## **Electronic Supporting Information**

## Controlled Production of Polymer Microspheres from Microgel-Stabilized High Internal Phase Emulsions

Zifu Li, Xiaoling Wei and To Ngai\*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

## **Experimental Details**

**Materials:** *N*-isopropylacrylamide (NIPAM, Fluka) was recrystallized from a toluene/nhexane mixture. *N*,*N*'-methylene bisacrylamide (MBAA, Fluka), methacrylic acid (MAA, Merck), perylene (Aldrich), and the fluorescent dye, methacryloxyethyl thiocarbamoyl rhodamine B (MRB, Polysciences, Inc.) were used as received. Styrene (St, Aldrich), benzene were dried over CaH<sub>2</sub>, degassed by high vacuum line for 3 times and distilled under vacuum. n-Butyllithium (n-BuLi, Acros) were used as received. Potassium persulfate (KPS, Merck) were used without further purification. Polycaprolactone (PCL,  $M_w \sim 14000$  g/mol) chains were purchased from Aldrich and used without further purification. Oils such as benzene, toluene and *O*-xylene were used as received. Deionized water was used in all the experiments. Note that benzene is a classified potent carcinogen and should be evaporated under highly controlled and contained conditions.

**PNIPAM-***co***-MAA microgel particles preparation and characterization:** PNIPAMbased microgel particles were synthesized using surfactant-free precipitation polymerization. Typically, 3.0893 g of NIPAM, 0.1075 g of MBAA, 0.1072 g of MAA and 0.0014 g MRB were dissolved into 140 mL of deionized water in a 250 mL two neck reactor fitted with a nitrogen bubbling inlet and outlet, and a reflux condenser and stirred with a magnetic stir bar. Then the solution mixture was adjusted to pH 10.88 with sodium hydroxide solution. After stirring the solution for 40 min at 70 °C under nitrogen bubbling, the polymerization was initiated by adding 0.031 g of KPS dissolved in 10 mL of deionized water. The reaction mixture was kept at 70 °C for 7 h. The pH of the dispersion after reaction was 9.27. The resultant microgels were dialyzed for 7 days to remove the unreacted reagents. The final pH of the microgel was ~ 6.0.

The size of the microgel particles was measured using laser light scattering (LLS) at an angle of 20° and shown in Figure S1. The apparatus used for LLS measurements was a modified commercial light-scattering spectrometer equipped with an ALV-5000 multi- $\tau$ digital time correlator and a He-Ne laser (output power =22 mW at  $\lambda_0$  = 632nm). The measurable angular range is 15-155°. In dynamic laser light scattering (DLS), the intensity-intensity time correlation function  $G^{(2)}(\tau)$  in the self-beating mode was measured in the scattering angle range 17.5°-150°. The Laplace inversion of  $G^{(2)}(\tau)$  can lead to a line-width distribution  $G(\Gamma)$ , which can be further converted to a translational diffusive coefficient distribution G(D) by  $\Gamma=Dq^2$  or a hydrodynamic radius distribution  $f(R_h)$  by use of the Stokes-Einstein equation,  $R_{\rm h} = k_{\rm B}T / 6\pi\eta D$ , where  $\eta$ ,  $k_{\rm B}$ , and T are the solvent viscosity, the Boltzmann constant, and the absolute temperature, respectively.



**Fig. S1.** Typical hydrodynamic radius distribution of the synthesized PNIPAM-*co*-MAA microgel particles measured by laser light scattering (LLS) at an angle of  $20^{\circ}$  and T = 25 °C.

**Polystyrene (PS) chains preparation and Characterization:** PS chains were prepared by anionic polymerization. The polymerization of styrene was carried out at 50 °C in benzene solvent with n-BuLi as initiator. The termination was done by adding ethanol (nitrogen bubbled for half an hour) and precipitated in ethanol. The final product was vacuum dried and characterized with GPC. The molar mass of PS chains is  $M_w \sim 1.9 \times 10^5$  g/mol.

The hydrodynamic radius of the PS chains was also measured using laser light scattering (LLS) in toluene at an angle of 20° and shown in Fig. S2. The PS chains have hydrodynamic radius of 11 nm. Since the PS chains are dissolved in toluene, the chains could be assumed as random coils, and  $\langle R_g^2 \rangle^{0.5} = 1.6 \langle R_h \rangle$ . According to the scaling relationship  $\langle R_g^2 \rangle^{0.5} = (1.107 \times 10^{-2}) M_w^{0.605}$ , we will get the  $M_w$  to be  $1.96 \times 10^5$ , which correlates well with the GPC results.



**Fig. S2.** Typical hydrodynamic radius distribution of the PS chains in toluene measured by laser light scattering (LLS) at an angle of  $20^{\circ}$  and T = 25 °C.

Preparation and characterization of microgel-stabilized High Internal Phase Emulsions (HIPEs): The stock aqueous solution contains PNIPAM-co-MAA microgel particles at the solid content of 2 wt%. PS chains or PCL chains were dissolved in various oils at the solid content of 5 wt%, and some perylene green dye was added into the oils for the visualization by confocal microscope. Microgel-stabilized HIPEs with an internal oil volume fraction of 0.8 were prepared by mixing the microgel dispersions (1 ml) with the oils (4 ml, dissolved within the PS chains) and then homogenizing the mixture for 30 seconds using an Ultra-Turrax T25 (Janke and Kunkel) rotor-stator mixer with an 10 mm dispersing head operating at 13500 rpm. The total emulsion volume was kept at 5 mL. The emulsion type was determined by measuring the conductivity and by observing whether a drop of emulsion dispersed when added to a small volume of pure water or oil. The confocal microscope images of the microgel-stabilized emulsions were taken on a Nikon Eclipse Ti inverted microscope (Nikon, Japan). Lasers with wavelengths of 543 nm and 408 nm were used to excite the fluorescent PNIPAM-co-MAA particles and perylene molecules, respectively. An oil immersion objective (60x, NA=1.49) was used to view the samples. The microgel-stabilized HIPEs were placed on the cover slides and a series of x/y layers were scanned before and after the evaporation of both of oils and water. The temperature was kept at 25 °C. For SEM observation, the microgel particles stabilized HIPEs were placed in a silica plate and dried at room temperature for 24 hours and then coated with Au before imaging on a FEI Quanta 400 FEG microscope operating at 10 kV.



**Fig. S3** Appearance of microgel particles stabilized HIPEs with benzene, toluene and *O*-xylene as the organic solvents (5wt% PS dissolved in oils). Confocal images of the HIPEs excited at laser of wavelength of 408 nm (the green color is due to the dissolved perylene in the oil phases: (a) HIPEs from benzene; (b) HIPEs from toluene; and (c) HIPEs from *O*-xylene.



**Fig. S4** a) SEM and b) confocal image of microspheres obtained from PCL chains in Benzene.



Fig. S5 a) SEM and b) confocal image of microspheres obtained from PCL chains in Toluene.



Fig. S6 a) SEM and b) confocal image of porous film obtained from PCL chains in *O*-xylene.