

## Supplementary Information

for

### **Preparation of Poly(methyl methacrylate)/Polystyrene/Poly(acrylonitrile-*co*-butadiene) Tri-layer Core-Shell Nanoparticles and Their Postpolymerization Modification via Catalytic Latex Hydrogenation**

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<b>Table of contents</b>	<b>Pages</b>
1. Experimental Section	S2-S4
2. Characterization	S5-S7
3. Figure	S8-S9
4. Reference	S9-S10

## **Experimental Section**

### **Materials Used in Synthesis of Polymer Nanoparticles**

Ammonium persulfate (APS, 98%), methyl methacrylate (MMA, 99%), acrylonitrile (AN, 99+%) and styrene (St, 99%) were purchased from Aldrich. The inhibitors were removed prior to polymerization by passing the monomer AN through an alumina column. The initiator APS was purified by recrystallization in ethanol and dried under vacuum at room temperature. The 1,3-Butadiene (BD) was provided by LANXESS Inc. The Gemini surfactant 12-3-12, i.e., trimethylene-1,3-bis(dodecyldimethylammonium bromide) with molar mass = 628.69 g/mol was synthesized by known procedures<sup>1</sup> and used after repeated recrystallization from acetone-ethyl acetate (1:1 volume). The ethanol, methanol, acetone, and ethyl acetate were all reagent grade and used without further purification. These four organic solvents and distilled water were obtained from the Department of Chemical Engineering, University of Waterloo, Canada.

### **Materials for Direct Hydrogenation in Latex Form**

Ultra-high purity hydrogen (99.999%, oxygen-free) was used as received (Praxair Inc. Mississauga, CA). Wilkinson's catalyst  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  was prepared according to the literature.<sup>2,3</sup> Triphenylphosphine (TPP, 99%) was obtained from Strem Chemicals, Inc. (Massachusetts, US) and further purified by recrystallization from ethanol to remove triphenylphosphine oxide.

### **Synthesis of PMMA/PS/NBR Nanoparticles**

The PMMA/PS/NBR tri-layer core-shell nanoparticles were prepared via a multistage semibatch emulsion polymerization, which was performed in a Parr 316 Stainless Steel Parr reactor (**Figure S1**). In the first stage of the preparation of PMMA seeded latex, 2.5

g of GS 12-3-12, 0.15 g APS, and 80 mL distilled water were charged into the stainless steel reactor equipped with an impeller stirrer, an addition tube, and a thermocouple. Oxygen was removed by purging a slow stream of nitrogen gas for 20 min while stirring was maintained at 200 rpm. The reactor was then heated up to the reaction temperature for the first stage at 70 °C. The monomer MMA (5 mL) was fed continuously to the reactor using a designed addition tube at a constant rate of 0.05 mL/min. After the MMA feeding was completed, the reaction system was allowed to proceed for an additional 1 h. Under the same temperature, the second monomer styrene (10 mL) was then fed in the reactor in an identical manner and with the same rate of addition as the MMA to prepare the PMMA/PS core-shell nanoparticles during this second stage of polymerization. After the completion of the addition of styrene, the temperature was decreased from 70 to 45 °C as the copolymerization temperature of AN and BD for the shell formation was set at 45 °C. The reaction system was aged for 1 h before proceeding to the third stage copolymerization of AN and BD. In the third stage, it is important to increase the pressure inside the reactor to at least 22 psi using nitrogen gas (80 psi used in our studies), since the saturated vapor pressure of BD in the addition tube is around 22 psi at room temperature. The addition tube filled with a 5 mL AN/15 mL BD mixture was then connected with the reactor (80 psi) and the pressure between the reactor and the addition tube was thereafter balanced. The mixture of AN and BD was added continuously at the same rate of 0.05 mL/min. After the completion of the addition, the polymerization was aged for a given time to reach a reasonable conversion.

### **Direct Hydrogenation of PMMA/PS/NBR Core-Shell Nanosized Latex**

The latex hydrogenation of diene-based nanoparticles in the presence of Wilkinson's catalyst  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  was carried out in the same Parr reactor as the polymerization for the synthesis of nanoparticle substrate (**Figure S1**). A measured volume of the latex (25 mL) with the added distilled water (75 mL) were first mixed with 1 wt%  $\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3$  on the basis of the amount of the NBR layer and the additive TPP with a weight ratio of 10:1 to catalyst. The TPP plays a vital role in the hydrogenation reaction as it maintains the activity of Wilkinson's catalyst.<sup>4</sup> The mixture was then degassed with three quick  $\text{N}_2$  cycles and subjected to bubbling  $\text{N}_2$  under about 1.38 MPa for 20 min at room temperature with an agitation speed of 200 rpm. The resulting mixture was heated up to 130 °C and stabilized for 2 h under 600 rpm stirring speed. The hydrogenation reaction was embarked on when hydrogen gas at a pressure of 6.89 MPa was introduced into the reactor. The hydrogen pressure (6.89 MPa), hydrogenation temperature (130 °C), and agitation speed (600 rpm) were maintained constant throughout the reaction period. Aliquots were taken at various time intervals through a dip tube for the characterization. After a given reaction time, the system was cooled down to room temperature and depressurized to obtain the final product.

## **Characterization Section**

### **Method to Obtain the Polymer Solid**

The polymer latexes were coagulated in ethanol. It is noted that GS 12-3-12 is easily dissolved in both ethanol and distilled water. The filtered solid was dried under vacuum in an oven at room temperature until constant weight was reached. The polymerization conversions of monomer(s) were calculated by a gravimetric method.

### **Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR)**

The <sup>1</sup>H NMR was also performed to investigate the composition and microstructure of the polymer NPs. The <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz Spectrometer (Bruker BioSpin Corp. Massachusetts, US) and chemical shifts were reported in ppm units with TMS as an internal standard. The sample solution was prepared by dissolving 15-20 mg dried polymer solid into 1 mL CDCl<sub>3</sub>.

### **Dynamic Light Scattering**

The size and number size distribution (non-negative least squares method) of the polymer particles of the synthesized latex were determined by dynamic light scattering (DLS) at 25 °C using a Nanotracs 150 particle size analyzer (BETATEK Inc., Canada) and reported as the number average diameter. The calculations of the particle size distributions were performed using Microtracs FLEX 10.2.14 software available from BETATEK Inc., which employed single-exponential fitting, non-negatively constrained least-squares (NNLS), cumulants analysis, and CONTIN particle size distribution analysis routines.

### **Transmission Electron Microscopy**

LEO 912 AB 100 kV Energy Filtered Transmission Electron Microscopy (EFTEM) (Carl Zeiss Inc. Germany) was used to examine the size and observe the morphology of the

nanoparticles. When preparing the specimens for TEM measurement, the nanosized latex was first diluted with distilled water and then 10  $\mu\text{L}$  of the diluted solution was incubated on a 400-mesh copper grid at room temperature. Excess solution was drawn off the edge of the grid with tissue paper. Next the grid was negatively stained with 2% (w/v) uranyl acetate for 1 min. After the excess stains were drawn off with tissue paper, the grid was delivered into the TEM chamber for imaging.

### **Cross Section TEM**

Before sending the samples for the analysis of cross section TEM, the samples were first carefully ground and then immersed in 100% ethanol for 2 hr with three changes of ethanol. The ethanol was then removed and replaced with a 50/50 (v/v) mixture of ethanol and LR White resin. This was left overnight with mixing. The 50/50 mixture was replaced by pure LR White resin and stirred for 3 hr. The sample was then put into a gelatin capsule. Once the sample had sunk to the bottom of the capsule the resin was polymerized at 60 °C overnight. Thin sections around 75 nm thick were cut with an ultramicrotome. The resulting sections were mounted on 100-mesh copper grids and stained with 2% (w/v) uranyl acetate (7 min) and Reynold's lead citrate (3 min). The prepared samples were viewed using a LEO 912 AB EFTEM.

### **Cross-linking Examination**

The cross-linking was estimated using a solvent extraction technique, which has been in detail described in El-Aasser and coworkers' reports.<sup>5,6</sup>

### **Zeta-potential**

The  $\zeta$ -potential measurements of core and core-shell latex particles were determined using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK) at 25 °C. The

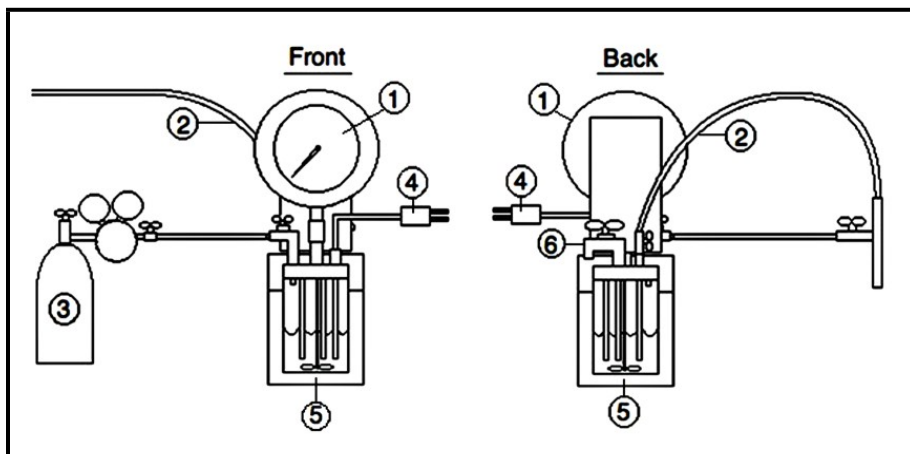
latex samples were injected into a disposable cell (folded capillary DTS-1060 from Malvern, Worcestershire, UK) with a volume of ~1 mL and analyzed at constant voltage. The  $\zeta$ -potential distribution (in mV) was automatically calculated from the electrophoretic mobility distribution based on the Smoluchowski formula. For each sample, the  $\zeta$ -potential measurement was repeated three times and the mean value was reported. The  $\zeta$ -potentials reported herein correspond to the average of the peak values of the  $\zeta$ -potential distributions.

### **Molecular Weight**

The molecular weight and polydispersity index were determined by size exclusion chromatography (SEC, Model 305 TDA, Viscotek, Houston, US). The dried polymers were first dissolved in THF and filtered through a 25 mm syringe filter with a 450 nm GHP membrane (Pall Corp. New York, US) and then 100  $\mu$ L of the solution was injected into the SEC analysis column using THF (GPC grade, stabilized with 250 ppm of 2,6-Di-tert-butyl-4-methylphenol (BHT)) as the eluent at a flow rate of 1.0 mL/min at 25  $^{\circ}$ C. The detectors are a triple detector system with a multi-angled laser light scattering setup equipped with an RI detector and a Viscometer detector. Polystyrene standard (PS 99 K,  $\overline{M}_w = 98251$ ,  $\overline{M}_n = 96722$ , IV = 0.477 in THF at 30  $^{\circ}$ C) was used for calibration.

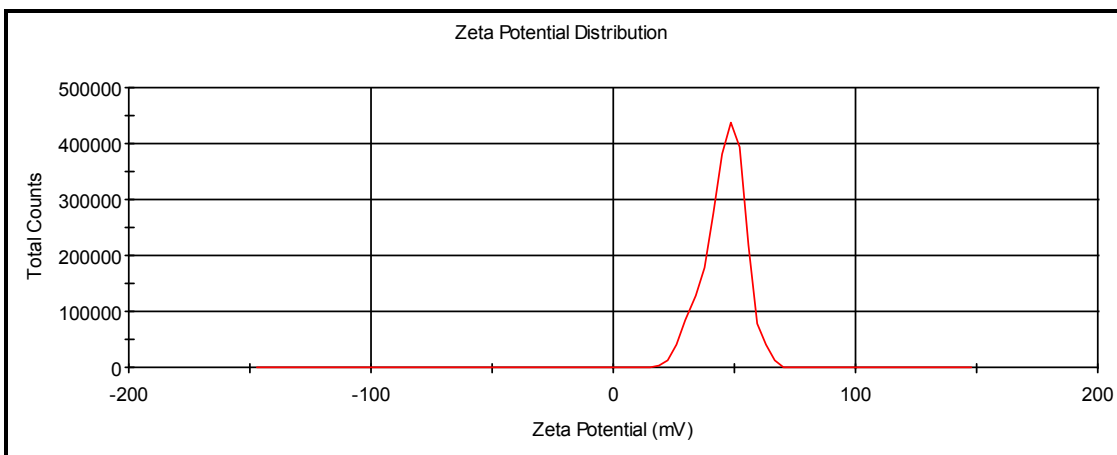
## Figure Section

The synthesis and hydrogenation of nanoparticles was performed in a modified Parr 316 Stainless Steel reactor (**Figure S1**).



**Figure S1.** Modified Parr 316 Stainless Steel Reactor. ① pressure gauge; ② monomer adding tube for polymerization of monomers or the hydrogen feeding for the hydrogenation reaction; ③ nitrogen cylinder; ④ thermocouple; ⑤ reactor autoclave; ⑥ sample taken outlet tube.





**Figure S2.** Zeta potential distribution of PMMA/PS/NBR latex nanoparticles. **Experimental conditions of synthesis of PMMA/PS/NBR nanosize latex:** APS = 0.15 g, Gemini Surfactant 12-3-12 = 2.5 g, MMA = 5.0 mL, T = 70 °C at the first stage; Styrene = 10 mL, T = 70 °C at the second stage; AN = 2.5 mL, BD = 7.5 mL, T = 45 °C at the third stage.

The average  $\zeta$ -potential was reported to be 46.1 mV at pH = 3.5 at 25 °C, which represents a good stability of the obtained latex.

## References

- 1 Zana, R.; Benraou, M.; Rueff, R. *Langmuir* 1991, 7, 1072-1075.
- 2 Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. J. *Chem. Soc. A.* 1966, 12, 1711–1732.
- 3 Parent, J. S.; McManus, N. T.; Rempel, G. L. *Ind. Eng. Chem. Res.* 1996, 35, 4417–4423.
- 4 Wang H, Yang L, Scott S, Rempel GL (2012) *J Polym Sci Part A Polym Chem* 50(22):4612.
- 5 He, Y.; Daniels, E. S.; Klein, A.; El-Aasser, M. S. *J Appl Polym Sci* 1996, 65, 511-523.

6 He, Y.; Daniels, E. S.; Klein, A.; El-Aasser, M. S. *J Appl Polym Sci* 1997, 64, 1143-1152.