Supporting Information

Synthesis and characterization of graft copolymers able to form polymersomes and worm-like aggregates

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Synthesis procedures

Synthesis of poly(glycerol adipate)-g-poly(ε-caprolactone) PGA-g-PCL. The PGA used for this reaction had M_n= 3400 g/mol determined by SEC. PGA (1.06 g, 5.5×10^{-3} mol with respect to OH group) was charged into a 50 mL Schlenk tube equipped with magnetic stirrer. This was followed by addition of ε-caprolactone (15.7 mL, 0.137 mol), 0.15 mL tin octoate, and 25 mL of anhydrous THF. The solution was degassed using three freeze-pump-thawing cycles. The resulting solution was stirred at 80°C for 20 h. Finally, the solution was diluted with THF and precipitated in 400 mL of methanol. Precipitation in methanol was repeated many times to remove the inevitably generated homopolymer poly(ε-caprolactone).[44] The resulting polymer was dried under vacuum at room temperature. Yield=46%.

Synthesis of alkyne-modified poly(glycerol adipate)-*g*-poly(ε-caprolactone), PGA-*g*-(PCL-alkyne). PGA-g-PCL (1 g, M_n= 32000 g/mol, 0.52 mmol) and 5-hexynoic acid (0.13 mL, 1.15 mmol) were dissolved in 25 mmol of anhydrous DCM and charged into 250 mL two neck round bottom flask. The solution was cooled using an ice bath. Then a solution of EDCI (220 mg, 1.15 mmol) and DMAP (28 mg, 0.23 mmol) dissolved in 7 mL DCM was added dropwise. The mixture was agitated using a magnetic stirrer and sealed using rubber a septum for 24 h at ambient temperature. The solution was filtered to remove the precipitate. This was followed by a concentration of the solution using rotary evaporation. The polymer solution was then precipitated two times into cold diethyl ether and dried under vacuum at room temperature. Yield=72%.

Synthesis of PGA-*g*-(PCL-*b*-PEO) using CuAAC. The typical procedure for the polymer synthesis can be described as the following; PGA-g-PCL (0.550 g, M_n=32000 g/mol, 0.289 mmol), mPEO-N_3 (0.618 g, M_n= 2000 g/mol, 0.301 mmol), and PMDETA (0.042 mL, 0.202 mmol) were dissolved in anhydrous DMF, and added to 25 mL Schlenk tube. The tube was degassed by bubbling nitrogen into the solution for 20 min. This was followed by addition of CuBr (29 mg, 0.202 mmol). Further degassing was carried out for 10 min. The solution was kept at room temperature for 48 h. The reaction was quenched finally by addition of 10 mL THF. The polymer solution was passed through an alumina column to remove CuBr. The resulting solution was concentrated and then dialyzed against water for 4 days using a dialysis membrane of MWCO= 3500 g/mol. The polymer was dried by freeze-drying. Yield=66%.

Synthesis of α-hydroxy-ω-alkyne end functional poly(ε-caprolactone) (Alkyne-PCL). The polymer was synthesized according to the procedure described by Hoogenboom et al.[75] The reaction was carried out at 85 °C.

Synthesis of poly(ε–caprolactone)-*b*-poly(ethylene oxide) PCL-*b*-PEO. Alkyne-PCL (0.5 g, M_n=2900 g/mol, 0.172 mmol) and mPEO-N_3 (0.141 g, M_n= 2000 g/mol, 0.206 mmol) were dissolved in 20 mL anhydrous DMF and added to an oven dried Schlenk tube. The tube was sealed by rubber septum and purged with nitrogen for at least 10 min. CuBr (15 mg, 0.1 mmol) and PMDETA (0.02 mL, 0.1 mmol) were then added. The solution was further purged with nitrogen for 10 min. The solution was kept at room temperature for 2 days. At the end of reaction the solvent was removed under vacuum using rotary evaporator, then 20 mL of THF was added and the solution was passed through an alumina column in order to remove copper bromide. The solution was dialyzed against acetone for 2 days using a dialysis membrane of MWCO=2000 g/mol. Finally, the solvent was removed and the resulting polymer was dried in an oven at 50°C under vacuum. Yield=58%.

Table S1. M_n and M_w/M_n Data of PGA-*g*-PCL Synthesized at Different Reaction Times.

Sample	Reaction Time (h)	$M_{n,PCL}$ [a] (g/mol)	$M_{n,total}$ [b] (g/mol)	M_w/M_n [c]
PGA_{17}-g-PCL_{13}	15	1500	28600	1.3
PGA_{17}-g-PCL_{15}	20	1700	32000	1.3
PGA_{17}-g-PCL_{24}	30	2700	48800	1.5

[a] M_n of PCL attached to the PGA backbone calculated by ^{1}H NMR spectroscopy. [b] M_n of the graft copolymer is obtained ^{1}H NMR spectroscopy. [c] Obtained by SEC. All subscripts in the sample coloumn refer to the number of repeat monomeric units.

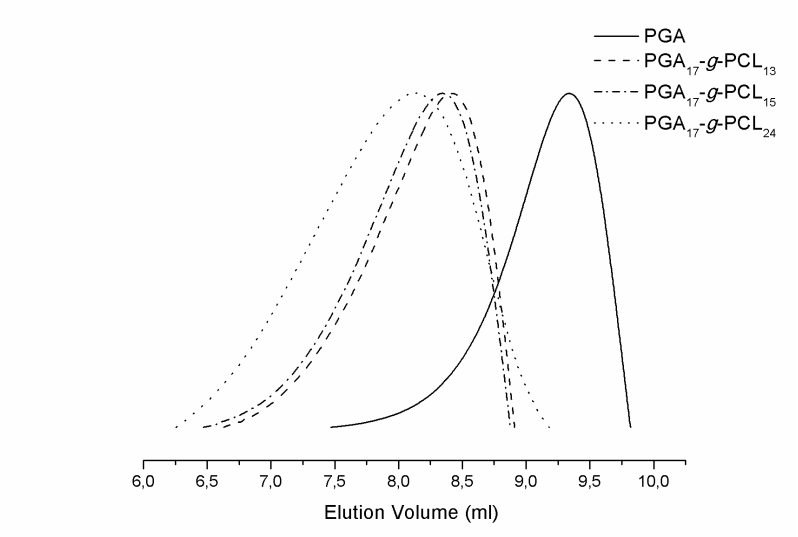

Fig. S1 Comparison of the SEC traces of PGA and PGA_{17}-*g*-PCL_{13}, PGA_{17}-*g*-PCL_{15}, PGA_{17}-*g*-PCL_{24} taken at room temperature in THF.

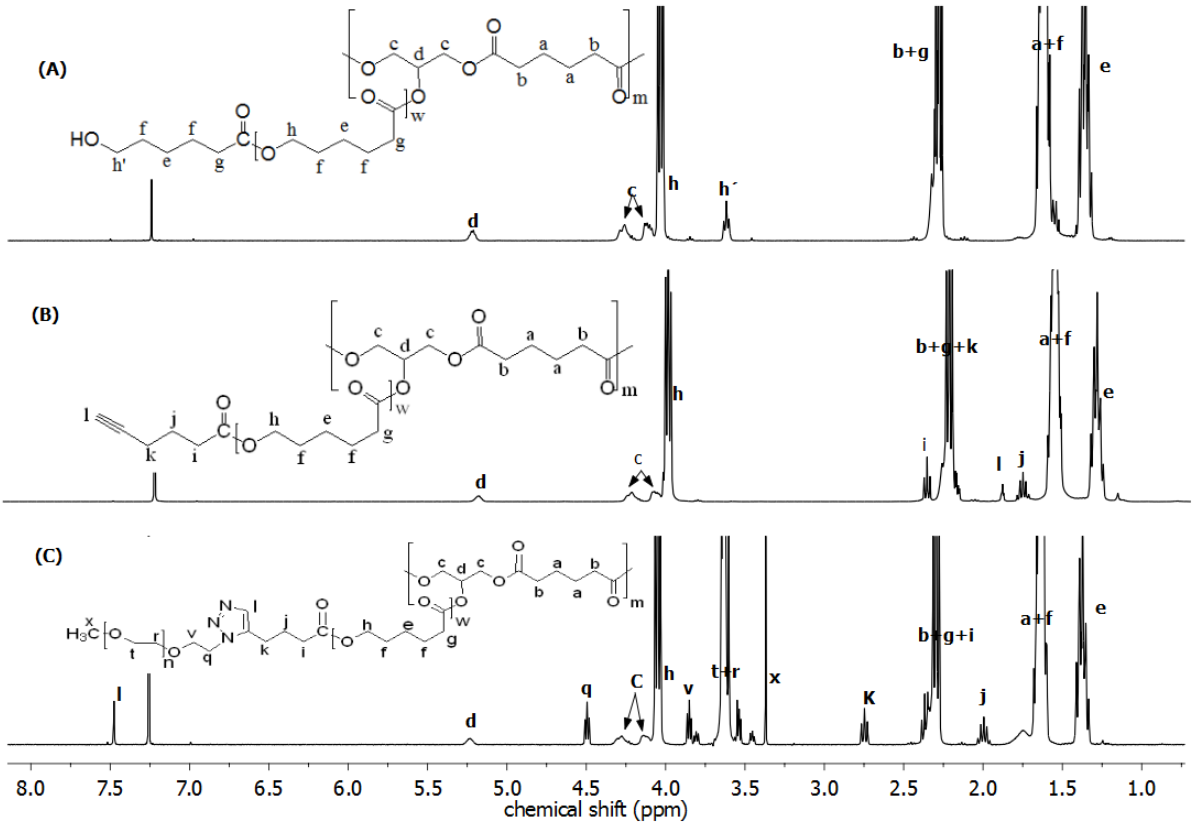

Fig. S2 ^{1}H NMR spectra of (A) PGA_{17}-*g*-PCL_{15}, (B) PGA_{17}-*g*-(PCL_{15}-alkyne) and (C) PGA_{17}-*g*-(PCL_{15}-*b*-PEO_{44}) measured at room temperature in $CDCl_3$.

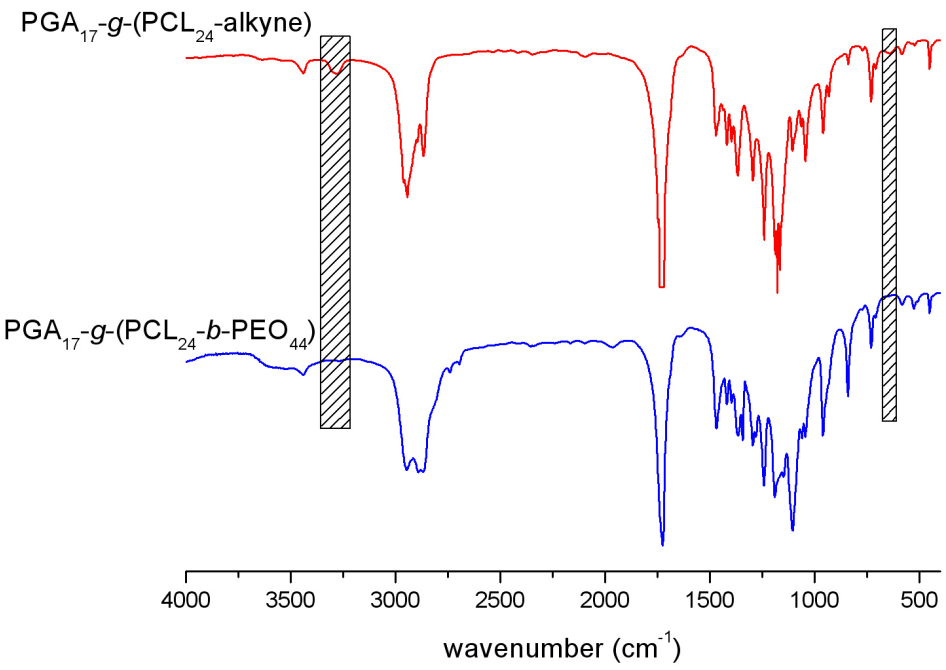

Fig. S3 FT-IR spectra of PGA_{17}-*g*-(PCL_{24}-alkyne) and PGA_{17}-*g*-(PCL_{24}-*b*-PEO_{44}). Shaded areas represent alkyne peaks.

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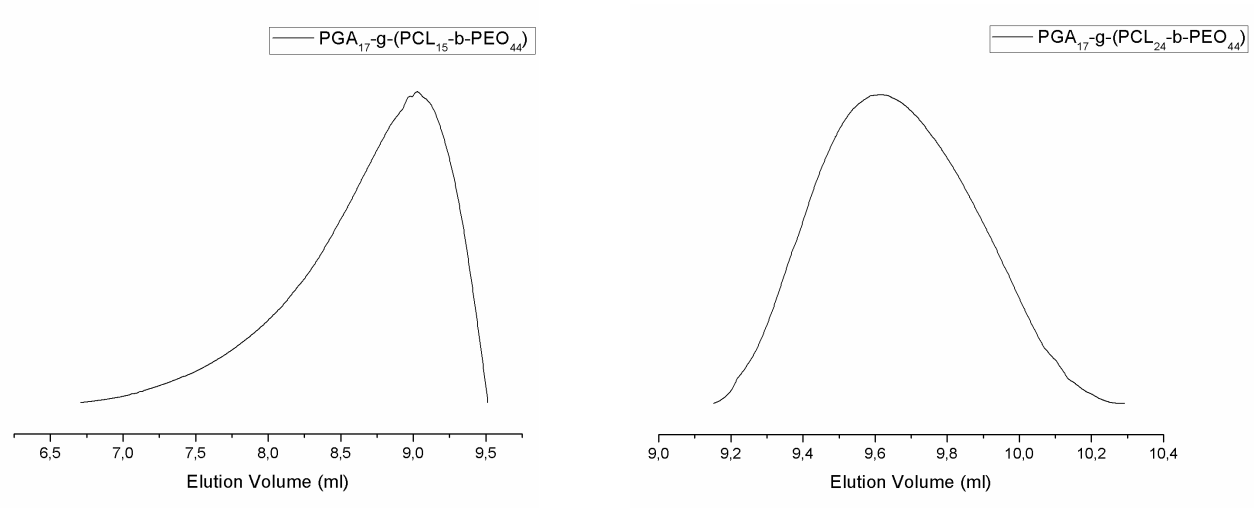

Fig. S4 The SEC traces of PGA_{17}-*g*-(PCL_{15}-*b*-PEO_{44}) and PGA_{17}-*g*-(PCL_{24}-*b*-PEO_{44}) taken at room temperature in THF.

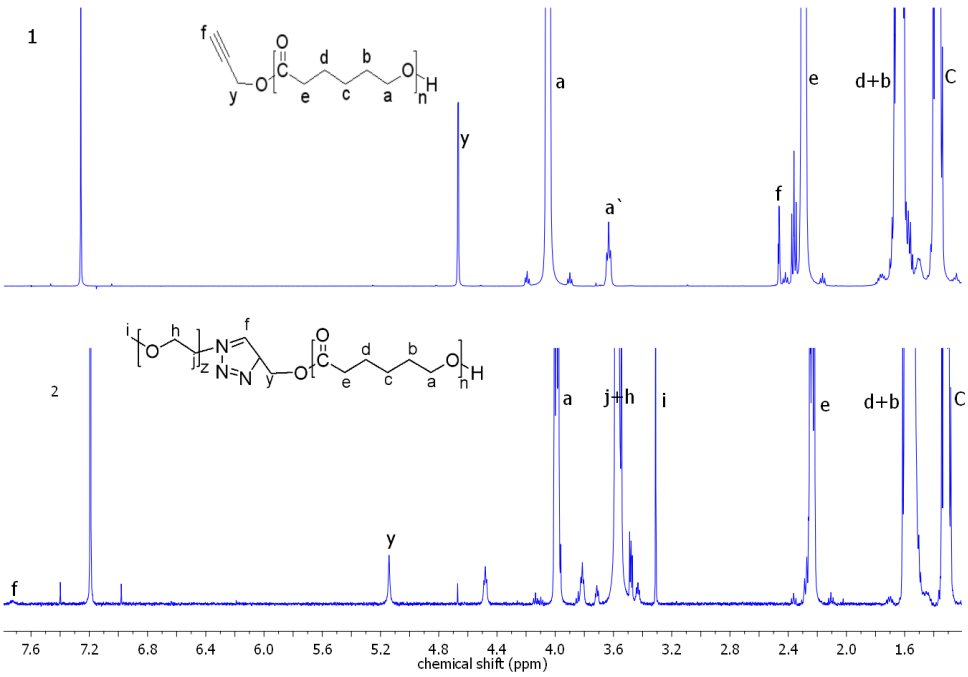

Fig. S5 ^{1}H NMR of 1- alkyne-PCL_{25} and 2- PCL_{25}-b-PEO_{44} measured in CDCl3 at 500MHz.

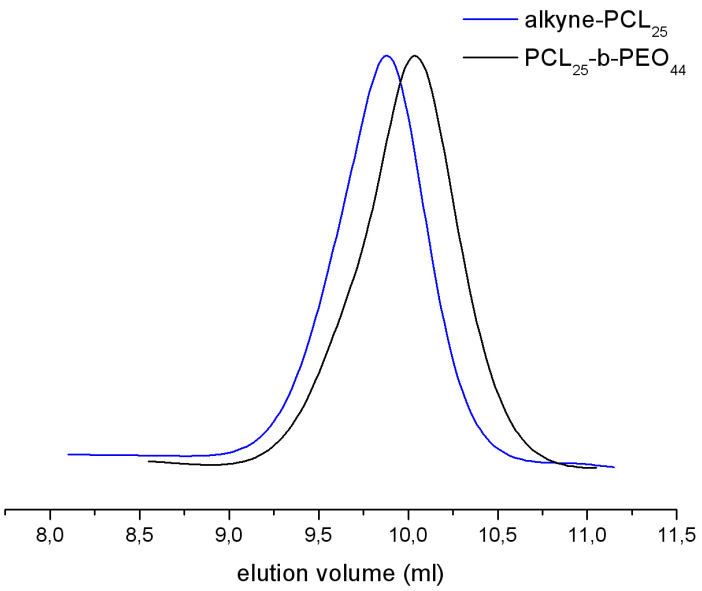

Fig. S6 SEC curves of alkyne-PCL_{25} and PCL_{25}-b-PEO_{44} recorded using THF as eluent.

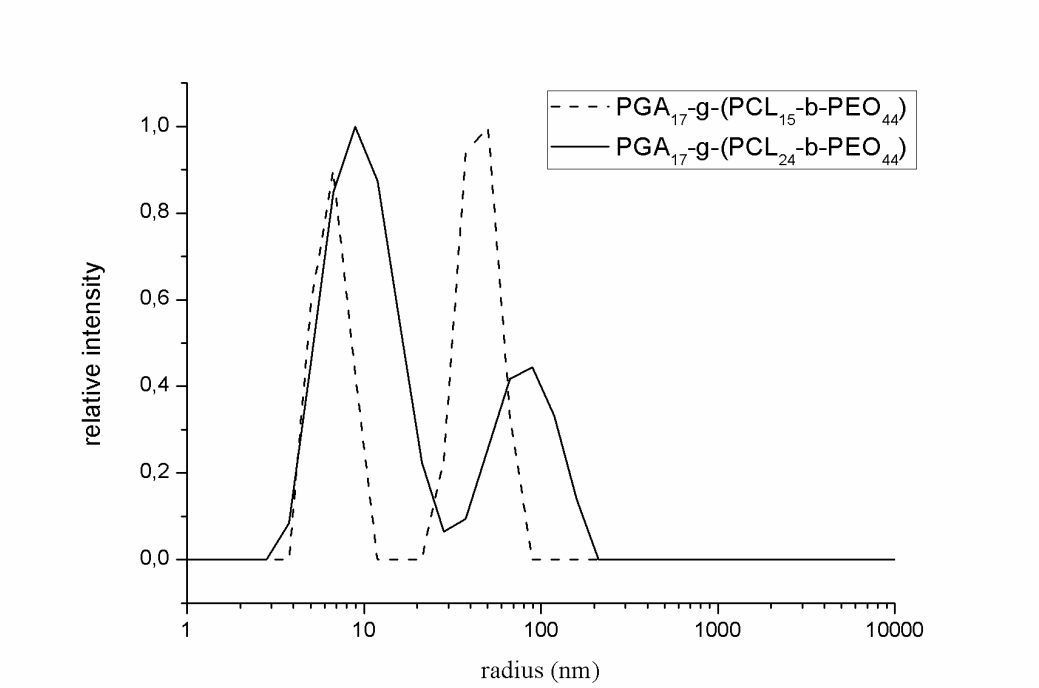

Fig. S7 Hydrodynamic radius distribution of PGA_{17}-*g*-(PCL_{15}-*b*-PEO_{44}) and PGA_{17}-*g*-(PCL_{24}-*b*-PEO_{44}) in water at a concentration of 1 g/L, scattering angle of 40°, and temperature of 25 °C.

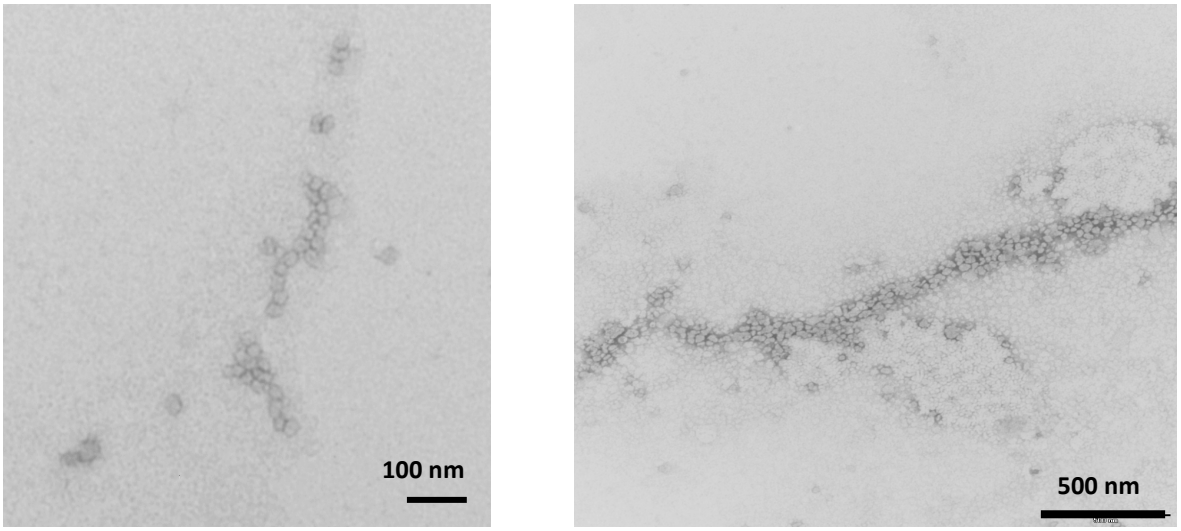

Fig. S8 TEM images of worm-like aggregates of PGA_{17}-g-(PCL_{24}-b-PEO_{44}).