Supporting Information

Designing new functional poly(*N*-vinylpyrrolidone) based (co)polymers via photoinitiated cobalt-mediated radical polymerization.

Antoine Debuigne,*[a] Matthieu Schoumacher,[a] Nicolas Willet,[b] Raphael Riva,[a] Xiaomin Zhu,[c] Stephan Rütten,[c] Christine Jérôme[a] and Christophe Detrembleur[a]

EXPERIMENTAL SECTION.

Materials. Isoprene (99%, Aldrich) and ε-caprolactone (99%, Alfa Aesar) were dried over calcium hydride, degassed by several freeze-pump-thaw cycles before being distilled under reduced pressure and stored under argon. *N*-vinyl-2-pyrrolidone (NVP, Aldrich) degassed by several freeze-pump-thaw cycles before being distilled under reduced pressure and stored under argon. Methanol (Aldrich) and toluene (99%, VWR) were dried over molecular sieves and degassed by bubbling argon for 15 minutes. 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, Wako), cobalt(II)acetylacetonate ($Co(acac)_2$, >98%, Acros), 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich), tin octoate ($Sn(Oct)_2$) were used as received. All polymerizations and coupling reactions were carried out under a protective argon atmosphere.

Characterization. Molecular parameters of polymers were determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) containing some LiBr (0.025 M) at 55°C (flow rate: 1 mL min^{-1}), with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (HR1, 100-5000; HR3, 500–30000; HR4, 5000–500000; HR5, 2000–4000000) using a polystyrene calibration. Absolute molecular weight of poly(*N*-vinyl pyrrolidone) (P*N*VP) samples were determined using a Multi-Angle Laser Light Scattering (MALLS) detector. The specific refractive index increment (d*n*/d*c*) of P*N*VP was determined as 0.064 $mL.g^{-1}$ by using a Wyatt Optilab rEXrefractive index detector (λ=658 nm). Data were processed with the Astra V software (Wyatt Technology). ^1H NMR spectra were recorded with a 400 MHz Bruker spectrometer. The consumption of *N*VP and ε-CL during the polymerizations were monitored by ^1H NMR at 298K in D_2O and $CDCL_3$, respectively. The ^{1}H NMR spectra of the poly(*N*-vinyl pyrrolidone)-poly(ε-caprolactone) copolymers were recorded at 298K in $CDCl_3$. Infrared spectra (IR) were recorded with a Perkin-Elmer FT-IR instrument with a NaCl disk coated by the polymer solutions in CH_2Cl_2. The size distribution of P*N*VP/PCL containing copolymers in water was estimated by dynamic light scattering (DLS) using a particle-size analyzer (Delsa Nano C, Particle Analyzer, Beckman Coulter) at 25°C. The intensity of scattered light was detected at an angle of 165°. Data were analyzed using the CONTIN method which is based on an inverse-Laplace transformation of the data and gives access to a size distribution histogram for the analyzed micellar solutions. Field emission scanning electron microscopy (FESEM) was carried out with an S-4800 Hitachi apparatus equipped with a and Cryo-transfer system (Alto 2500, Gatan). Samples were prepared by depositing a drop of the sample into a preparation tube (5mm length and 1.5mm diameter) using a pipette. Then it was chocked frozen by throwing the tube into a pre-cooling chamber of the cryo-transfer system (Alto 2500, Gatan) which was filled with liquid nitrogen (-196°C). Subsequently it was transferred into a cooling device of the preparation chamber which was attached to the FESEM. Then the top of the drop was broken by using a cooled scalpel. In order to eliminate ice crystals, the sample was sublimated by - 90°C for 5 min. Afterwards the temperature was reset to -156°C. Finally, the fractured sample was transferred into the FESEM, and analyzed under the accelerating voltage 1kV.

Cobalt-mediated radical polymerization of *N*-vinyl pyrrolidone photoinitiated by VA-086. $Co(acac)_2$ (0.204 g, 0.80 mmol) and VA-086 (0.460 g, 1.60 mmol) were placed under argon in a reactor designed for photochemistry, an immersion-well reactor in which the lamp is surrounded by the solution in a quartz tube. Dried and degassed methanol (7.5 mL) and *N*VP (7.5 mL, 7.80g, 70.2 mmol) were added under argon. The medium was then stirred at 0°C under UV irradiation (UV lamp TQ 150: 150W, λ= 200-280 nm). After 4h, the irradiation was stopped and the reaction mixture was allowed to warm to room temperature for polymerization. Samples were regularly withdrawn with a syringe prior to quenching by TEMPO. Monomer conversions and macromolecular parameters were determined by ^{1}H NMR spectroscopy and SEC/MALLS, respectively (See Figure 1).

Synthesis of the α-hydroxy-PNVP (5). $Co(acac)_2$ (0.204 g, 0.80 mmol) and VA-086 (0.460 g, 1.60 mmol) were placed under argon in a reactor designed for photochemistry, an immersion-well reactor in which the lamp is surrounded by the solution in a quartz tube. Dried and degassed methanol (15.0 mL) and *N*VP (15.0 mL, 15.6g, 140 mmol) were added under argon. The medium was then stirred at 0°C under UV irradiation (UV lamp TQ 150:

150W, λ= 200-280 nm). After 4h, the irradiation was stopped and a sample was withdrawn with a syringe prior to quenching by TEMPO. Monomer conversion reached 16%. TEMPO (0.31 g, 2.0 mmol) in solution in degassed methanol (2 mL) was added to the reaction mixture and stirred at 0°C for 30 minutes. The final polymer was precipitated in diethyl ether and dried under vacuum at 40°C. The polymer was then solubilized in bidistilled water, dialyzed through a Spectra pore membrane (6000/8000 g/mol) against pure water for 3 days and recovered by lyophilisation. The final α-hydroxy-PNVP **2** was analyzed by SEC ($M_{n\ MALLS}$ = 27400 g/mol, M_w/M_n = 1.11, $M_{n\ SEC\ cal\ PS}$ = 38500 g/mol, M_w/M_n SEC = 1.17).

Synthesis of the α,ω-hydroxy-telechelic PNVP (4). $Co(acac)_2$ (0.408 g, 1.60 mmol) and VA-086 (0.920 g, 3.20 mmol) were placed under argon in a reactor designed for photochemistry, an immersion-well reactor in which the lamp is surrounded by the solution in a quartz tube. Dried and degassed methanol (20.0 mL) and *N*VP (20.0 mL, 20.8g, 187 mmol) were added under argon. The medium was then stirred at 0°C under UV irradiation (UV lamp TQ 150: 150W, λ= 200-280 nm). After 4h, the irradiation was stopped and a sample was withdrawn with a syringe prior to quenching by TEMPO. Part of the sample was used to evaluate the NVP conversion (11%) by ^{1}H NMR in D_20. The rest of the aliquot was analyzed by SEC-MALLS in order to measure molecular parameters of PNVP (M_n = 26200 g/mol, M_w/M_n = 1.07). In parallel, the polymerization medium was treated at 0°C with isoprene (5 ml, 3.405 g, 50 mmol) without removing the unreacted NVP and stirred for 2 h at 0°C. A sample was withdrawn with a syringe in order to measure the NVP conversion (11%) and molecular parameters of PNVP ($M_{n\ SEC\ MALLS}$ = 45400 g/mol, M_w/M_n = 1.08). The crude mixture was then poured into diethyl ether and the final PNVP was filtered and dried under vacuum. The polymer was then solubilized in bidistilled water, dialyzed trough a Spectra pore membrane (6000/8000 g/mol) against pure water for 3 days and recovered by lyophilisation. The α,ω-hydroxy-telechelic PNVP **4** was analyzed by SEC ($M_{n\ MALLS}$ = 44600 g/mol, M_w/M_n = 1.08)

Synthesis of the P*N*VP-*b*-PCL diblock copolymer (6). The α-hydroxy-P*N*VP **3** (0.500 g, 27400 g/mol, 1.82 10^{-5}mol) was placed under argon in a reactor and dried by three azeotropic distillations with anhydrous toluene. The P*N*VP was then added with a dry and degassed mixture of toluene (3.0 mL) and ε-caprolactone (0.750 g, 6.5 10^{-3}mol). The medium was stirred and heated at 110°C before addition of $Sn(Oct)_2$ solution in toluene (0.25 mL of a 0.1M solution, 2.5 10^{-5} mol). After 22h, the ε-CL conversion measured by ^{1}H NMR in $CDCl_3$ reached 94%. The crude mixture was then poured into diethyl ether and the expected PNVP-

b-PCL copolymer was filtered and dried under vacuum at 40°C. The final copolymer **5** was analyzed by SEC (Figure 3a), IR (Figure S5) and NMR (Figure S6). The composition of the copolymer was determined by ^{1}H NMR in $CDCl_3$: P*N*VP(27400 g/mol)-*b*-PCL(32700 g/mol).

Synthesis of the symmetrical PCL-*b*-P*N*VP-*b*-PCL triblock copolymer (7). The α,ω-hydroxy-telechelic P*N*VP **4** (0.500 g, 44600 g/mol, 1.12 10^{-5}mol) was placed under argon in a reactor and dried by three azeotropic distillations with toluene. The PNVP was then added with a dry and degassed mixture of toluene (3.0 mL) and ε-caprolactone (0.500 g, 4.38 10^{-3} mol). The medium was stirred and heated at 110°C before addition of $Sn(Oct)_2$ solution in toluene (0.25 mL of a 0.1M solution, 2.5 10^{-5} mol). After 18h, the ε-CL conversion measured by ^{1}H NMR in $CDCl_3$ reached 73%. The crude mixture was then poured into diethyl ether and the expected PCL-*b*-P*N*VP-*b*-PCL copolymer was filtered and dried under vacuum at 40°C. The final copolymer **6** was analyzed by (Figure 3b), IR (Figure S5) and NMR (Figure S6). The composition of the copolymer was determined by ^{1}H NMR in $CDCl_3$: PCL(18600 g/mol)-*b*-P*N*VP(44600 g/mol)-*b*-PCL(18600 g/mol).

Solution behavior study of the P*N*VP/PCL copolymers 6 and 7. A sample of P*N*VP-PCL **6** or PCL-P*N*VP-PCL **7** (20 mg) was solubilized in DMF (1 mL) before dropwise addition of milli-Q water (Millipore) (1 mL) under stirring. The solution was stirred for 1 h before addition of a second portion of water (4 mL). The resulting solutions were dialyzed through Spectra/Por ® membranes (cut-off 6000-8000 g/mol) against pure water before CryoSEM analyses. The solutions were diluted 10 times before DLS measurements.

SUPPLEMENTARY DATA.

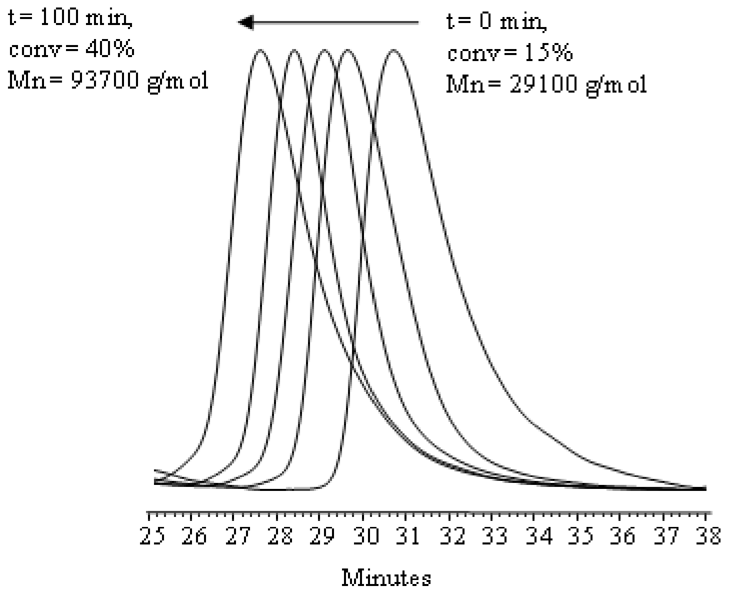

Figure S1. Evolution of SEC chromatograms with the time for the photoinitiated CMRP of NVP at room temperature. Conditions : [VA-086]/[Co(acac)$_2$]/[*N*VP] : 2/1/88; V_{NVP}/V_{MeOH} =1; UV irradiation for 4h at 0°C, then polymerization at rt.

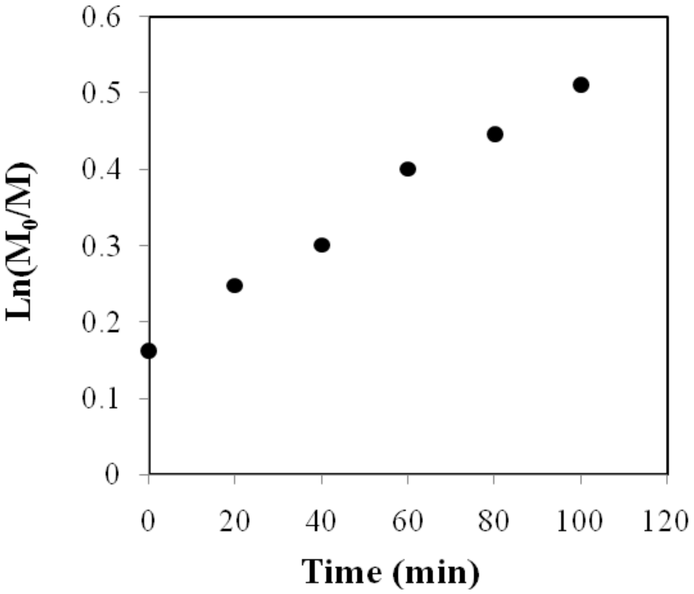

Figure S2. Dependence of ln[M]$_0$/[M] versus time for the photoinitiated CMRP of NVP at room temperature. Conditions : [VA-086]/[Co(acac)$_2$]/[*N*VP] : 2/1/88; V$_{NVP}$/V$_{MeOH}$ =1; UV irradiation for 4h at 0°C, then polymerization at rt.. t$_0$ corresponds to the moment of the temperature increase from 0°C to rt.

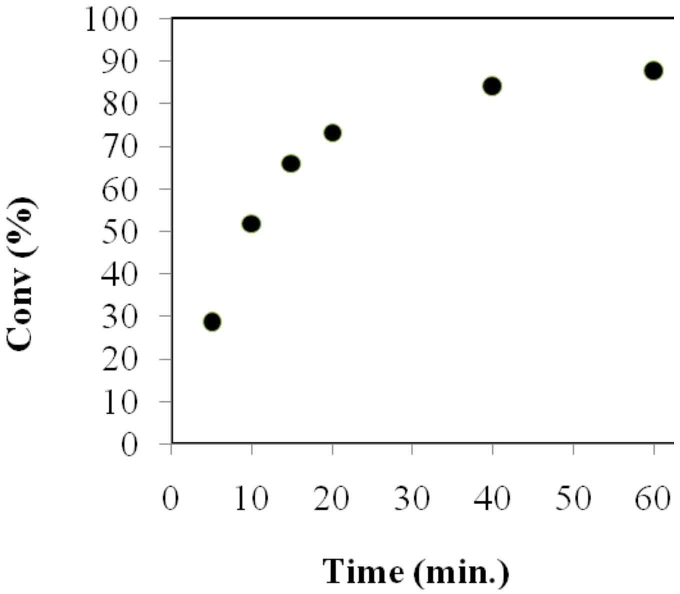

Figure S3. Kinetic of the photodecomposition of VA-086 monitored by measuring the N_2 volume produced along the irradiation in methanol at 0°C. Conditions : UV irradiation at 0°C, 50ml of degassed methanol, 144 mg of VA-086 (0.5 mmol).

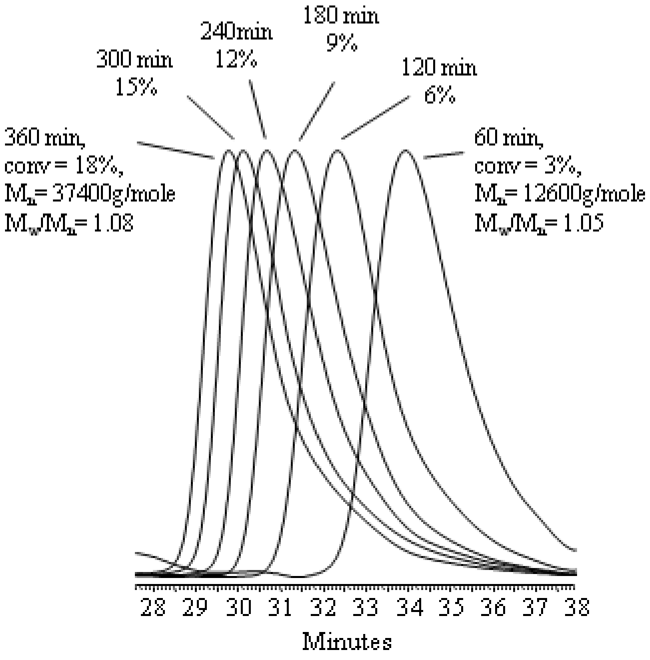

Figure S4. Evolution of SEC chromatograms with the time for the CMRP of NVP under UV irradiation at 0°C. Conditions : [VA-086]/[Co(acac)$_2$]/[*N*VP] : 2/1/176; V_{NVP}/V_{MeOH} =1; UV irradiation at 0°C.

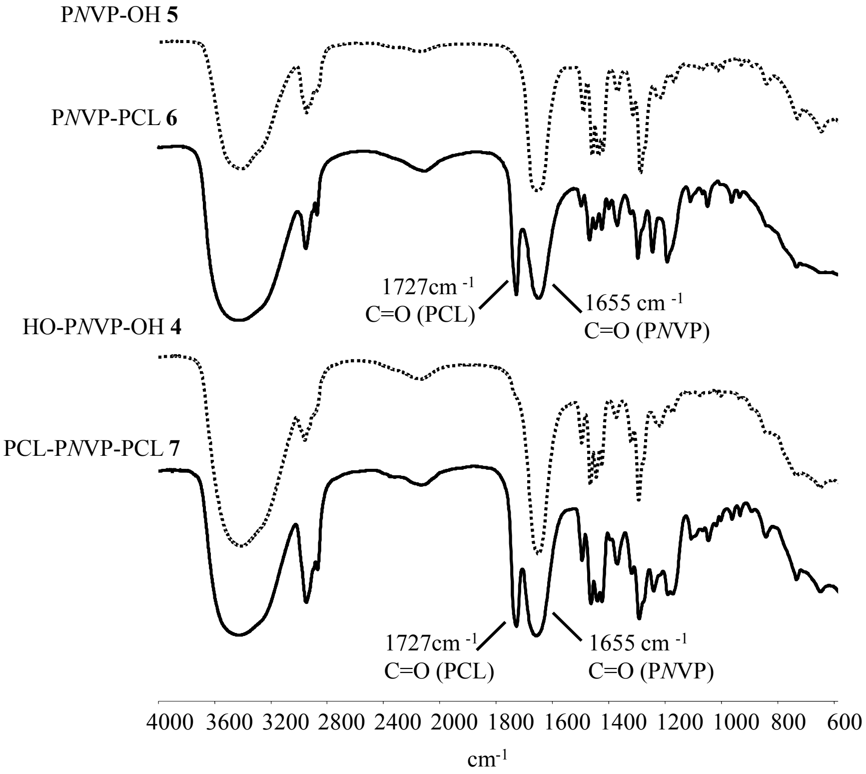

Figure S5. IR infrared spectra of the α-hydroxy-PNVP **5**, α,ω-dihydroxy-telechelic PNVP **4**, the diblock PNVP-b-PCL **6** and the triblock PCL-b-PNVP-b-PCL **7**.

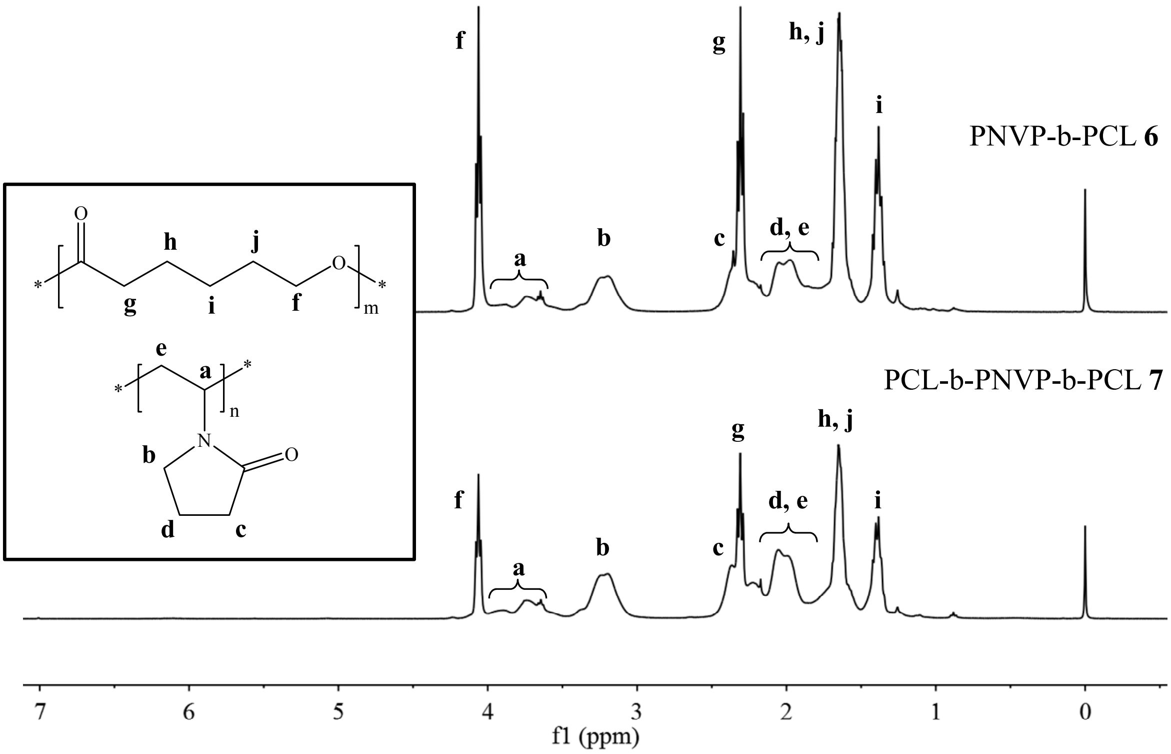

Figure S6. ^{1}H NMR spectra in $CDCl_3$ of the diblock PNVP-b-PCL **6** and the triblock PCL-b-PNVP-b-PCL **7**.