Supporting Information

Maltopentaose-Conjugated CTA for RAFT Polymerization Generating Nanostructured Bioresource-Block Copolymer

Daichi Togashi, † Issei Otsuka, ^{‡,§} Redouane Borsali, ^{‡,§} Koichi Takeda, †

Kazushi Enomoto, † Seigou Kawaguchi, † Atsushi Narumi*, †

[†]Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Jonan 4-3-16, Yonezawa 992-8510, Japan

[‡]Univ. Grenoble Alpes, CERMAV, F-38000 Grenoble, France [§]CNRS, CERMAV, F-38000 Grenoble, France

*Corresponding author; e-mail: narumi@yz.yamagata-u.ac.jp

Tel & Fax: +81-(0)238-26-3829

Experimental Section

Instrument

The purity of Mal₅-N₃ was determined by a size exclusion chromatography (SEC, pump: Jasco PU-2080 Plus, degasser: Jasco DG-2080-53, column oven: Jasco CO-2060 Plus, temperature of the column oven: 40 °C) in an aqueous solution containing 0.05 M NaNO₃. This SEC was equipped with the columns [Tosoh TSK-GEL G2500 PW_{XL} (size: 7.8 mm \times 300 mm, average bead size: 7 μ m, exclusion limit: 5.0 kg mol⁻¹), Tosoh TSK-GEL G4000 PW_{XL} (size: 7.8 mm \times 300 mm, average bead size: 10 μ m, exclusion limit: 1.0 \times 10³ kg mol⁻¹), and Tosoh TSK-GEL G6000 PW_{XL} (size: 7.8 mm \times 300 mm, average bead size: 13 μ m, exclusion limit: 5.0 \times 10⁴ kg mol⁻¹)], and a refractive index detector (RI: Jasco RI-2031 Plus).

Results and Discussion

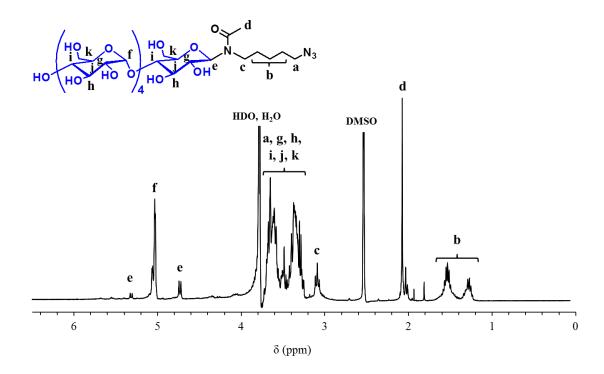


Figure SI-1. 1 H NMR spectrum of Mal₅-N₃ in DMSO- d_6 /D₂O.

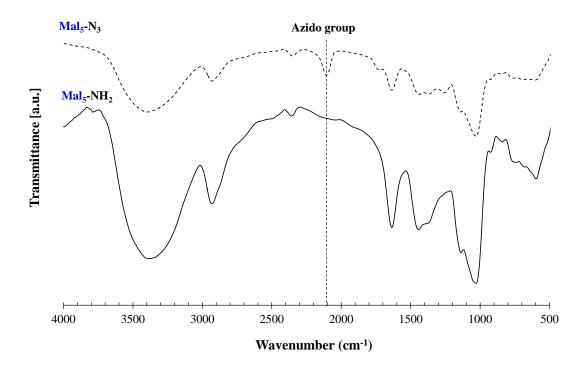


Figure SI-2. IR spectra of Mal₅-N₃ (dashed line) and Mal₅-NH₂ (solid line).

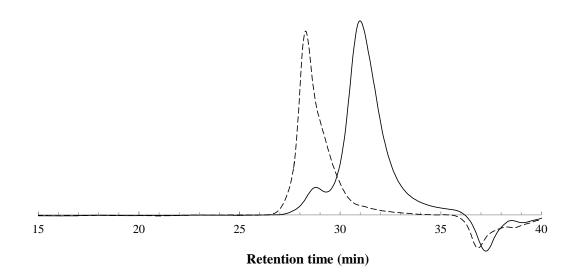


Figure SI-3. SEC traces of Mal_5 - N_3 (solid line) and Mal_5 (dashed line) in 0.05 M $NaNO_3$ aqueous solution.

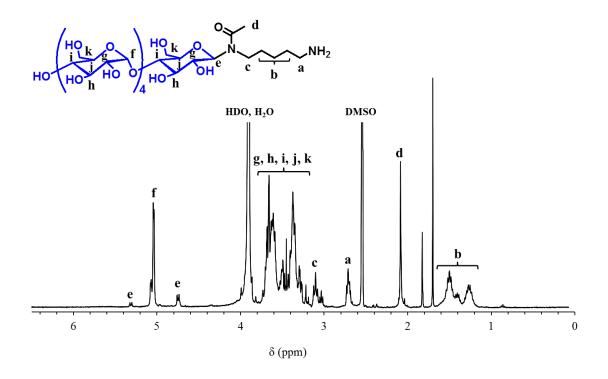


Figure SI-4. ¹H NMR spectrum of Mal₅-NH₂ in DMSO-*d*₆/D₂O.

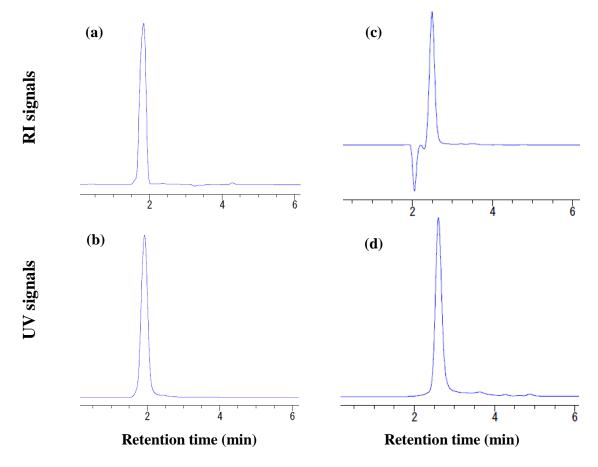


Figure SI-5. HPLC traces of (a and b) $\bf 1a$ in $CH_3CN/H_2O=2/3$ and (c and d) $\bf 1b$ in MeOH.

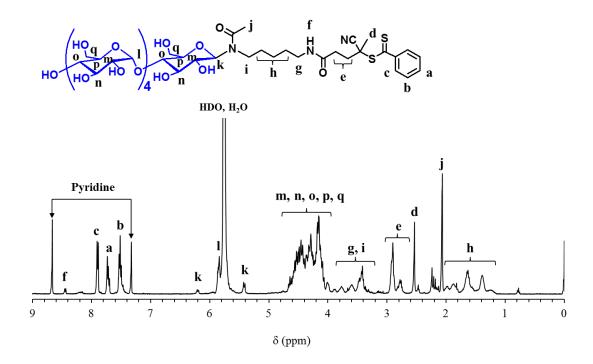


Figure SI-6. ¹H NMR spectrum of **1a** in pyridine- d_5/D_2O .

Table SI-1. Solubility of Mal₅-CTAs (1) ^a

Mal ₅ -CTAs	H_2O	CH ₃ OH	DMF	DMSO	Toluene	CHCl ₃	1,4-dioxane	THF
1a	+	+	+	+	_	_	_	_
1 b	+	+	+	+	_	_	_	+

^a +, clear solution; —, suspension or precipitate.

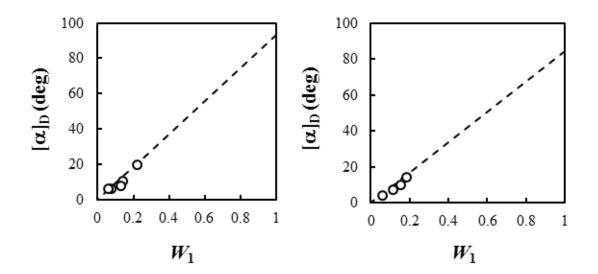


Figure SI-7. Plots of specific rotations for **2a** (left) and those for **2b** (right) as a function of their weight fractions of **1** (W_1 s).

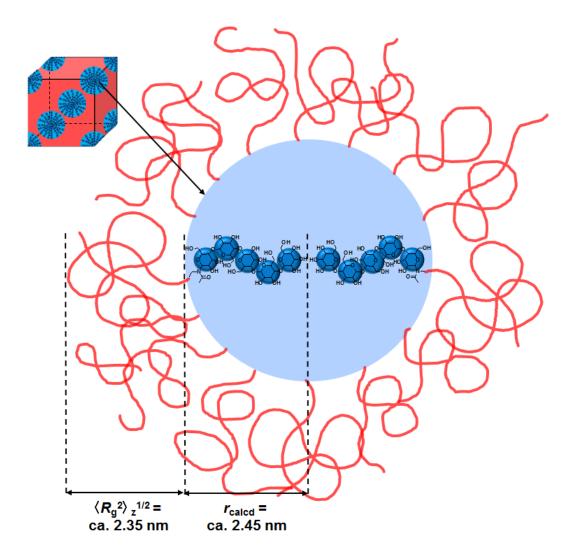


Figure SI-8. Supporting illustration representing $r_{\rm calcd}$ and z-averaged mean-square radius of gyration $\langle R_{\rm g}^{\, 2} \rangle_{\rm z}^{\, 1/2}$ for the phase separated structures formed by **2b-I**. The $r_{\rm calcd}$ was calculated on the basis of the bound lengths; C-C bound: 0.154 nm, C-O bound: 0.145 nm. The $\langle R_{\rm g}^{\, 2} \rangle_{\rm z}^{\, 1/2}$ was calculated by adopting the following equation.¹

$$\langle R_{\rm g}^2 \rangle_{\rm z}^{1/2} = 1.12 \times 10^{-2} \ M_{\rm w}^{0.60} \ ({\rm nm})$$

Reference

(1) Konishi, T.; Yoshizaki, T.; Saito, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1990**, *23*, 290-297.