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

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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 hydroperoxide (tBuOOH, Aldrich, 70 wt. % in water) and L(+) Ascorbic Acid (AscAc, Acros, 99%) were used as received. O-ethyl-S-(1-methoxycarbonyl)ethylthiokarbonate (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 (Mₙ,SEC = 14 600 g.mol⁻¹, 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 (Mₙ,RMN = 1200 g.mol⁻¹) and by SEC in DMF/LiCl with PMMA standards (Mₙ,POE = 3600 g.mol⁻¹, D = 1,07).

Redox-initiated RAFT/MADIX block copolymerisation of NVP. Pam (prepared according to the procedure described above) (300 mg, 6 × 10⁻³ 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 (Mₙ,SEC = 12200 g.mol⁻¹, 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 D₂O. A SEC system, comprising two Shodex K-805L columns (8mm*300mm, 13µm), 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.
$DP_{n,\text{RMN}} = \frac{e+j}{i} = \frac{i + (a+c+f) - 3i}{3}$

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. $M_n_{\text{NMR}}=1600$ g.mol$^{-1}$. A = $\text{CH}_3OCOCH_2CH_-(\text{NVP})_{n-1}-CH=CH(C_6H_5NO)$ ($\text{Na}^+$), B = $\text{CH}_3OCOCH_2CH-(\text{NVP})_{n-1}-CH=CH(C_6H_5NO)$ ($\text{K}^+$), C = $\text{CH}_3OCOCH_2CH-(\text{NVP})_{n-1}-S(C=\text{S})OCH_2CH_3$ ($\text{K}^+$).