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Effect of copolymer composition of controlled (*N*-vinylcaprolactam/*N*-vinylpyrrolidone) statistical copolymers on formation, stabilization, thermoresponsiveness and catalytic properties of gold nanoparticles

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Highlights

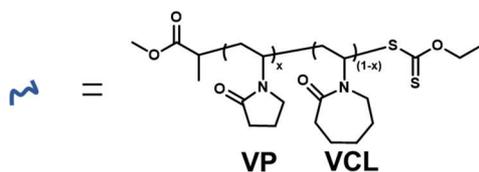
- A series of P(VCL/VP)_{20k} statistical copolymers of different compositions were used to prepare gold nanohybrids either from preformed gold nanoparticles or by an *in situ* approach.
- Increasing the fraction of VCL in copolymer promotes its ability to act as efficient growth control agent of gold nanoparticles.
- Thermoresponsiveness, colloidal stability and catalytic properties of obtained AuNPs@P(VCL/VP) can be tuned by adjusting VP and VCL content.

Abstract

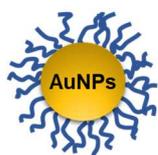
The insertion of an increasing amount of *N*-vinylpyrrolidone (VP) in statistical copolymers based on thermoresponsive poly(*N*-vinylcaprolactam) (PVCL) enables one to modulate the properties of the copolymer and those of the corresponding AuNPs-polymer hybrid materials. The incorporation of VP not only affects the growth of gold nanoparticles synthesized in the presence of the polymers (*in situ* route), but also the properties (stabilization, optical, catalytic...) of preformed nanoparticles coated by these polymers. Hence, at a molar fraction of VP in copolymer less than 40%, it was possible to increase the transition temperature of the hybrid material and improve its catalytic properties compared to counterparts comprising PVP and PVCL homopolymers. The structural difference of the two monomers allows the best compromise between the hydration level and the

interaction strength of the copolymer with the surface of gold particles for a chosen application.

Graphical abstract



Effect of copolymer composition on:



Stability ?
Thermoresponsiveness ?
Catalytic properties ?

Keywords. nanohybrids, thermoresponsive polymer, poly(*N*-vinylpyrrolidone), poly(*N*-vinylcaprolactam), gold nanoparticles

1. Introduction

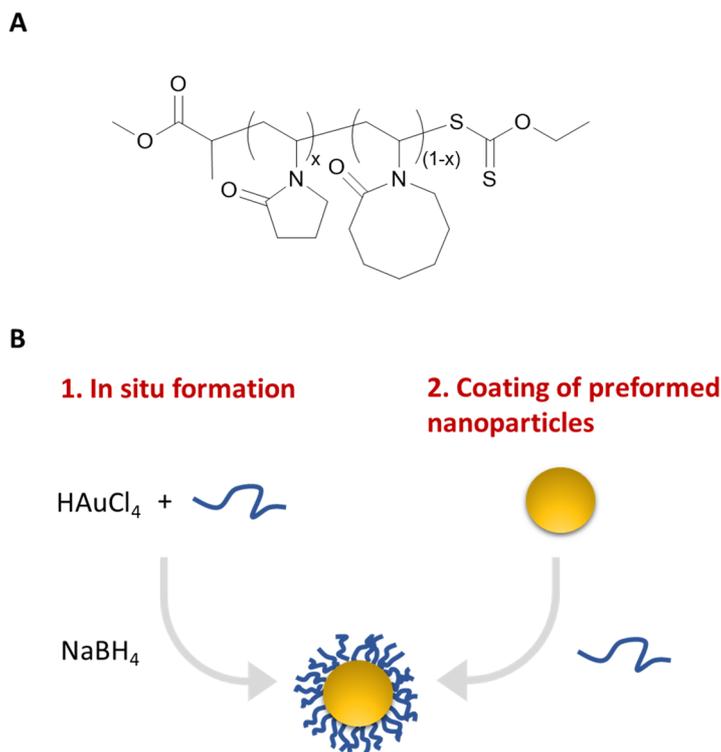
Metal nanoparticles,[1] especially gold nanoparticles (AuNPs), have attracted much attention because of their unique electronic, optical and catalytic properties resulting in their wide application ranging from optoelectronics to biology.[2-3] These properties strongly depend on the particle size and shape, the nature of the protecting organic shell and the interparticle distance.[4] AuNPs are colloiddally unstable and are susceptible to irreversible aggregation. To stabilize them, they can be coated with small organic molecules such as citrates, surfactants, ligands or polymers. These organic molecules provide an additional tool to modulate physico-chemical properties. To this end, polymers have proved to be a material of choice due to their flexibility for tailoring specific uses and also for their greater long-term stabilizing properties compared to small molecules such as citrates. Notable examples include responsive polymers. Indeed, coating AuNPs with stimuli-responsive is a convenient way to change reversibly the properties of AuNPs. Thermoresponsive polymers of LCST-type have been grafted on AuNPs without losing their thermoresponsiveness.[5-9]

Such hybrid materials can be obtained through the grafting or adsorption of a thermoresponsive polymer around AuNPs. This confers to the obtained hybrid material not only a steric stability, but also a capacity to control the NPs properties (drug delivery, optical, catalytic properties...) in response to a change of temperature.[10-12] Hence different families of thermoresponsive polymers like poly(*N*-isopropylacrylamide),[13-18] poly(methyl vinyl ether),[19] poly(*N*-acryloyl-*N'*-propyl piperazine)[20] and copolymers based on oligo(ethylene glycol) (meth)acrylate[21-23] or poly(*N*-vinyl caprolactam) (PVCL)[24, 25] were used to obtain such hybrids. The use of this last family is of special interest for the formation of hybrid nanoparticles presenting a sharp reversible response to temperature. Moreover, the cloud point temperature of PVCL and corresponding hybrid materials can be easily tuned either by adjusting polymer chain length or by changing its concentration.[24]

PVCL belongs to the family of poly(*N*-vinyl lactams) like poly(*N*-vinylpyrrolidone) (PVP), which is not thermoresponsive but is one of the most commonly used polymers for the stabilization of NPs of different nature for diverse applications.[26] The structure of *N*-vinylcaprolactam (VCL) monomer only differs from *N*-vinyl pyrrolidone (VP) by the inclusion of two additional methylene groups. Reversible-

deactivation radical polymerization has recently made it possible to synthesize copolymers of VCL and VP of controlled architecture and tunable thermoresponsive properties.[25, 27-29] Detrembleur and coworkers synthesized PVCL-*b*-P(VCL-*stat*-VP)-*b*-PVCL with adjustable hydration/dehydration properties by cobalt-mediated radical polymerization followed by a radical coupling reaction, and then studied their solution behavior.[28, 29] Hoogenboom et al. have used reversible addition-fragmentation chain transfer (RAFT)-derived P(VCL-*stat*-VP) to stabilize preformed AuNPs surrounded by citrate via a 'grafting to' approach. The polymer-coated AuNPs showed a larger hydrodynamic size in comparison to pristine citrate@AuNPs. In presence of 0.1 M NaCl, a color change depending on the copolymer composition and ultimately on the cloud point temperature of the polymers was observed.[25]

The objective of this paper is to study the influence of composition of narrowly dispersed VCL/VP statistical copolymers of controlled molar mass for the formation, stabilization and modulation of the properties of AuNPs. For this purpose, a series of VCL/VP statistical copolymers containing different amounts of VP (between 0 and 100%) was synthesized by RAFT/MADIX polymerization (MADIX standing for Macromolecular design by interchange of xanthates). The effect of the copolymer composition was evaluated, as shown in **Scheme 1**, both on the growth of gold nanoparticles synthesized in the presence of the polymers (*in situ* route) or on the properties (stabilization, optical, catalytic...) of preformed nanoparticles coated by these polymers.



Scheme 1. A) Structure of copolymer and B) the two synthetic pathways used for the formation of nanohybrids (*in situ* formation and coating of preformed nanoparticles).

Materials and methods

2.1. Materials

Sodium tetrachloroaurate dihydrate ($\text{AuCl}_4\text{Na}\cdot 2\text{H}_2\text{O}$) and sodium borohydride (NaBH_4) were purchased from Aldrich and were used without further purification. 1,4-dioxane (Aldrich, 99%) was passed through basic alumina to remove BHT inhibitor prior to polymerization, *N*-vinylcaprolactam (VCL, Aldrich, 98%) and *N*-vinylpyrrolidone (VP, Aldrich, > 99%) were both distilled over CaH_2 and stored under argon prior to use. 2,2'-azobisisobutyronitrile (AIBN, Fluka, 98%) was recrystallized twice from methanol. O-ethyl-S-(1-methoxycarbonyl)-ethylthiocarbonate (X1) was synthesized as previously described.[30] Ultrapure water ($\rho = 18 \text{ M}\Omega\cdot\text{cm}^{-1}$) was obtained from Aquadem apparatus.

2.2. General procedure for the synthesis of a $P(\text{VCL}/\text{VP})_{20k, 25/75}$

A Schlenk tube containing VP (1.54 g, 1.4 mmol), AIBN (6.8 mg, 0.041 mmol), X1 (21 mg, 0.1 mmol), VCL (0.51 g, 3.7 mmol) and dioxane (4.12 g) was degassed by

three freeze-pump-thaw cycles, place under argon flow and heated at 65 °C for 20h in an oil bath. After cooling down to room temperature, the polymerization was stopped and the solution was precipitated in diethyl ether. The precipitated polymer was dried under vacuum and analyzed by SEC-RI-MALS in THF and DMF-LiBr to determine \underline{M}_n and dispersity.

2.3. Characterization of synthesized polymers

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 at 400.13 MHz and at 100.61 MHz, respectively. Number-average molecular weights (\underline{M}_n) and dispersities (Đ) of copolymers were determined in THF by size exclusion chromatography (SEC) on an apparatus equipped with a multi-angle light scattering (MALS) detector MiniDawn TREOS (Wyatt Technology Corporation), a Waters 2414 refractive index (RI) detector and a set of 2 Shodex columns (K-804L, K-802.5) at a flow rate of 1 mL·min⁻¹. Alternatively, samples were analyzed in DMF-LiBr (10 mM) comprising a Waters 410 refractive index detector, a Varian ProStar 325 UV, a MiniDawn TREOS and a set of two Shodex K-805 L columns. All polymer concentrations were calculated as % weight/weight (w/w).

The thermal properties of the copolymers in solution were determined by Differential Scanning Calorimetry (DSC) using a Mettler Toledo DSC 1 STARe System Thermal Analysis calorimeter equipped with a Gas Controller GC200. Solution samples were sealed in impermeable crucibles of 120 μL . Transition temperatures were taken at the top of the peak on the thermogram on heating after extrapolation of the values obtained at different heating rates to 0 °C·min⁻¹. The variation of enthalpy was measured as the temperature increased at a rate of 1 °C·min⁻¹.

Transmittance of polymer aqueous solutions was recorded at 500 nm and different temperatures with a Cary 100 Bio spectrophotometer at different heating/cooling rates (0.5, 1, 2.5 and 5 °C·min⁻¹). Cloud point temperatures were calculated from the determination of inflection point of each transmittance curve, extrapolated to 0 °C·min⁻¹. For Transmission Electron Microscopy (TEM) measurements, a drop of solution was placed on a formvar carbon-coated copper TEM grid (200 mesh, Ted Pella Inc.) and dried. A Hitachi HT7700 transmission electron microscope operating at 80 kV accelerating voltage was used. Obtained images were analyzed using WCIF Image J software and confidence intervals were given as average diameter \pm standard

deviation. Hydrodynamic diameter was determined via Dynamic Light Scattering measurements (DLS) using a Zetasizer Nano-ZS (Malvern Instruments, France). The reported apparent equivalent hydrodynamic diameter (D_h) is obtained by analysing measured correlation function (on 5 different samples) via non-negative least square algorithm and using the Stokes-Einstein equation.

2.4. Formation of nanohybrids

2.4.1. *In situ* formation of nanohybrids

The *in-situ* formation was performed by addition of a NaBH_4 solution (final concentration equal to $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) upon a mixture of an HAuCl_4 solution (final concentration equal to $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) and polymer at different concentrations (10^{-3} , 10^{-2} , 0.1 and 0.5 wt.%) under vigorous stirring. The color of the solution turned immediately from pale yellow to red or pale yellow depending on the nature of the polymer and its concentration. The nanohybrids were purified by dialysis before further analysis.

2.4.2. Coating of preformed nanoparticles

Preformed AuNPs were prepared by the addition to 0.5 mL of a AuCl_4Na solution ($10^{-2} \text{ mol} \cdot \text{L}^{-1}$), 9.4 mL of MilliQ water and 25 μL of an aqueous solution of sodium hydroxide ($1 \text{ mol} \cdot \text{L}^{-1}$) of 50 μL a fresh NaBH_4 solution ($0.1 \text{ mol} \cdot \text{L}^{-1}$) under vigorous stirring. The solution turned immediately dark red, indicating the formation of AuNPs. These colloidal solutions were stable but rapidly aggregated by addition of salt. Then, a series of stock aqueous solutions of copolymer solutions at 2×10^{-3} , 2×10^{-2} , 0.1, 0.2 wt.% and a stock solution of preformed AuNPs at $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ were prepared separately. Experiments were performed using a 96-well plate (Costar 96) with a well final volume equal to 200 μL . Typically, 100 μL aliquots of a AuNPs solution were introduced in each well then completed with an appropriate volume of an aqueous polymer solution to reach the chosen final concentration. This experiment was repeated for the different polymer compositions. After a brief shaking of the plate, UV-vis spectra were recorded ($[\text{polymer}]_{\text{final}} = 10^{-4}$, 10^{-3} , 5×10^{-3} or 10^{-2} wt.% and $[\text{Au}^0]_{\text{final}} = 2.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$). In order to test the colloidal stability of the obtained nanohybrids, the same experiments were repeated with a complementary addition of

NaOH (stability in basic conditions) or by adding 40 μL of a 5 $\text{mol}\cdot\text{L}^{-1}$ NaCl aqueous solution (effect of ionic strength) in complement to the other reactants.

2.5. Catalytic efficiency

The kinetics of reduction of *p*-nitrophenol to *p*-aminophenol was monitored by *in situ* UV-vis spectroscopy. In a standard quartz cuvette, 1730 μL deionized water and 200 μL AuNPs (0.5 $\text{mol}\cdot\text{L}^{-1}$) were mixed with 10 μL polymer solution (1%) under continuous stirring, the catalyst of Au@polymer was therefore obtained. Then 20 μL *p*-nitrophenol (10⁻² $\text{mol}\cdot\text{L}^{-1}$) was injected into the mixture. After 10 min of equilibrium at a given temperature, 60 μL fresh NaBH₄ solution (0.1 $\text{mol}\cdot\text{L}^{-1}$) was added quickly to start the catalytic reaction. Meanwhile, the UV-vis spectra were recorded in the range of 200 - 700 nm at an interval of 30s. The kinetic constant of reduction was determined by absorbance change of band at 400 nm where the phenolate form of *p*-nitrophenol were (the NaBH₄ provided basic environment). The final concentration of Au, *p*-nitrophenol, NaBH₄ and polymer were 5 \times 10⁻⁵ $\text{mol}\cdot\text{L}^{-1}$, 10⁻⁴ $\text{mol}\cdot\text{L}^{-1}$, 3 $\text{mol}\cdot\text{L}^{-1}$ and 5 \cdot 10⁻³%, respectively.

3. Results and discussion

3.1. Polymer synthesis and characterization

A series of statistical copolymers of VCL and VP of predetermined M_n (20000 $\text{g}\cdot\text{mol}^{-1}$) and compositions was synthesized by RAFT/MADIX polymerization as previously described,[27] taking advantage of the adequate reactivity of xanthates towards *N*-vinyl monomers. Their properties in aqueous solution were determined by differential scanning calorimetry (DSC). The main characteristics of the synthesized copolymers are summarized in **Table 1** (see **Fig. S1-S4**).

Table 1. Copolymer composition and main characteristics of the polymers.

| Entry | Theoretical copolymer structure | Composition ^a | | $\frac{M_n}{\text{THF(DMF)}}$ | Dispersity $\frac{D}{\text{THF(DMF)}}$ | DSC (solution 2%) ^c | |
|-------|---------------------------------|--------------------------|--------------------|-------------------------------|--|--------------------------------|---|
| | | VCL/VP weight ratio | VCL/VP molar ratio | | | T _c (°C) | ΔH (J \cdot g ⁻¹ of VCL) |
| 1 | PVCL | 100/00 | 100/00 | 14350 | 1.09 | 36.7 | -30 |
| 2 | P(VCL/VP) _{75/25} | 75/25 | 70/30 | 16000 (13850) | 1.04 (1.12) | 50.8 | -8 |
| 3 | P(VCL/VP) _{60/40} | 63/37 | 58/42 | 17000 (18500) | 1.04 (1.19) | 62.0 | -3 |
| 4 | P(VCL/VP) _{50/50} | 51/49 | 45/55 | (18400) | (1.07) | / ^b | / ^b |
| 5 | P(VCL/VP) _{25/75} | 26/74 | 22/78 | (19000) | (1.13) | / ^b | / ^b |
| 6 | P(VCL/VP) _{10/90} | 10/90 | 8/92 | (23200) | (1.12) | / ^b | / ^b |

| 7 | PVP | 0/100 | 0/100 | (22000) | / ^b | / ^b |
|--|-----|-------|-------|---------|----------------|----------------|
| ^a Determined by ¹ H NMR. ^b no transition detectable. ^c T _c was evaluated at the maximum of the peak on heating after extrapolation to 0 °C·min ⁻¹ , standard deviation on T _c = ± 0.2 J·g ⁻¹ ; ΔH obtained on heating with a heating rate of 2.5 °C·min ⁻¹ , standard deviation on ΔH = ± 2 J·g ⁻¹ . | | | | | | |

The cloud point temperature increased non-linearly from 36.7 to 50.8 and 62.0 °C for a VP content of 0, 25 and 40 wt.% respectively (Entry 1-3 in **Table 1**). This resulted from the introduction of the hydrophilic VP monomer. No transition occurred for a VP content higher than 40%. Further insight on the effect of VP introduction within PVCL chain was obtained through the measurement of associated variation of enthalpy ΔH normalized with respect to VCL content. When the fraction of VP in copolymer increased, a strong decrease of ΔH was measured (**Table 1**). This variation is clearly not proportional to VCL content. This behavior was ascribed to a mechanism of dehydration involving the whole macromolecule structure, and not short sequences of VCL units: indeed, insertion of VP units within the PVCL backbone strongly impeded dehydration phenomenon by preventing the release of water molecules from the polymer chains and therefore the formation of hydrophobic regions responsible for the aggregation process and the formation of mesoglobules.[27] Consequently, only copolymers with a low VP content (below 40%) can present a thermoresponsive behavior in solution.

3.2. *In situ* formation of nanohybrids

The first evidence of the interaction of the different polymers with AuNPs was given by performing *in-situ* growth of AuNPs. Whereas PVP-based polymers can act solely as both reducing agent and stabilizer, its use as a reductant led to the formation of large particles with broad particles size distribution poorly adapted to catalytic applications.[31] Therefore, NaBH₄ was used here as a reducing agent to have fast access to AuNPs with better control of particle size and dispersity. For this a solution of NaBH₄ was added to a mixture of gold salt and polymer at different concentrations (10⁻³, 10⁻², 0.1 and 0.5 wt.%). The formation of AuNPs was followed visually, by UV-vis measurements and by transmission electron microscopy (TEM). As can be seen on **Fig. S5** from the different colors of the colloidal solutions, the polymer concentration

drastically modifies the particles growth. At the lowest polymer concentration (10^{-3} wt. %), a sharp surface plasmon band (SPB) was visible for all polymers. TEM analysis evidenced in this case the formation of AuNPs with an average size at 5 ± 2 nm close to that of AuNPs obtained in the absence of polymer. Increasing the polymer concentration led to a progressive decrease of the intensity of this plasmon band whatever the nature of polymer (**Fig. S6**). This decrease results from the formation of smaller NPs as demonstrated by TEM measurements. This difference in size as a function of the polymer concentration confirms that the presence of polymer plays an important role in the control of NPs growth by interacting with the gold nuclei/gold precursor at the early stage of the NPs growth. This adsorption is favored on the one hand by the interactions of the thioester groups present at the end of the polymer chains [18] and on the other hand by the interactions of the polymer chain with the surface of AuNPs. This latter interaction occurred from the carbonyl group and nitrogen atom within the lactam ring as demonstrated on PVP based polymers by combination of X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy and Raman spectroscopy [31].

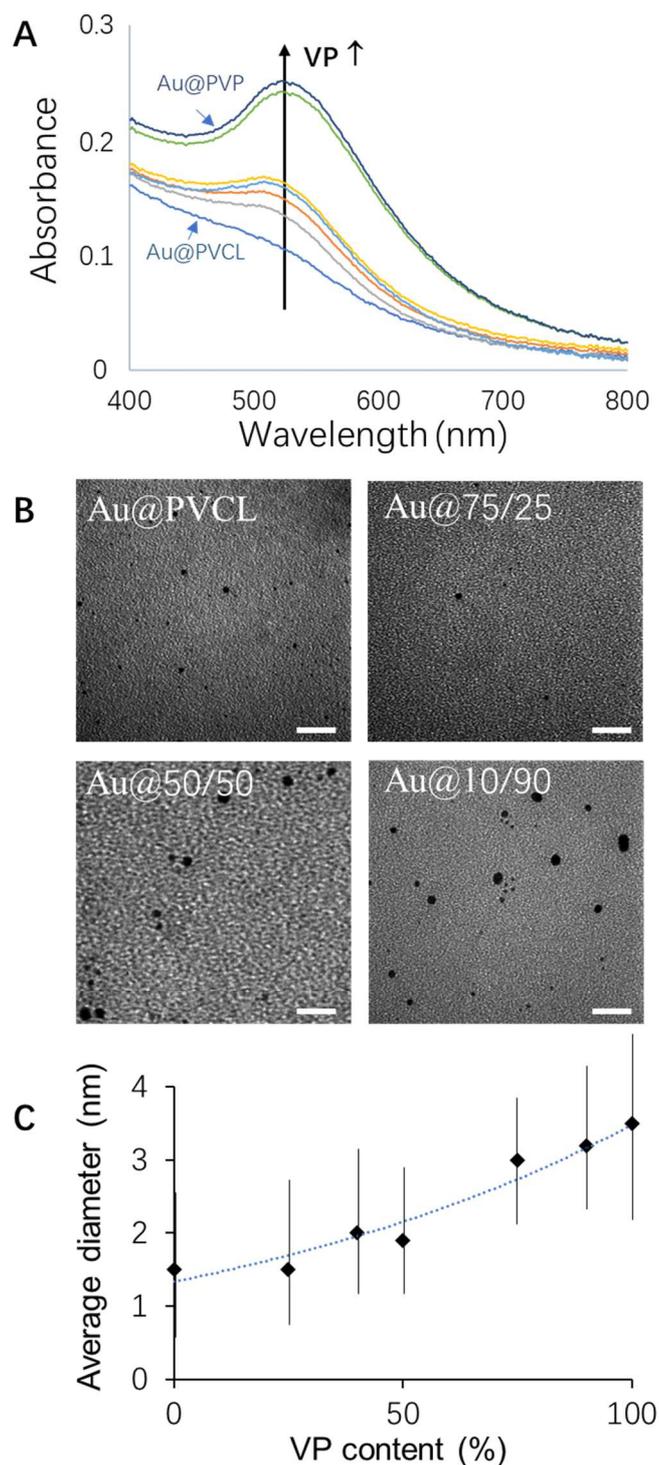


Fig. 1. *In situ* formation of AuNPs in presence of P(VCL/VP)_{20k} with $[Au^0] = 5 \times 10^{-4}$ mol·L⁻¹ and [polymer] = 10⁻² wt.%. A) Changes in absorption spectra as a function of the VP content within the polymer (increasing from 0, 25, 40, 50, 75, 90 and 100 %) observed 5 days after NPs formation. B) TEM images for Au@PVCL, Au@75/25, Au@50/50 and Au@10/90 and C) Evolution of average size as a function of VP content (the line is only a guide for the eyes).

The effect of polymer composition for a given polymer concentration was then considered. As illustrated in **Fig. 1A**, an increase of the intensity of the measured plasmon band with an increase of the VP fraction in copolymer was observed. TEM analysis (**Fig. 1B** and **1C**) confirmed that the observed trend is related to a progressive increase of the average size of formed AuNPs from 1.5 to 3.2 nm when VP content increases from 0 to 100 %. The different copolymers having the same end groups, the differences observed can only be attributed to a difference in composition: a higher VCL content leading to a better control of NPs growth. In comparison with VP, VCL presents two additional methylene group per monomer in the lactam ring. The increased

hydrophobicity of VCL (i.e a lower hydration level in solution) thus favors the interaction with the surface of AuNPs thus blocking the growth of the particles at an early stage. TGA measurement on purified AuNPs enables to evaluate roughly a polymer content of 20 wt.% corresponding to density coverage of 0.3 polymer per nm² in agreement with previous published from literature [31].

3.3. Stabilization of preformed nanoparticles

To evaluate solely the effect of the copolymer composition on the different properties of AuNPs of interest (stabilization, catalysis, optical properties) a second series of nanohybrids were prepared by coating preformed AuNPs with a chosen amount of each polymer (**Scheme 1**). Pristine AuNPs with controlled size and dispersity were synthesized by reduction of NaAuCl₄ by NaBH₄. [13, 32] Whereas no additional stabilizing agent was added, experimental conditions including pH (around 8.0) and gold precursor concentration (2.5×10^{-4} mol·L⁻¹) were carefully adjusted to yield AuNPs with good colloidal stability and controlled size (5 ± 2 nm). These nanoparticles are coated with the different copolymers presented in **Table 1**. As stated above, interactions with preformed AuNPs come from both lactam ring and thioester group. [18, 31] Four different polymer concentrations are used for each polymer (final concentration equal to 10^{-4} , 10^{-3} , 5×10^{-3} and 10^{-2} wt.%). As illustrated in **Fig. 2** and **S7** (A₁, B₁, C₁ and D₁ columns), all solutions remain stable. The surface plasmon resonance band revealed a slight red shift (2 nm) after polymer coating ([polymer] = 10^{-3} wt.%) of the AuNPs due to a decrease in local polarity (**Fig. S8A** and **B-left**).

After coating, nano hybrids with an average hydrodynamic diameter around 9 ± 2 nm are obtained as measured from DLS measurements (**Fig. S9**). This size corresponds to colloidal solutions made of AuNPs surrounded by a polymer corona preventing aggregation through steric hindrance. These nano hybrids obtained from preformed AuNPs were further studied to evaluate the effect of polymer composition on their colloidal stability, thermoresponsiveness and catalytic activity.

Colloidal stability. The effect of the copolymer composition on the colloidal stabilization of solution of particles subjected to an increase in pH or ionic strength is evaluated after addition of NaOH (A_2 , B_2 , C_2 , D_2) or NaCl solution (A_3 , B_3 , C_3 , D_3) as shown in **Fig. 2** and **S7**. In this experiment, a progressive change of color related to the modification of the plasmon band of the particles due to aggregation or sedimentation phenomena reflects a low colloidal stability. Increasing the polymer concentration enables to increase the stability of AuNPs toward modification of pH or addition of salt due to a higher steric hindrance. Moreover, for a chosen concentration PVCL promotes the NPs with a slightly higher colloidal stability as can be seen on B_2 and C_2 columns for instance, or by the evolution of absorbance spectra in **Fig. 2B**. This is in agreement with stronger interactions of VCL than VP toward the surface of AuNPs as previously evidenced for the *in situ* formation of AuNPs.

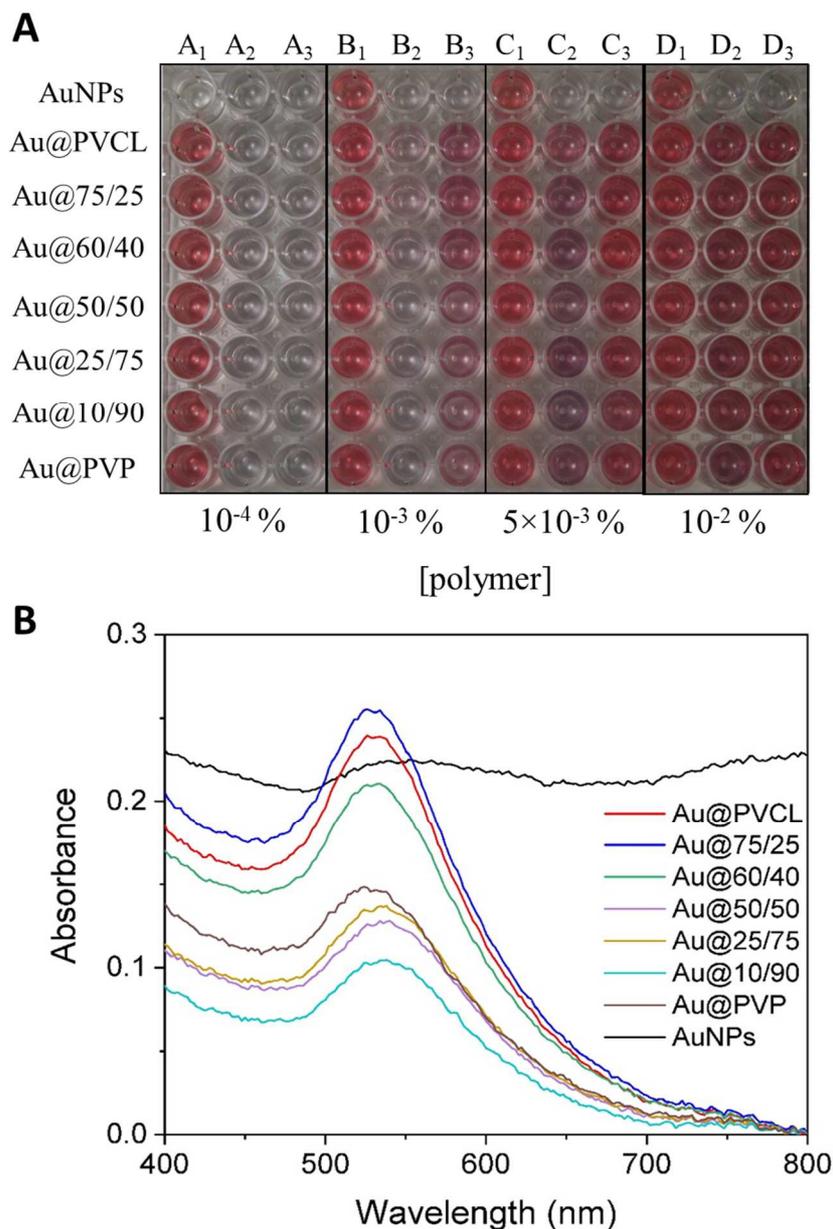


Fig. 2. A) Colloidal stability of aqueous solutions of AuNPs@P(VCL/VP)_{20k} observed for four different polymer concentrations (A: 10⁻⁴ wt.%, B: 10⁻³ wt.%, C: 5 × 10⁻³ wt.% and D: 5 × 10⁻² wt.%) and different polymer compositions 2 weeks after the addition of NaOH (A₂, B₂, C₂, D₂, final pH = 10), NaCl (A₃, B₃, C₃, D₃, [NaCl]_{final} = 1 mol · L⁻¹) compared to a control (A₁, B₁, C₁, D₁). [Au⁰] = 2.5 × 10⁻⁴ mol · L⁻¹. B) Evolution of absorption spectra as a function of polymer nature between 400 and 800 nm two weeks after the addition of salt ([polymer] = 10⁻³ wt.%).

Effect of temperature on AuNPs properties. The effect of temperature on the resulting dialyzed hybrid materials is then evaluated by DLS (**Fig. S10**) and, as shown in **Fig. 3**, by measuring the absorbance of the solutions at 520 nm between 20 and 70 °C as a function of the copolymer composition.

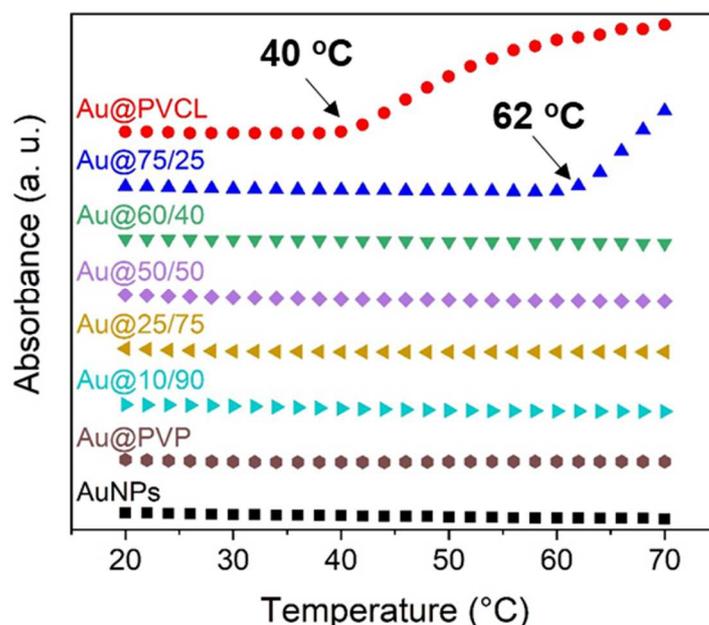


Fig. 3. Evolution of absorbance (an arbitrary unit was chosen) at 520 nm as a function of temperature for pristine AuNPs and AuNPs covered by different polymers ($[\text{polymer}] = 2.5 \times 10^{-2} \text{ wt.}\%$ and $[\text{Au}^0] = 2.5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$).

Only Au@PVCL and Au@75/25 systems present a significant increase of absorbance induced by the increase of temperature (**Fig. S11B**) and the presence in solution of large aggregates in solution above the cloud point temperature. Increasing the VP content induced two main effects on thermoresponsive properties: a shift of transition temperature to higher values as observed in **Fig. 3** and a lower variation of enthalpy during the transition phenomenon. As a result, only the hybrids obtained with polymers with a VP content below 40% present thermoresponsive properties in solution at the chosen concentration. Additionally, only the colloidal solution of Au@PVCL shows a significant change in the wavelength of the maximum absorbance when temperature is increased from 20 to 70 °C (**Fig. S11C**) as previously observed.[27] Thus, increasing VP content in $\text{P}(\text{VCL}/\text{VP})_{20\text{k}}$ is detrimental to thermoresponsive properties and to the aggregation of NPs.

In addition, temperature changes are likely to induce changes in the state of aggregation of colloidal solutions. In order to evaluate the ability of different copolymers to effectively and reversibly stabilize gold nanoparticles, the absorbance spectra at 20 °C are compared before and after a temperature rise to 70 °C (**Fig. S11A**). The two homopolymer-based colloidal solutions Au@PVCL and Au@PVP show the smallest variation in absorbance and are therefore the least sensitive to temperature variation.

Catalytic efficiency of AuNPs@P(VCL/VP)_{20k}. The catalytic performances of all Au@P(VCL/VP)_{20k} systems were further tested at different temperatures (20, 30, 40, 50, 60 and 70 °C) in the reduction of *p*-nitrophenol to *p*-aminophenol in water using sodium borohydride (**Fig. 4A**).^[12] The color changes associated with the conversion of *p*-nitrophenol to *p*-aminophenol enables one to easily monitor the reaction kinetics by UV-vis spectroscopy at 400 nm. As expected, the catalytic reduction was not triggered when only NaBH₄ was present. **Fig. 4A** shows absorbance spectra as a function of time for Au@75/25 catalyst at 20 °C. From the absence of measured diffusion at 800 nm, it is noteworthy that the colloidal stability of the catalytical systems is not affected by the presence of reactant and products. The observed rate constant (k_{obs}) for all kinetics were extracted from linear relationship between $\ln(A_t/A_0)$ versus time *t* assuming pseudo first-order kinetics for this reaction in the presence of an excess of sodium borohydride. **Fig. 4B** and **Fig. S12** display the fits of the experimental data obtained at different temperatures for Au@75/25 and Au@PVCL catalysts, respectively. At first, there is an induction period which is related to a surface restructuring of the nanoparticles before the catalytic reaction starts.^[33] The reaction can occur only between species adsorbed on the surface. Results suggest that the catalytic activity increases with temperature until the cloud point is reached from which no catalytic efficiency is observed (**Fig. 4C**). The results of other fits taken at 20 °C for all the Au@polymer systems are given in the Supporting Information (**Fig. S13**).

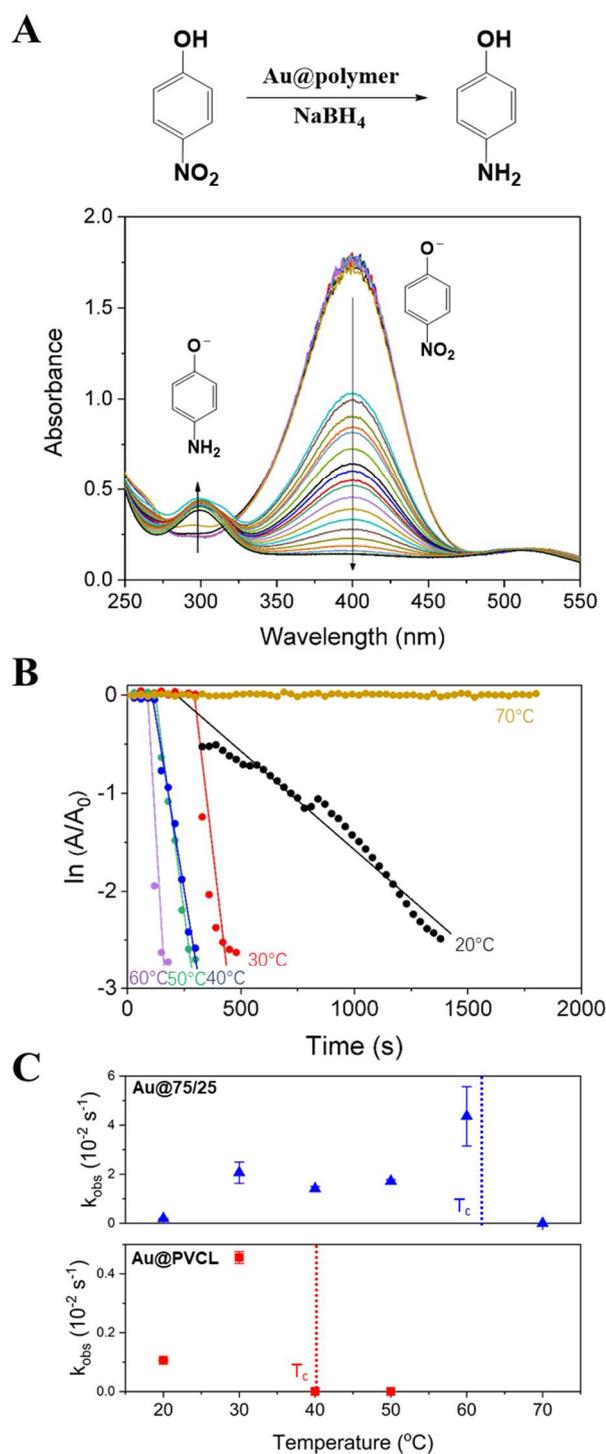


Fig. 4. A) UV-vis spectra of the reduction of *p*-nitrophenol to *p*-aminophenol by NaBH₄ catalysed by Au@75/25 at 20 °C. B) Plots of $\ln(A/A_0)$ vs time for Au@75/25 at different temperatures and C) pseudo-first order kinetic constant (k_{obs}) as a function of temperature for Au@PVCL and Au@75/25 (the blue and red lines are only a guide for the eyes) ($[p\text{-nitrophenol}] = 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $[\text{Au}^0] = 5\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, $[\text{NaBH}_4] = 3\times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{polymer}] = 5\times 10^{-3} \text{ wt.}\%$).

Interestingly, at 20 °C, hybrid nanoparticles based on statistical copolymers present higher k_{obs} values than those evaluated for Au@PVCL and Au@PVP. Moreover, an optimum of measured pseudo-first order kinetic constant, k_{obs} , is measured for a VP content equal to 50%. From the results of kinetics of the catalyst systems within the polymer (**Fig. 4C** and **S13**), the trend of catalytic efficiency as a function of the copolymer composition could be rationalized as a compromise between two opposite effects. On the one hand, higher VCL content increased the hydrophobic character of the organic shell surrounding AuNPs and thus favored the diffusion of reactants towards the AuNPs surface. On the other hand, at the same time, the stronger adsorption of VCL compared to VP limits the catalytic efficiency of resulting nanohybrids.

4. Conclusion

The stabilization of AuNPs based on PVCL enables the access to hybrid thermosensitive materials with modular properties.[24, 25] Though structurally close to PVP, studies on PVCL are much less prevalent. In order to compare the ability of these two families for the formation, stabilization and modulation of the properties of AuNPs, a series of VCL/VP statistical copolymers of controlled molar mass and low dispersity, containing variable amounts of VP (between 0 and 100%), was synthesized by RAFT/MADIX polymerization. The effect of the composition was evaluated, both on the growth of gold nanoparticles synthesized in the presence of the polymers (*in situ* route) and on the properties (stabilization, optical, catalytic...) of preformed nanoparticles coated by these polymers. With two additional methylene group per monomer unit in comparison with PVP, PVCL demonstrates strong differences concerning its ability to interact with AuNPs. As demonstrated through this study, its increased hydrophobic character enables PVCL to act as a more effective growth control agent than PVP for the *in situ* synthesis of AuNPs. Moreover, whatever the method of preparation of nanohybrids used (*in situ* or coating of preformed NPs), statistical copolymerization of VCL and VP makes it possible to modulate to some extent the properties of the polymer, and thus of the obtained hybrid materials. Hence, at a molar fraction of VP in copolymer less than 40%, it was possible to increase the transition temperature of the hybrid material and improve its catalytic properties compared to counterparts comprising PVP and PVCL homopolymers. In addition,

incorporation of higher fraction of VCL units in the VCL/VP copolymers promotes an increased colloidal stability of gold nanohybrids.

The results obtained on gold particles can be used to extent the scope of PVCL-based copolymers for the synthesis of functional colloidal materials based on different inorganic supports as described for PVP [31] or for the formation of thermosensitive hybrid nanogels [34,35].

CRedit authorship contribution statement

Fang Yin: Investigation, Formal analysis, Data curation. **Hong Hanh Nguyen:** Investigation, Formal analysis. **Olivier Coutelier:** Investigation, Formal analysis. **Mathias Destarac:** Investigation, Formal analysis. **Nancy Lauth-de Viguerie:** Project administration, Supervision, Writing - original draft, Writing - review & editing **Jean-Daniel Marty:** Conceptualization, Project administration, Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

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