

Electronic Supplementary Information (ESI)

Aqueous RAFT/MADIX Polymerisation of *N*-Vinyl Pyrrolidone at Ambient Temperature.

Aymeric Guinaudeau,^a Stéphane Mazières,^a D. James Wilson^b and Mathias Destarac^{*a}

Summary of the Supplementary Information document

I. Materials, Synthesis, Characterisation	2
II. ¹ NMR spectroscopy analysis of PVP-XA1	4
III. MALDI-TOF mass spectrometry analysis of PVP-XA1	5

^aUniversité Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée, UMR-CNRS 5069, Bât 2R1, 118, route de Narbonne, 31062 Toulouse Cedex 9, France

^bRhodia Opérations, Centre de Recherches et Technologies d'Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers Cedex, France

To whom correspondence should be addressed:

E-mail: destarac@chimie.ups-tlse.fr

Materials. N-Vinylpyrrolidone (NVP, Acros, 98%) was dried over anhydrous magnesium sulphate and distilled under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was recrystallized three times in methanol. Ethanol (EtOH, Normapur), *t*-butyl hydroperoxyde (*t*BuOOH, Aldrich, 70 wt. % in water) and L(+) Ascorbic Acid (AscAc, Acros, 99%) were used as received. *O*-ethyl-S-(1-methoxycarbonyl)ethylthiocarbonate (XA1) and Acrylamide (Am, 50 wt. % in water) were supplied by Rhodia and used as received.

Redox-initiated, aqueous RAFT/MADIX polymerisation of NVP. A typical polymerisation was performed as follows: XA1 (122 mg, 5.8×10^{-4} mol), NVP (5 g, 4.5×10^{-2} mol), distilled water (2,5 mL) and *t*-BuOOH (85 mg, 6.6×10^{-4} mol) were placed in a 15-mL Schlenk flask. The polymerisation mixture was degassed by purging with ultra-high purity argon during 20 minutes. AscAc (115 mg, 6.5×10^{-4} mol) was added one-pot under a stream of argon. The reaction was stopped after 24 h at room temperature. NVP conversion was determined by ^1H NMR (97%). Molecular weight and dispersity were determined by SEC in DMF/LiCl with PMMA standards ($M_{n,SEC} = 14\,600 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1,30$).

Redox-initiated RAFT/MADIX polymerisation of acrylamide. An acrylamide prepolymer was synthesized as follows to perform a further block copolymerisation: XA1 (220 mg, 1.1×10^{-3} mol), Ethanol (EtOH, 3.3 g, 7.2×10^{-2} mol), Am (10 g, 7×10^{-2} mol), distilled water (2,5 mL) and *t*-BuOOH (171 mg, 1.3×10^{-3} mol) were placed in a 15-mL Schlenk flask. The polymerisation mixture was degassed by purging with ultra-high purity argon during 20 mn. AscAc (182 mg, 1.2×10^{-3} mol) was added one-pot under a stream of argon. The reaction was stopped after 24h at room temperature. The monomer conversion reached 99% (determined by ^1H NMR). Ethanol was then evaporated under reduced pressure. Molecular weight and dispersity were determined by ^1H NMR ($M_{n,RMN} = 1200 \text{ g}\cdot\text{mol}^{-1}$) and by SEC in DMF/LiCl with PMMA standards ($M_{n,POE} = 3600 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1,07$).

Redox-initiated RAFT/MADIX block copolymerisation of NVP. Pam (prepared according to the procedure described above) (300 mg, 6×10^{-5} mol), *t*-BuOOH (19 mg, 1.5×10^{-4} mol), distilled water (1,3 mL) and NVP (0.5 g, 3.5×10^{-3} mol) were placed in a 15-mL Schlenk flask. The polymerisation mixture was degassed by purging with ultra-high purity argon during 20 mn. AscAc (23 mg, 1.3×10^{-4} mol) was added one-pot under a stream of argon. The reaction was stopped after 8 h of stirring at room temperature. Molecular weight and dispersity were determined by SEC in DMF/LiCl with PMMA standards ($M_{n,SEC} = 12200 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1,25$).

PVP purification. PVP was isolated by diluting the sample in dichloromethane and precipitating in diethylether (three times). The polymer was then dried under vacuum at 40°C during 10 h.

Characterization

^1H -NMR were recorded on Bruker AMX 300, at 300 MHz, in D_2O .

A SEC system, comprising two Shodex K-805L columns (8mm*300mm, 13 μm), a UV detector and a RI detector using DMF/LiCl (0,1 N) as the eluent at 40°C with a flow rate of 1mL.min $^{-1}$ was used. This system was calibrated using narrow poly(methyl methacrylate) standards ranging from 900 to 625 000 g.mol $^{-1}$. Toluene was used as a flow marker.

MALDI-TOF MS measurements were performed on an applied Biosystems Voyager System 4243. Positive-ion spectra were acquired in the reflector mode. The matrix was 4-(4-nitrophenylazo)resorcinol. There was no cationisation agent. The polymer sample and the matrix were dissolved in dichloromethane and premixed in a 1:10 ratio.

$$DP_{n, RMN} = \frac{e) + i)}{i)} = \frac{i) + \frac{(a) + e) + f)}{3} - 5i)}{i)} \quad (4.1)$$

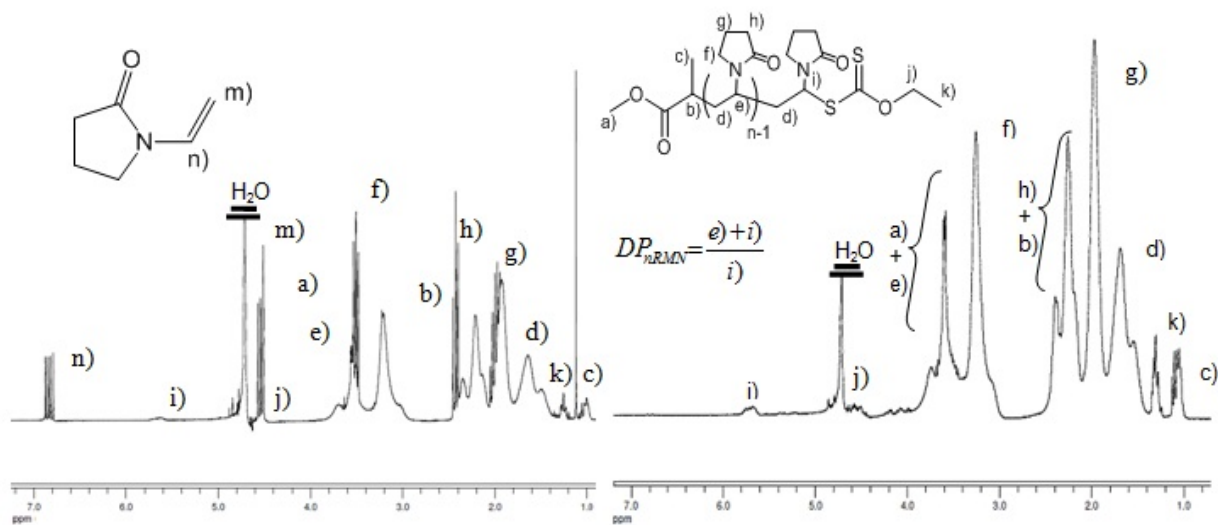


Fig. S1 ¹H NMR spectrum of a PVP synthesized by XA1-mediated RAFT/MADIX polymerisation in water at 25°C, reaction medium (left) and purified polymer (right)

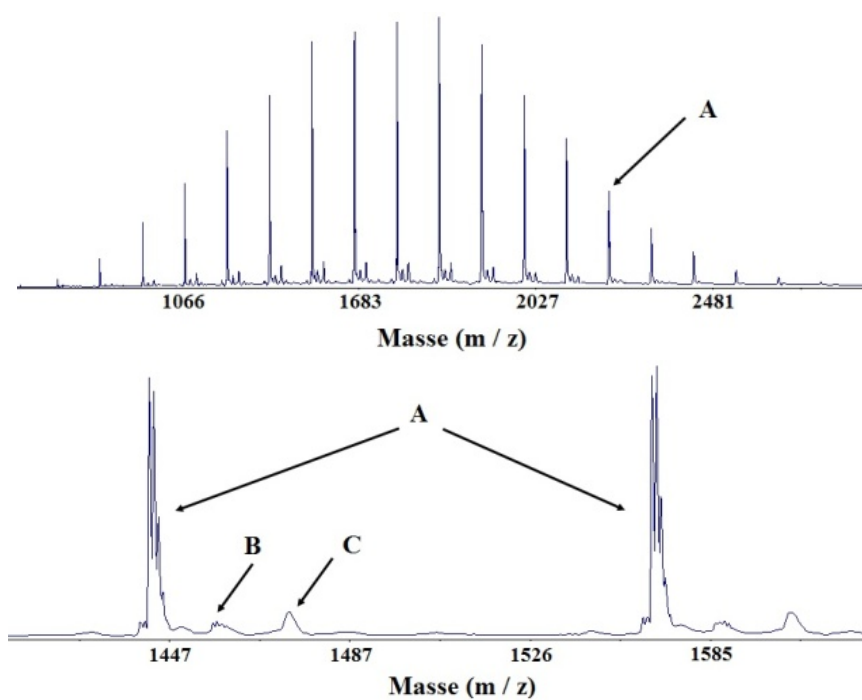


Fig S2 MALDI-TOF mass spectrum of a PVP synthesized by XA1-mediated RAFT/MADIX polymerisation in water at 25°C for 24h, then left in the reaction medium for 5 additional days. M_n NMR=1600 g.mol⁻¹. A=CH₃OCOCH₃CH-(NVP)_{n-1}-CH=CH(C₄H₆NO) (Na⁺), B=CH₃OCOCH₃CH-(NVP)_{n-1}-CH=CH(C₄H₆NO) (K⁺), C = CH₃OCOCH₃CH-(NVP)_n-S(C=S)OCH₂CH₃ (K⁺).