Supporting Information for

Functionality- and Size-dependent Target-Differentiation of Nanoporous Carboxylated Polystyrenes in Polar Protic Solvents

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SUPPORTING INFORMATION
Experimental Details

Methods. \(^1\)H- and \(^13\)C-NMR spectra were recorded at room temperature on Varian 200 and 500 spectrometers, using chloroform-\(d\) (CDCl\(_3\)) as the solvent, and tetramethylsilane (TMS) as the internal reference for chemical shifts. Gel permeation chromatography (GPC) measurements were performed on a Waters system equipped with a Waters 510 HPLC pump, a Waters M486 tunable absorbance detector, a Waters M410 differential refractive index detector, and three waters styragel HR columns with a continuous porosity of \(10^{-2}-10^{-4}\) Å. Monodisperse linear polystyrene standards were used for calibration. THF (with 2% v/v N,N-dimethylacetamide) was used as the mobile phase, and the rate was 1.0 mL/min at 35 °C. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC-7 instrument. Indium and zinc standards were used for temperature and enthalpy calibrations, and nitrogen (10 mL/min) was used as the purge gas. The scan rate was 10 °C/min. Data were collected from a second heating scan. The glass transition temperatures \(T_g\) of PS and PLA were calculated at a midpoint of thermograms. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 10C1 beamline of the Pohang Accelerator Laboratory (PAL), Korea. The sample was held in an aluminum sample holder with polyimide films on both sides. Absorption spectra were obtained on a Perkin Elmer spectrum Lambda 25 UV/Vis spectrophotometer. Transmission electron microscopy (TEM) experiments were performed using a JEM-2100F (JEOL) using acceleration voltage of 200 kV. Scanning electron microscopy (SEM) samples were analyzed with a Hitachi S-4300 FE-SEM using acceleration voltage of 15 kV. The secondary electron images were collected in ultra-high resolution mode at a working distance of ~5 mm. The platinum coating thickness was about 2 nm, which was estimated from a calculated deposition rate and experimental deposition time. Nitrogen adsorption measurement was performed on an ASAP 2010 volumetric adsorption analyzer at 323 K. The specific surface area and pore size distribution were calculated through the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The fluorescence microscopy image was obtained by Nikon Eclipse TE2000-U, inverted fluorescence microscope equipped with DXM1200C digital camera.

**Scheme S1.** Synthesis of the dendritic block copolymer, (PS)\(_2\)-b-PLA.

**Synthesis.** The dendritic block copolymer, (PS)\(_2\)-b-PLA, was synthesized in Scheme S1, and the details of the synthetic procedure were described previously.\(^\text{S1}\)

(PS)\(_2\)-b-PLA. \(M_w/M_n\) (GPC) = 1.05. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.85 (s, H-triazole), 7.28-6.36 (br, Ar-H of PS), 5.44 (s, triazole-CH\(_3\)OOC-Ar), 5.29-5.08 (br, OOCCH(CH\(_3\))O, repeating unit of PLA), 5.07 (triazole-CH\(_3\)O-Ar), 4.52 (s, NCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)O), 4.36 (m, OOCCH(CH\(_3\))OH, end group of PLA), 4.27 (s, NCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OOCCH(CH\(_3\))O), 3.93 (br, NCH\(_2\)CH\(_2\)), 3.86 (s,
NCH₂CH₂OCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O, 3.62 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O), 3.56 (s, NCH₂CH₂OCH₂CH₂OCH₂CH₂OOCCH(CH₃)O), 2.69 (d, OOCCH(CH₃)OH, end group of PLA), 2.31-1.19 (br, OOCCH(CH₃)O repeating unit of PLA and CHCH₂ of PS backbone), 1.18-0.49 (br, PS-CH(phenyl)CH₂CH(CH₂CH₃)CH₃).

**Macroscopic alignment by a channel die.** The macroscopic alignments were performed with a home-built channel die 3 mm wide and 60 mm long. Hot pressed pieces of (PS)₂-b-PLA were placed in the center of the channel die, then heated to 130 °C in a laboratory press. The samples were subjected to compression with a constant load (compression ratio ~ 10) and allowed to cool to room temperature over a period of 1 hour before removing them from the channel die. The thicknesses of aligned samples were between 0.5 mm and 1 mm.

**Degradation of PLA block in (PS)₂-b-PLA samples.** The degradation of PLA was performed by placing aligned samples in a 0.5 M NaOH solution (methanol/water = 40/60 vol %). Then, the solution was stirred in an oil bath at 55 °C (This temperature is higher than the T_g (52.1 °C) of the PLA block but lower than the T_g (88.5 °C) of the PS block) for about 1 week. The etched samples were washed with water and methanol, and dried under vacuum for 24 hours at room temperature.

**Preparation of 2 nm AuNP solution.** A solution of HAuCl₄·3H₂O (50 mg) dissolved in water (15 mL) was added to a solution of tetraoctylammonium bromide (210 mg) dissolved in toluene (15 mL). The mixture was stirred for 10 minutes at ambient temperature until the toluene layer turned red. To this solution, a solution of pentanethiol (37 mg) dissolved in toluene (2 mL) was added, and then the mixture solution was stirred for another 10 minutes. To this solution, 8 mL of aqueous sodium borohydride (190 mg) solution was slowly added, and stirred overnight. The organic layer was collected and concentrated. The resulting solid was dissolved in a small amount of hexane, and precipitated by ethanol. Then, the suspension was placed in a freezer for 1 day. The crude product was purified by repeating a sonication-centrifugation-decantation cycle three times in ethanol, and the solid was dried under vacuum at ambient temperature for 10 hours. To change the surface functional groups of the prepared AuNPs, a solution of mercaptoundecanoic acid (71 mg) dissolved in dichloromethane (5 mL) was added to 4.5 mL of 2 nm AuNP solution (dichloromethane), and the mixture was stirred at ambient temperature for 2 days. After that, the above mentioned sonication-centrifugation-decantation cycle was performed three times in dichloromethane to remove the remaining mercaptoundecanoic acid. Then, AuNP was dried under vacuum at ambient temperature for 10 hours. Finally, a methanolic 10 µM AuNP (2 nm) solution was prepared by dissolving appropriate amount of the AuNP powder in water and methanol. The average size of the AuNPs was determined to be 2 nm by a transmission electron microscopy.

**Preparation of 16 nm AuNP solution.** A solution of HAuCl₄·3H₂O (5 mg) dissolved in water (95 mL) was brought to reflux with stirring. Aqueous sodium citrate solution (1%) was added to the solution. The mixture solution was further heated until the color turned deep red. The solution was concentrated to be 56 nM. The average size of the AuNPs was determined to be 16 nm by a transmission electron microscopy. The concentration of the 16 nm AuNP solution was confirmed by Beer’s law calculation based on the surface plasmon resonance (SPR) peak from the UV-vis absorption.

**Reference**
Figure S1. One-dimensional and two-dimensional SAXS data of (a) oriented (PS)$_2$-b-PLA and (b) porous PS (1). The oriented polymer and porous PS are monolithic in nature. When the X-ray beam was perpendicular to the shear direction (i.e., cylinder axes), two intense spots were observed in the two dimensional small angle X-ray scattering (SAXS) data, indicative of a macroscopic orientation.

Figure S2. Calculation of the pore diameter on the basis of the SAXS data.

Figure S3. DSC thermogram of (PS)$_2$-b-PLA.
**Figure S4.** (a) $^1$H NMR spectra before and after hydrolysis of (PS)$_2$-b-PLA. (b) GPC elugrams of dibranched PS, (PS)$_2$-b-PLA, and the porous PS obtained after hydrolysis. In (a), the methine protons of the PLA at 5.1-5.2 ppm completely disappeared after the chemical etching. In (b), the GPC data of the etched sample was identical to that of the dibranched PS.

**Figure S5.** Scanning electron micrographs of 1: (a) parallel and (b) perpendicular to the cylinder axes. The side-view image (a) displayed cylindrical channels over the entire area, and the top-view image (b) exhibited hexagonally arrayed nanopores. The average pore diameter from the SEM image was approximately 10.0 nm. However, considering the thickness of the Pt coating (ca. 2.0 nm), the actual pore diameter can be assumed to be 14.0 nm.
Figure S6. (a) Nitrogen adsorption-desorption curves, and (b) pore size distribution of 1. From a type IV isotherm with an H1 type hysteresis loop between the adsorption and desorption curves, a specific surface area was determined to be 135 m$^2$/g using the Brunauer-Emmett-Teller (BET) method. The Barrett-Joyner-Halenda (BJH) method determined the average pore diameter of 12.1 nm, which was somewhat underestimated. It is well known that the BJH method gives a smaller pore diameter than the actual value [Zalusky, A. S.; Olayo-Valles, R.; Wolf, J. H.; Taylor, C. J.; Hillmyer, M. A. J. Am. Chem. Soc. 2002, 124, 12761].

Figure S7. Bright field micrograph (5 x) of the non-porous PS sample after immersion in the aqueous rhodamine 6G solution for 24 hours.

Figure S8. Size distributions of a) 16 nm and b) 2 nm AuNP samples on the basis of the obtained TEM images.