Supporting Information for

Interfacial Photocrosslinking of Polymer Particles Possessing Nucleobase Photoreactive Groups for Hollow/Capsule Fabrication

Yukiya Kitayama*, Akali Dosaka, and Atsushi Harada*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1,

Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

Corresponding Authors

- * Yukiya Kitayama: kitayama@chem.osakafu-u.ac.jp
- * Atsushi Harada: harada@chem.osakafu-u.ac.jp



1. ¹H-NMR and ¹³C-NMR spectra of VBT

Figure S1. ¹H-NMR (a) and ¹³C-NMR spectra (b) of VBT in d_6 -DMSO.

2. UV-Vis spectrum of VBT



Figure S2. UV-Vis spectrum of VBT in DMF (1 nM).

3. ¹H-NMR spectrum of P(S-VBT)



Figure S3. ¹H-NMR spectra of P(S-VBT)-25 (a), P(S-BNT)-33 (b), and P(S-VBT)-50 (c) (d₆-DMSO)

4. Solubility of Photoreactive Polymers

	P(S-VBT)-25	P(S-VBT)-33	P(S-VBT)-50
Hexane	×	×	×
Toluene	×	×	×
Dichloromethane	×	×	×
Chloroform	0	×	×
MeOH	×	×	×
Acetone	×	×	×
THF	0	\bigcirc	×
Ethyl acetate	×	×	×
DMF	0	\bigcirc	\bigcirc
DMAc	0	\bigcirc	\bigcirc
DMSO	0	0	0

 Table S1 Solubility of photoreactive polymers (10 mg/mL)

5. Photocrosslinking property of P(S-VBT)-25



Figure S4. Particle size distributions (a) and optical microscope image (b) of spherical P(S-VBT)-25 particles after solvent evaporation method using homogenizer (9000 rpm, 5 min)

6. ¹H-NMR spectrum of Fluorescein Acrylamide



Figure S5. ¹H-NMR spectrum of fluorescein acrylamide in d₆-DMSO.

7. Fluorescence spectrum of Fluorescein-labeled P(S-VBT)-25



Figure S6. Fluorescence spectrum of fluorescein-labeled P(S-VBT)-25 in DMF (1 μ g/mL). Excitation wavelength: 488 nm. The purification of fluorescein-labeled P(S-VBT)-25 was confirmed by thin layer chromatograpy.

8. Effect of incubation periods for removal of non-crosslinked polymers

P(S-VBT)-25 dispersion in PVA aqueous solution (6.67 mg/mL, 6 mL) was photoirradiated for 2 h. The photoirradiated particles were collected by centrifugation, and THF (6 mL) were added to the particles. After certain incubation periods (0.5, 1, 2, 4 h), the dispersion (1 mL) was corrected, and the supernatant was corrected by centrifugation. The supanatant was measured by UV-Vis after ten times dilution.



Figure S7. UV-Vis spectra of supernatant of P(S-VBT)-25 particle dispersion, prepared by photoirradiation for 2 h, in THF for various incubation times Photoirradiation wavelength: 254 nm, Power: 2 mW/cm^2

9. Effect of solvent mixture ratio for removal of non-crosslinked polymers

P(S-VBT)-25 dispersion in PVA aqueous solution (2 mg/mL, 10 mL) prepared by homogenization (6,000 rpm for 3 min) and subsequent SPG membrane emulsification process (30 times) was photoirradiated for 2 h or 4 h. The photoirradiated particles were collected by centrifugation, and DMF/THF mixture (vol/vol:1:1, 1 mL) were added to the particles. After 1h incubation, the dispersion (1 mL) was corrected, and the supernatant was corrected by centrifugation. The supanatant was measured by UV-Vis after ten times dilution. The washing process was repeated once, twice, or thrice.



Figure S8. UV-Vis spectra of supernatant of P(S-VBT)-25 particle dispersion, prepared by photoirradiation for 2 (a, b) or 4 h (c, d), in DMF/THF mixture (vol/vol:1:1) after 1 h incubation for 1^{st} , 2^{nd} , and 3^{rd} washing processes. Photoirradiation wavelength: 254 nm, Power: 2 mW/cm²

10. Effect of solvent mixture ratio for removal of non-crosslinked polymers

P(S-VBT)-25 dispersion in PVA aqueous solution (6.67 mg/mL, 3 mL) was photoirradiated for 2 h. The photoirradiated particles were collected by centrifugation, and THF or DMF, or DMF/THF mixture (3 mL) were added to the particles. After 1 h incubation, the dispersion (1 mL) was corrected, and the supernatant was corrected by centrifugation. The supanatant was measured by UV-Vis after ten times dilution.



Figure S9. UV-Vis spectra of supernatant of P(S-VBT)-25 particle dispersion, prepared by photoirradiation for 2 h, in different solvents after 1 h incubation. Photoirradiation wavelength: 254 nm, Power: 2 mW/cm^2

11. Particle Size of Hollow Polymer Particles Prepared with Different Photoirradiation Times



Figure S10. Average particle size of the P(S-VBT)-25 hollow particles at different photoirradiation times. The number of particle counts is more than 50.