Supplementary Material (ESI) for Chemical Communications
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Supporting Information for

Thermoresponsive poly(*N*-vinyl caprolactam)-coated Gold nanoparticles: sharp reversible response and easy tunability.

Mariana Beija[†], Jean-Daniel Marty[†]* and Mathias Destarac[‡]*

[†]*Laboratoire IMRCP, CNRS UMR 5623,University of Toulouse, 118 route de Narbonne, 31062 Toulouse, France.* [‡]*Laboratoire HFA, CNRS UMR 5069, University of Toulouse,* 1 18 route de Narbonne, 31062 Toulouse, France.

e-mails: marty@chimie.ups-tlse.fr; destarac@chimie.ups-tlse.fr

A – Experimental Part

Materials. *N*-vinyl caprolactam (98%, VCL) was supplied from Aldrich and distilled over hydroquinone. The MADIX agent, *O*-ethyl-*S*-(1-methoxycarbonyl) ethyl-dithiocarbonate (Rhodixan A1) was obtained from Rhodia and used as received and the 2,2'-azobis-(isobutyronitrile) initiator (98%, AIBN) was purchased from Janssen Chimica and recrystallized from ethanol. 1,4-dioxane (99%, Sigma-Aldrich) was distilled before use. Tetrachloroauric acid trihydrate ($HAuCl_4$, $3H_2O$), sodium borohydride ($NaBH_4$), sodium chloride (NaCl) and sodium hydroxide (NaOH) were purchased from Aldrich and were used without further purification. Using a Purite device, water was purified through a filter and ion exchange resin (resistivity ≈ 16 MΩ.cm).

Polymer synthesis. A typical procedure for the synthesis of PVCL is as follows: VCL (1 g; 7.2 mmol), Rhodixan A1 (11 mg; 0.05 mmol), AIBN (1.7 mg; 0.01 mmol) and 1,4-dioxane (2 g) are placed in a Schlenk flask equipped with a magnetic stirrer. The solution is then degassed by four freeze-pump-thaw cycles and set under argon atmosphere. It is then heated at 60 °C for several hours and samples are periodically withdrawn from the polymerization medium for determination of monomer conversion by ^{1}H NMR. The polymerization is stopped by quenching in liquid nitrogen. The PVCL samples are then purified by precipitation in hexane and recovered by filtration.

Characterization of polymer samples. Number-average molecular weights (M_n) and dispersities ($Đ$) were determined by size-exclusion chromathography (SEC) in THF flow rate: 1 mL min^{-1}) using two Shodex KF804 and KF802.5 columns (8 mm×300 mm, 6-7 µm) on an apparatus comprising a Waters 2414 refractive index detector (35 ºC), a three-angle (47º, 90º, 130º) light scattering detector (MiniDAWN, Wyatt, operating at 690 nm) and a viscometer (Viscostar II, Wyatt). ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz.

Determination of cloud points. Transmittance of polymer aqueous solutions at 700 nm with increasing temperature was recorded by a Cary 100 Bio spectrophotometer (3 cycles; heating/cooling rate: 1 °C min^{-1}). Because the responses were very sharp, the cloud points were taken from the onset of the transmittance decrease.

Absorption spectra. To follow the changes in the surface plasmon band (SPB) of AuNPs as a function of temperature, absorption spectra of aqueous dispersions of Au@PVCL were recorded between 400 and 800 nm at increasing temperatures (from 20 to 55 ºC). The influence of the solution turbidity was removed by first subtracting the increase in absorbance at 800 nm, then by normalizing the curves at 400 nm and multiplying by a factor in a way that these absorbances vary from 1 to 0.

Formation of AuNPs. Preformed NPs were synthesized as previously described. Briefly, to 5 mL of a 1×10^{-2} mol L^{-1} $HAuCl_4$ solution were added 94 mL of distilled water and 250 µL of a 1 mol L^{-1} aqueous solution of sodium hydroxide. Then, the pH was adjusted (if necessary) around 7.5-8 and 500 µL of a fresh $NaBH_4$ solution (0.1 mol L^{-1}) were subsequently added under manual stirring. The solution color immediately turned into dark red, indicating the formation of AuNPs.

Coating of Preformed NPs. Typically, for a final polymer concentration of 0.1 wt.%, 0.9 mL of deionized water and 0.1 mL of a 1 wt.% aqueous stock solution of polymer were added to 1 mL of an aqueous AuNPs stock solution ($[Au^0]=5\times10^{-4}$ mol L^{-1}) to yield coated AuNPs.

Dynamic Light Scattering measurements (DLS). DLS measurements were carried out at different temperatures with a Malvern Instrument Nano-ZS equipped with a He-Ne laser (λ = 633 nm). Samples were introduced into cells (pathway: 10 mm) after filtration through 0.45 µm PTFE micro-filters. The correlation function was analyzed via the general purpose method (NNLS) to obtain the distribution of diffusion coefficients *(D)* of the solutes, and then the apparent equivalent hydrodynamic diameter ($<D_h>$) was determined using the Stokes–Einstein equation. Mean diameter values were obtained from three different runs. Standard deviations were evaluated from hydrodynamic diameter distribution.

Transmission Electron Microscopy (TEM). A drop of the aqueous dispersion was placed on a carbon-coated copper TEM grid and left to dry under air. Then, the samples were negatively stained. The TEM grid was successively placed on a drop of the sample solution for 2 min, on a drop of an aqueous solution of uranyl acetate (2 wt.%, 2 min) and finally on a drop of distilled water, after which the grid was then air-dried before introduction into the electron microscope. The samples were viewed with a HITACHI HU12 operating at 70 kV. Size distribution was determined by manual counting on ca. 100 particles, using WCIF Image J software.

B – Polymer Synthesis and Characterization

In order to prepare PVCL samples of different M_n, polymerizations were carried out using fixed concentrations of monomer and AIBN and varying concentrations of Rhodixan A1 (Table S1).

Table S1. Polymerization conditions and results for the synthesis of PVCL samples in 1,4-dioxane at 60 °C. [VCL]=3.7 M; [AIBN]=5.2 mM.

Sample	$[Rhodixan\ A1]_0$ (mM)	$M_{n,target}$ (g mol^{-1})[a]	t(h)	Conv. (%)	$M_{n,theor}$ (g mol^{-1})[b]	$M_{n,exp}$ (g mol^{-1})[c]	$Đ$[c]
$PVCL_{18k}$	27	19 500	20	83	16 000	18 000	1.1
$PVCL_{50k}$	11	48 000	20	93	45 000	50 000	1.1
$PVCL_{71k}$	5.7	92 000	20	89	80 000	71 000	1.2
$PVCL_{148k}$	3.3	155 000	20	97	150 000	150 000	1.1

[a] $M_{n,target}=([VCL]_0/[Rhodixan\ A1]_0)\times MW_{VCL}+ MW_{Rhodixan\ A1}$
[b] $M_{n,theor}=([VCL]_0/[Rhodixan\ A1]_0)\times conversion\times MW_{VCL} + MW_{Rhodixan\ A1}$
[c] Determined by SEC-MALS in THF. dn/dC (PVCL)=0.109 mL g^{-1}.

Although high conversions were obtained after 20 h of polymerization, the polymerization kinetics was retarded for increasing $[Rhodixan\ A1]_0$ as also reported by Wan et al. (Figure S1).[1] By contrast, no induction period was observed with the Rhodixan A1 MADIX agent.

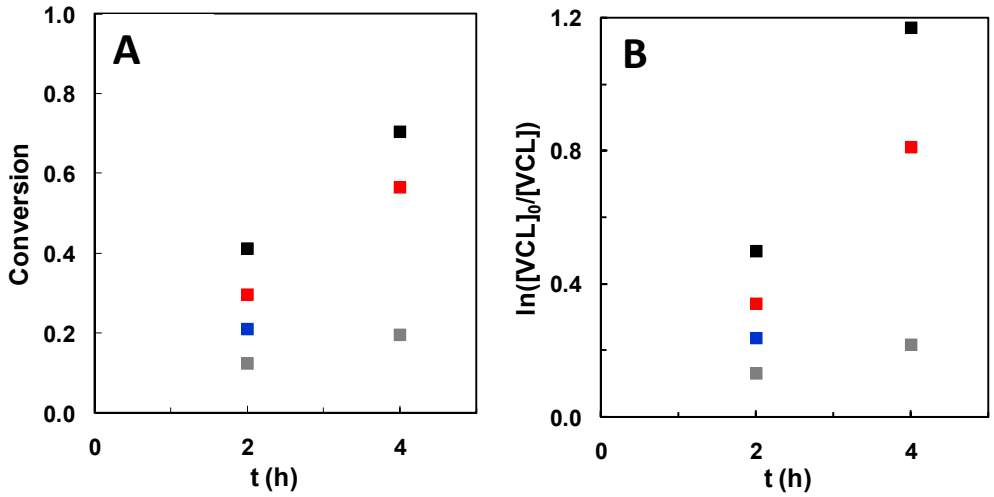

Figure S1. (**A**) Time evolution of VCL conversion and (**B**) pseudo-first order kinetics plots for the polymerization of VCL in 1,4-dioxane initiated by AIBN at 60 °C, with $M_{n,target}$=10 000 g mol^{-1} (■); 19 500 g mol^{-1} (■); 48 000 g mol^{-1} (■); 92 000 g mol^{-1} (■) and 155 000 g mol^{-1} (■).[VCL]=3.7 M; [AIBN]=5.2 mM.

The experimental M_n values were very close to those theoretically predicted and the dispersities of the polymer samples were very low ($Đ$<1.2, Table S1). However, it is important to note that the characterization of PVCL by SEC is not simple since in most eluents, the separation is also driven by some affinity to the stationary phase. Thus, when using calibration curves some deviations can be observed. Figure S2 shows the M_n values obtained by both SEC/RI-MALS and by SEC/RI-

viscometer. An evident a downward curvature deviation from linearity over the course of the polymerization was observed for the M_n values obtained by SEC/RI-viscometer detection.

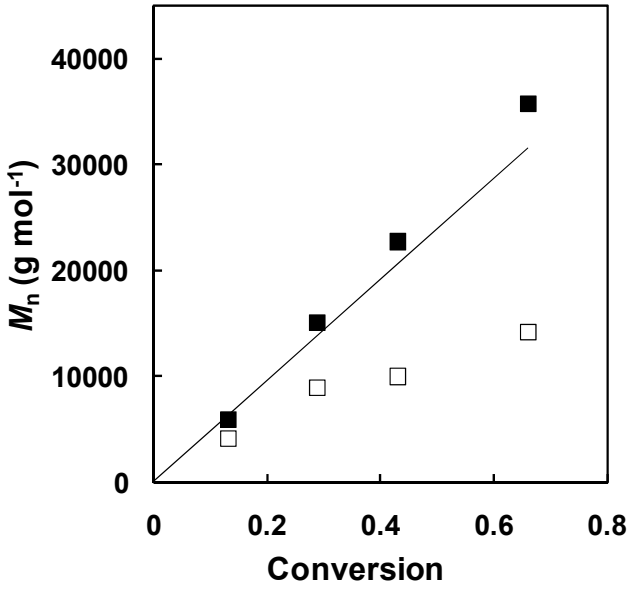

Figure S2. Evolution of M_n with monomer conversion for the MADIX polymerization of VCL in 1,4-dioxane at 60 °C mediated by Rhodixan A1 and initiated by AIBN. [VCL]=3.7 M; [AIBN]=5.2 mM; [Rhodixan A1]=12 mM. Molecular weight characterization by SEC/RI-MALS (■) and by SEC/RI-viscometer(□). The solid line represents the dependence of theoretical M_n on monomer conversion.

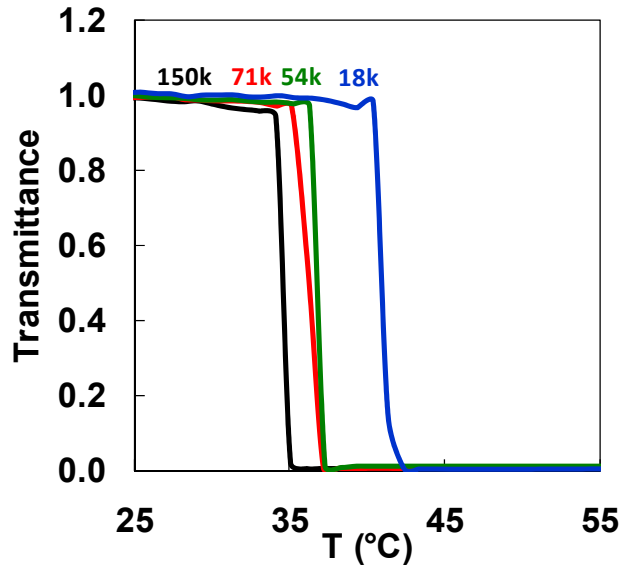

Figure S3. Turbidimetry curves of aqueous solutions of PVCL samples with controlled M_n at [PVCL] = 0.5 wt% and heating rate=1 °C min^{-1}.

C – Nanohybrids characterization

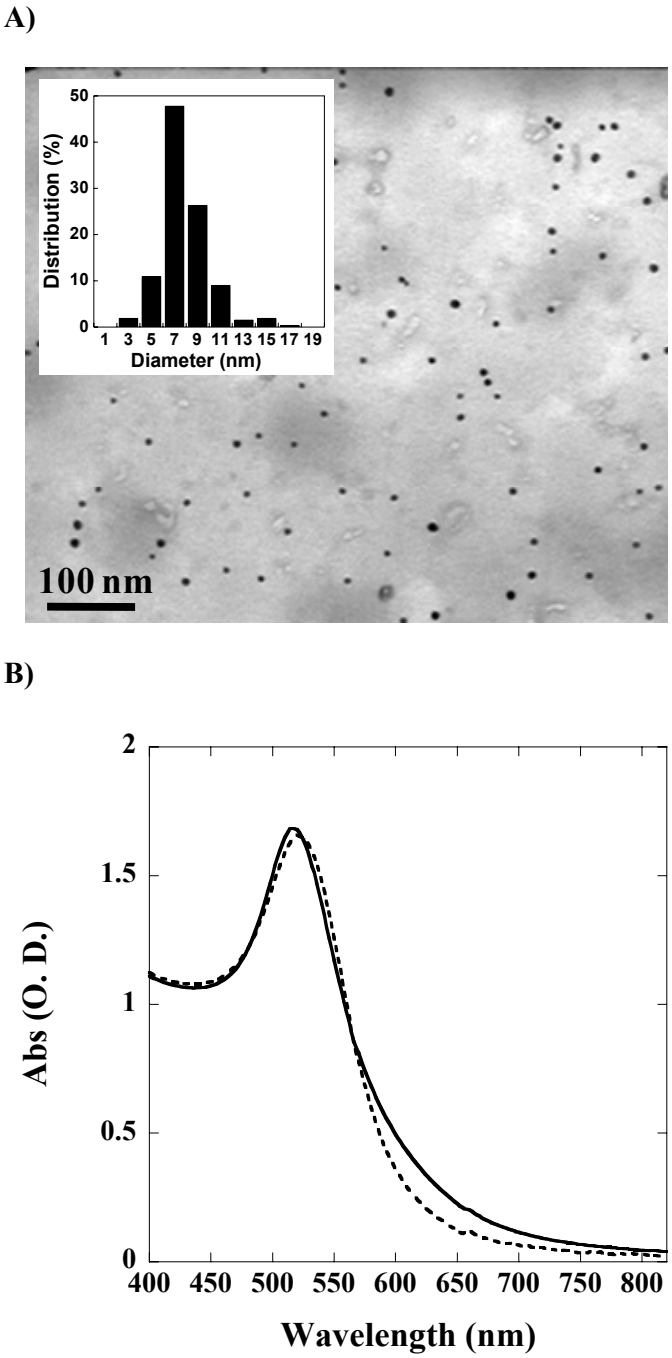

Figure S4. A) Representative TEM image and analysis of preformed AuNPs (synthesized by reduction of $HAuCl_4$ solutions (5×10^{-4} mol·L^{-1}) with one equivalent of $NaBH_4$). Mean diameter: 7.9 ± 2.3 nm. B) UV-vis spectra of colloidal dispersions of AuNPs synthesized by reduction of $HAuCl_4$ solutions (5×10^{-4} mol·L^{-1}) with one equivalent of $NaBH_4$ obtained after 1 hour (solid line) and 1 month (dotted line).

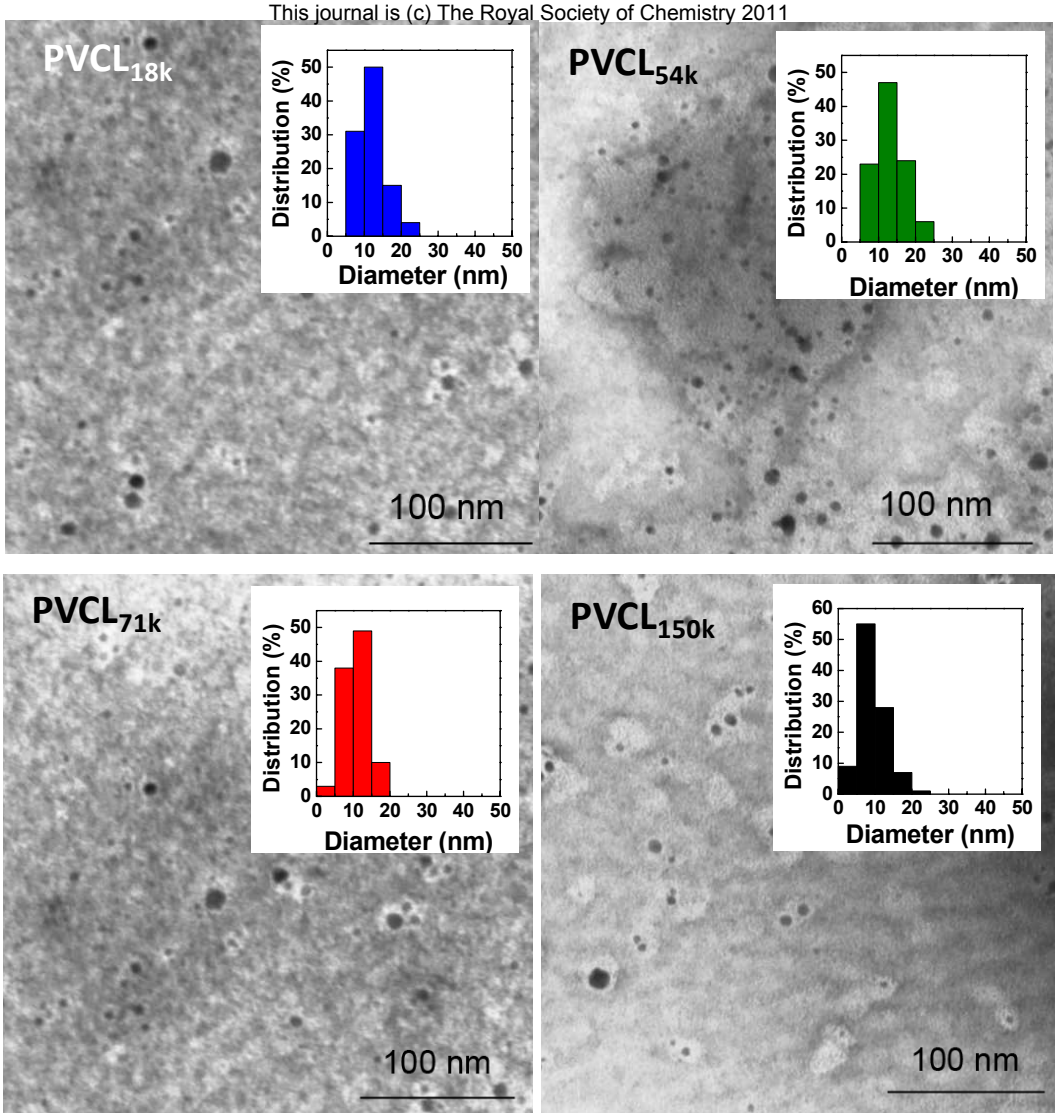

Figure S5. TEM images and distribution of Au@PVCL nanohybrids. Size distribution was determined by manual counting on ca. 100 particles

DLS measurements.

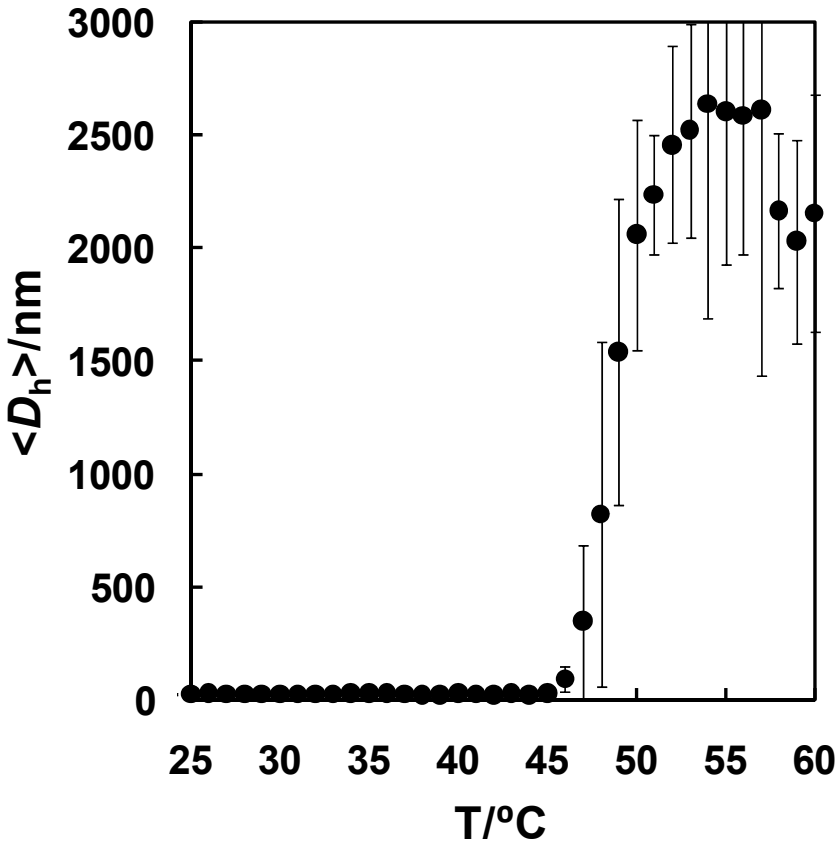

Figure S6. Variation of hydrodynamic radius of Au@$PVCL_{18k}$ nanohybrids at [PVCL] = 0.02 wt% obtained while heating. The errors correspond to the dispersity of particles multiplied by hydrodynamic radius.

Additional turbidimetry measurements.

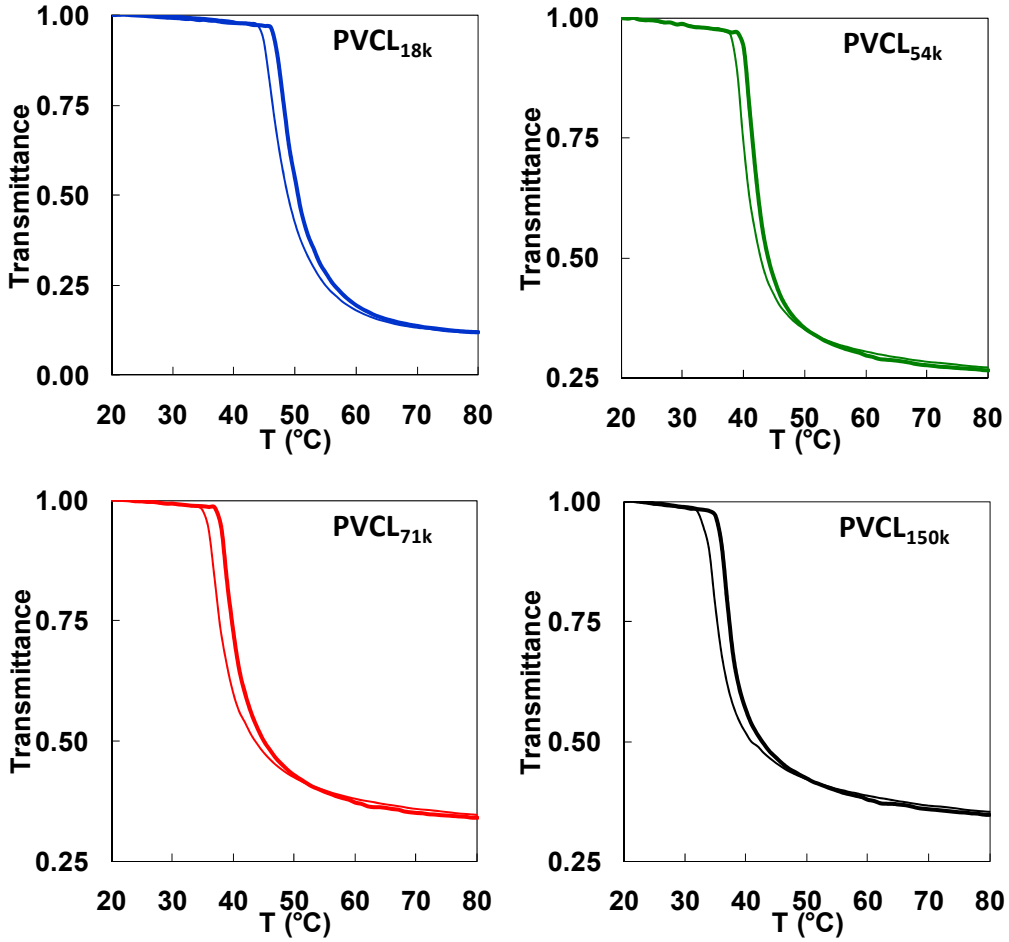

Figure S7. Turbidimetry curves of aqueous solutions of Au@PVCL nanohybrids coated with PVCL with controlled M_n at [PVCL] = 0.02 wt% obtained while heating (heavy lines) and cooling (solid lines), showing the very low hysteresis of the system. Heating/cooling rate=1 °C min^{-1}