Electronic Supplementary Material (ESI) for Soft Matter.

Gold Nanoparticles Endowed with Low-Temperature Colloidal Stability by Cyclic Polyethylene Glycol in Ethanol

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Experimental

Fast scanning calorimetry. FSC experiments were performed in nitrogen atmosphere by using a Flash DSC 1 of Mettler Toledo based on chip calorimetry technology and equipped with a two-stage intracooler allowing for temperature control between -90 and 450 °C. Dry AuNP@PEG 11k samples with mass about 100 ng were heated at 1000 K s^{-1} from -80 °C to 80 °C after quenching all samples from 80 °C at the same rate.

Supporting Figures

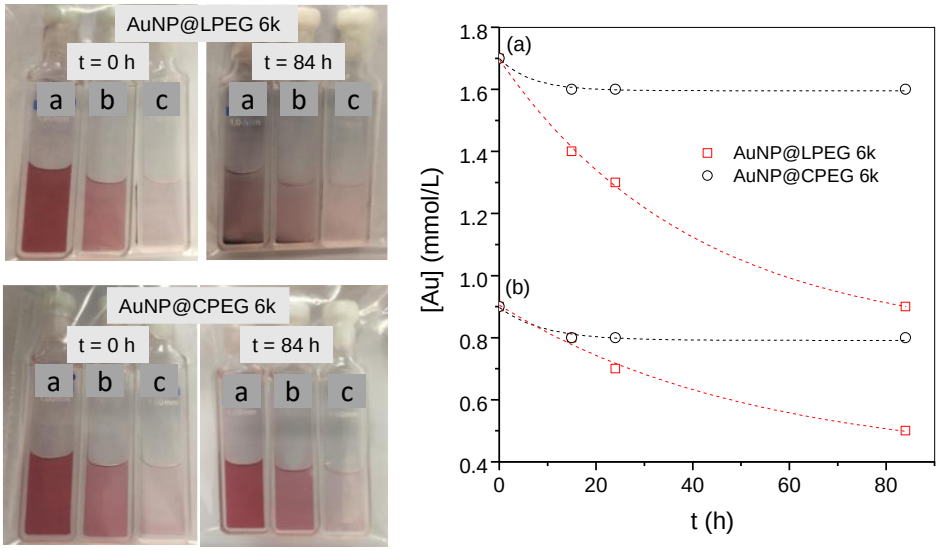


Figure S1. Left: Pictures of AuNP@LPEG 6k and AuNP@CPEG 6k dispersed in ethanol at different concentrations at the initial state and after cooling at -25 ºC in a freezer for 84 h. (a) [Auº] = 1.7 mM, (b) [Auº] = 0.9 mM and (c) [Auº] = 0.2 mM. Changes in sample (c)

were not visually observed due to the low AuNP concentration. Right: Concentration of AuNP remaining in the supernatant as a function of time, determined by UV-Vis. Note that the whole concentration of AuNP in the sample remains constant.

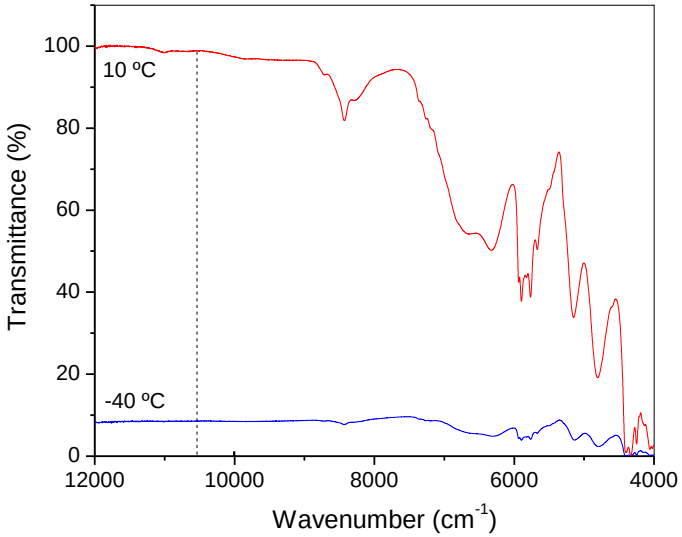


Figure S2. NIR transmittance of LPEG 6k in ethanol (5 wt%) at 10 and -40 ºC. Optical path = 1 mm. Dash line shows the wavelength (10500 cm^{-1}) at which the solution transmittance was measured as a function of temperature (see main text). The observed bands correspond to ethanol, the major component.

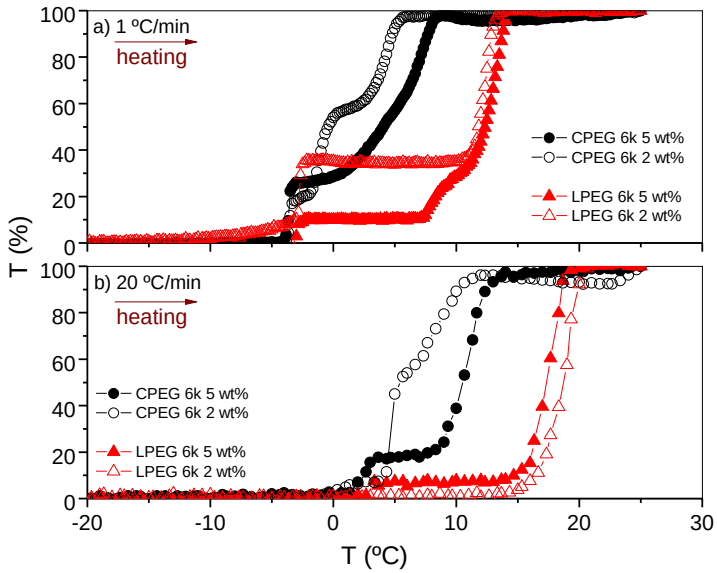


Figure S3. Solution transmittance, $T(\%)_{heating}$, of CPEG 6k and LPEG 6k in ethanol (c = 2 and 5 wt%) at heating rates of a) 1 ºC/min and b) 20 ºC/min.

Under heating, the light transmittance increases but not monotonously (Figure S3). In all cases, the transition temperature for CPEG occurs at lower temperatures than for LPEG. The steps of T (%) detected during heating are related to the different stages

visually observed during the change from the solid-like paste to a transparent liquid solution. First, a liquid starts moving and then the turbidity disappears (Figure S4). In the microscope we could detect the advance of the liquid front before the disappearance of the spherulite-like structures. These results are in line with the existence of long-range network structures in PEG/ethanol mixtures.[1]

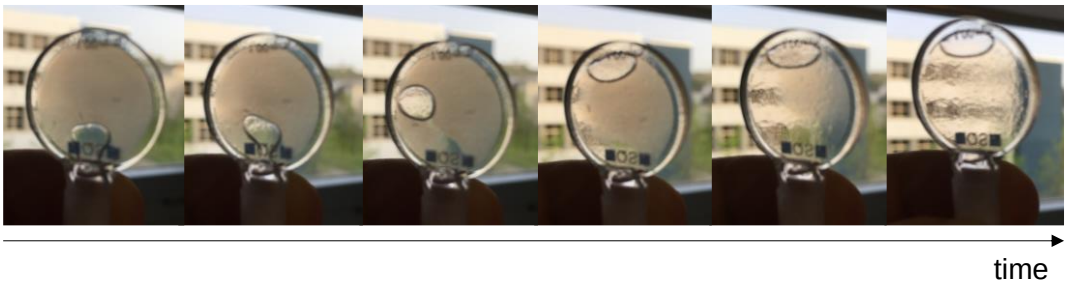


Figure S4. Pictures of CPEG 6k / ethanol (2 wt%) cooled at -60 ºC and then exposed to air to see how the solid-like paste evolve in about 1 min. First, the liquid starts to move (the bubble moves up) and then, the turbidity disappears. Droplets in the cuvette glass are due to water condensation.

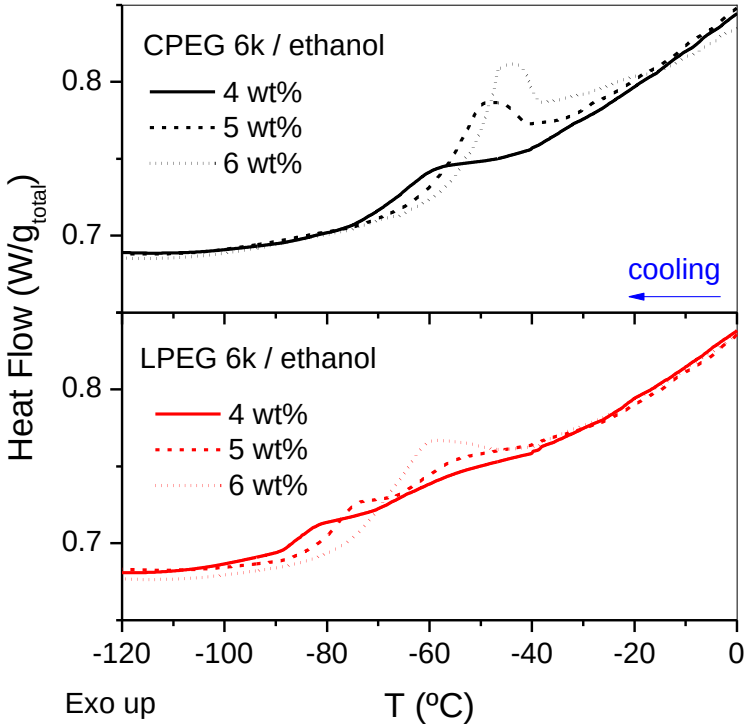


Figure S5. Cooling DSC scans (20 ºC/min) of CPEG 6k and LPEG 6k solutions in ethanol at different polymer concentrations. Heat flow is referred to the total mass of sample (PEG + ethanol). At lower polymer concentrations, a peak was difficult to detect.

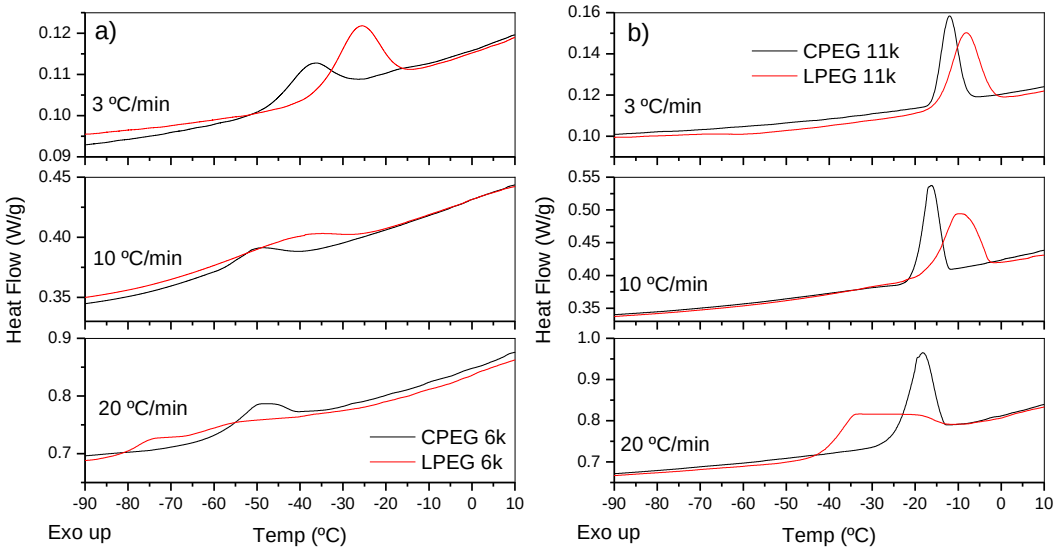
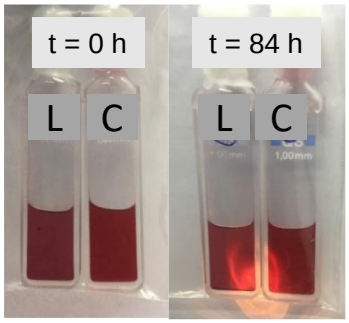


Figure S6. Cooling DSC scans of CPEG and LPEG in ethanol (5 wt%) at different cooling rates (3, 10 and 20 ºC/min). a) M_n= 6 kg/mol and b) M_n = 11 kg/mol.



L = AuNP@LPEG 6k / EtOD
C= AuNP@CPEG 6k / EtOD

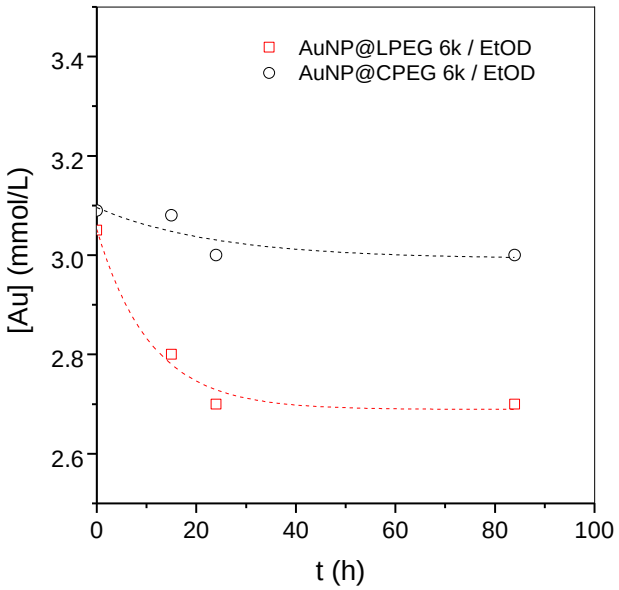


Figure S7. Left: Pictures of AuNP@LPEG 6k and AuNP@CPEG 6k dispersed in deuterated ethanol (EtOD) at the initial state and after cooling at -25 ºC in a freezer for 84 h. Right: Concentration of AuNP remaining in the supernatant as a function of time, determined by UV-Vis. Note that the whole concentration of AuNP in the sample remains constant.

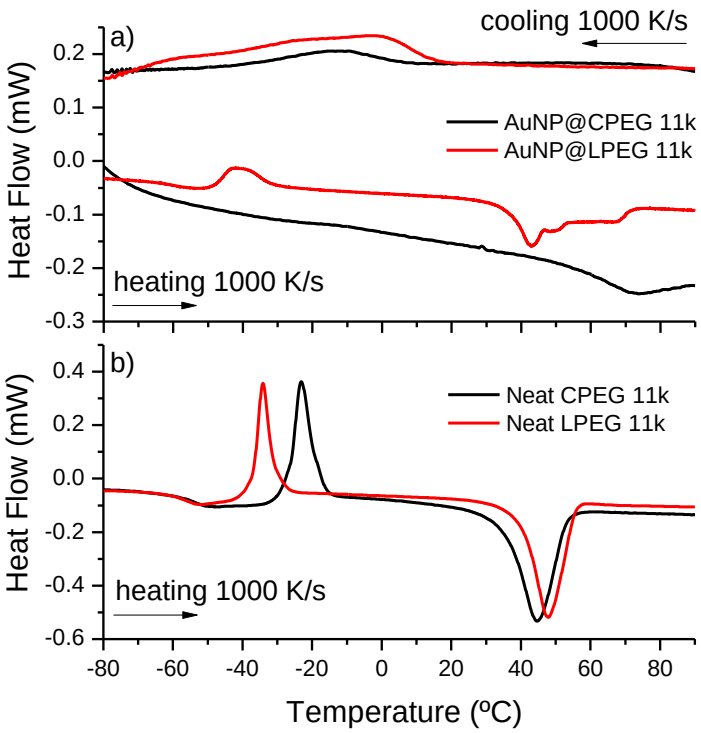


Figure S8. a) FSC data of dry AuNP@CPEG 11k and AuNP@LPEG 11k obtained by cooling and heating at 1000 K/s. b) Heating run of neat CPEG and LPEG 11k samples.

References

1. D. L. Ho, B. Hammouda, S. R. Kline and W.-R. Chen, *J. Polym. Sci. B Polym. Phys.*, 2006, **44**, 557-564.