

Article

Synthesis and Hydrogelation of Star-Shaped Graft Copolypeptides with Asymmetric Topology

Thi Ha My Phan ^{1,†}, Yu-Hsun Yang ^{1,†}, Yi-Jen Tsai ¹, Fang-Yu Chung ¹, Tooru Ooya ^{2,3}, Shiho Kawasaki ² and Jeng-Shiung Jan ^{1,4*}

¹ Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan; n36087113@gs.ncku.edu.tw (T.H.M.P.); e34074093@gs.ncku.edu.tw (Y.-H.Y.); n36094704@gs.ncku.edu.tw (Y.-J.T.); f54081036@gs.ncku.edu.tw (F.-Y.C.)

² Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan; ooya@tiger.kobe-u.ac.jp (T.O.); shihoshi@stu.kobe-u.ac.jp (S.K.)

³ Center of Advanced Medical Engineering Research & Development (CAMED), Kobe University, Kobe 657-8501, Japan

⁴ Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan 70101, Taiwan

* Correspondence: jsjan@mail.ncku.edu.tw

† These authors contributed equally to this work

Table S1. Characterization of star-shaped poly (Z-L-lysine) homopolypeptides (s-PZLL). The degree of polymerizations (DP), number-averaged molecular weights (M_n), and ratio of weight-averaged molecular weight to number-averaged molecular weight (M_w/M_n) were calculated from proton nuclear magnetic resonance (¹H NMR) and gel permeation chromatography-light scattering (GPC-LS) analyses.

Polypeptides	Feed ratio	¹ H NMR		GPC		
		DP	M_n (g mol ⁻¹)	M_n (g mol ⁻¹)	M_w/M_n	D P
6s- PZLL ₃₂	1:90	32.1	50654	50800	1.16	32.0
12s- PZLL ₁₂	1:180	11.9	34121	32200	1.99	10.0
24s- PZLL ₁₂	1:480	12.3	72109	55600	1.52	8.6

Table S2. Radius of gyration (R_g) of nano-assemblies in star-shaped graft copolypeptides. The concentration of all samples was 8.0 wt%. The data was fitted from Small-angle X-ray scattering (SAXS) analysis using SasView software (version 5.0.4).

Polypeptide	R_g (Å)
12s-PLL ₁₂ -g-Indo _{0.10}	151
12s-PLL ₁₂ -g-Phenyl _{0.08}	161
24s-PLL ₁₂ -g-Indo _{0.11}	215
24s-PLL ₁₂ -g-Phenyl _{0.13}	192

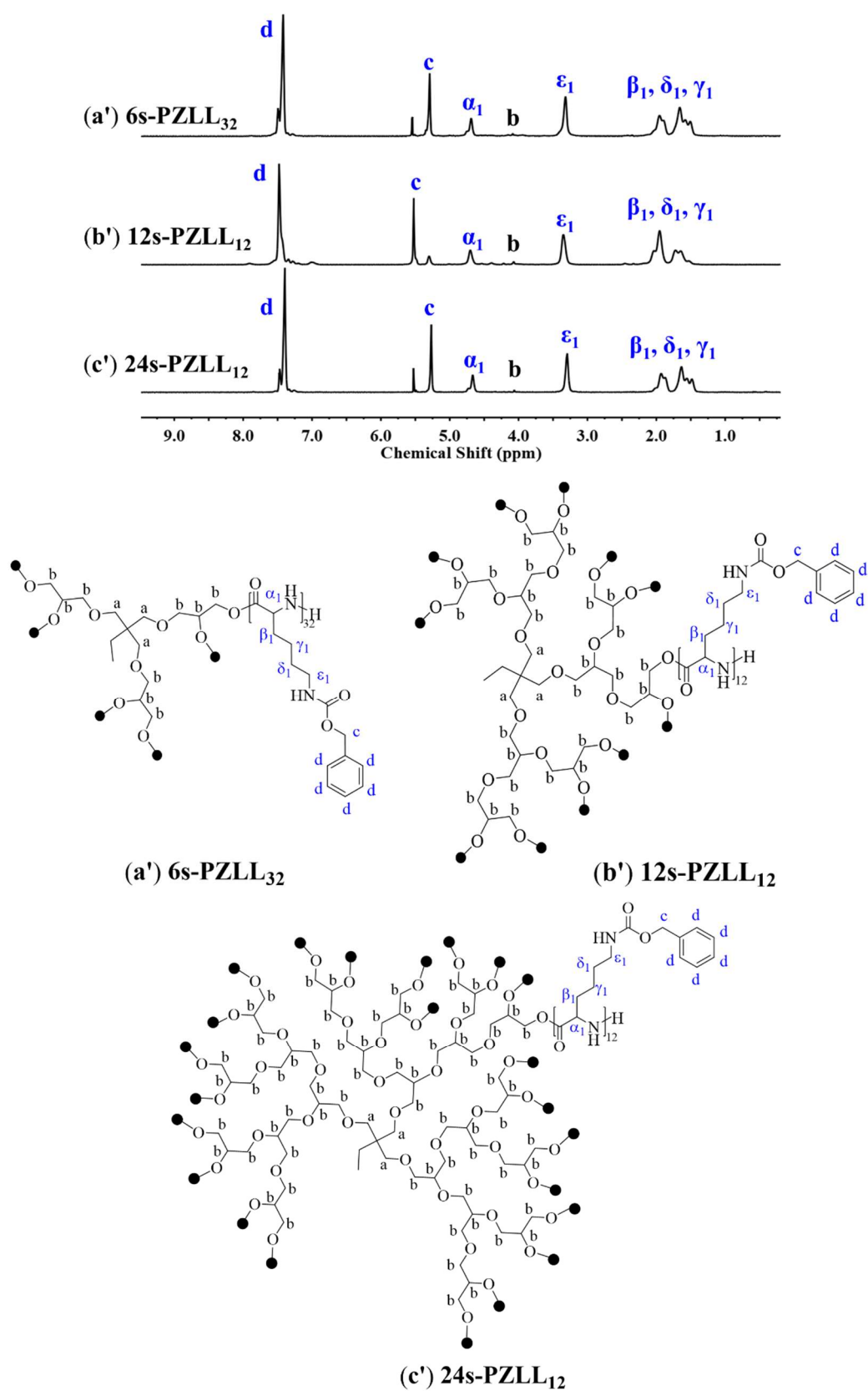


Figure S1. ^1H NMR of (a') 6s-PZLL₃₂, (b') 12s-PZLL₁₂, and (c') 24s-PZLL₁₂ homopolypeptides in trifluoroacetic acid- d_1 (TFA- d_1). The symbols were used to represent the different protons.

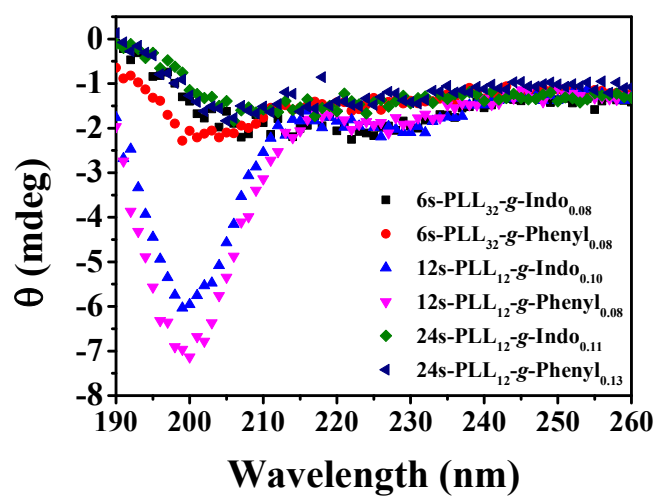


Figure S2. Circular dichroism (CD) spectra of graft polypeptides at 0.1 mg/mL.

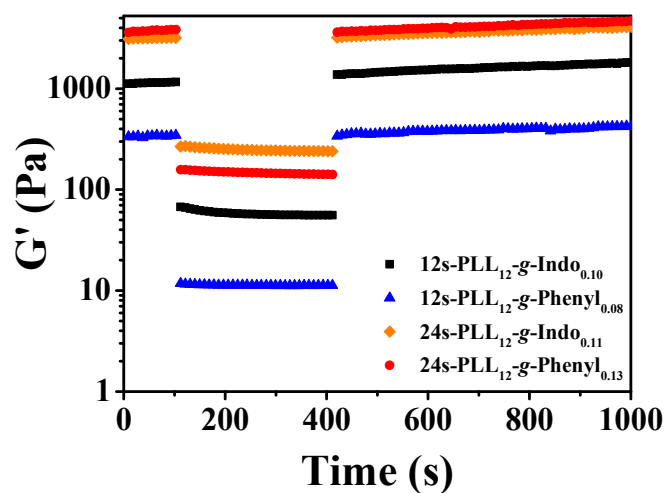


Figure S3. Recovery behavior of 12-armed and 24-armed polypeptide hydrogels. The concentration of hydrogel samples was 8.0 wt%. The rheological measurement was operated at 1 rad/s of frequency, room temperature and various strain at three continuous periods: 1.0% for 100s, 100.0% for 300s, and 1.0% for 600s.