

Supporting Information

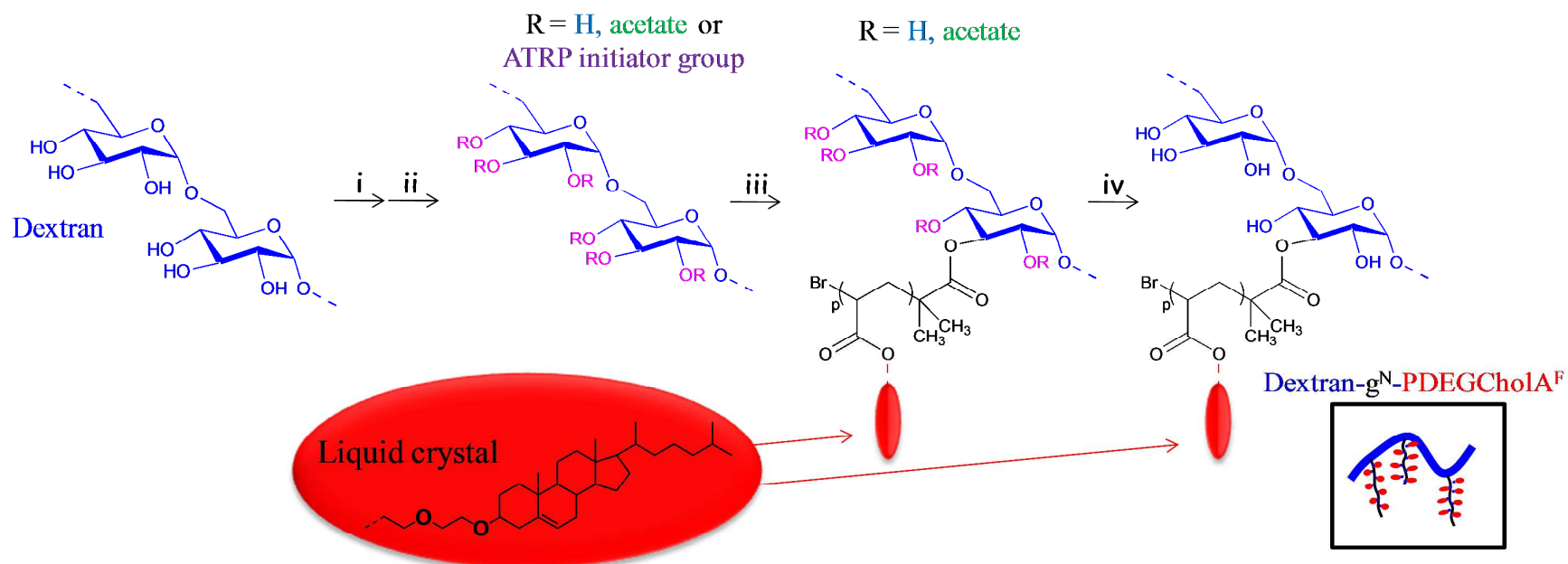
Polymersomes from amphiphilic glycopolymers containing polymeric liquid crystal grafts

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Copolymers synthesis strategy



Scheme S1: Synthesis of Dex-g^N-PDEGCholA^F glycopolymers. i) Partial acetylation. ii) Esterification by 2-bromoisobutyryl bromide. iii) Controlled ATRP of DEGCholA. iv) Deprotection of acetate groups. Details are given in reference [1]. In boxes are given the mesomorphic DEGChol part formula and the schematic draw of such glycopolymers.

Interfacial Tension Measurements

Interface (toluene/water) tension measurements were carried out at 25 °C with a Krüss Easy Dyne tensiometer equipped with a platinum ring. In a typical experiment, copolymer was solubilized in freshly distilled toluene, then interface was prepared by adding water slowly on the toluene solution. Afterward, mixture was stored in the dark for 24 hours to reach equilibrium before measurements. Finally, interfacial tension versus copolymer concentration was determined by using Lecomte de Noüy method (figure S1).

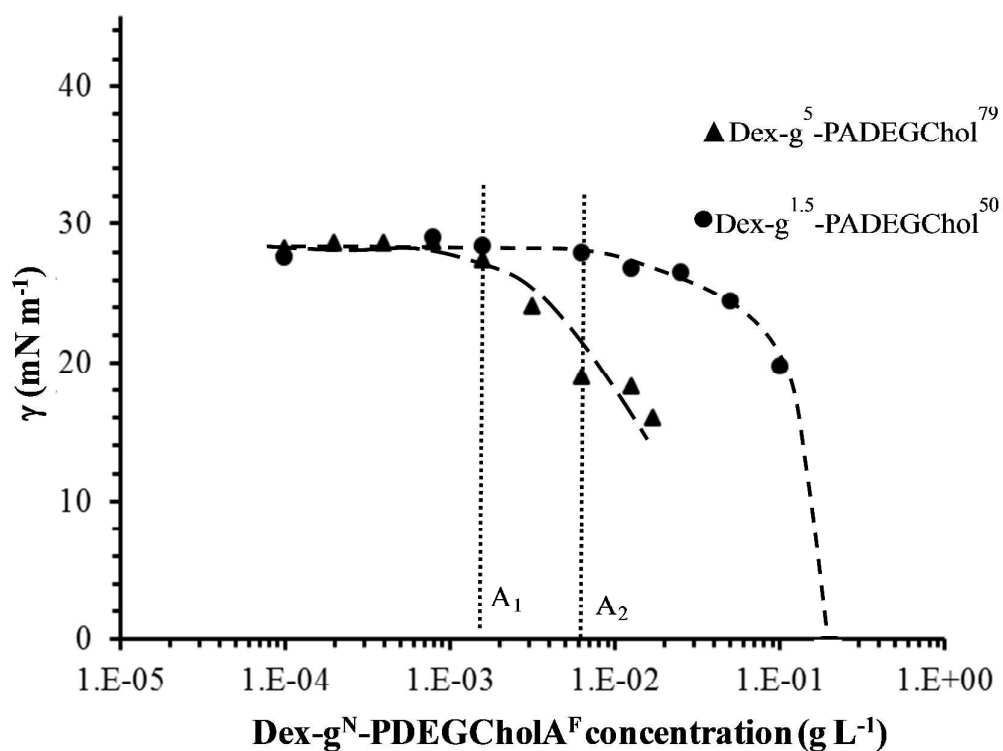


Figure S1: Toluene/water interfacial tension (γ) versus Dex-g^N-PDEGCholA^F concentration.

Copolymers self-assembly procedure

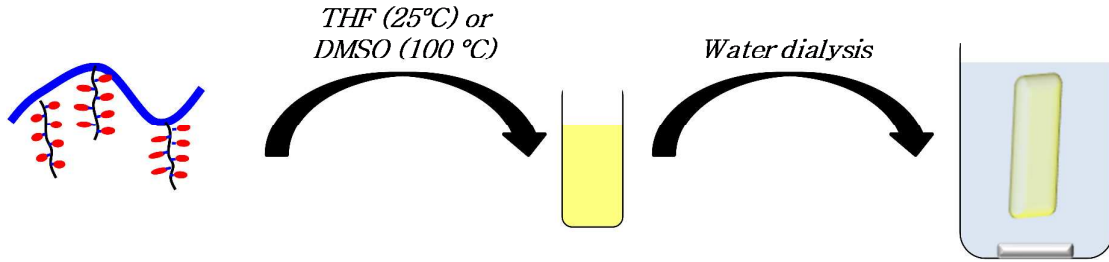


Figure S2. Self-assembly of copolymers in aqueous medium using selective solvent followed by water dialysis.

Dynamic and static light scattering (SLS and DLS)

Measurements were recorded with a ALV-5000 multibit, multitaue, full digital correlator in combination with a Spectra-Physics laser (emitting vertically polarized light at $\lambda = 632.8$ nm) and a thermostated bath controller (20 °C). The autocorrelation functions ($g_1(t)$) were analyzed in terms of relaxation time distribution (τ) (equation S1) according to the REPES Routine.^[2] Measurements were made at angles (θ) ranging between 20 and 150° corresponding to a scattering vector $q = 4.6 \times 10^{-3} \text{ nm}^{-1}$ to $2.55 \times 10^{-2} \text{ nm}^{-1}$.

$$g_1(t) = \int A_{(\tau)} \exp\left(-\frac{t}{\tau}\right) d\tau \quad (\text{S1})$$

Hydrodynamic radius (R_H) was estimated using the Stokes-Einstein relation (Equation S2), where D_0 is diffusion coefficient, K_B is the Boltzmann constant, T is absolute temperature and η_s is the viscosity of the solvent (water). D_0 was determined from the slope of the q^2 dependence of $1/\tau$ as shown in figure S3. The polydispersity (given in Table 1) of the distributions of the relaxation times may be estimated from the product $\langle \tau \rangle \times \langle \frac{1}{\tau} \rangle$.

$$R_H = \frac{K_B \times T}{6 \times \pi \times \eta_s \times D_0} \quad (\text{S2})$$

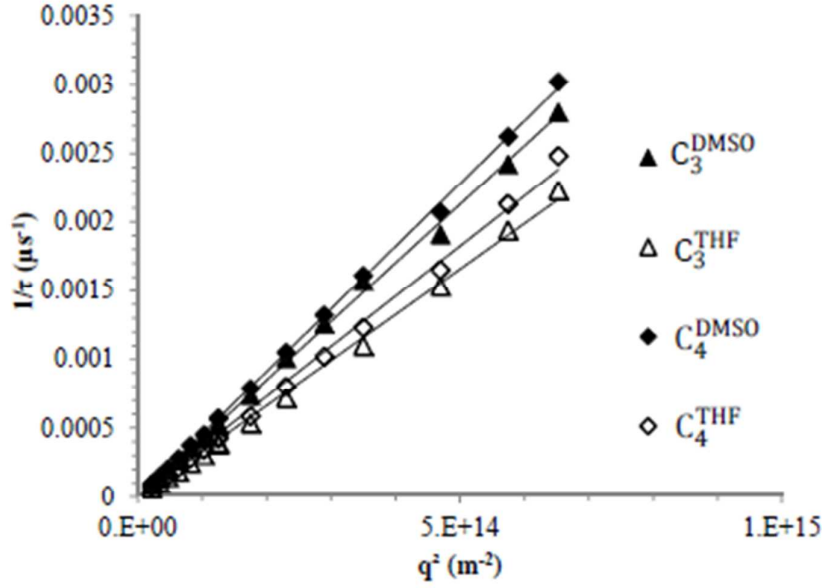


Figure S3. q^2 dependence with $1/\tau$.

The Rayleigh ratio (R_θ) of the solution was measured by SLS using (Equation S3) and was fitted by a modified RGD approach of the total scattered intensity I for a coated sphere (Equation S4) ^[3-4].

$$R_\theta = \frac{I_{\text{solution}}(\theta) - I_{\text{water}}(\theta)}{I_{\text{toluene}}(\theta)} \times \left(\frac{n_{\text{water}}}{n_{\text{toluene}}} \right)^2 \times R_{\text{toluene}} \quad (\text{S3})$$

with I_{solution} , I_{water} , and I_{toluene} the intensities scattered by the solution, water (solvent) and the reference (toluene), respectively. $n_{\text{water}} = 1.33$ and $n_{\text{toluene}} = 1.496$ are the refractive indexes, and $R_{\text{toluene}} (1.35 \times 10^{-5} \text{ cm}^{-1})$ is the Rayleigh ratio of toluene for a wavelength $\lambda = 632.8 \text{ nm}$.

$$I = \left((m_1 - 1) \left(\frac{3 \times j_1(x)}{x} + f^3 \times \frac{1 - m_1}{m_1 - 1} \times \frac{3 \times j_1(f \times x)}{f \times x} \right) \right)^2 \quad (\text{S4})$$

where $f = 1 - \frac{t}{R}$ with R the vesicle radius and t the thickness of polymeric bilayer. $x = R \times q$ with q the scattering vector. $j_1(x)$ and $j_1(f \times x)$ are the first-order spherical Bessel function.

$m_1 = \frac{n_m - n_0}{n_0}$ with n_0 and n_m the refractive indexes of aqueous medium (1.33) and of the polymeric membrane (1.382), respectively.

Transmission Electronic Microscopy

Cryo-TEM –Specimens for cryo-TEM observation were prepared using a cryo-plunge cryo-fixation device (Gatan, USA) in which a drop of the aqueous suspension was deposited onto glow-discharged holey-type carbon-coated grids (Ted Pella Inc., USA). The TEM grid was then prepared by blotting the drop containing the specimen to a thin liquid layer remained across the holes in the support carbon film. The liquid film was vitrified by rapidly plunging the grid into liquid ethane cooled by liquid nitrogen. The vitrified specimens were mounted in a Gatan 910 specimen holder (Gatan, USA) that was inserted in the microscope using a CT-3500-cryotransfer system (Gatan, USA) and cooled with liquid nitrogen. TEM images were then obtained from specimens preserved in vitreous ice and suspended across a hole in the supporting carbon substrate. The samples were observed under low dose conditions ($< 10 \text{ e}^-/\text{Å}^2$), at -178 °C , using a JEM 1230 'Cryo' microscope (Jeol, Japan) operated at 80 kV and equipped with a LaB6 filament. All the micrographs were recorded on a Gatan 1,35 K x 1,04 K x 12 bit ES500W CCD camera.

Conventional TEM - A drop of 50 μL of each aqueous dispersion specimen was first placed on a carbon-coated TEM copper grid (Quantifoil, Germany) previously submitted to a glow-discharge to ensure hydrophilicity. The sample was then negatively stained with uranyl acetate (Merck, Germany). For that, the sample-coated TEM grid was successively placed on a drop of an aqueous solution of uranyl acetate (2 % w/w) and on a drop of distilled water. The grid was then air-dried before introducing them in the electron microscope. The samples were viewed using a JEOL JEM-1230 TEM operating at 80 kV.

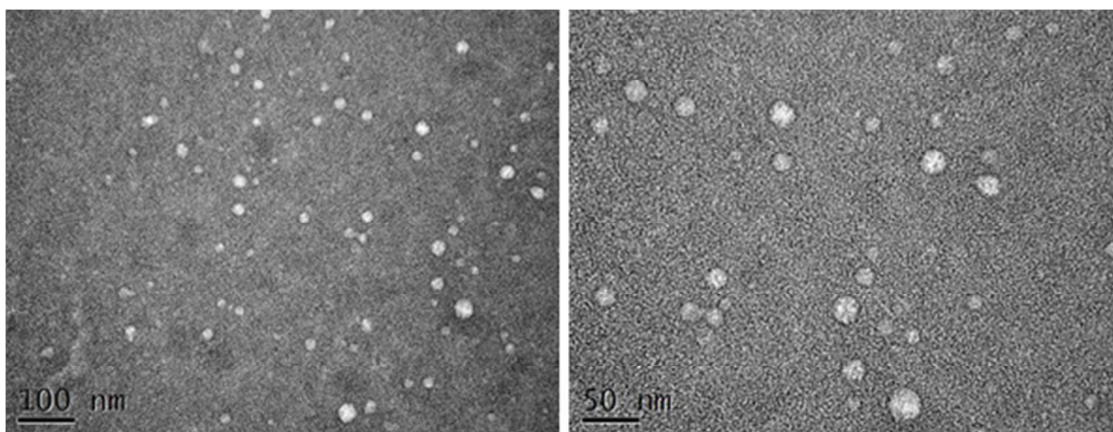


Figure S4. TEM images(different scales) of polymersomes obtained in water after dialysis of Dex-g⁵-PADEGChol⁷⁹ dispersed in THF (case of C₃^{THF}). Average diameter was estimated equal to 27 nm, according method described in ref [5].

References :

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