Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Novel self-assembling organogelators by combination of double chain-alkylated L-glutamide and polymeric head group

Hirotaka Ihara,*[a,b] Makoto Takafuji,[b] Toshihiko Sakurai,[b]

Masahiro Katsumoto,[b] Noriko Ushijima,[b] Tomohiro Shirosaki,[b]

and Hiroshi Hachisako[c]

[a] *Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.*

Fax: 81-92-642-2715; Tel: 81-92-642-2713; E-mail:

ihara@chem.kumamoto-u.ac.jp

[b] *Kumamoto University, 2-39-1 Kirokami, Kumamoto 860-8555, Japan. Fax:*

81-96-342-3662; Tel: 81-96-342-3661; E-mail:takafuji@chem.kumamoto-u.ac.jp

[c] Sojo University, 4-22-1 Ikeda, Kumamoto 860-0082. Fax: 81-96-323-1331; Tel:

81-96-326-3111; *E-mail: hatisako@life.sojo-u.ac.jp*

Table SM1 Gel-to-sol transition temperature of **G**$_{12}$-containing polymers

G$_{12}$-derivative	Composition of MA	T_{GS} (˚C) [a)	
		in benzene	in a mixture[b)
G$_{12}$-vinyl	0	>70	53
copoly-**G**$_{12}$	2	55	37
copoly-**G**$_{12}$	4	50	32
copoly-**G**$_{12}$	12	36	30
t-**G**$_{12}$	10	61	41
t-**G**$_{12}$	25	53	39

a) Gel-to-sol transition temperature (T_{GS}) was estimated by an inverse fluid method. The heating rate was approximately 1 ˚C min^{-1}.

b) A cyclohexane-ethanol (9 : 1) mixture was used.

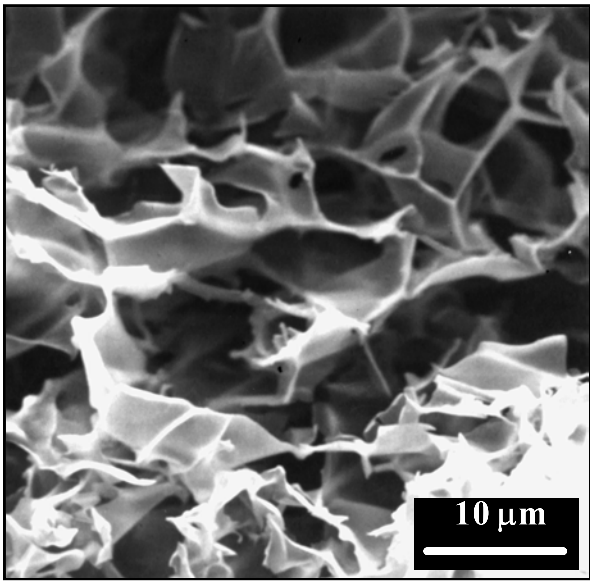

Fig. SM1 SEM image of xerogel from a copoly-**G12** (m/n = 12) benzene gel.

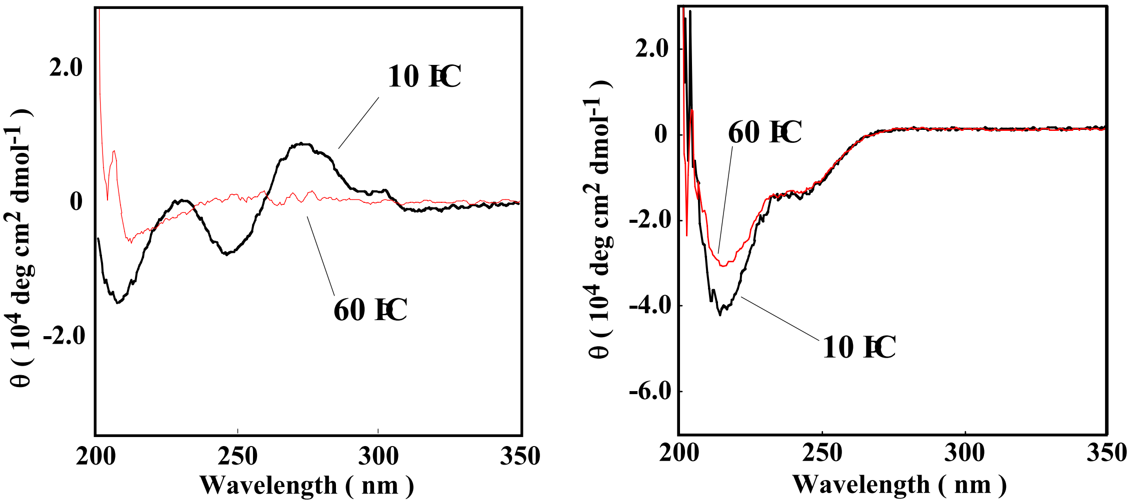

Fig. SM2 Temperature dependence of CD spectra of (a) $\mathbf{G}_{12}$-vinyl and (b) copoly-$\mathbf{G}_{12}$ (n/m = 4).

Experimental and Characterization

Synthesis of **G_{12}**-a:

Ten g of *N*-benzyloxycarbonyl-L-glutamic acid and 14.5 g of dodecylamine were dissolved in 250 ml of dry THF. After the mixture was cooled to 0 ˚C, 15 ml of triethylamine and 19.3 g of diethyl cyanophosphate were added to the mixture and then stirred for 30 min at 0 ˚C and 6 h at room temperature. The resultant precipitates were gathered by filtration and then recrystallized from ethyl acetate. Yield: 11.1 g, 51 %. mp 135 ˚C. Anal. Calc. for $C_{37}H_{65}N_3O_4$: C, 72.2; H, 10.6; N, 6.8. Found C, 72.0; H, 10.8; N, 6.9.

11.1 g of didodecyl *N*-benzyloxycarbonyl-L-glutamide obtained was dissolved in hot 400 ml of DMF and then cooled to 40 ˚C. After 0.1 g of Pd was added to the solution, hydrogen gas was bubbled to the solution for 8 h at 40 ˚C. Pd was removed by filtration and then the solution was concentrated *in vacuo*. The precipitates were obtained by hexane and recrystallized from methanol. Yield: 5.9 g, 68 %. mp 122 ˚C. Anal. Calc. for $C_{29}H_{59}N_3O_2$: C, 72.3; H, 12.3; N, 8.7. Found C, 72.0; H, 12.3; N, 8.7.

Four g of didodecyl-L-glutamide obtained and 2.8 g of *N*-benzyloxycarbonyl β-alanine were dissolved in 400 ml of hot THF. After the solution was cooled to 0 ˚C, 2.5 ml of triethylamine and 2.1 g of diethyl cyanophosphate were added to the mixture and then stirred for 1 d at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in 100 ml of chloroform. After the solution was washed with 0.2N-HCl, 5% $NaHCO_3$ and water. The product was obtained by concentration and recrystallization from methanol. Yield: 5.2 g, 93 %. mp 170 ˚C. Anal. Calc. for $C_{40}H_{70}N_4O_5$: C, 69.9; H, 10.3; N, 8.2. Found C, 69.6; H, 10.3; N, 8.0. IR adsorptions: ν_{max}/cm^{-1} 3292 (NH), 2919 and 2851 (CH), 1698 (CO), 1635 (NH,CO), 1551 (CN). NMR data: δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, Me), 4.33 (1 H, m, C^*H), 3.03 (2 H, m, CH_2-NHCOO), 5.09 (2 H, s, CH_2-Ph).

Synthesis of **G_{12}**-b:

Five g of **G_{12}**-a was dissolved in 400 ml of ethanol. 0.1 g of Pd was added to the solution and hydrogen gas was bubbled to the solution for 8 h at room temperature. Pd was removed by filtration and then the solution was concentrated *in vacuo*. The precipitates were obtained by hexane and recrystallized from methanol. Yield: 3.6 g, 90 %. mp. 196 ˚C. Anal. Calc. for $C_{32}H_{64}N_4O_3$ $3H_2O$: C, 63.3; H, 11.6; N, 9.2. Found C, 63.4; H, 11.2; N, 9.2. IR adsorptions: ν_{max}/cm^{-1} 3288 (NH), 2919 and 2850 (CH), 1635 (NH,CO), 1560 (CN). NMR data: δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, Me), 4.38 (1 H, m, C^*H), 3.03 (2 H, t, CH_2-NH_2).

Synthesis of **G_{12}**-vinyl:

Two g of **G_{12}**-b and 0.64 g of 4-vinylbenzoic acid were dissolved in 150 ml of dry THF. After the solution was cooled to 0 ˚C, 1 ml of triethylamine and 1 g of diethyl cyanophosphate were added to the mixture and then stirred for 1 d at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in 100 ml of chloroform. After the solution was washed with 0.2N-HCl, 5% $NaHCO_3$ and water. The product was obtained by concentration and recrystallization from methanol. Yield: 1.6 g, 65 %. mp 144 ˚C. Anal. Calcd for $C_{32}H_{64}N_4O_3$: C, 69.5; H, 11.7; N, 10.1. Found C, 68.4; H, 11.4; N, 9.5. IR adsorptions: ν_{max}/cm^{-1} 3585 (NH), 2920 and 2852 (CH), 1633 (CO), 1633 (NH,CO), 1548 (CN). NMR data: δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.88 (6 H, t, Me), 4.38 (1 H, m, C^*H), 3.03 (2 H, t, CH_2-NHCO-Ph), 5.35 – 5.82 (2 H, q, CH_2=C).

Synthesis of copoly-**G_{12}** (n/m = 4)

0.2 g of **G_{12}**-vinyl and 0.13 ml of methyl acrylate were dissolved to 30 ml of dry THF and N_2 gas was bubbled to the solution for 20 min. AIBN as an initiator was added to the solution and then heated to 60 ˚C. Under N_2 bubbling, the solution was stirred for 48 h at 60 ˚C. The solution was concentrated *in vacuo* and poured into 100 ml of diethyl ether. The resultant precipitates were gathered by filtration and washed successively with methanol. Yield: 0.19 g, 79 %. IR adsorptions: ν_{max}/cm^{-1} 3587 (NH), 2951 and 2851 (CH), 1734 (CO), 1633 (NH,CO), 1548 (CN). NMR data: δ_H (400 MHz; $CDCl_3$; Me_4Si) 4.35 (1 H, s, CH of the chiral center), 3.65 (12 H, s, OCH_3).