Electronic Supplementary Information (ESI)

Aqueous RAFT/MADIX polymerisation of vinylphosphonic acid

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I Experimental

Materials

All reagents were used without further purification. Vinyl phosphonic acid (VPA, 97%), was purchased from Aldrich. Acrylic acid (AA, 99.5%) and 2,2'-Azobis(isobutyramidine) dihydrochloride (AIBA, 98%) was supplied by Acros. The other reagents were obtained from Aldrich. 2-[(ethoxythiocarbonyl)thio] propionic acid (X1) was prepared according to a procedure described elsewhere.[1]

Instrumentation

NMR spectra of PVPAs were obtained in D_2O on a Bruker AC-500 and AC-300 spectrometers. Size exclusion chromatography (SEC) was performed on an Agilent 1100 HPLC system, a 18 angle Multi-Angle Light Scattering (MALS) DAWN-Heleos-II (Wyatt Technology, Santa Barbara, CA, US), an OptilaRex Refractometer (Wyatt Technology, Santa Barbara, CA, US) and a set of 2 columns (Shodex SB-806M and SB-802.5) thermostated at 30°C. Number-average molar masses ($M_{n\ MALS}$) and dispersities ($Đ=M_{w\ MALS}/M_{n\ MALS}$) were determined with the SEC-RI-MALS described above. Water (NaCl 100 mmolL^{-1}, NaH_2PO_4 25 mmolL^{-1}, Na_2HPO_4 25 mmolL^{-1}, buffer solution at pH=7) was used as eluent with a flow rate of 1.0 mL min^{-1}.

Synthesis of VPA-X1 1:1 adduct.

Xanthate X1 (719 mg, 3.7 mmol), VPA (200 mg, 1.85 mmol), AIBA (3.74 mg, 0.013 mmol) and distilled water (245 mL) were added to a Schlenk flask. The solution was then degassed by gently bubbling argon for 15 min. After that, the reaction mixture was heated at 65°C for 24 hours in a thermostated oil bath. The mixture was then purified by extraction of the residual amount of xanthate X1 with dichloromethane. The aqueous phase was then freeze-dried to remove water. Monoadduct was obtained as a mixture of diastereisomers (viscous oil, 280 mg, 51% yield).
^{1}H-NMR (D_2O, 300.13. MHz): δ (ppm) =1.05 (m, 3H, **CH_3**-CH), 1.35 (m, 3H, **CH_3**-CH_2O), 1.62, 1.98 and 2.28 (m, 2H, CH-**CH_2**-CH), 2.65 (m, 1H, **C**H-CO_2H), 4.01 (m, 1H, **C**H-PO(OH)$_2$), 4.55 (m, 2H, CH_3 **CH_2**-O).
^{31}P-NMR (D_2O, 121.50 MHz): δ (ppm) =19.5 (d).

RAFT/MADIX polymerisation of VPA

A typical polymerisation procedure is as follows: X1 (34.6 mg, 0.178 mmol), VPA (500 mg, 4.62 mmol), AIBA (9.35 mg, 0.034 mmol) and distilled water (615 mL) were put together in a Schlenk flask. The solution was then degassed by gently bubbling argon for 15 mins. After that, the reaction mixture was heated at 65°C for 24 hours in a thermostated oil bath. 78.4% of VPA was converted into polymer at the end of the reaction as determined by ^{31}P NMR. $M_{n\ th}$=2400 g mol^{-1}, $M_{n\ NMR}$=2700 g mol^{-1}, $M_{n\ MALS}$=3420 g mol^{-1}, $Đ$=1.30.

RAFT/MADIX block copolymerisation of AA and VPA

Synthesis of PAA_8-X1

The synthesis of the macro-MADIX agent PAA_9-X1 was carried out as follows: Xanthate X1 (698 mg, 3.6 mmol), AA (2 g, 27.77 mmol), AIBA (11.9 mg, 0.044 mmol) and distilled water (1640 mL) were added to a Schlenk flask. The reaction mixture was then degassed by bubbling argon for 15 min and heated at 70 °C. The reaction was stopped after 3 h. The monomer conversion was greater than 99.9% (determined by ^{1}H NMR).The reaction mixture was then freeze dried to remove water.
^{1}H-NMR (D_2O, 300.13. MHz): δ (ppm) =4.55 (-O-C**H$_2$**-CH_3), 4.25 (-C**H**-S-), 2.7-1.35 (-C**H$_2$**-C**H**-), 1.3 (-O-CH_2-C**H$_3$**), 1.05 (CH_2-C**H$_3$**).
$M_{n\ NMR}$=900 g mol^{-1}, $M_{n\ MALS}$= 850 g mol^{-1}, $Đ$=1.2.

Synthesis of PAA_9-$PVPA_5$-X1

PAA_9-X1 (210.9 mg, 0.237 mmol), VPA (0.5 g, 4.62 mmol), AIBA (9.35 mg, 0.034 mmol) and distilled water (615 mL) were added to a Schlenk flask. The reaction mixture was then degassed by bubbling argon for 15 min and heated at 65°C. The reaction was stopped after 24 h. Monomer conversion of 30.1% was determined by ^{31}P NMR.
$M_{n\ PAANa}$ = 1020 g mol^{-1}, $Đ$=1.61.

1. [1] R. Fleet, J. B. McLeary, V. Grumel, W. G. Weber, H. Matahwa, R. D. Sanderson, *Macromol. Symp.* 2007, **255**, 8-19.

II. Figures S1 to S6.

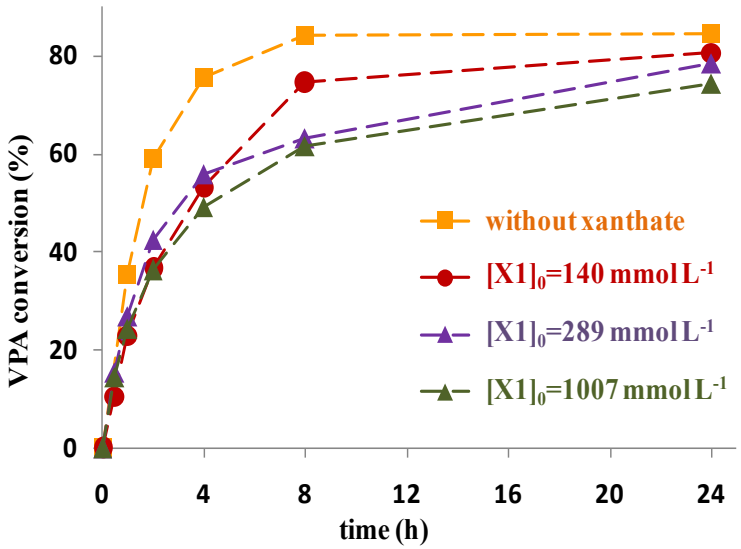


Fig S1. *Time-conversion curves during the RAFT/MADIX polymerisation of VPA in water at different initial X1 concentrations. $[VPA]_0$=7.52 mol L^{-1}, $[AIBA]_0$=56 mmol L^{-1}, T=65 °C.*

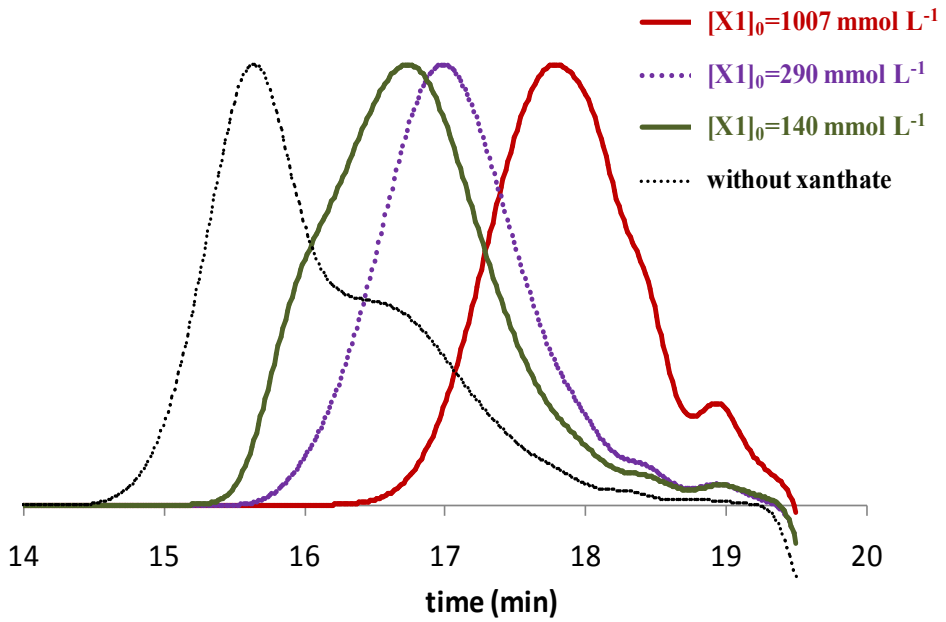


Fig. S2. *SEC-RI chromatograms of PVPAs synthesized in the presence of various concentrations of X1 after 24h reaction. Entries 4, 8, 11 and 15 of Table1.*

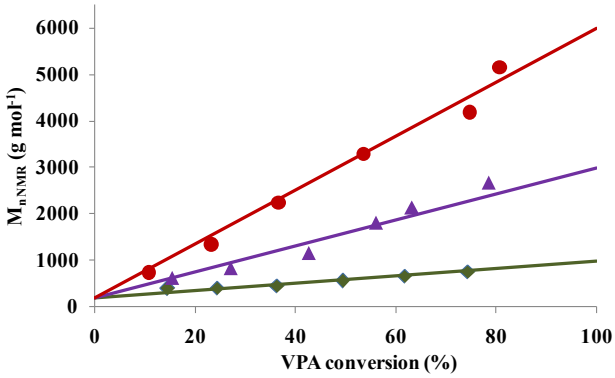


Fig. S3. *Evolution of $M_{n\ NMR}$ during the RAFT/MADIX polymerisation of VPA in water at different initial concentrations of X1. $[VPA]_0$=7.52 molL^{-1}, $[AIBA]_0$=56 mmolL^{-1}, T=65 °C. Full lines represent the theoretical evolution of M_n for a controlled MADIX polymerisation. $M_{n\ th}$=($[VPA]_0/[X1]_0$) *Conv*M(VPA)+ M(X1). $M_{n\ th}$=1000 g mol^{-1} (diamonds), 3000 g mol^{-1} (triangles), 6000 g mol^{-1} (circles).*

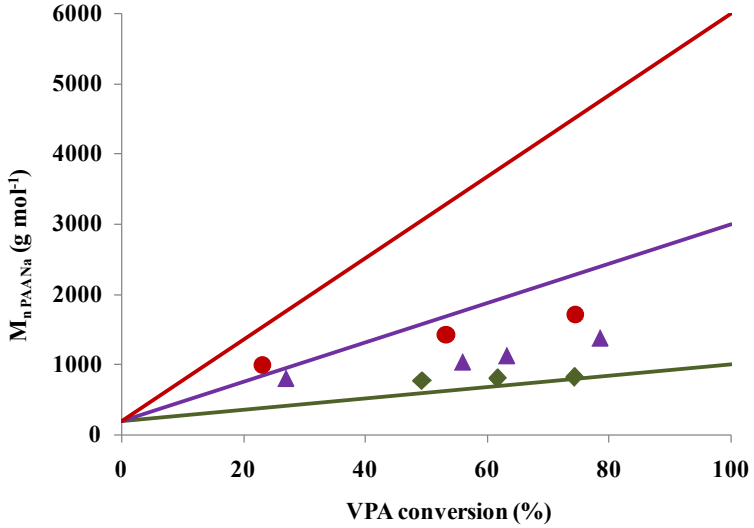


Fig.S4. *General Evolution of $M_{n\ PAANa}$ during the RAFT/MADIX polymerization of VPA at different initial X1 concentrations. $[VPA]_0$ = 7.52mol L^{-1}, $[AIBA]_0$ =56 mmol L^{-1}, T = 65°C. Solid lines represent the theoretical evolution of M_n for a controlled MADIX polymerization. $M_{n\ th}$ = ($[VPA]_0/[X1]_0$)*Conv*M(VPA)+ M(X1). $M_{n\ th}$ = 1000 g mol^{-1} (diamonds), 3000 g mol^{-1} (triangles), 6000 g mol^{-1}(circles).*

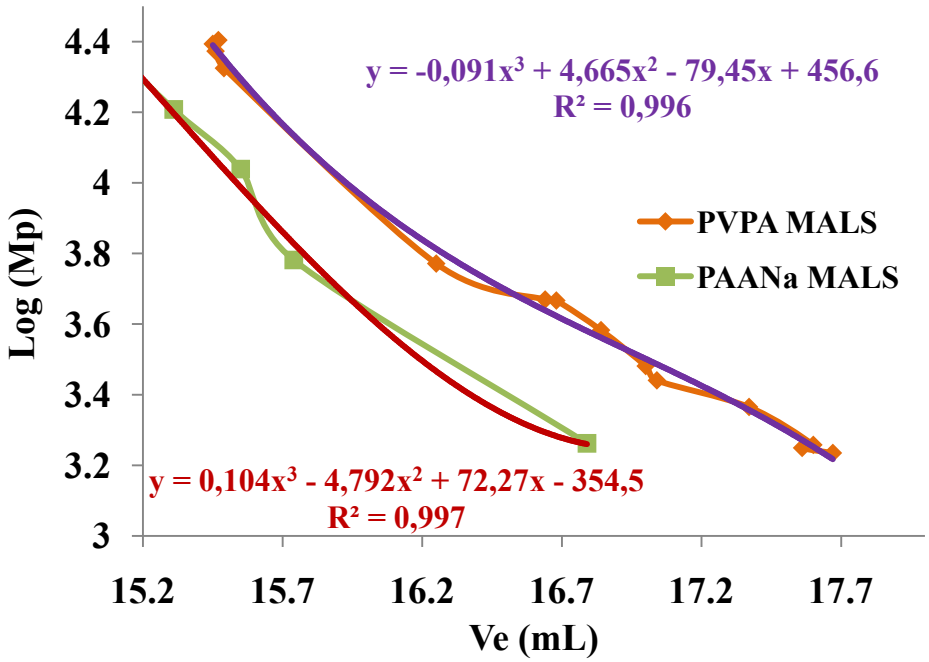


***Fig.S5**. Comparison of Log(M) versus elution volume for narrow PAANa standards and PVPA in Water (NaCl 100 mmolL^{-1}, NaH_2PO_4 25 mmolL^{-1}, Na_2HPO_4 25 mmolL^{-1}, buffer solution at pH=7).*

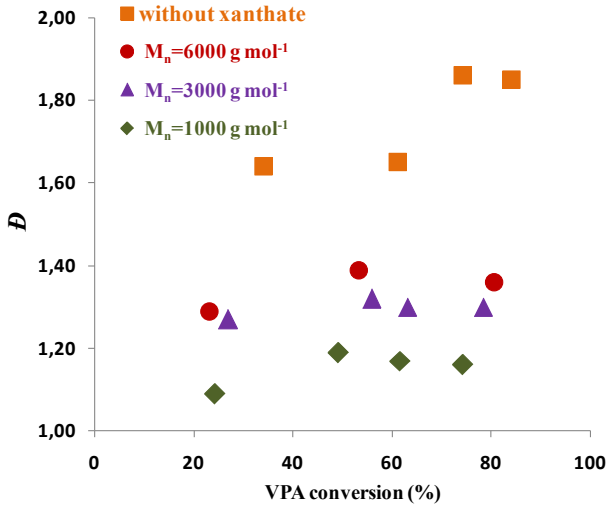


***Fig. S6**. Evolution of the polymer dispersity during aqueous RAFT/MADIX polymerisation of VPA for different theoretical molecular weights. $[VPA]_0$ = 7.52 mol L^{-1}, $[AIBA]_0$ =5 6 mmol L^{-1}, T=65 °C.*

III. NMR spectroscopy of PVPA, Figures S7 and S8.

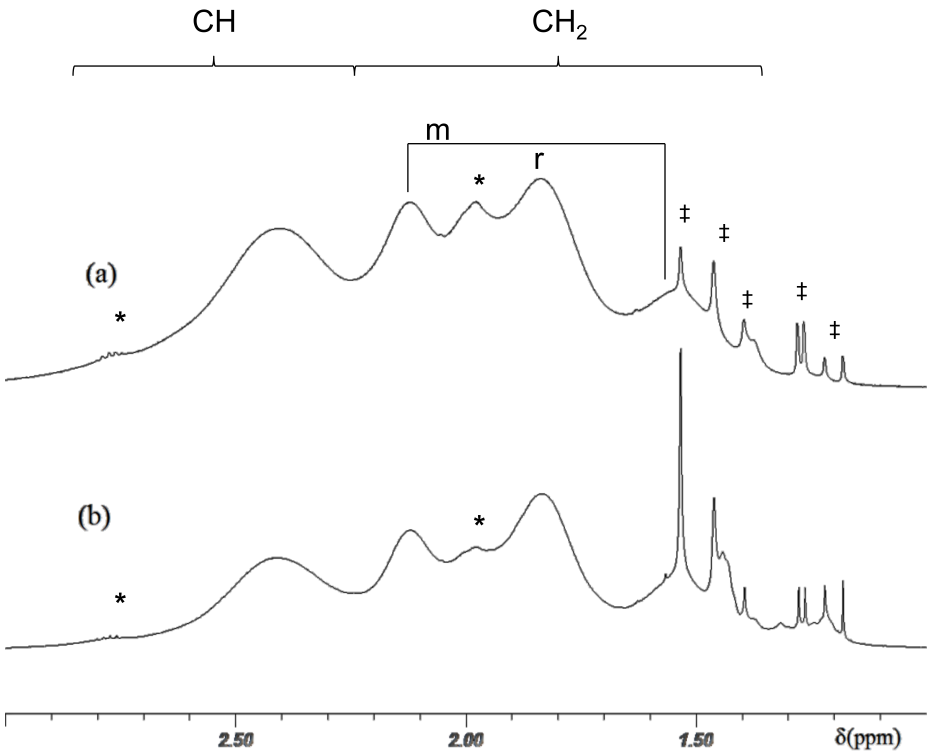


Fig.S7. *[1]H NMR spectrum of (a) PVPA obtained by RAFT/MADIX polymerisation and (b) PVPA obtained by conventional radical polymerisation.*denote the position of structural defects, m and r stand for meso and racemo respectively. ‡ denote the position of end group signals.*

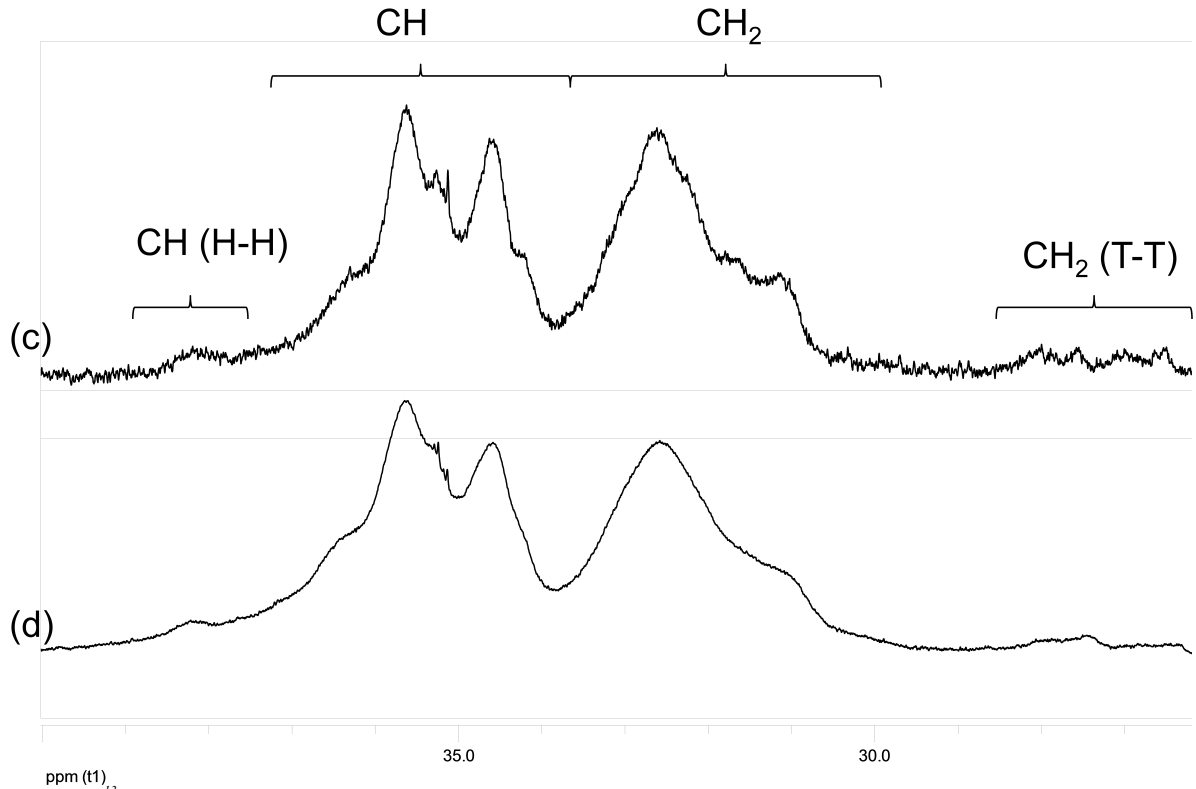
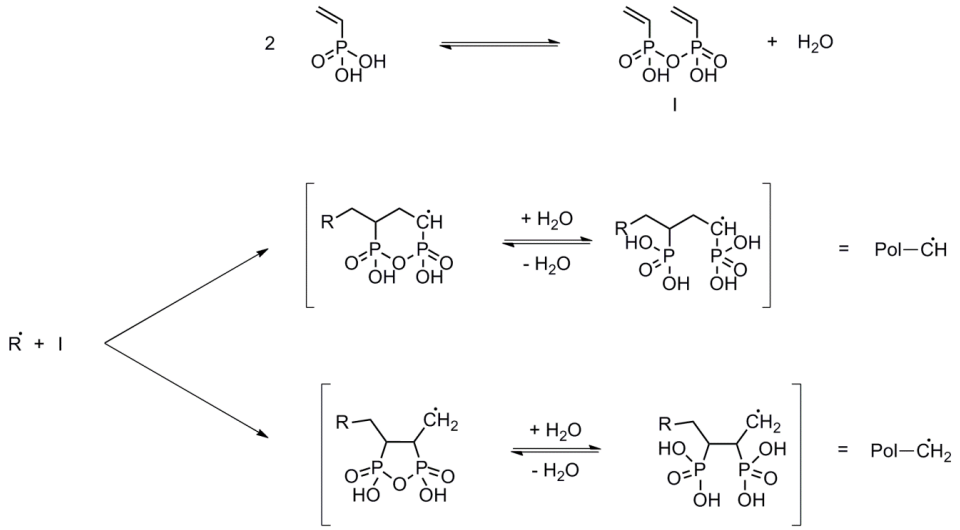


Fig.S8. *[13]C NMR spectrum of (c) PVPA obtained by RAFT/MADIX polymerisation and (d) PVPA obtained by conventional radical polymerisation. H-H and T-T stand for Head-to-Head and Tail-to-Tail defects signals, respectively.*

IV. Scheme S1.



Scheme.S1. *General mechanism for the polymerisation of VPA involving both conventional polymerisation and cyclopolymerisation.*