Electronic Supplementary Information

for

Construction of reverse vesicles from pseudo-graft poly(glycerol methacrylate)s *via* cyclodextrin-cholesterol interaction

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Contents

1. Instruments

2D-NOESY NMR measurements were carried out on 500 MHz NMR spectrometer (Bruker AVANCE-III500). LPGMA10K-CD and PLA-Chol mixed in a CD/Chol molar ratio of 1:1 were prepared DMSO-d_6. Inverted microscope image was collected on Nikom Edipse Ti instrument.

2. Synthesis and Characterization

2.1. Synthesis and characterization of 5-arm initiator. With five functional hydroxyl groups, *a*-D-glucose was used as the precursor of 5-arm initiator. 2-Bromoisobutyryl bromide (0.108 mol) and *a*-D-glucose (0.014 mol) were dispersed in a mixture of pre-distilled anhydrous pyridine (25 mL) and chloroform (50 mL). The dispersion was refluxed for 3 h at 70 °C, and cooled down to react further for 15 h at 25 °C. Then, the mixture was poured into a separating funnel with dichloromethane (200 mL). The organic layer was washed, in turn, with ice-cold water, 25% HCl, 0.1 M NaOH, brine solution, and dried over anhydrous magnesium sulfate. After removing the solution by vacuum rotary evaporation, the solid was dissolved in dichloromethane (10 mL), and precipitated in methanol to obtain the pure product.

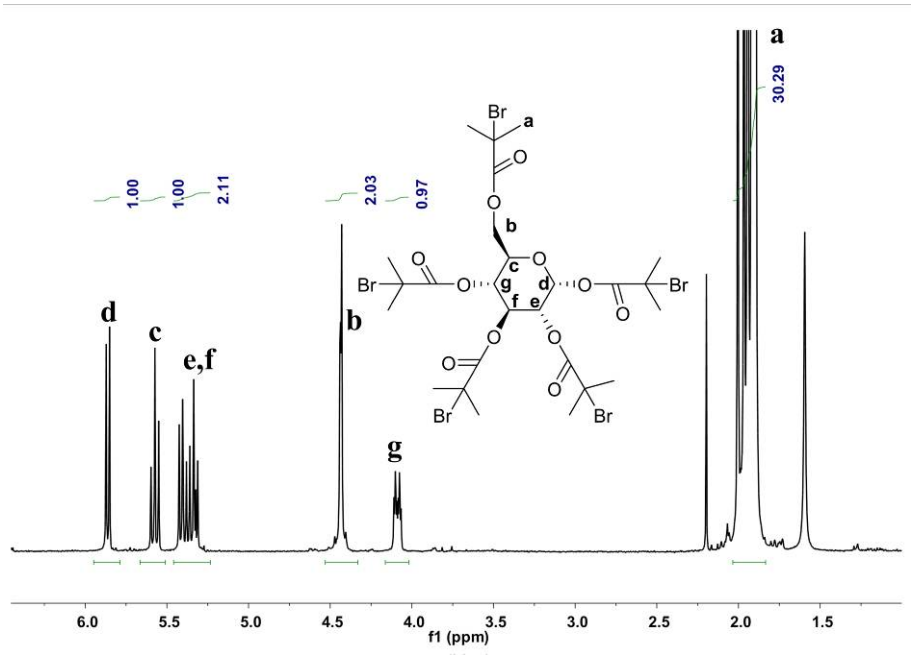


Figure S1. ^{1}H NMR spectrum of 5-arm initiator in $CDCl_3$.

2.2. Synthesis and characterization of linear and 5-arm PGMAs. Linear PGMA (LPGMA) and 5-arm PGMA (SPGMA) were synthesized by atom transfer radical polymerization

(ATRP). GMA (105 or 175 equiv), bipyridyl (1 equiv), ATRP initiator (1 equiv), CuBr (1 equiv) were successively added into THF in a three-necked flask. The mixture was refluxed for 24 h at 90 ^{o}C under nitrogen. The mixture was then passed through a silica gel column using THF as an eluent. The leaching liquor was concentrated by vacuum rotary evaporation, and precipitated twice in diethyl ether to obtain white solid product.

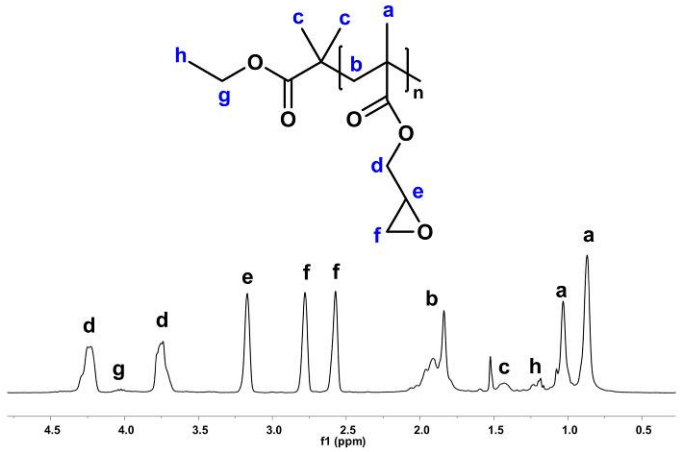
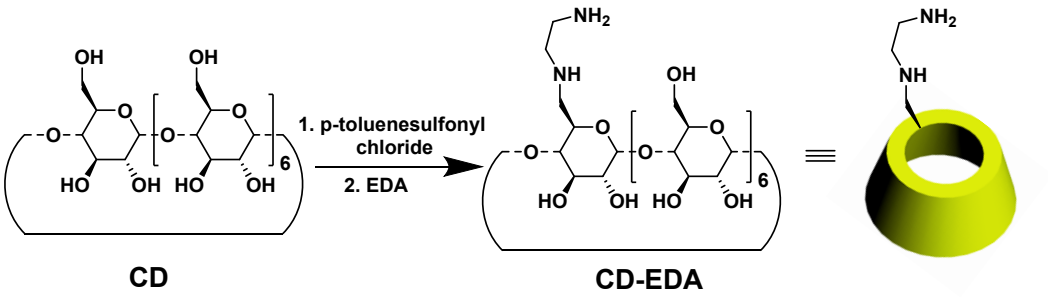


Figure S2. ^{1}H NMR spectrum of LPGMA10K in $CDCl_3$.

2.3. Synthesis and characterization of mono(6-(ethanediamine)-6-deoxy)-β-CD (CD-EDA). CD-DEA was synthesized in two steps. Typically, β-CD (20.0 g, 17.6 mmol) was suspended in a beaker with double-distilled water (150 mL) in an ice-water bath. The solution was white emulsus mixture with good dispersibility. NaOH solution (containing 2.19 g NaOH, 54.7 mmol) in deionized water (7 mL) and p-toluenesulfonyl chloride (3.36 g, 17.6 mmol) in acetonitrile (10 mL) were successively added into the reaction solution. After stirring for 5 h, the suspended solids was removed by suction filtration, and the filtrate was adjusted with 10% HCl solution to be approximately pH=6, and refrigerated overnight at 4 ^{o}C. The resulting white precipitate, i.e. the intermediate product mono-6-deoxy-6-(p-tolylsulfonyl)-β-cyclodextrin (6-OTs-β-CD), was recovered by suction filtration. To obtain CD-EDA, 6-OTs-β-CD reacted with distilled EDA (30 mL) for 4 h at 75 ^{o}C. Subsequently, the mixture was precipitated in cold ethanol (200 mL). The precipitate was collected by suction filtration, dissolved in water (30 mL), poured into cold ethanol (200 mL) three times to obtain purified product. Total yield: 10-15%. ^{1}H NMR (δ, ppm, D2O): 2.66-2.70 (t, 2H), 2.78-2.82(t, 2H), 3.40-3.61 (m, 14H), 3.84-3.95 (m, 21H), 5.02-5.03 (d, 7H).



Scheme S1. Synthesis of CD-EDA

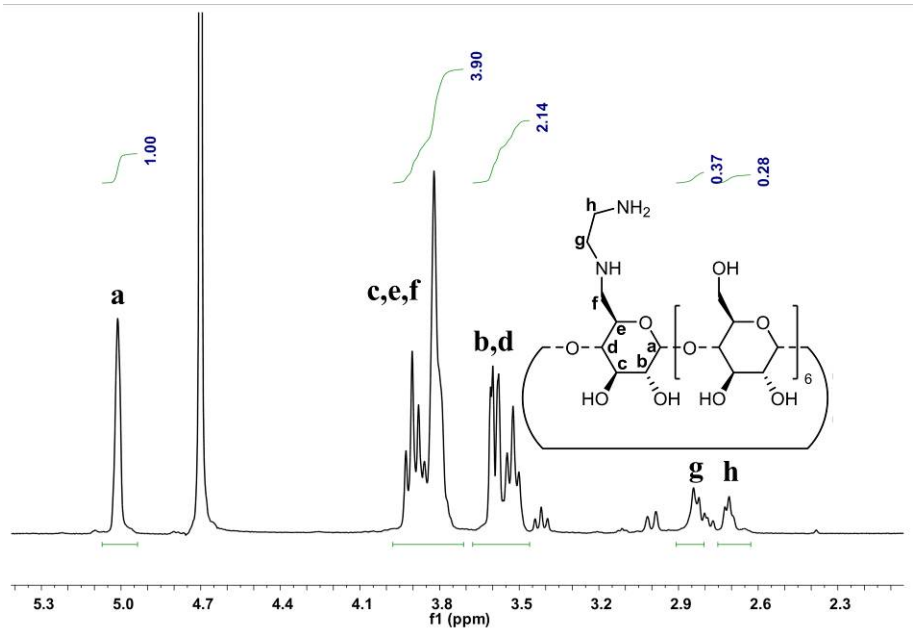
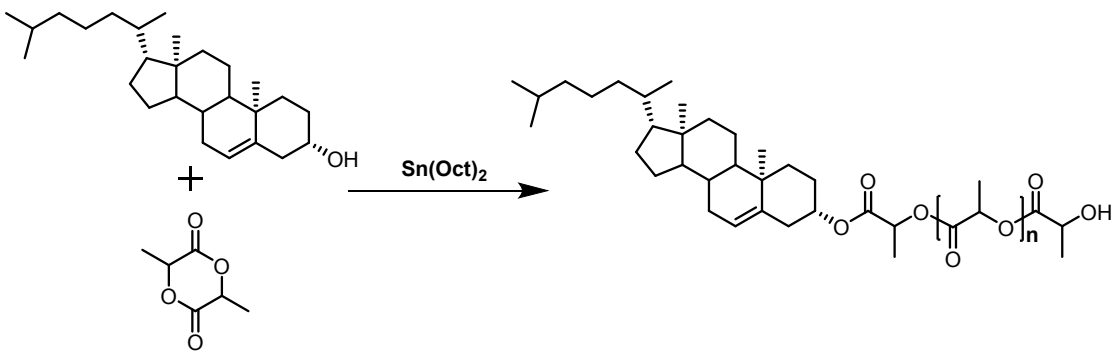


Figure S3. ^{1}H NMR spectrum of CD-EDA in D_2O.

2.4. Synthesis and characterization of PLA-Chol. PLA-Chol was synthesized through the ring-opening reaction of lactide using cholesterol as an initiator. D,L-Lactide (2.66 g), cholesterol (0.11 g) and $Sn(Oct)_2$ (0.03 wt%) as a catalyst were sealed in an airtighted tube after being vacuumed. The tube was dipped in an oil bath for 5 h at 150 °C, and cooled to room temperature, dissolved in acetone (10 mL), and precipitated in cold water three times to obtain the pure product.



Scheme S2. Synthesis of PLA-Chol

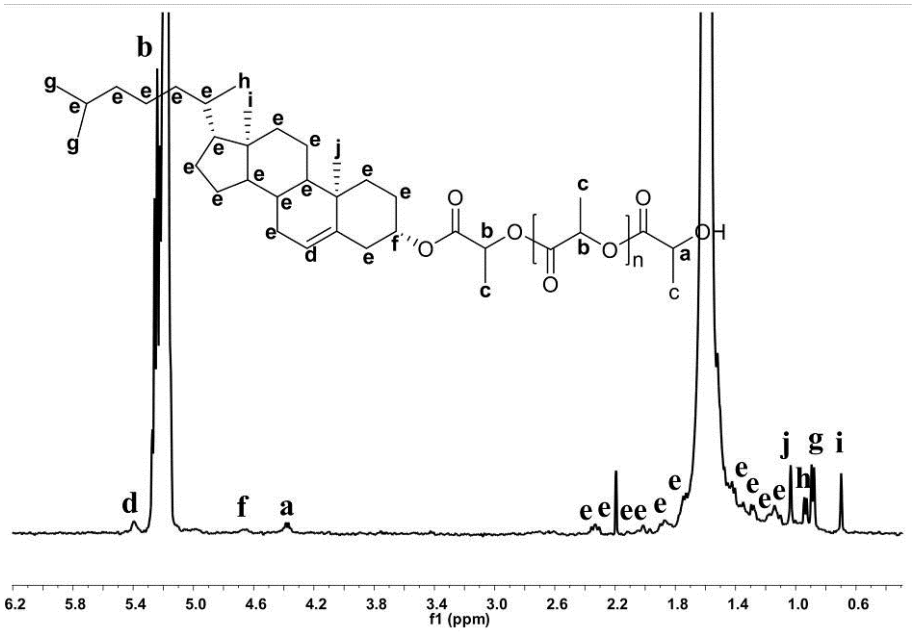


Figure S4. ^{1}H NMR spectrum of PLA-Chol in $CDCl_3$.

3. Preparation and Characterization of Reverse Vesicles

3.1. Preparation of reverse vesicles

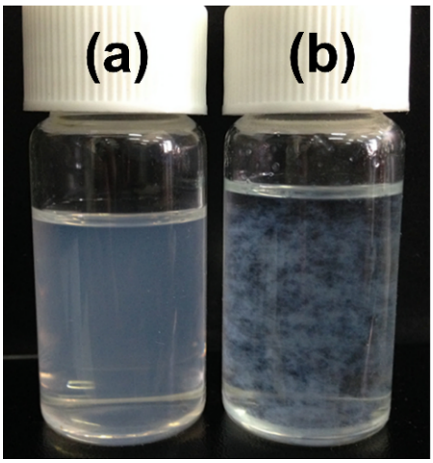


Figure S5. Photograph of (a) reverse vesicles prepared from LPGMA10K-CD and PLA-Chol, (b) flocculent aggregates prepared from LPGMA10K-CD and PLA.

3.2. 2D-NOESY NMR study of reverse vesicles

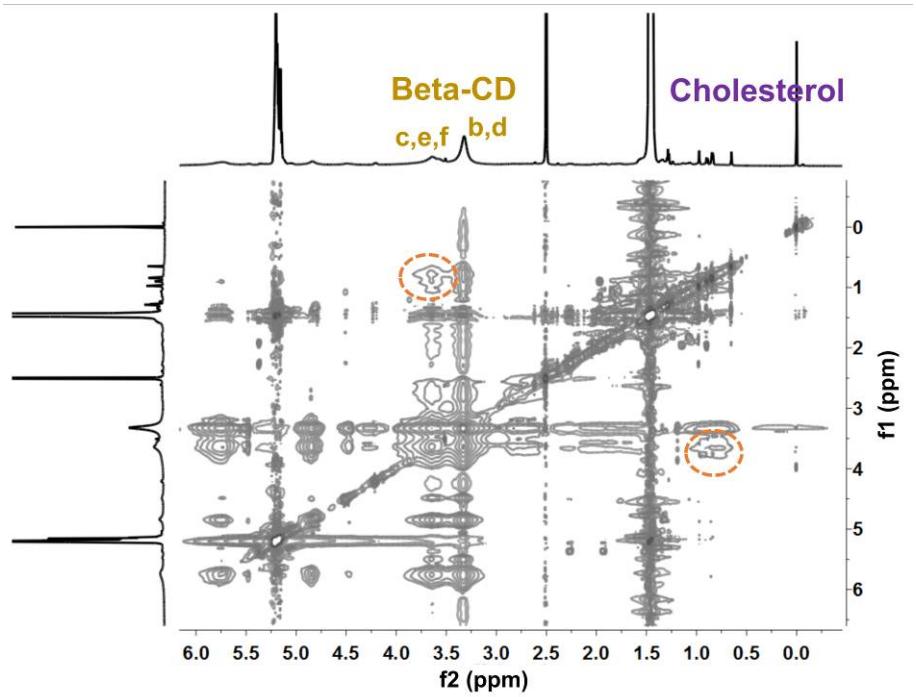


Figure S6. 2D ^{1}H-^{1}H NOESY spectrum of LPC10K-g-LC reverse vesicles in DMSO-d_6.

3.3. SEM study of reverse vesicles

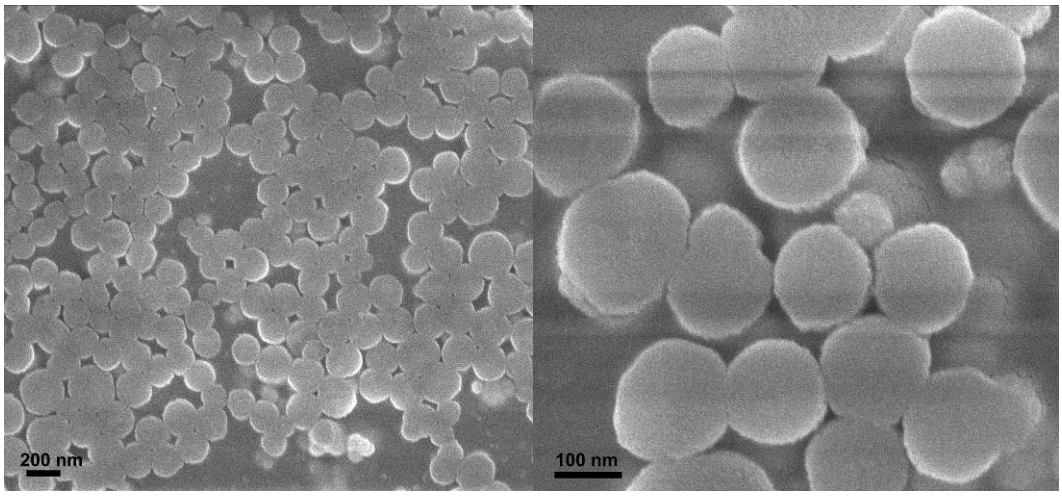


Figure S7. SEM images of LPC10K-g-LC reverse vesicles.

3.4. DLS study of reverse vesicles. The DLS results exhibited that the copolymers were able to form stable particles from LPC10K-g-LC at the molar ratio of CD/cholesterol ranged from 1 to 10. Figure S4 shows the size distribution by intensity.

Table S1. DLS results of LPC10K-g-LC with different CD/cholesterol molar ratio

Samples (CD/cholesterol)	Z-average diameter (nm)	PDI
1:1	229	0.12
2:1	237	0.18
3:1	225	0.12
6:1	249	0.13
10:1	267	0.19

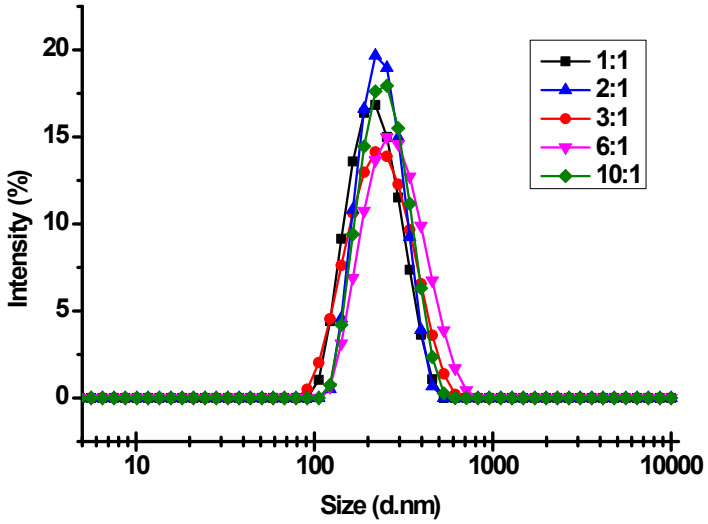


Figure S8. Size measurement of LPC10K-g-LC with different CD/Chol molar ratio.

4. Transformation and characterization of organogels.

4.1 Transformation from reverse vesicles into organogels. Gelatinization was observed in tubes, and gel settled at the tube bottom when the sample tubes were inverted.

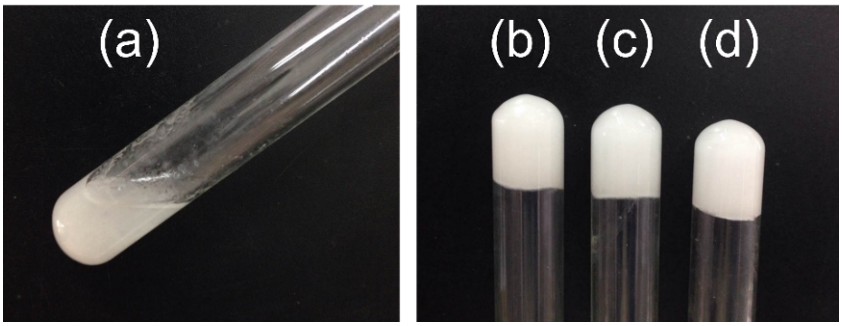


Figure S9. Representative photos of (a) free-flowing milky suspension, (b)-(d) white gels, with concentration of reverse vesicles at (a) 1 mg/ml, (b) 1.5 mg/ml, (c) 2 mg/ml, and (d) 2.5 mg/ml. DCM-H_2O ratio (*v*/*v*) is 8:1.

4.2. Inverted microscope of organogels.

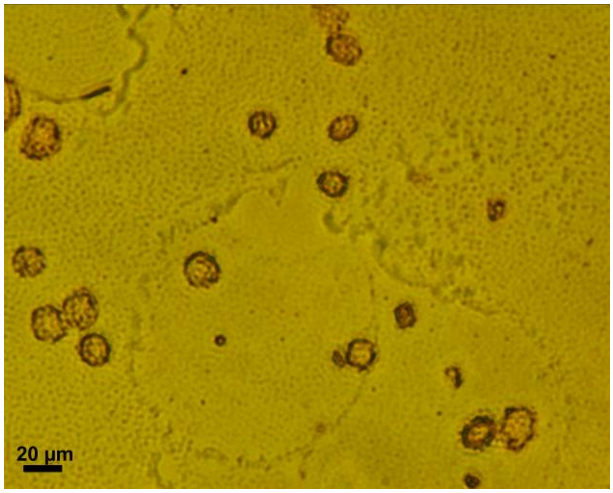


Figure S10. Inverted microscope image of LPC10K-g-LC organogels encapsulated with CR.

4.3. Release of encapsulated Congo red

Extraction experiments were performed as described in the manuscript. The organic phase was then carefully transferred to a new vial. Then, 1 mL of the organic phase was sampled and exposed to 1 mL of water. Interestingly, no Congo red could be released into the aqueous phase, probably owing to the physical cross-linking of the organogels.