

Supporting Information for

A Novel Approach to the Fabrication of Macroporous Polymers and Its Use as a Template for Crystalline Titania Nano Rings

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Experimental Section

Colloid Monodispersed **PSDVB** colloids with a diameter of 500 nm were kindly donated by Otsuka co. The colloids were synthesized by dispersion polymerization.¹ Mole fraction of divinylbenzene / styrene in feed was 8 / 92. Gel Permeation Chromatography (GPC) analysis revealed that soluble parts of polymer had $M_n = 118,000$, and the PDI value was 1.39. FT-IR characterization was carried out using SPECTRUM 2000, Perkin Elmer. Colloid dispersion in distilled water was dried for 48 h at 50 °C and mixed with KBr powder. The powder was ground and shaped as a disc for IR analysis. Compared with homo **PS**, **PSDVB** showed an aliphatic C=C stretch peak at 1637 cm^{-1} because it contains divinylbenzene (**DVB**) as the cross-linker: monoreacted or nonreacted free **DVB** could be the origin of the C=C peak (arrow, Figure SI-1a). Thermal analysis was carried out using a differential scanning calorimetry (DSC) 2010, TA Instrument. The reported glass transition temperature (T_g) was the arithmetic mean of upper and lower bounds from intersecting tangents in the DSC thermogram. The T_g of

PSDVB was determined to be 123 °C from a second scan (Figure SI-1b).

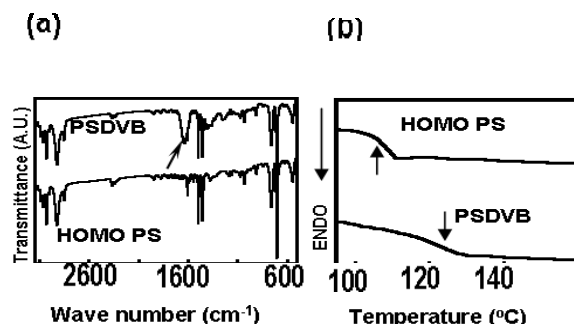


Figure SI-1 (a) Unreacted **DVB** monomer showed an aliphatic C=C stretching peak at 1637 cm⁻¹ (arrow) in the FTIR spectra of **PSDVB**, however no aliphatic C=C stretching peak was observed in homo **PS**. (b) Cross-linking effect caused an increase in T_g (indicated by arrows) of **PSDVB** in comparison with that of homo **PS**.

The measured value was higher than that of homo polystyrene ($T_g \sim 108$ °C, Polysciences catalog number 07307) due to the cross-linking of **DVB** monomers. Glans *et al.* reported that T_g was elevated by 25 °C at a **DVB** mole fraction of 7.5 % in a **DVB**-styrene system.² In our experiment, although **PSDVB** was synthesized using a mole fraction of 8.0 %, the T_g was increased only by 15 °C. This relatively small elevation in T_g could be due to the low degree of cross-linking (see free **DVB** C=C stretch in IR spectra). Glans *et al.* used γ -radiation for complete cross-linking.² The cross-linked **PSDVB** showed a decreased prominence in DSC thermogram, which was in agreement with data reported by Glans *et al.*

Colloid crystal An epoxy based azo functionalized polymer was spun on the quartz plate in the form of a thin film, thickness ~ 1 μ m. Figure SI-2 shows the schematic view of the synthesis of epoxy based azo functionalized polymer. Colloidal crystals were formed on the flat film of azo functionalized polymer for a 2D monolayer or 3D layers by convective crystallization, as described previously.³ Azo functional polymer was used to fix colloidal

assembly during dissolution by indenting colloids toward the depth of the film. Figure 3g shows the traces of indented colloids as concavities on the azo functional polymer film. However, the colloidal crystal on the glass slide was swept away during dissolution. The fabricated crystals were dried for 48hs in air at room temperature.

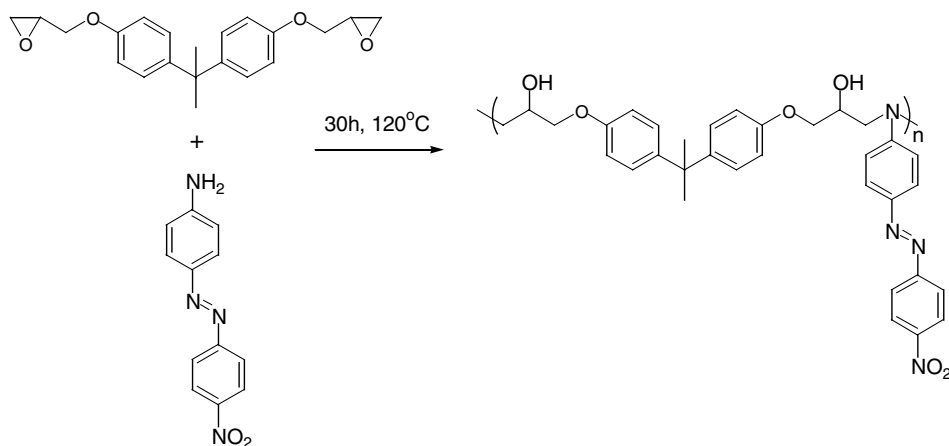


Figure SI-2 A schematic view of synthesis of an epoxy based azo functionalized polymer.

Colloid sintering and selective dissolution Colloid crystals were sintered at 125 °C or 150 °C (above T_g of the colloid) for 1hr and selectively dissolved in cyclohexane: sintered assembly was dip into cyclohexane bath at 40 °C for 30 min, and exposed in ambient environment to evaporate residual cyclohexane at room temperature for 3hr. Cross-linked **DVB** is insoluble in common organic solvents such as THF.⁴ Compared with the UV-VIS spectra of neat cyclohexane, no increase in the absorbance was observed after treating the azo functionalized polymer in cyclohexane at 40 °C for 10hs, thereby confirming the insolubility of azo

functionalized polymer in cyclohexane. The structures of colloid assembly were measured using SEM, Jeol 5800.

Titania deposition and calcination A honeycomb and an inverse opal were used as templates for fabricating the nano rings. Titanium isopropoxide in isopropanol (titanium isopropoxide, 4 vol %) was spun on the honeycomb or the inverse opal templates at 2500 rpm and calcined at 700 and 900 °C, respectively, in air for 5hr. Elemental analysis was carried out using EDX interfaced with SEM. The crystalline phase was analyzed using Cu-K α radiation in film mode running at 40 kV and 40 mA (Rigaku RAD-C).

References

- (1) Okubo, M.; Ikegami, K.; Yamamoto, Y.; *Colloid Polym. Sci.* **1989**, 267, 193.
- (2) Glans, J. H.; Turner, D. T. *Polymer* **1981**, 22, 1540.
- (3) Kralchevsky, P. A ; Nagayama, K. *Langmuir* **1994**, 10, 23. Dekov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992**, 8, 3183. Yi, D. K.; Seo, E. M.; Kim, D. Y. *Appl. Phys. Lett.* **2002**, 80, 225. Yi, D. K.; Kim, M. J.; Kim, D. Y. *Langmuir* **2002**, 18, 2019.
- (4) page 4536-4537 in Downey, J. S.; Mcisaac, G.; Frank, R. S.; Stover, H. D. H. *Macromolecules*, **2001**, 34, 4534.