

Supporting Information

Self-Assembly of Gold Nanoparticles With Oppositely Charged, Long, Linear Chains of Periodic Copolymers

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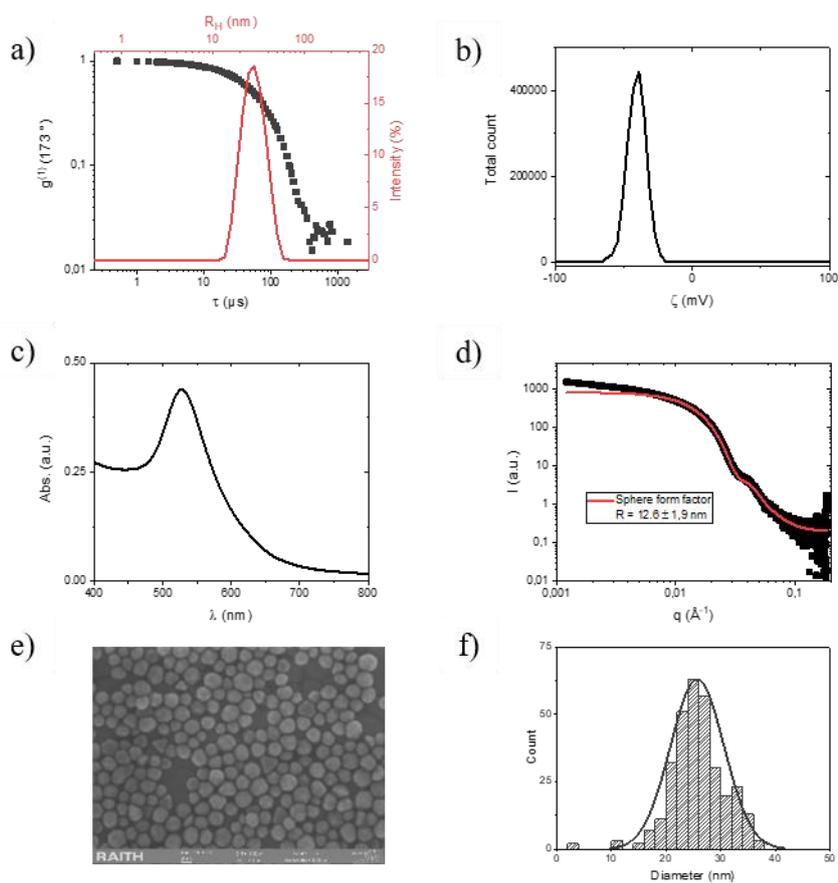


Figure S1. Characterizations of the gold nanoparticles after ligand exchange (AuNP(MUA)).
 (a) Scattered electric field autocorrelation function (black square) and corresponding normalized size distribution (red line) of the gold nanoparticle suspension;
 (b) Zeta potential distribution of the gold nanoparticle suspension;
 (c) UV-Vis absorption spectrum of the gold nanoparticle suspension;
 (d) SAXS curve of the gold nanoparticle suspension (black square) and best fit of the data using the form factor of spheres with log normal size distribution (red line);
 (e) Typical SEM-FEG image of the gold nanoparticles;
 (f) corresponding size distribution with gaussian fit (line).

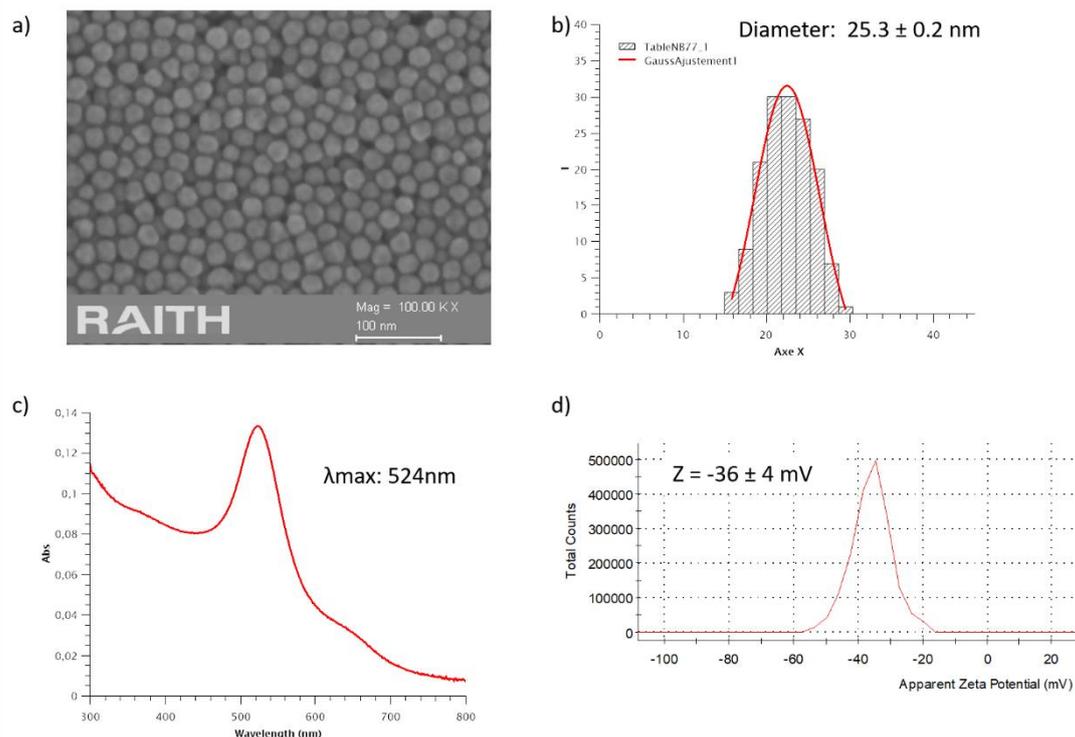


Figure S2. characterisation of the gold nanoparticles used for Au-CP n°4:
 a) SEM-FEG image; b) size distribution; c) UV-vis spectrum; d) zeta potential

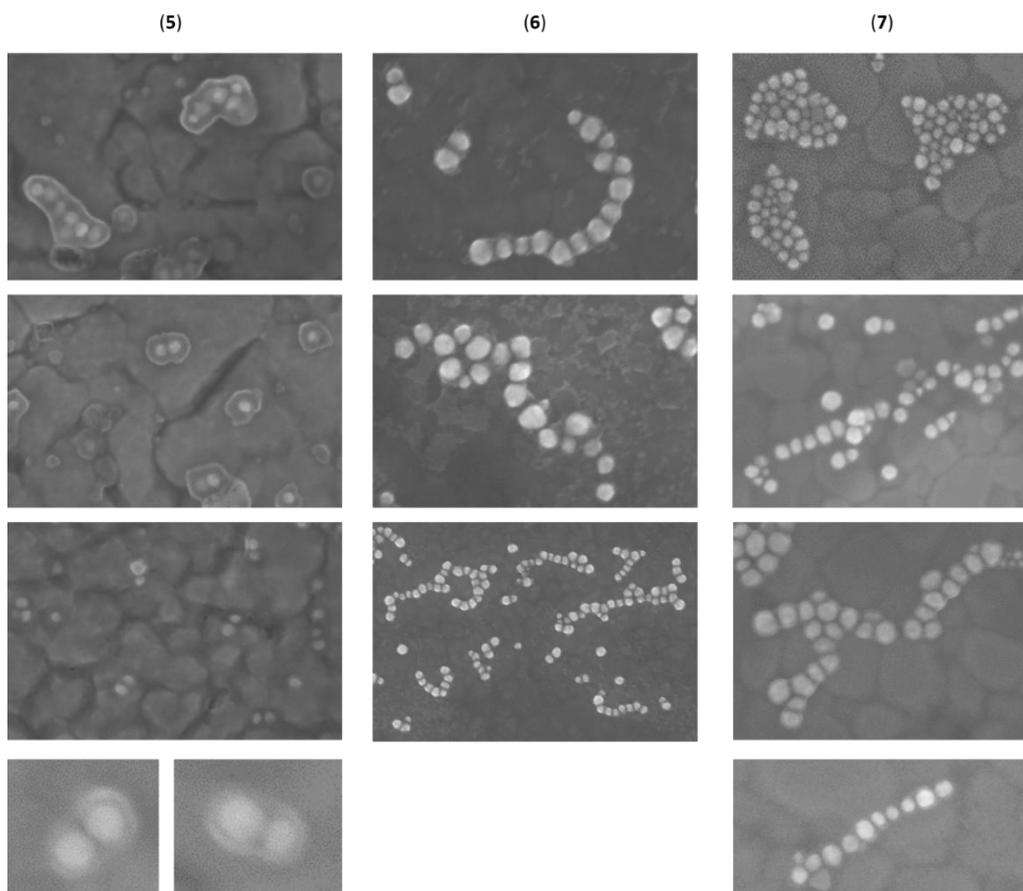
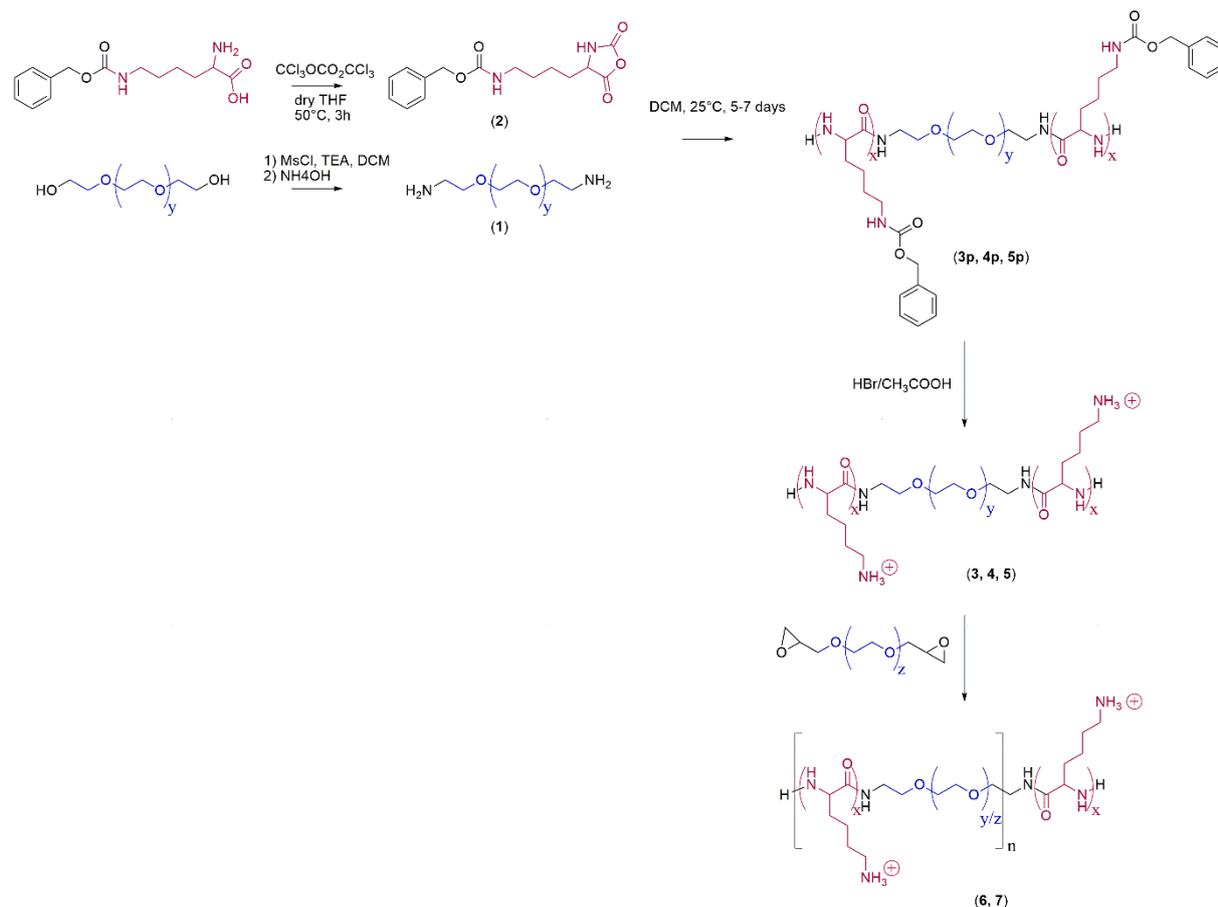


Figure S3. Deposition of the nanoparticles AuMUA (a) and dried patterns of the colloidal oligomer formation obtained at $\chi < 1$ using copolymer 5; 6 and 7

Detailed synthesis of the copolymers.



Scheme S1. Synthesis route for the polylysine-poly(ethyleneglycol) copolymers

(1) H₂N-PEG-NH₂. Amination of the dihydroxy-PEG (PEG-3400: M_w=3400g/mol and PEG-10000: M_w=10000g/mol) was achieved in two steps. **Ms-PEG-Ms.** The mesyl-terminated-PEG was synthesized first. The dihydroxy-PEG (1 mmol, 10 g for PEG-10000 or 3.4 g for PEG-3400) was dissolved in 50mL of DCM and triethylamine (20 mmol, 2.02 g, 2.79 mL). A solution of methanesulfonyl chloride (6 mmol, 0.46 mL) in 20 mL DCM was slowly added to the PEG solution that turned cloudy, and was stirred for 2 h at room temperature to complete the reaction of the Ms-PEG-Ms. The TEACl precipitate was filtered off, the filtrate was concentrated and precipitated in a 30-fold volume of diethyl ether. The polymer was collected by filtration Yield 60-70%. **Ms-PEG₁₀₀₀₀Ms** :¹H NMR (CDCl₃, 400MHz): δ/ppm, 3.07 (s, O-SO₂-CH₃), 3.44-3.81 (PEG, m, -O-CH₂CH₂-), 4.35-4.38 (m, CH₂-O-SO₂CH₃)

(1) H₂N-PEG-NH₂. Ms-PEG-Ms (2 g) was dissolved in 160 mL of ammonium hydroxide solution concentration 25%) and reacted at room temperature for 4 days. The flask was then left to stir in air to remove excess of ammonia and KOH was added until

the pH reached 13. The polymer was extracted in DCM, dried with MgSO₄ and concentrated before being precipitated in diethylether and collected by filtration. The resulting PEG diamine (H₂N-PEG-NH₂) was dissolved in water and dialyzed (MWCO: 1kDa) against deionized water. Finally, the polymer was lyophilized from water. Yield 71% (from HO-PEG-OH)

H₂N-PEG₁₀₀₀₀NH₂: ¹H NMR (CDCl₃, 400MHz): δ/ppm, 2.86-2.89 (m, 4H, -CH₂-NH₂), 3.45-3.83 (PEG, m, -O-CH₂CH₂-)

(2) CBz-lysine-N-carboxyanhydride (CBz-lysine-NCA). The protected CBz-lysine (CBz = carboxybenzyl protecting group) and the triphosgene were dried separately under vacuum for 30 min. The protected CBz-lysine (1 g, 3.57 mmol, 1 eq.) was suspended in 30 mL of dry THF in a schlenck tube connected to a KOH trapping solution. The solution was warmed to 50°C and a solution of triphosgene (0.481 g, 2.07 mmol, 0.58 eq) in 10 mL of THF was added. The suspension became transparent after approx. 30min and was left reacting for an additional 2 hours to complete the reaction. The reaction system was purged with nitrogen to eliminate chlorine hydride gas generated by the reaction. The CBz-lysine-NCA was poured in hexanes (200 mL) and left to crystallize at 4°C overnight. The white powder was collected and two more recrystallizations were performed to complete purification of the product. Finally, the compound was dried under vacuum. Yield 81%

¹H NMR (CDCl₃, 400MHz): δ/ppm, 7.26-7.37 (m, 5H, -C₆H₅), 6.28 (s, 1H, -CH-NH-CO-), 5.08-5.15 (m, 2H, C₆H₅-CH₂-O-), 4.83 (m, 1H, C₆H₅-CH₂-O-CO-NH₂-), 4.29 (m, 1H, CO-CH-NH), 3.15-3.28 (m, 2H, C₆H₅-CH₂-O-CO-NH₂-CH₂-), 1.41-1.59 (m, 6H, C₆H₅-CH₂-O-CO-NH₂-CH₂-(CH₂)₃-)

(3p, 4p, 5p) Protected-PLL-PEG-PLL triblock. The synthesis of the triblock copolymers was achieved by ring-opening polymerization of the protected aminoacid-NCA. Typically, a solution of **H₂N-PEG-NH₂ (1)** (0,015 mmol) in dry DCM (10 mL) was added to a 0,12 M solution of **CBz-lysine-NCA (2)** and left to stir under a nitrogen atmosphere at 25°C for 5-7 days. The solution was concentrated under reduced pressure and the polymer was precipitated in anhydrous diethyl ether. The polymer was collected by filtration. Yield ~85%. The protected triblocks polymers **(3p)**, **(4p)** and **(5p)** were obtained by varying the molar ratio **NH₂-PEG-NH₂/CBz-lysine-NCA (2)** (**(3p)** : **NH₂-PEG₃₄₀₀-NH₂/(2)** =100/1; **(4p)** : **NH₂-PEG₁₀₀₀₀-NH₂/(2)** =100/1, **(5p)** : **NH₂-PEG₁₀₀₀₀-NH₂/(2)** = 400/1).

(3p): ^1H NMR (CDCl_3 , 400MHz): δ/ppm , 7.23 (m, 5H, $-\text{C}_6\text{H}_5$), 5.47 (s, 1H, $\text{CO}-\text{CH}(\text{NH}_2)-(\text{CH}_2)_4-\text{NH}_2$), 4.99 (s, 4H, $-(\text{OCH}_2\text{CH}_2)-\text{CH}_2-\text{CH}_2-\text{NH}-$), 3.64 (PEG, m, 4H- $\text{O}-\text{CH}_2\text{CH}_2-$), 3.11 (s, 2H, $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-\text{CO}-\text{NH}_2-\text{CH}_2-$), 1.59 (m, 6H, $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-\text{CO}-\text{NH}_2-\text{CH}_2-(\text{CH}_2)_3-$)

(3, 4, 5) PLL-PEG-PLL. Typical deprotection of the polymer consisted in hydrolysing the benzyl ester by reacting 100mg of the triblock copolymer with HBr (4 mL, 33 wt% in acetic acid solution). The polymer was left reacting for approx. 1h before being collected by filtration and washed numerous times with acetone. The polymer was redissolved in a THF/water mixture and dialyzed (cellulose ester, MWCO: 1kDa). Finally, lyophilisation from water afforded a fluffy white powder. Completion of the deprotection was attested by the disappearance of the benzyl protons at 7.3 ppm in ^1H NMR. Yield ~90%.

(3): ^1H NMR (D_2O , 400MHz): δ/ppm , 4.32 (s, 1H, $\text{CO}-\text{CH}(\text{NH}_2)-(\text{CH}_2)_4-\text{NH}_2$), 3.71 (PEG, m, 4H, $-\text{O}-\text{CH}_2\text{CH}_2-$), 3.07 (s, 2H, $\text{H}_2\text{N}-\text{CH}_2-(\text{CH}_2)_3-$), 1.44-1.91 (m, 6H, $\text{H}_2\text{N}-\text{CH}_2-(\text{CH}_2)_3-$)

(6, 7) (PLL-PEG-PLL) $_n$ multiblock. The protected-PLL-PEG-PLL triblock was solubilized in 20mL of dry DCM under inert atmosphere. Separately, 1eq of polyethyleneglycol diglycidyl ether (Mw = 500 g/mol) was solubilized in dry DCM (5mL) and added in one time, and the reaction was left stirring for 2 days under ambient temperature. The polymer was precipitated in diethylether and dried for several hours. Deprotection was carried out as presented above, and the polymer was purified by dialysis. Polymers **(6)** and **(7)** were obtained by varying the concentration of initial precursors.

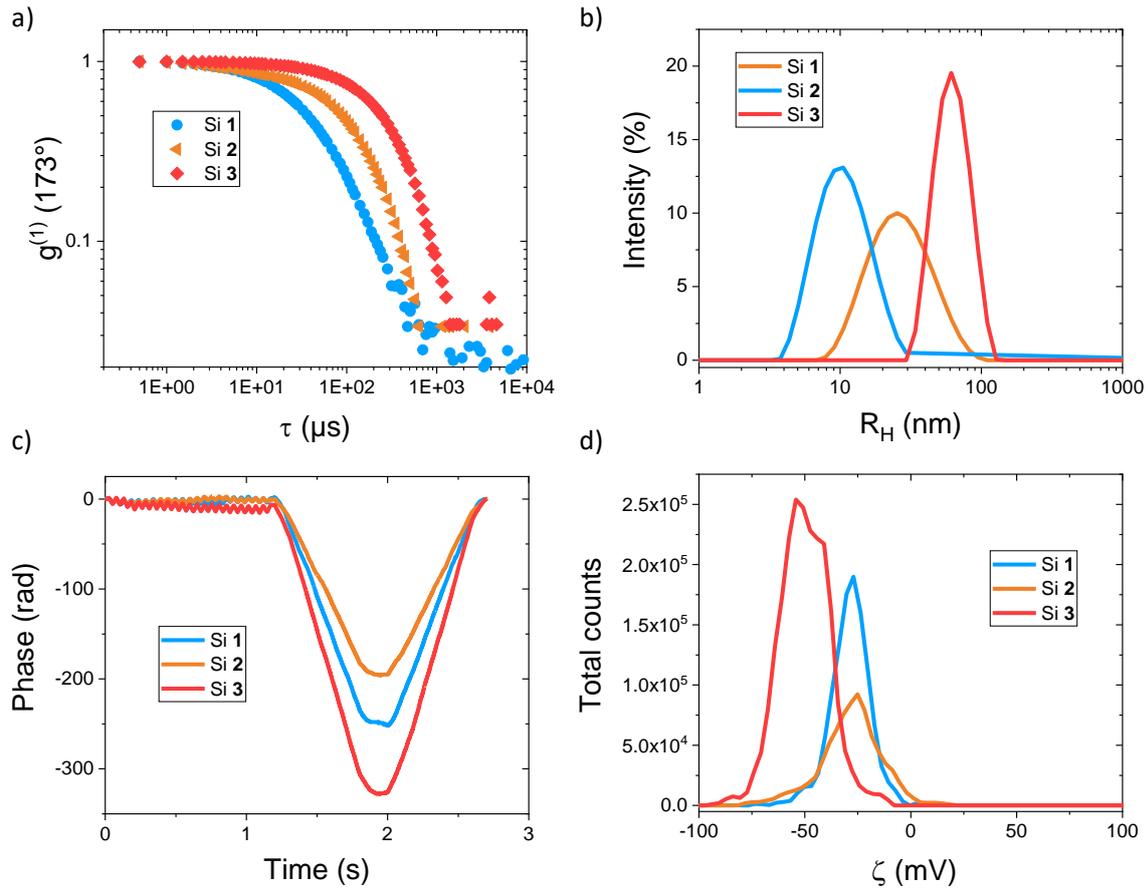


Figure S4. Characterizations of the silica nanoparticles. (a) Scattered electric field autocorrelation function and (b) corresponding size distribution of the silica nanoparticle suspensions; (c) Time evolution of the phase for electric field oscillating at 20 Hz ($t \leq 1.2$ s) and 0.2 Hz ($t > 1.2$ s); (d) Zeta potential distribution of the silica nanoparticle suspensions.

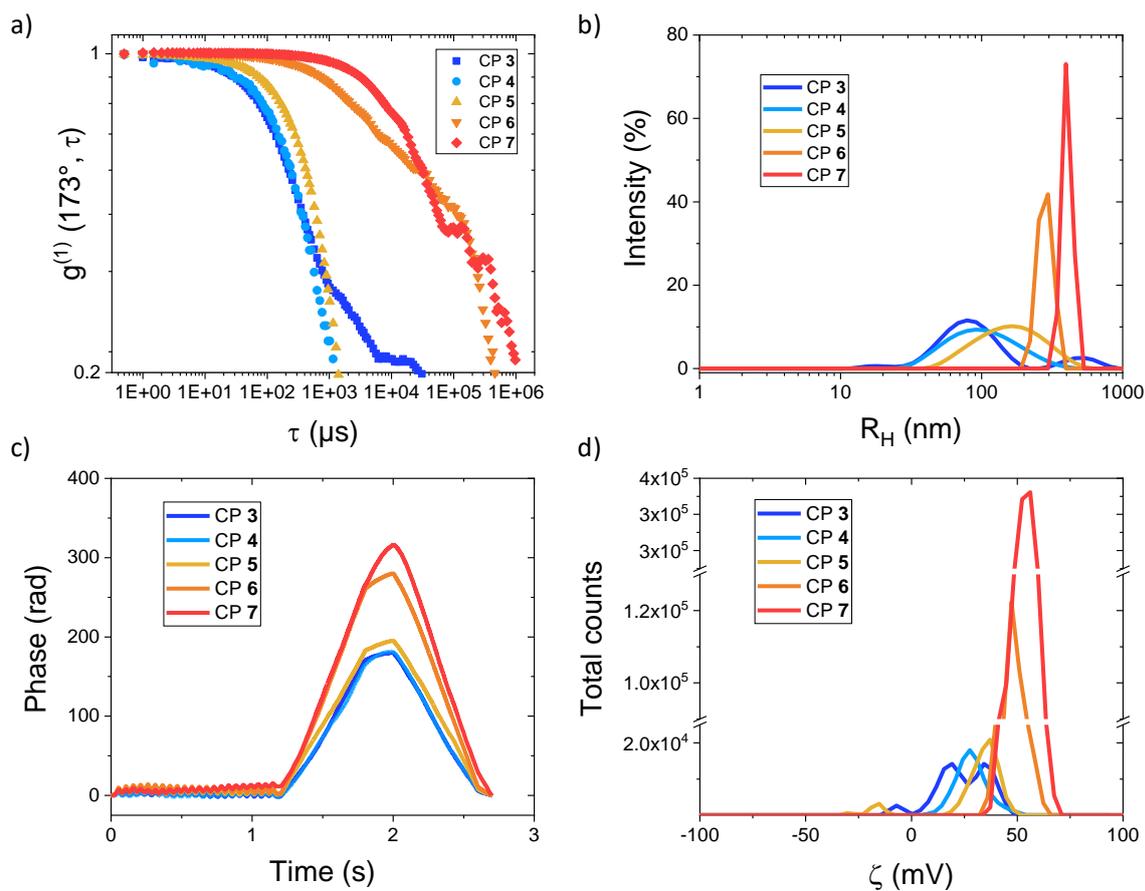


Figure S5. Characterizations of the copolymers dilute solutions ($c = 0.025$ g/L). (a) Scattered electric field autocorrelation function and (b) corresponding size distribution; (c) Time evolution of the phase for electric field oscillating at 20 Hz ($t \leq 1.2$ s) and 0.2 Hz ($t > 1.2$ s); (d) Zeta potential distribution.