplementary Information**

# **Design of Polystyrene Latex Particles Covered with Polyoxometalate Clusters** *via* **Multiple Covalent Bonding**

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## Materials and sample preparation.

Sodium tungstate dehydrate (Sigma, Aldrich), Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%, Fisher Scientific,), Glacial acetic acid (GR), 3-(Trimethoxysilyl) propyl methacrylate (Sigma-Aldric), Acetonitrile (Sigma-Aldric), Hydrochloric Acid (HCl, Fisher Scientific), Potassium chloride (KCl, Sigma-Aldric,), Styrene (Sigma-Aldric,), Potassium chloride (KCl, Sigma-Aldric), Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Sigma-Aldric).

## Synthesis of the Sodium Tungstophosphate, Na<sub>9</sub>[A-PW<sub>9</sub>O<sub>34</sub>]·14H<sub>2</sub>O

The procedure was based on the classic literature. A mixture of 120 g (0.36 mol) of sodium tungstate dihydrate  $Na_2WO_4$ ·2H<sub>2</sub>O and 150 g of water was stirred in a 300 mL beaker with a magnetic stirring bar until the solid is completely dissolved. Phosphoric acid (85%) was added dropwise with stirring (4.0 ml, 0.06 mol). Glacial acetic acid (22.5 ml, 0.40 mol) was added dropwise with vigorous stirring. Large quantities of white precipitate formed during the addition. The solution was stirred for 1h, and the precipitate is collected and dried by suction filtration.

Yield: 87%. FTIR (KBr): 2135 (w, broad), 1637 (m), 1577 (m), 1461 (m), 1057 (s), 1016 (m), 937 (s), 888 (m), 760 (s, broad), 645 (m), 594 (m), 508 (m), 462 (m). TGA: Na<sub>9</sub>[A-PW<sub>9</sub>O<sub>34</sub>]·xH<sub>2</sub>O, measured from TGA, x = 14. <sup>31</sup>P NMR (300 MHz, D<sub>2</sub>O)  $\delta$  10.78.

#### Synthesis of POM surfactant, K<sub>3</sub>[A-(RSiO)<sub>3</sub>(SiR)] (R = {H<sub>2</sub>C=C(CH<sub>3</sub>)O(CH<sub>2</sub>)<sub>3</sub>})

3-(Trimethoxysilyl) propyl methacrylate (1.5 mL, 6.3 mmol) was added to 200 mL of a solvent mixture of CH3CN/H2O (150 mL/50 mL, v/v). The solution was acidified with 5 mL of 6 M aqueous HCl solution. To it was slowly added the precursor Na<sub>9</sub>[A- PW<sub>9</sub>O<sub>34</sub>]·14H<sub>2</sub>O (it was synthesized in the previous step) (2.7 g, 1.0 mmol) with a small portion. The resulting colorless clear solution was concentrated to ca. 60 mL in volume with a water bath at 80 °C. To it was added KCl (3.0g, 40.2 mmol). Large quantities of precipitate formed during the addition. After keeping in the fridge for 12 h, the water was poured out and evaporated at reduced pressure. The obtained compound was dissolved in 50 ml acetonitrile followed by centrifugation at 6000 rpm for 30 min. The supernatant was poured into a glass petri dish. After all the solvent evaporated, the resulted transparent product was kept in fridge.

Yield: 89%. FTIR (KBr): 2963 (s, -CH<sub>3</sub>, as), 2936 (m, -CH<sub>2</sub>-, as), 2877 (w, -CH<sub>3</sub>, as), 2741 (vw, -OH in H<sub>2</sub>PO4<sup>-</sup>, s), 2361 (w, CO<sub>2</sub><sup>-</sup>, s), 2342 (w, CO<sub>2</sub><sup>-</sup>, s), 1891 (vw, C=O, s, coupling), 1716 (vs, C=O in ester, s), 1637 (w, -OH in H<sub>2</sub>PO4<sup>-</sup>, s), 1484 (w), 1437 (w, -CH<sub>2</sub>-,), 1405 (w, -COO<sup>-</sup>, s), 1381 (w, -CH<sub>2</sub>-, w), 1322 (m, -C-C-H, d), 1298 (m), 1167 (s, PO<sub>2</sub> in PO<sub>3</sub><sup>-</sup>, s), 1094 (vs, Si-O, s), 1056 (s, P-O, as), 977 (vs, W=O, as) 954 (vs, W=O, as), 922 (m, P-OH in H<sub>2</sub>PO4<sup>-</sup>, s), 868 (s, W-O<sub>a</sub>-W, as), 818 (m, W-O<sub>b</sub>-W, as) 746 (vs)

670 (w) 593 (vw), 527 (w), 471 (vw). [Note: O<sub>a</sub> atoms are shared by two W atoms of different W<sub>3</sub>O<sub>3</sub> units; O<sub>b</sub> atoms are shared by two W atoms from the same Mo<sub>3</sub>O<sub>13</sub> unit.]. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO) δ 5.98 (d, J = 9.3 Hz, 4H), 5.59 (s, 4H), 4.03 (t, J = 15.8 Hz, 7H), 3.26 (d, J = 19.7 Hz, 19H), 2.56 – 2.42 (m, 14H), 2.05 (s, 4H), 2.03 – 1.66 (m, 16H), 1.66 (s, 4H), 0.58 (d, J = 5.4 Hz, 10H). <sup>31</sup>P NMR (300 MHz, [D<sub>6</sub>]DMSO) δ 18.19. ESI-MS (Acetonitrile): m/z: 965.9 ([POM hybrid]<sup>3-</sup> Calc. 966.2), 1449.8([H + POM hybrid]<sup>2-</sup> Calc.1449.8), 2900.6 ([2H + POM hybrid]<sup>-</sup> Calc.2900.6). <sup>13</sup>C NMR (500 MHz, d<sub>2</sub>o) δ 167.30 (s), 135.22 (s), 125.21 (s), 118.29 (s), 65.83 (s), 21.44 (s), 16.99 (d, J = 8.3 Hz), 8.46 (s), 0.00 (s).

#### Emulsion copolymerization of POM surfactant and styrene

The synthesized POM surfactant is further used in the emulsion copolymerization. The polymer reaction was carried out based on traditional emulsion polymerization protocol except we used hybrid as surfactant. Hybrid was added to 9 mL H<sub>2</sub>O, and stirred for 10 min. Then added 1 mL styrene to the solution and allowed for 30 min stirring to form the emulsion (r = 1000 r / min). After 24 hrs polymerization reaction at 70 °C with potassium persulfate as initiator (50 mg), the obtained milk-like solution was centrifuged and the obtained solid sample was washed with water.

#### **TGA analysis**

The solid sample obtained was put into the 60°C oven for 24 h to allow it fully dried. Thermogravimetric (TGA) analysis was performed on a TA Instruments Q50 Thermogravimetric Analyzer at a heating rate of 10 °C/min from room temperature to 800 °C under a nitrogen purge.

#### Zeta Potential analysis

The suspension of the POM-latex (synthesized with hybrid concentration as ca. 15 mg/mL) was used for measurement. The experiments were done by using Malvern Instruments Zetasizer Nano-ZS90 with disposable curvette.

#### Calculation of area that each POM head occupies on the POM-Polymer nanobeads:

In Figure 9, assume that before the point A, the mass loss is only due to the water or other small molecules absorbed on the surface of the nanobeads. Between the A and B, the mass loss is due to the decomposition of polystyrene (Mass loss of tracer of organic tails attached to POM is ignored to simplify the calculation). After point B, only POM part exists.

A (260.83°C, 90.31%), B (489.86°C, 9.984%), Sample size: 0.6700 mg, density of polystyrene<sup>4</sup>: 1.057 g cm<sup>-3</sup>.

Weight of polystyrene

 $m_{ps} = m_{total} \times (w_A - w_b) = 0.6700 \times (90.31\% - 9.984\%) = 0.5381 (mg)$ 

Where  $m_{total} = 0.6700 \ mg$ ,  $w_A = 90.31\%$ ,  $w_b = 9.984\%$ .

Weight of POM

 $m_{POM} = m_{total} \times w_b = 0.6700 \times 9.984\% = 0.06689 \ (mg)$ 

Total volume of polystyrene

$$V_{total} = \frac{m_{ps}}{\rho} = 0.5381 \times 10^{-3} \div 1.057 = 5.091 \times 10^{-4} (cm^3)$$

Where  $\rho = 1.057 \ g \ cm^{-3}$ .

For R=78 nm, the volume of one nanobead

$$V_{single} = \frac{4}{3}\pi R^3 = \frac{4}{3}\pi \times (78 \times 10^{-7})^3 = 1.998 \times 10^{-15} \ (cm^3)$$

Total number of nanobeads

$$N_{total} = \frac{V_{total}}{V_{single}} = \frac{5.091 \times 10^{-4}}{1.998 \times 10^{-15}} = 2.561 \times 10^{11}$$

The average mass of POM on each nanobead

$$\bar{m}_{POM} = \frac{m_{POM}}{N_{total}} = \frac{0.06689 \times 10^{-3}}{2.561 \times 10^{11}} = 2.612 \times 10^{-16} (g)$$

The average number of POM on each nanobead

$$N_{POM} = \frac{\bar{m}_{POM}}{M_{POM}} \times N_A = \frac{2.612 \times 10^{-16}}{2269} \times 6.022 \times 10^{23} = 6.932 \times 10^5$$

Where  $M_{POM}$  is the average molecular weight of [A-PW<sub>9</sub>O<sub>34</sub>] plus three K

The surface area of each nanobead

$$S_{single} = 4\pi R^2 = 4\pi \times 78^2 = 7.645 \times 10^5 (nm^2)$$

The average area occupied by one POM on each nanobead

$$\mathcal{F}_{POM} = \frac{S_{single}}{N_{POM}} = \frac{7.645 \times 10^5}{6.932 \times 10^5} = 1.103 \ (nm^2)$$

The average distance between the centers of POM on the surface of nanobead

$$l = \sqrt{S_{POM}} = \sqrt{1.103} = 1.05 \ (nm)$$

Hybrid **2** is compatible with the length of lacunary Keggin  $Na_9[A-PW_9O_{34}]$ , around 0.7 nm. This indicates the fully coverage of POM on the surface of nanobeads.



Firgue S1. FT-IR of POM-organic hybrid



Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR of POM surfactant,  $K_3[A-(RSiO)_3(SiR)]$  (R = {H<sub>2</sub>C=C(CH<sub>3</sub>)O(CH<sub>2</sub>)<sub>3</sub>}). The labels of the peaks ascribe the corresponding peak to the C/H atom in Figure S4.



Figure S3. Plot of conductivity to concentration of the hybrid water solution.



Figure S4. Molecular structure of POM-based hybrid.



Figure S5. DLS results of the assemblies of POM-hybrid surfactant in water.



Figure S6 top) TEM images of the POM-polymer latex; bottom) EDS results of the surface area of the latex beads.



Figure S7 SEM image of the POM-polymer latex.



Figure S8. FT-IR of POM-Polymer nanobeads (KBr).



Figure S9. The appearance blue color of the suspension of the latex after UV radiation.



Figure S10. The recycling of the latex sample from its suspension by using centrifugation.





Figure S11. SEM elemental mapping of the solid sample of hybrid **2**. up) SEM images of the solid sample; midde) mapping of potassium; bottom) mapping of tungsten.



Figure S11. DLS measurement of the formed emulsions before the polymerization reactions. The two major peaks at ca. 4000 and 100 nm are ascribed to the sizes of formed emulsions and monomer droplets. Hybrid concentration, 15 mg/mL.