

## Supporting Information

# Synthesis of Transition-Metal-Free and Odour-Free Nanoparticles and Nanocapsules via Reversible Complexation Mediated Polymerization (RCMP) and Polymerization Induced Self-Assembly (PISA)

*Sarkar Jit,<sup>a</sup> Longqiang Xiao,<sup>a</sup> Alexander W. Jackson,<sup>b</sup> Alexander M. van Herk,<sup>b\*</sup> Atsushi Goto<sup>a\*</sup>*

<sup>a</sup>Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,  
Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

<sup>b</sup>Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research, 1  
Pesek Road, 627833, Singapore

## Experimental Section

**Materials.** Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), methacrylic acid (MAA) (>99%, TCI), ethylene glycol dimethacrylate (EGDMA) (98%, Sigma Aldrich), iodo-2-methylpropionitrile (CP-I) (>95%, TCI), NaI (>99.5%, Kanto), 2,2'-azobis(2,4-dimethyl valeronitrile) (V65) (95%, Wako Pure Chemical, Japan), and (trimethylsilyl)diazomethane (10% in hexane) (TCI) were used as received.

**Measurements.** PMAA-I and PMAA-PMMA-I were methylated for the GPC analysis.<sup>1</sup> PMAA-I (purified by reprecipitation) (15 mg) or PMAA-PMMA-I (not purified but dried after the polymerization) (15 mg) was dissolved in tetrahydrofuran (THF) (1 mL). (Trimethylsilyl)diazomethane (1.5 equivalents to the COOH group) was added into the solution. The solution was stirred overnight at room temperature and analyzed with GPC. The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was THF at a flow rate of 1.0 mL/min. Sample detection was conducted using a Shodex differential refractometer RI-101. The column system was calibrated with standard poly(methyl methacrylate)s (PMMA)s.

The NMR spectra were recorded on a Bruker (Germany) AV500 spectrometer (500 MHz) and Bruker BBFO400 spectrometer (400 MHz) at ambient temperature. DMSO-*d*<sub>6</sub> (Cambridge Isotope Laboratories (CIL), USA) and D<sub>2</sub>O (CIL) were used as the solvents for the NMR analysis.

Transmission electron microscopy (TEM) images were obtained on a JEM-1400 transmission electron microscope (JEOL, Japan) operated at 100 kV. The TEM grid was carbon-coated on 200 mesh (copper) (Ted Pella, USA).

The cryogenic TEM (cryo-TEM) image was obtained in a FEI Titan Krios transmission electron microscope equipped with an auto sampler and a field emission gun (FEG) and performed under 300 kV. The image was captured with a Falcon II camera (4\*4) with magnification of 29,000 and a pixel size of

2.873 Å. The vitrification of the sample was performed using a vitrification robot (FEI Vitrobot Mark IV, Hillsboro, OR, USA). A 5  $\mu$ L stock solution was added on a grid (Quantifoil, R2/2, Holey Carbon film) which was freshly glow-discharged before use at 20 mA for 60 s. An excess sample was blotted away with a filter paper at room temperature, in 100% humidity, in a blotting time of 2 s, and with a blotting force of 1. Then it was vitrified in liquid ethane and immediately transferred to a cryo-holder.

The dynamic light scattering (DLS) measurement was carried out on a Malvern Zetasizer Nano ZSP (Worcestershire, UK). The test angle for the DLS analysis was 173° (backscattering detection). Water was used as the solvent.

**Preparation of PMAA-I Macroinitiator.** A mixture (2 g) of MAA (8 M), CP-I (160 mM), V65 (266 mM), NaI (160 mM), and water (50 wt% of the mixture) was heated in a Schlenk flask at 45 °C under argon atmosphere with magnetic stirring. The reaction mixture was diluted with 1 mL ethanol. The polymer was reprecipitated in diethyl ether and dried under vacuum.

**PISA.** A mixture (1.5 g) of MMA (8 M), PMAA-I (27 mM), NaI (40 mM), V65 (40 mM), and ethanol (90 wt% of the mixture) was heated in a Schlenk flask at 60 °C under argon atmosphere with magnetic stirring. After the prescribed time  $t$ , an aqueous solution (50  $\mu$ L) of NaHCO<sub>3</sub> (0.9 equivalents to the COOH group) was added to the reaction mixture. An aliquot (0.1 mL) of the solution was dried under vacuum, methylated, and analyzed with GPC. Another aliquot (0.1 mL) was diluted with DMSO- $d_6$  (0.9 mL) and analyzed with <sup>1</sup>H NMR for obtaining the monomer conversion. Another aliquot (0.1 mL) was diluted with an aqueous solution (0.5 mL) of KCl (1 mM), which is a stock solution. The stock solution (50  $\mu$ L) was further diluted with water (0.6 mL) and analyzed with DLS. The stock solution (10  $\mu$ L) was also dropped on a TEM grid, dried under vacuum, and analyzed with TEM.

## Reference.

1. L. Couvreur, C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet, *Macromolecules*, 2003, **36**, 8260–8267.