Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Self-assembly of Amphiphilic Copolymers Containing Polysaccharide: PISA versus Nanoprecipitation, and the Temperature Effect.

Djallal Ikkene,[a] Ana Andreea Arteni,[b] Malika Ouldali,[b] Jean-Luc Six, [a] and Khalid Ferji*[a]

a. Université de Lorraine, CNRS, LCPM, F-54000 NANCY, France.

b. Université Paris-Saclay, CEA, CNRS, Institute for Integrative Biology of the Cell (I2BC), Cryo-electron Microscopy Facility, CRYOEM-Gif, 91198, Gif-sur-Yvette, Franc

E-mail: khalid.ferji@univ-lorraine.fr

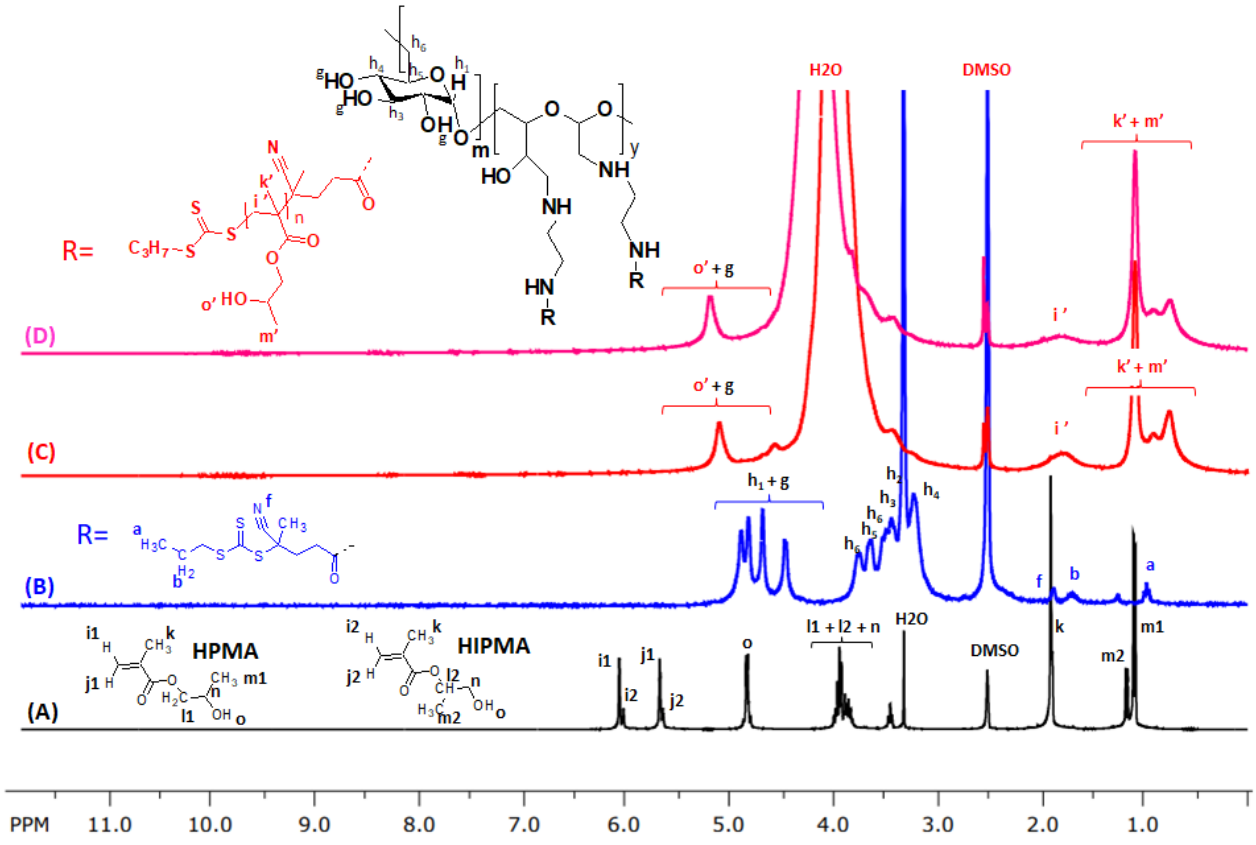
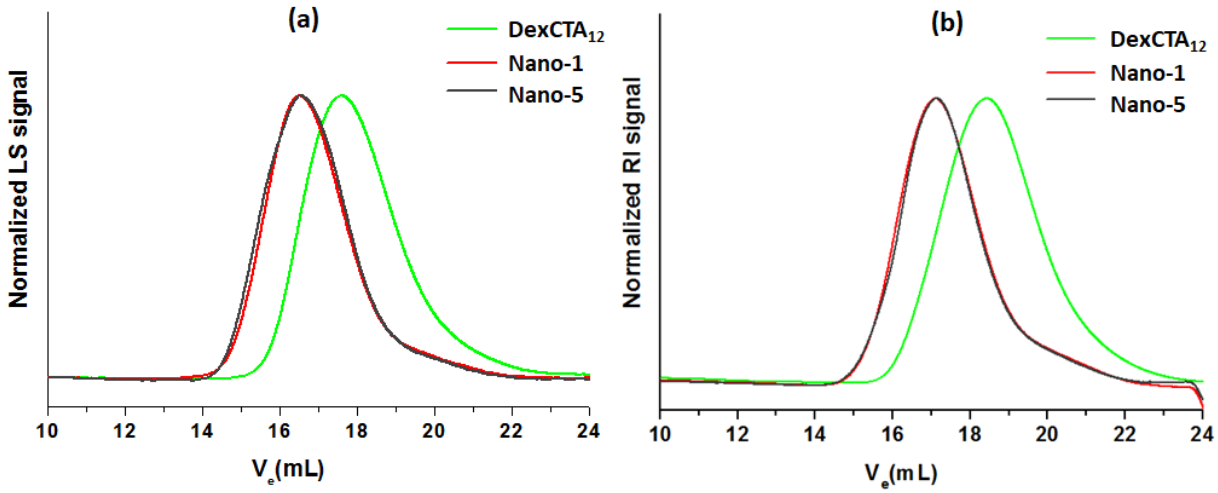


Fig. S1. ^{1}H NMR spectra in DMSO-d_6 of (A) Mixture of isomers (2-hydroxypropyl methacrylate-HPMA and 2-hydroxyisopropyl methacrylate-HIPMA), (B) Macromolecular chain transfer agent ($DexCTA_{12}$), (C) Crude Nano-1 suspension prepared *via* photo-PISA at RT, (D) Crude Nano-5 suspension prepared *via* photo-PISA at 60°C.

The number of CTA groups per dextran chain (Y) was determined from Fig. S1B using Eq-S1, where $\overline{M_{n,Dex}}$ = 32000 g mol^{-1} and M_{GU}=162 g mol^{-1} are the number average molar mass of dextran T_{40} and the molecular weight of glucopyranosic unit, respectively.

$$Y = \frac{\frac{A_a}{3}}{\frac{A_{(h_1+g)}}{4}} \times \frac{\overline{M_{n,Dex}}}{M_{GU}} \qquad \text{Eq-S1}$$



(c)

Sample	$\overline{M_n}$ (g/mol)	Đ
$DexCTA_{12}$	37500	1.27
Nano-1	135000	1.21
Nano-5	134000	1.22

Fig. S2. SEC traces (DMSO/$NaNO_3$, 70°C) of $DexCTA_{12}$, and Dex-g^{12}-$PHPMA_{400}$ glycopolymers produced by photo-PISA of HPMA at room temperature (Nano-1) and at 60°C (Nano-5). (a) Light scattering (LS) and (b) refractive index (RI) detections, respectively. (c) Macromolecular characteristics of (co)polymers analyzed.

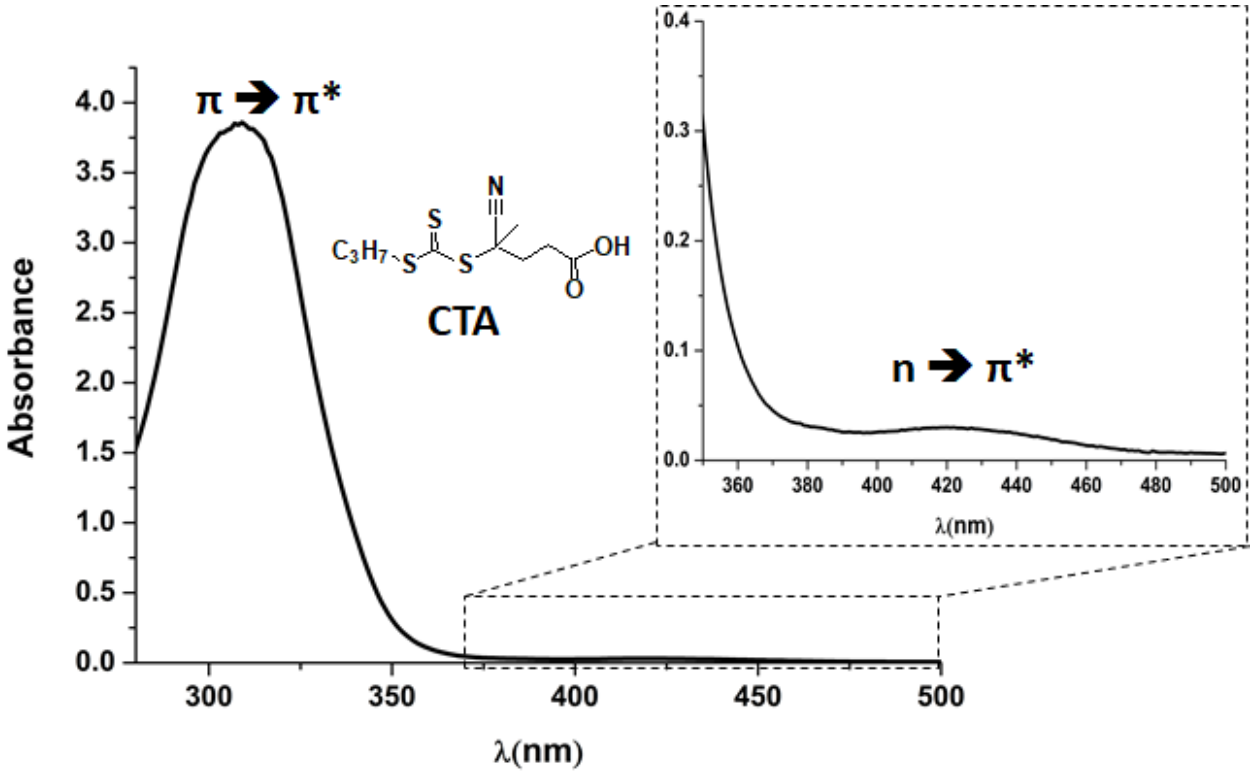


Fig. S3. UV-Visible absorbance spectrum of thiocarbonate RAFT agent (CTA) in DMSO ([CTA]= 0.1 mM).

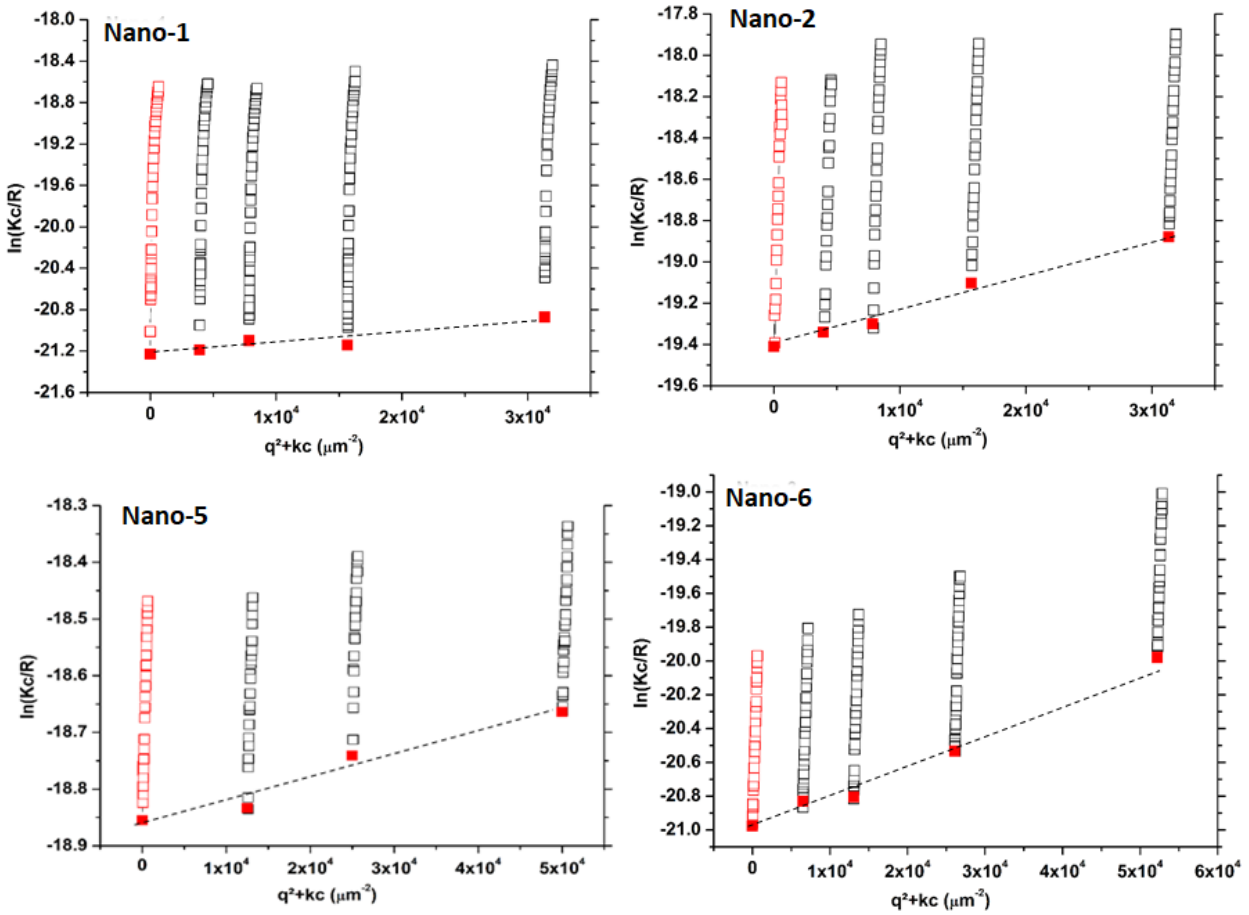


Fig. S4. Zimm plot (black open squares) intensity measured and (red open squares) extrapolation to zero concentration and to zero angle (red closed squares) for different glyco-nanoobjects suspensions (see Table 1) at 20°C.

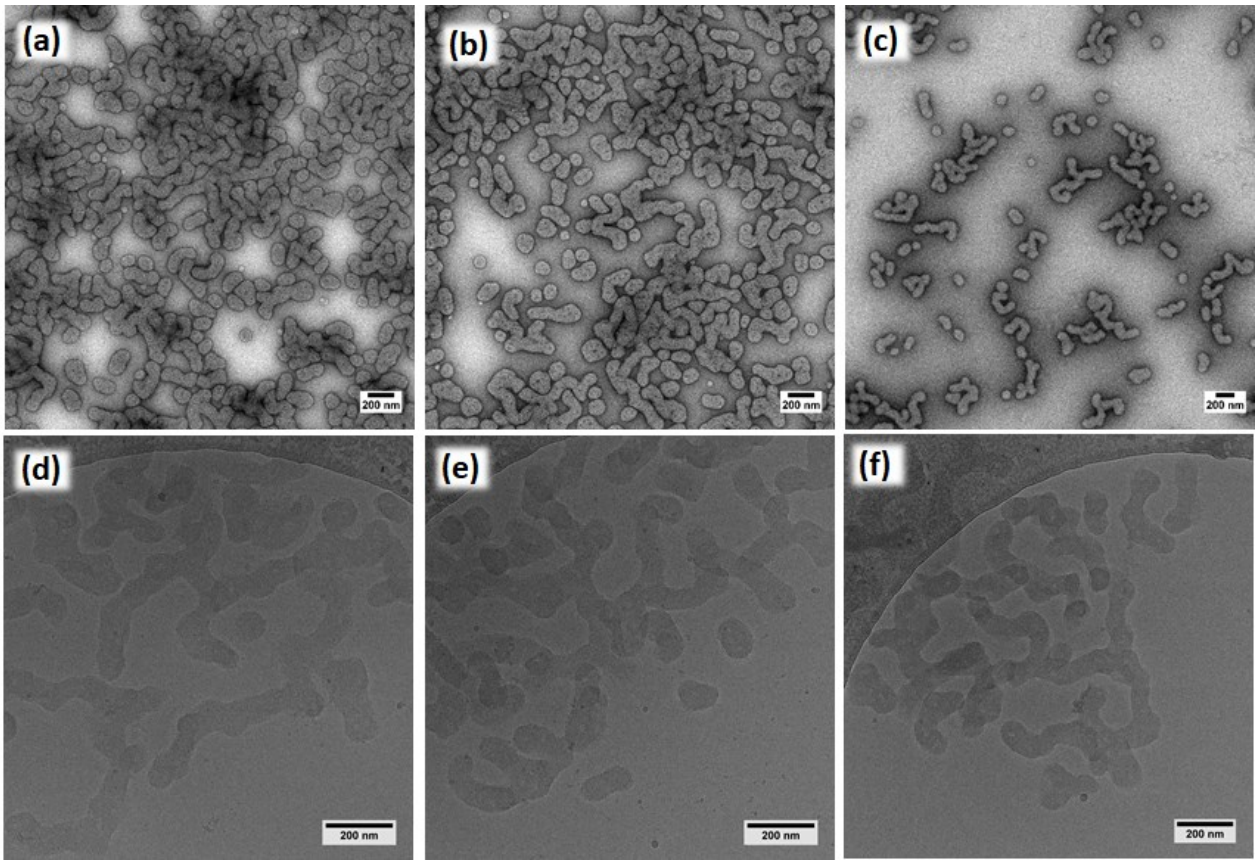


Fig. S5. (a, b, and c) negative stain and (d, e, and f) cryo TEM images of Dex-g^{12}-PHPMA$_{400}$ glyco-nanostructures suspension (Nano-1) prepared by photo-RAFT polymerization of HPMA at RT in aqueous medium using DexCTA$_{12}$ at 10% w/w solids.

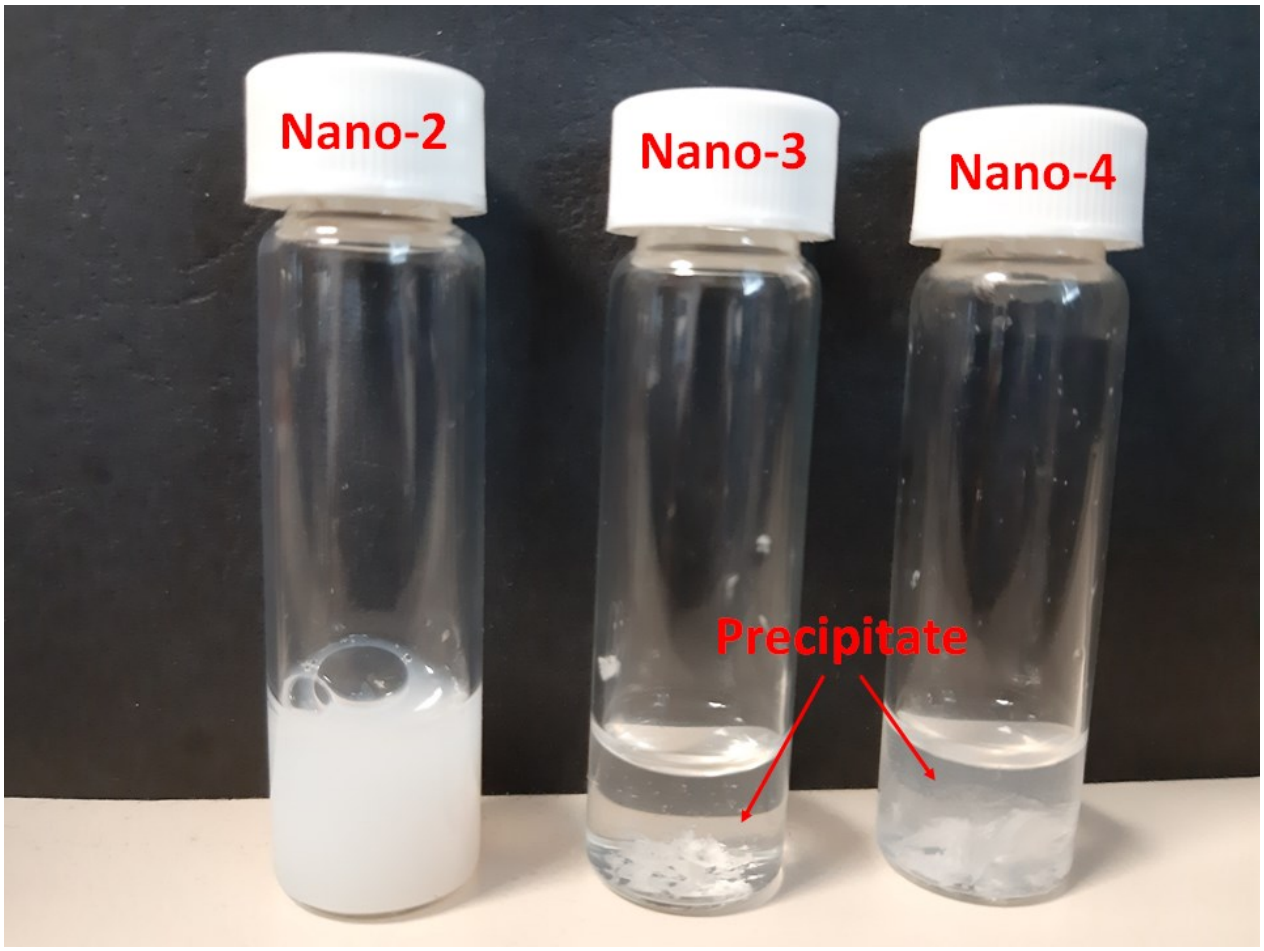


Fig. S6. Digital photographs recorded for a series of Dex-g^{12}-PHPMA$_{400}$ glyco-nanostructures suspensions prepared using conventional methods: nanoprecipitation (Nano-2), emulsion -solvent-removing (Nano-3), and film-rehydration (Nano-4).

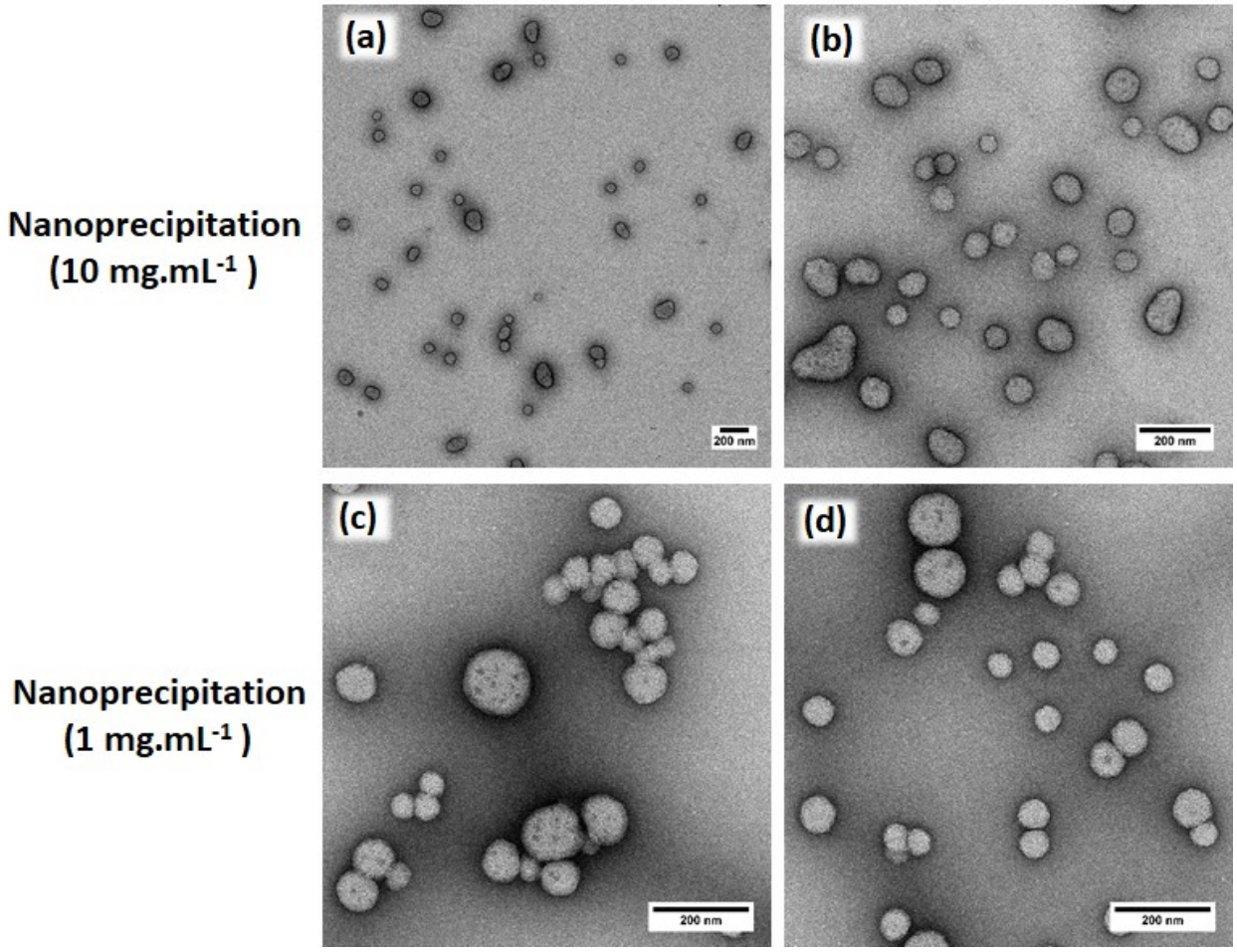


Fig. S7. Negative stain TEM images of suspensions (diluted to 1 mg.mL^{-1} for imaging) prepared by nanoprecipitation of dried Dex-g^{12}-PHPMA$_{400}$. The final concentration after removing of water was (a, b) 10 mg.mL^{-1}, and (c, d) 1 mg.mL^{-1}.

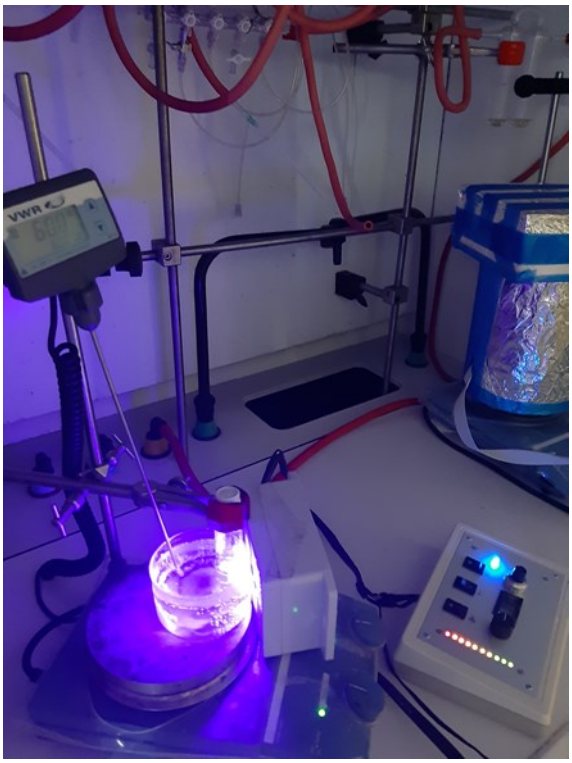


Fig. S8. Experimental setup for photopolymerization using visible light at 60°C

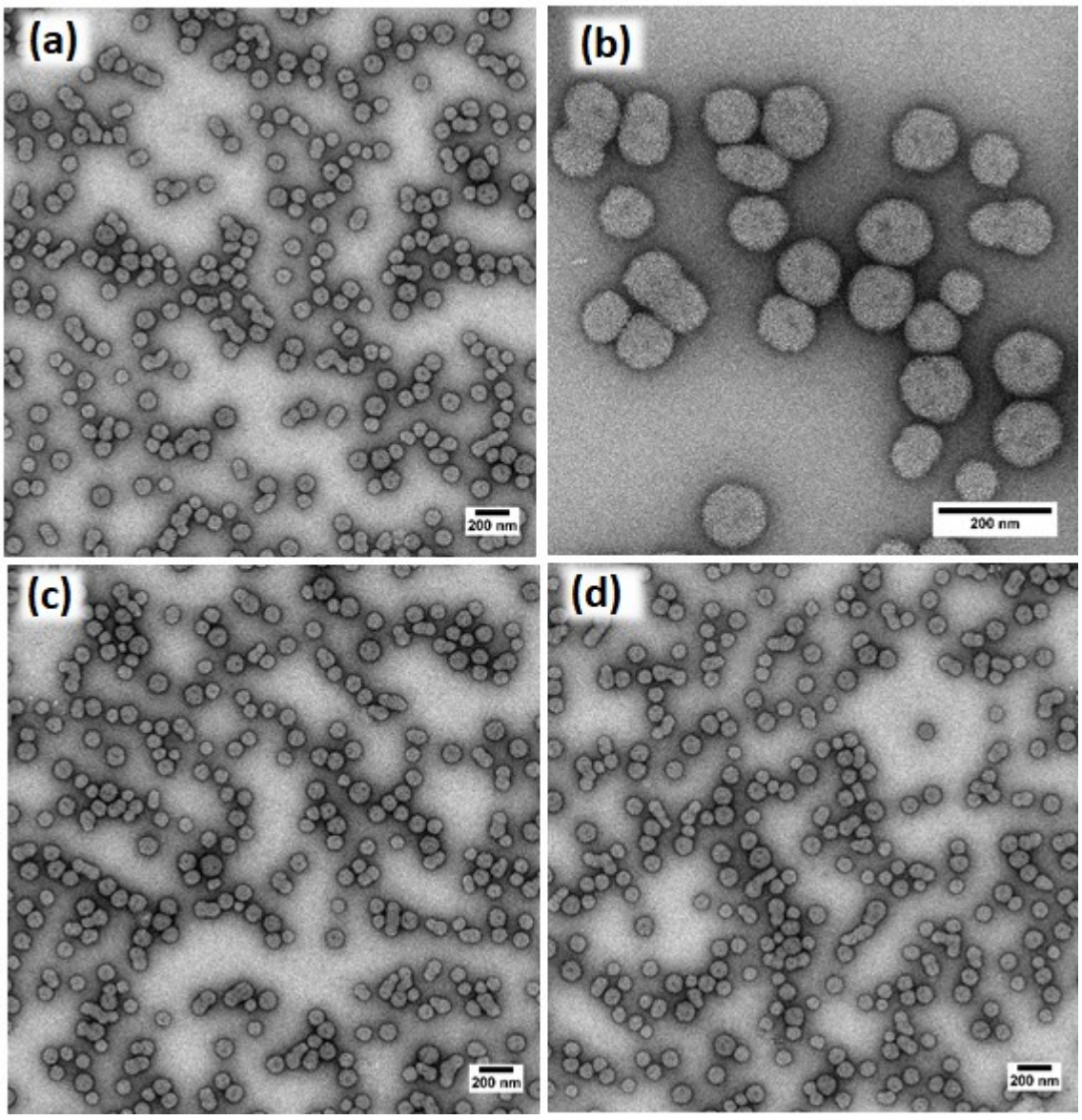


Fig. S9. TEM images of Dex-g^{12}-PHPMA$_{400}$ suspension of Nano-5 prepared by photo-PISA polymerization of HPMA at 60°C in aqueous medium using DexCTA$_{12}$ at 10% w/w solids. Analysis was performed on samples at room temperature.

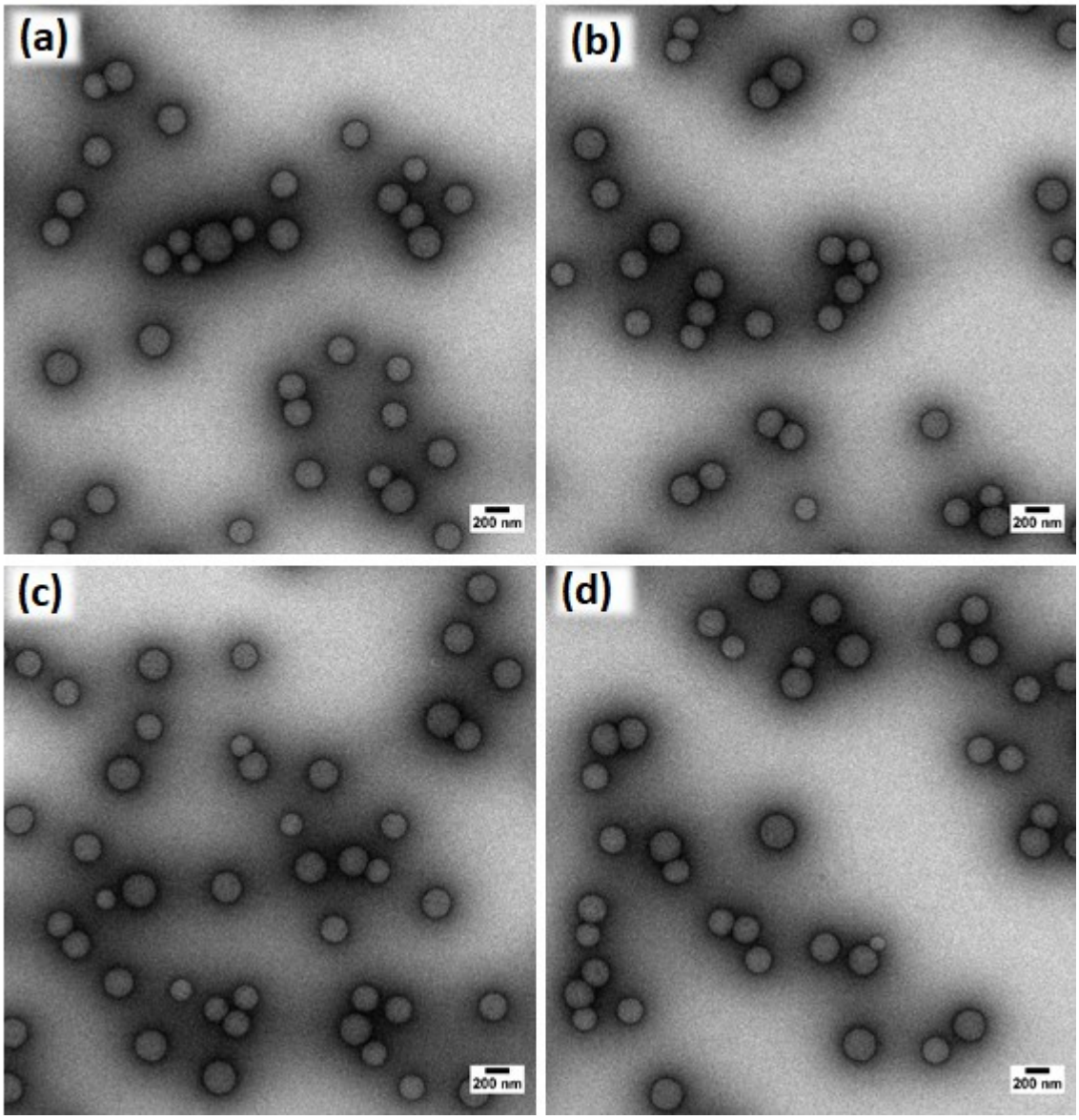


Fig. S10. TEM images of Dex-g^{12}-PHPMA$_{400}$ glyco-nanostructures suspension (Nano-6) prepared by heating Nano-1 suspension at 60°C for 40 days.