

Supporting Information

Cation-Condensed Microgel-Core Star Polymers as Polycationic Nanocapsules for Molecular Capture and Release in Water

Kaoru Fukae, Takaya Terashima,* Mitsuo Sawamoto*

*Corresponding Author

Polymer Chemistry, Graduate School of Engineering, Kyoto University

Kyotodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Tel: +81-75-383-2600

Fax: +81-75-383-2601

E-mail: terashima@living.polym.kyoto-u.ac.jp, sawamoto@star.polym.kyoto-u.ac.jp

Contents:

Figure S1.	Synthesis of Cation-Condensed Microgel Star Polymers (S1)	2
Figure S2.	¹ H NMR spectra	2
Figure S3.	Synthesis of Microgel Star Polymers with a Non-Ionic Linking Agent (2')	3
Figure S4.	Conformation Analysis by MO-G with AM-1	3
Figure S5.	DSC Thermograms	4
Table S1.	DSC analysis	4
Table S2.	Encapsulation of Orange G into Polymers in Water	5
Figure S6.	UV-vis spectra of Methyl Orange in Water	5
Figure S7.	¹ H DOSY spectra	6
Figure S8.	DLS Measurements	6
Table S3.	Release of Orange G from Polymers with NaCl Aqueous Solution	7

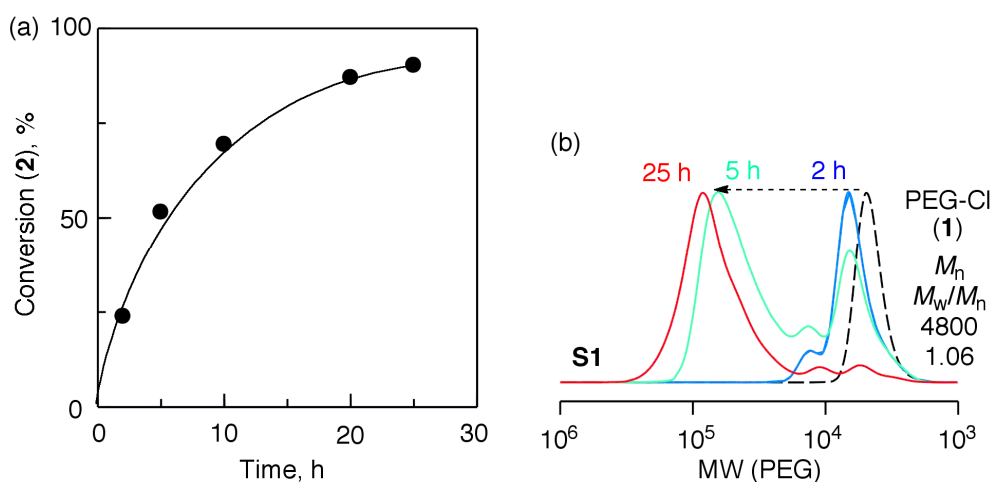


Figure S1. (a) Time-conversion curves and (b) SEC curves of the samples obtained from the linking reaction of PEG-Cl (**1**) with **2** and $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$: $[\text{1}]/[\text{2}]/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]/[\text{2-DMAE}] = 20/200/2.0/40$ mM in EtOH/DMF (3/1, v/v) at 40 °C.

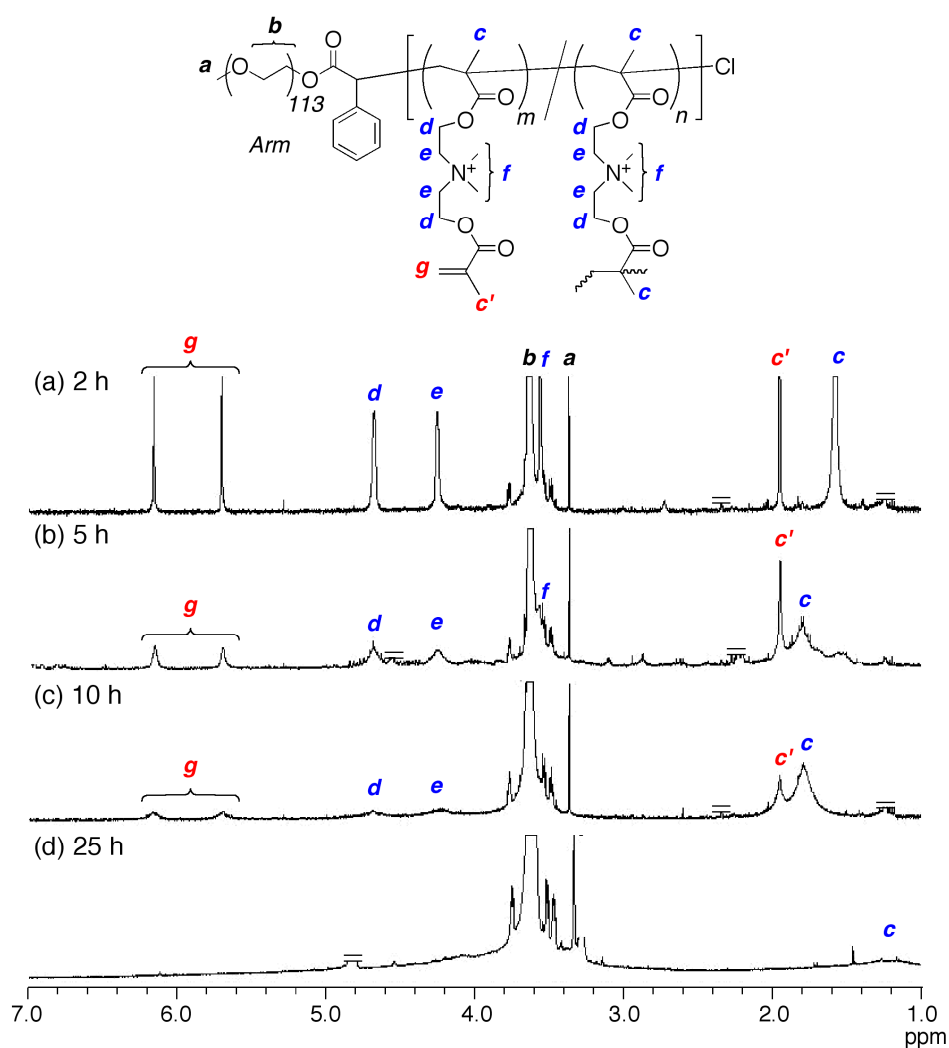


Figure S2. ^1H NMR spectra (500 MHz, in CDCl_3 at 25 °C) of the samples obtained from the linking reaction of **1** with **2** and $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$: (a) 2 h; (b) 5 h; (c) 10 h; (d) 25 h.

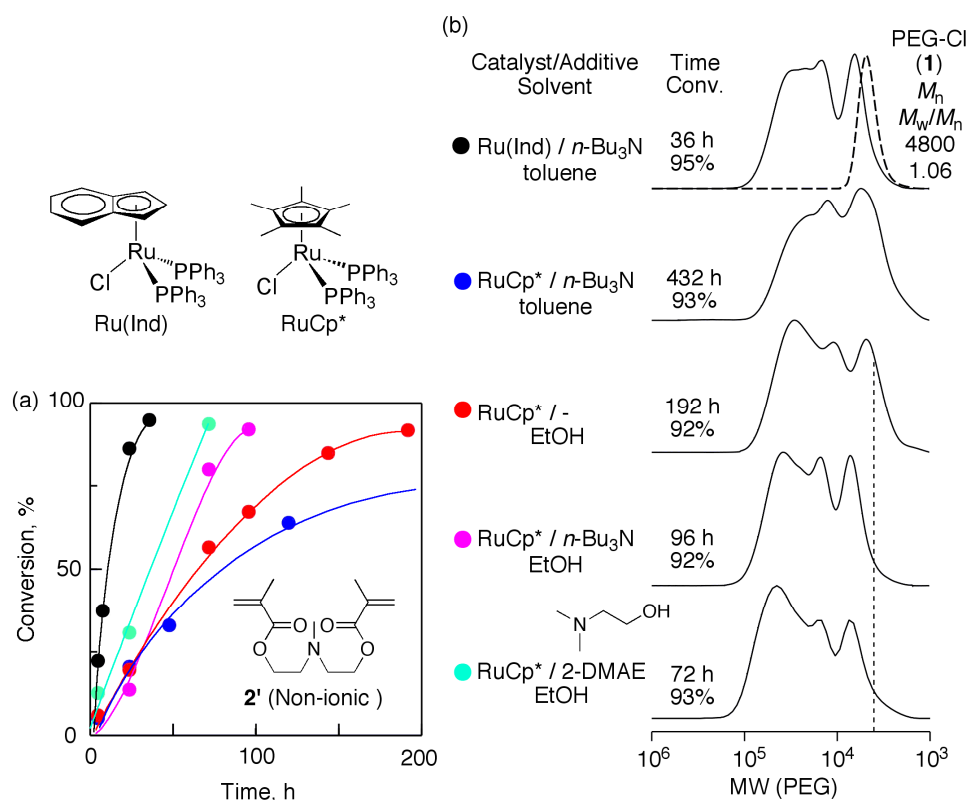


Figure S3. (a) Time-conversion curves and (b) SEC curves of the samples obtained from the Ru-mediated linking reaction of **1** with a non-ionic **2'**: [**1**]/[**2'**]/[Ru]/[additive] = 20/200/2/40 mM in toluene at 80 °C or in EtOH at 40 °C.

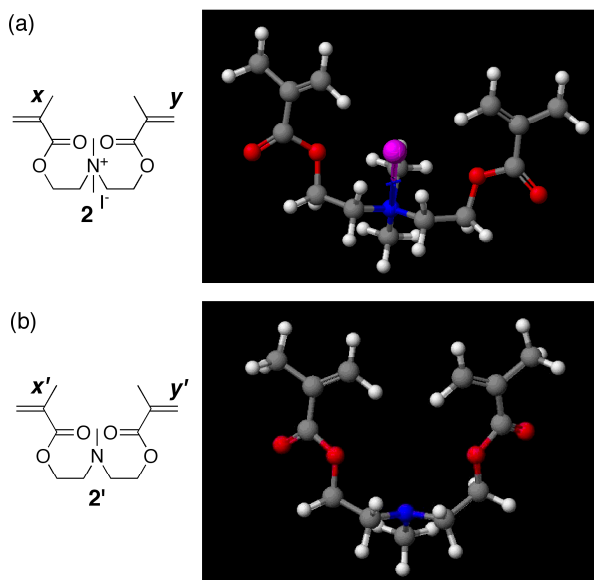


Figure S4. Most stable conformations of **2** and **2'**, calculated by MO-G (a semiempirical molecular orbital program) coupled with AM1 (Hamiltonian). The distance between two olefins of **2** (*x*-*y* = ~6.8 Å) was longer than that of **2'** (*x'*-*y'* = ~5.1 Å).

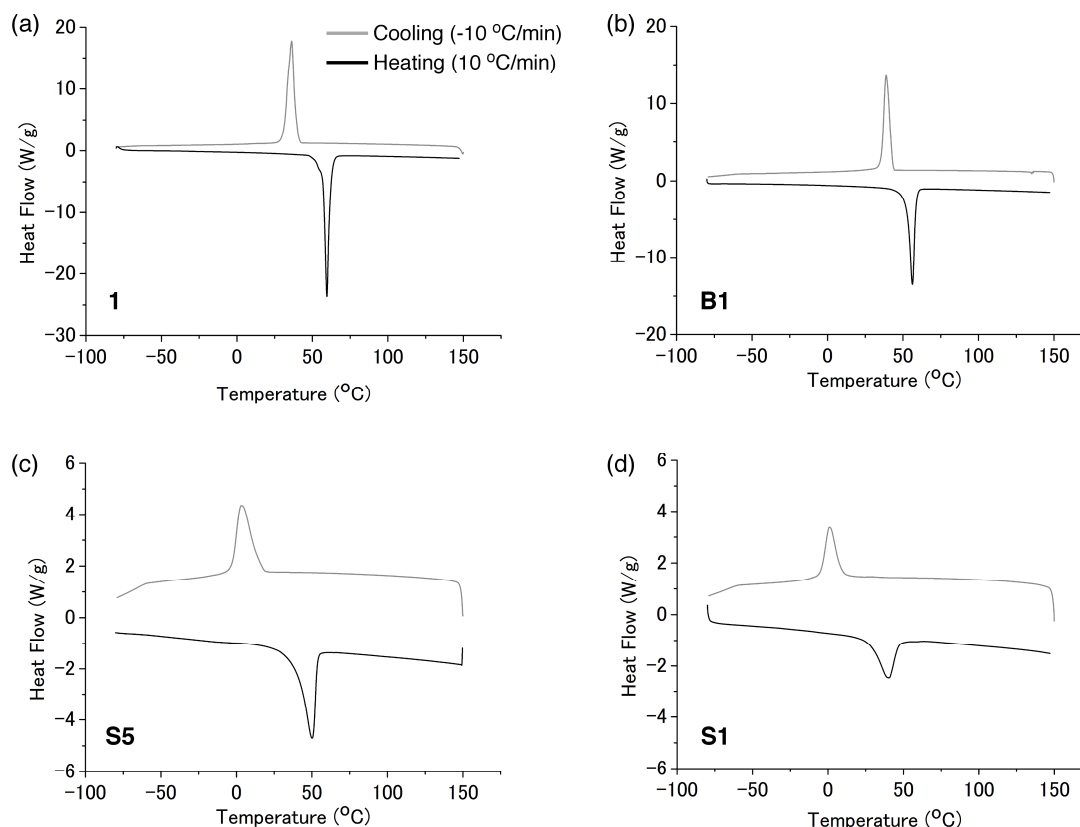


Figure S5. DSC thermograms recorded on (a) **1**, (b) **B1**, (c) **S5**, and (d) **S1** via the cooling scan from 150 °C to -80 °C (gray line, cooling rate: -10 °C/min) and the second heating scan from -80 °C to 150 °C (black line, heating rate: 10 °C/min).

Table S1. DSC Analysis of Samples (**1**, **B1**, **S5**, **S1**)

Samples	T_c (°C) ^a	T_m (°C) ^a	$\Delta H_{m,total}$ (J/g) ^b	w^c	$\Delta H_{m,calcd}^0$ (J/g) ^d	Fractional Crystallinity (%) ^e
1	36.3	59.6	187	0.97	191	~100
B1	38.8	56.2	139	0.65	128	~100
S5	3.2	49.4	69	0.73	144	~48
S1	1.0	40.3	45	0.58	114	~40

^a T_c and T_m were determined by DSC measurements at the second heating step from -80 °C to 150 °C with 10 °C/min, respectively.

^b Melting enthalpy ($\Delta H_{m,total}$) was obtained from integration of endothermic peaks.

^c Weight fraction of PEG segments in samples.

^d Calculated melting enthalpy: $\Delta H_{m,calcd}^0 = \Delta H_m^0 \times w$; $\Delta H_m^0 = 197$ J/g.

^e Fractional crystallinity (%) = $100\Delta H_{m,total}/\Delta H_{m,calcd}^0$.

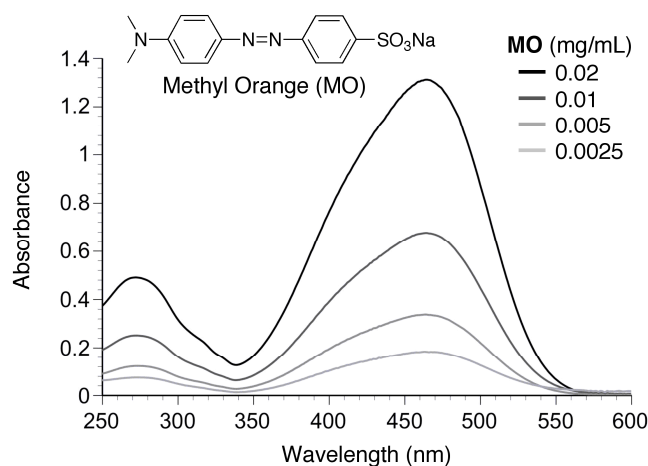


Figure S6. UV-vis spectra of MO in H₂O at r.t.: [MO] = 0.02, 0.01, 0.005, 0.0025 mg/mL (6.1×10^{-5} - 7.6×10^{-6} M).

Table S2. Encapsulation of Orange G into Polymers in Water^a

Entry	Polymer	[OG] ₀ /[Polymer] ₀ (mg/mL)	Time (h)	OG _{polymer} ^b (μmol/g)	N _{OG/polymer} ^c	N _{N+/OG} ^d
1	S1	5/10	2	652	402	1.9
2	S1	0.5/1	2	672	414	1.8
3	S1	0.5/1	24	721	445	1.6
4	S1	0.05/0.1	2	637	392	1.9
5	S1	0.05/0.1	10	756	466	1.5
6	S1	0.05/0.1	24	780	482	1.5
7	B1	5/10	2	420	3.3	3.3
8	B1	0.5/1	2	477	3.8	2.9
9	B1	0.5/1	24	475	3.8	2.9
10	B1	0.05/0.1	2	197	1.6	9.1
11	B1	0.05/0.1	10	323	2.6	4.5
12	B1	0.05/0.1	24	475	3.8	2.9

^a Polymers (**S1**, **B1**) and Orange G (OG) were stirred in H₂O at r.t., followed by the dialysis of the mixture with H₂O.

^b The amount of OG per a gram polymer, determined by UV-vis analysis of OG-bearing polymers in H₂O with the calibration plot of OG at 478 nm.

^c The number of OG in a single polymer:

$$N_{\text{OG/polymer}} = \text{OG}_{\text{polymer}} \times [M_{\text{w,star}} (\text{MALLS}): \mathbf{S1} \text{ or } M_n (\text{NMR}): \mathbf{B1}] \times 10^{-6}.$$

^d The number ratio of polymer-bound cations to polycation-bound OGs:

$$N_{\text{N+/OG}} = N_{\text{N+}} / (N_{\text{OG/polymer}} - N_{\text{OG/PEG}}); N_{\text{OG/PEG}} = N_{\text{arm}} \times [N_{\text{OG/polymer}} (\mathbf{S5})/74].$$

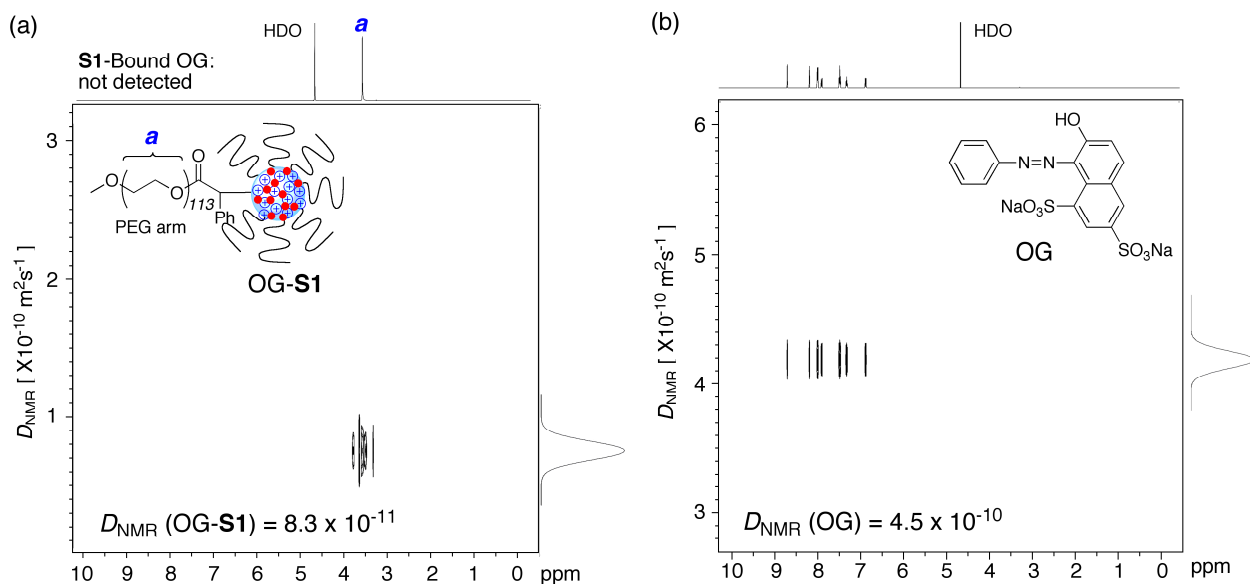


Figure S7. ^1H DOSY spectra (500 MHz) of (a) OG-bearing **S1** and (b) OG alone in D_2O at 30 °C. Diffusion coefficient (D_{NMR}) was calculated by the following software: Delta v4.3.6, JEOL.

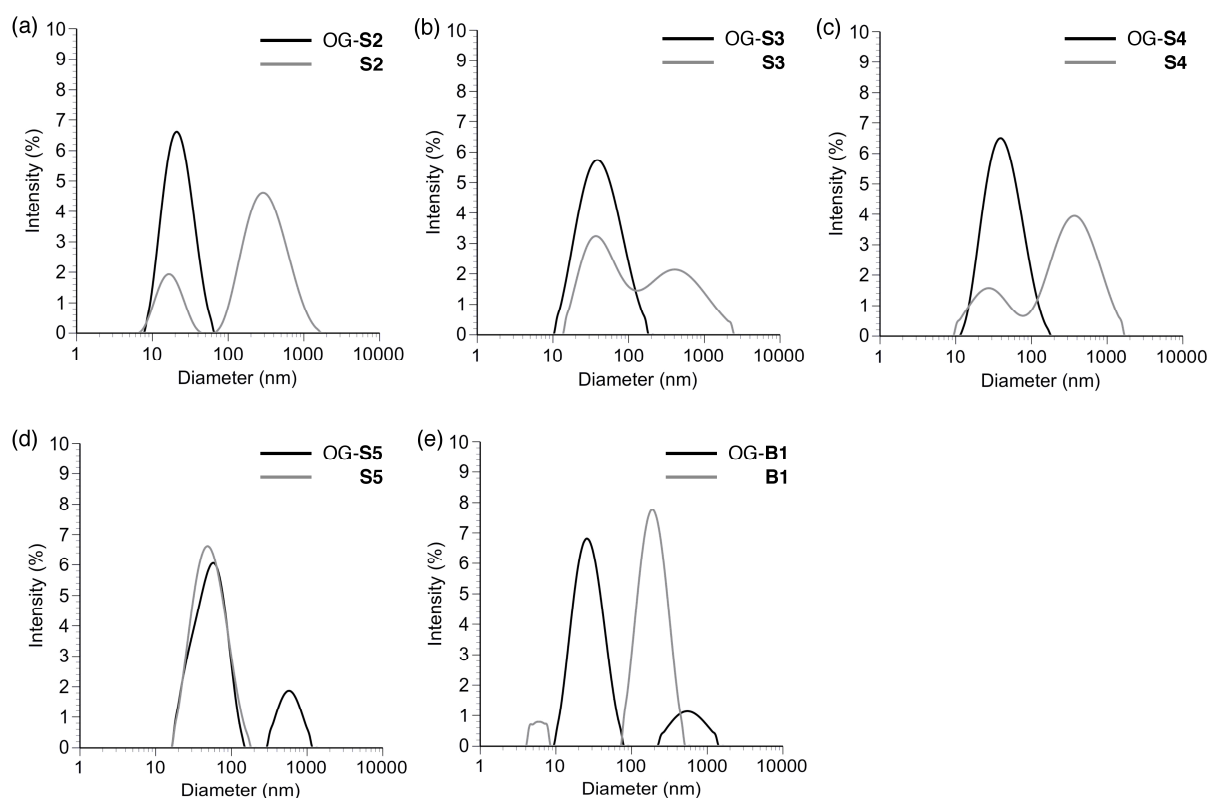


Figure S8. DLS intensity distributions of (a) OG-S2 and **S2**, (b) OG-S3 and **S3**, (c) OG-S4 and **S4**, (d) OG-S5 and **S5**, and (e) OG-B1 and **B1** in H_2O at 25 °C: [OG-bearing polymer] (black line) = 1 (**S2-S5**), 10 (**B1**) mg/mL; [polymer] (gray line) = 0.1 mg/mL.

Table S3. Release of Polymer-Bound OG from **S1** and **B1** with NaCl aqueous solutions^a

Entry	Polymer	Time (h)	$N_{\text{OG/polymer}}^b$	OG in Polymer (%) ^c
1	S1	0	414	100
2	S1	2	224	54
3	S1	5	107	26
4	S1	24	48	12
5	B1	0	3.8	100
6	B1	2	0.65	17
7	B1	5	0.15	4.0
8	B1	24	0.033	0.88

^a Aqueous solutions of OG-bearing polymers (**S1**, **B1**) ([polymer] = 1 mg/mL, 1 mL) were charged in dialysis tubes and the tubes were placed in 0.1 M NaCl aqueous solutions (100 mL). At the predetermined periods, the inner solutions were sampled for UV-vis analysis to determine the amount of polymer-bound OGs ($\text{OG}_{\text{polymer}}$: $\mu\text{mol/g}$) with the calibration plot of OG at 478 nm.

^b The number of OG in a single polymer:

$$N_{\text{OG/polymer}} = \text{OG}_{\text{polymer}} \times [M_{\text{w,star}} (\text{MALLS}): \textbf{S1}, M_{\text{n}} (\text{NMR}): \textbf{B1}] \times 10^{-6}.$$

^c Mole percent of OG remaining in polymers: $100 \times N_{\text{OG/polymer}}(t)/N_{\text{OG/polymer}}(t = 0)$.