

Electronic Supplementary Information (ESI)

Influence of macromolecular characteristics of RAFT/MADIX poly(vinyl acetate)-based (co)polymers on their solubility in supercritical carbon dioxide

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I. Experimental section

Materials

Sodium trifluoroacetate (NaTFA, Fluka, for HPLC, > 99.0 %), *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Aldrich, matrix substance for MALDI-MS, > 99.0 % (HPLC)), *trans*-3-indoleacrylic acid (IAA, Fluka, matrix substance for MALDI-MS, > 99.0 % (HPLC)), dilauroyl peroxide (Acros Organics, 99 %), tetrahydrofuran (THF, Sigma-Aldrich, anhydrous, > 99.9 %, inhibitor-free) and propan-2-ol (Acros Organics, 99.5+ %) were used as received.

MALDI-TOF mass spectrometry

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 DCTB and NaTFA was used as a cationization agent for the PVAc samples. IAA and NaTFA were used for the PDMA oligomers. The polymer sample, the matrix and the salt were dissolved in THF and premixed in a 10:1.5:10 ratio.

Removal of the xanthate terminal group of PVAc

A PVAc (PVAc_{4k}-Xa, $M_{n\text{ theo}} = 4200 \text{ g.mol}^{-1}$) was synthesized with Rhodixan A1. A sample of this polymer (0.5 g, 0.11 mmol) was mixed with dilauroyl peroxide (113.6 mg, 0.285 mmol) in THF (1.5 mL) and propan-2-ol (3 mL). The mixture was degassed via four freeze-pump-thaw cycles, backfilled with argon, sealed and placed in an oil bath at 80 °C. After 4 h, the reaction was cooled in liquid nitrogen. The polymer was dried *in vacuo*.

II. MALDI-TOF characterization of PVAc-Xa

The PVAc samples synthesized with increasing chain lengths were characterized via MALDI-TOF MS measurements to assess their ω -functionalization by a xanthate moiety. A MALDI-TOF mass spectrum of a PVAc_{1.8k}-Xa is given in Figure S1.

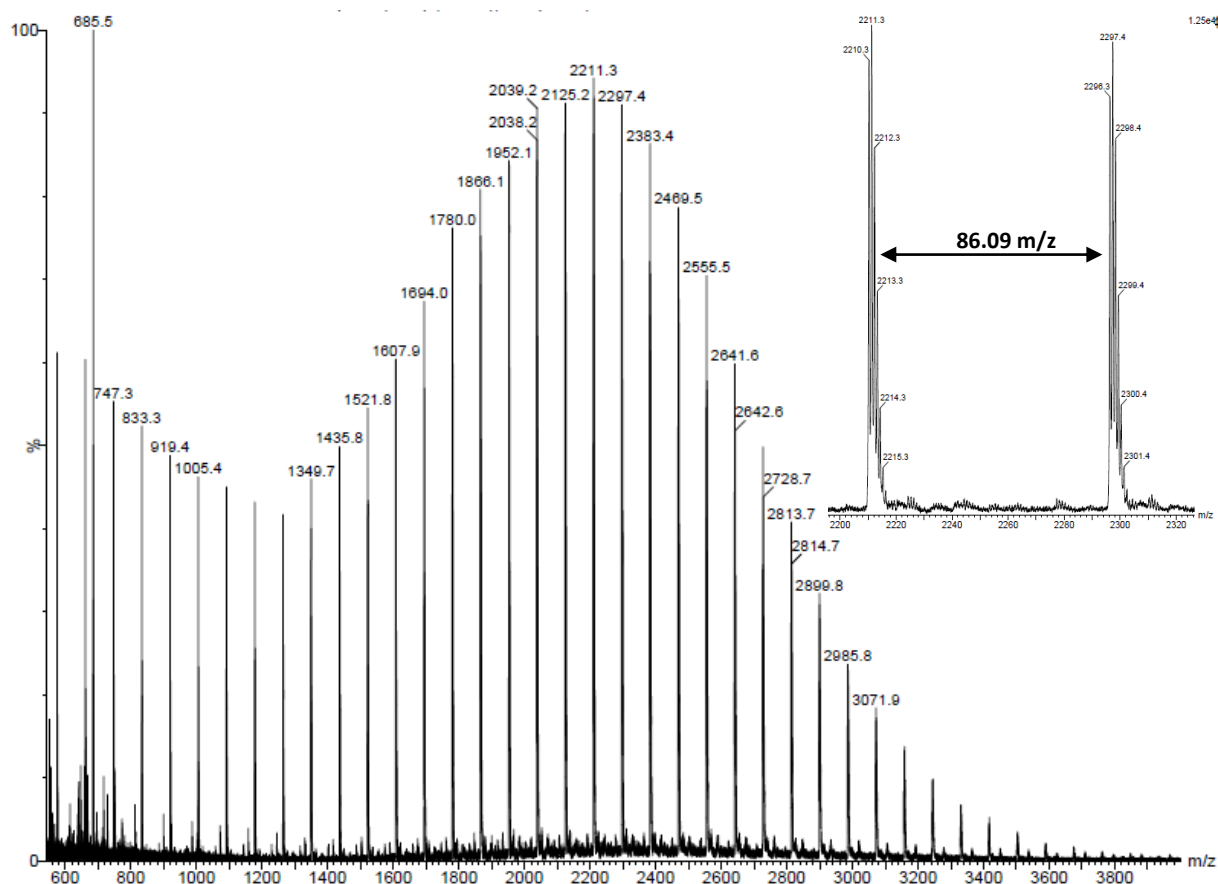


Figure S1 MALDI TOF spectrum of a PVAc_{1.8k} capped with a *O*-ethyl xanthate moiety

Each peak is 86.1 Da apart from each other corresponding to the molar mass of a vinyl acetate monomer unit. The main population was attributed to PVAc polymers initiated by a methyl propionyl radical and capped with a *O*-ethyl xanthate chain end (see Table S1). Interestingly, no fragmentation of the chain end was induced by the MALDI-TOF MS analysis. In the low molecular weight range, the relatively high intensities may be related to the formation of the PVAc chains terminated with an inverted VAc unit (head-to-head addition) and a xanthate.¹ Similar experiments with samples of higher M_n (PVAc_{3.8k}-Xa and PVAc_{5.8k}-Xa) led to significant mass discriminations. This was attributed to dispersities higher than 1.3.²

α end	ω end	DP _n	Cation	M _{n,theo}	M _{n,exp}
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	22	Na ⁺	2125.3	2125.2
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	23	Na ⁺	2211.4	2211.3
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	24	Na ⁺	2297.5	2297.4

Table S1 Peak assignments in the MALDI-TOF spectrum of PVAc_{1.8k}-Xa.

III. MALDI-TOF characterization of PDMA RAFT/MADIX Agents

MALDI-TOF measurements were also performed on poly(*N,N*-dimethylacrylamide) samples synthesized by RAFT/MADIX polymerization to assess the chain end-functionalization with a xanthate moiety. An example of a PDMA RAFT/MADIX Agent ($M_n = 1200 \text{ g.mol}^{-1}$) is given in Figure S2.

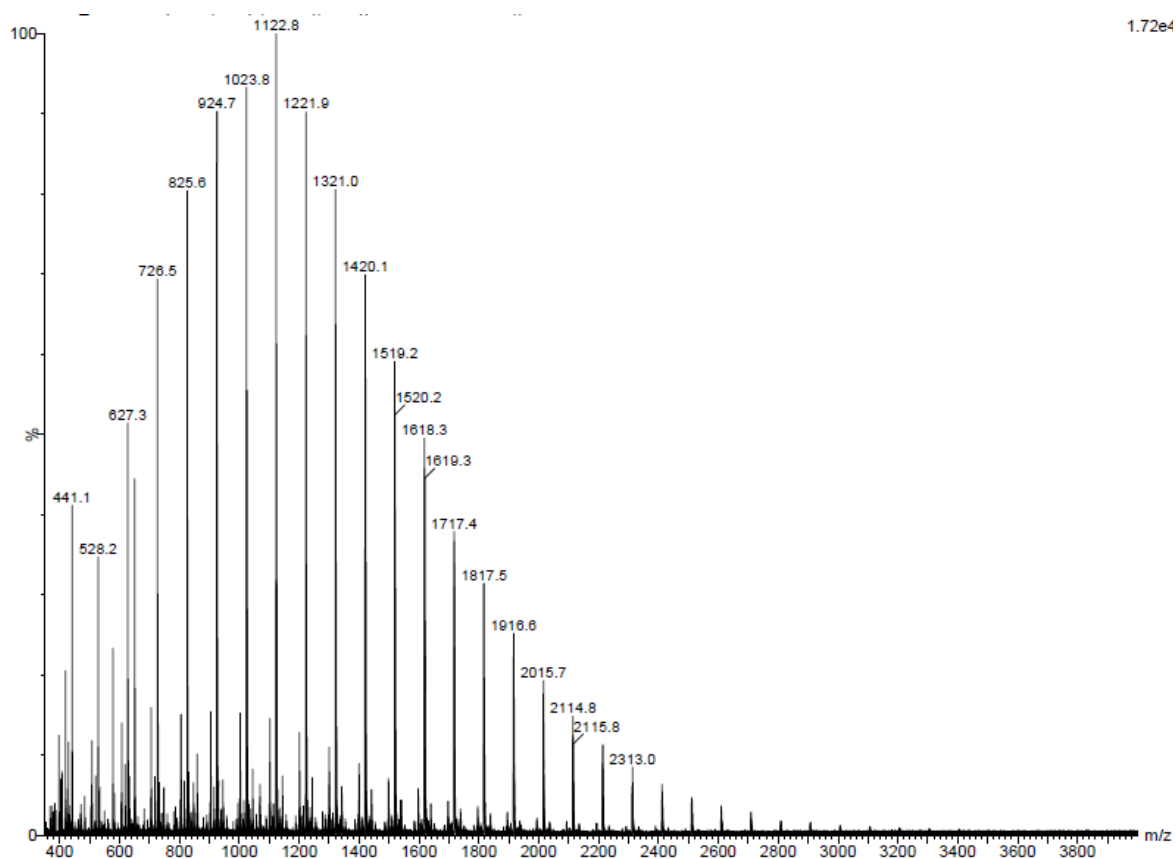


Figure S2 MALDI TOF spectrum of a PDMA RAFT/MADIX Agent ($M_{n,theo} = 1200 \text{ g.mol}^{-1}$)

The peaks are 99.1 Da apart from each other, which corresponds to the molar mass of a *N,N*-dimethylacrylamide monomer unit. The main population was attributed to PDMA chains initiated by a methyl propionyl radical and capped with a xanthate chain end (see Table S2).

α end	ω end	DP _n	Cation	M _{n,theo}	M _{n,exp}
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	9	Na ⁺	1123.2	1122.8
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	10	Na ⁺	1222.3	1221.9
CH ₃ -O-C(=O)-CH-CH ₃	-SC(=S)-OCH ₂ CH ₃	11	Na ⁺	1321.4	1321.0

Table S2 Assignment of the peaks in the MALDI-TOF spectrum of a PDMA MADIX Agent ($M_{n,theo} = 1200 \text{ g.mol}^{-1}$)

IV. Radical reduction of the xanthate chain-end group of PVAc

To probe the effect of a xanthate end-group on the solubility PVAc in supercritical carbon dioxide, the xanthate moiety was removed from a sample of PVAc_{4k}-Xa by radical reduction. The reaction was monitored by size exclusion chromatography using UV detection at 290 nm. The UV signal corresponding to the xanthate moiety in the PVAc_{4k}-Xa sample disappeared after reduction (see Figure S3a)) as no UV signal was evidenced for the PVAc_{4k}-H sample at similar elution volumes. No radical coupling or change in the molecular weight distribution were detected with RI detection (see Figure S3b)).

Additional experimental evidence of the disappearance of the xanthate moiety was given by MALDI-TOF MS analysis. Again, significant mass discriminations appeared due to a dispersity of 1.4. However, the detailed zooms evidenced the shift of the peak from 3244.7 m/z (Figure S4a)) to 3124.9 m/z (Figure S4b)). This difference of 119.8 m/z was attributed to the loss of $-\text{SC}(=\text{S})-\text{OCH}_2\text{CH}_3$ and the creation of a PVAc_{4k}-H chain via a hydrogen atom transfer to propan-2-ol.

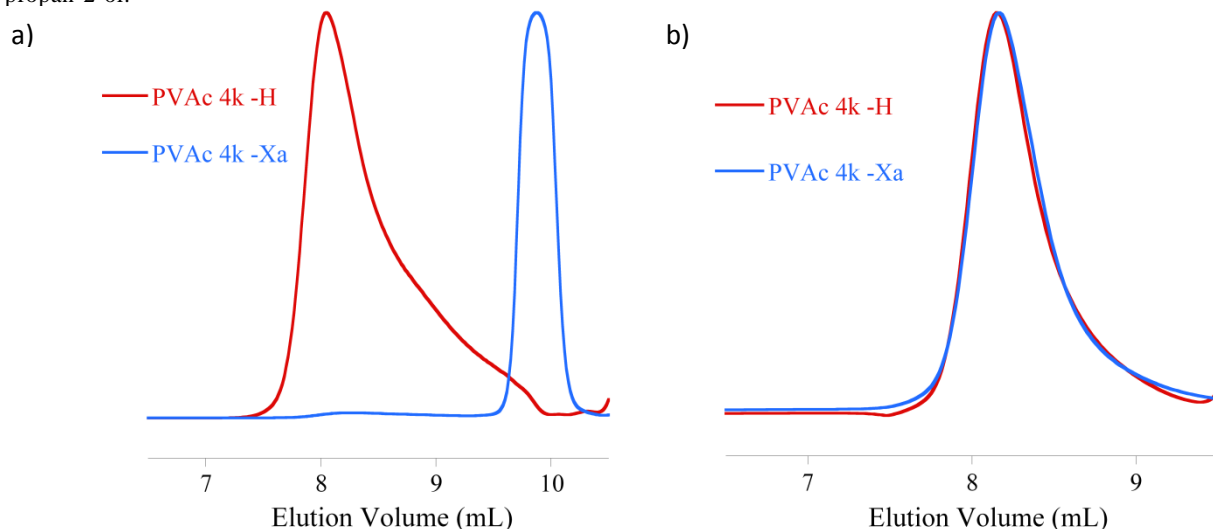


Figure S3 Overlays of SEC chromatograms for PVAc_{4k}-Xa (blue line) and a PVAc_{4k}-H (red line) in a) UV detection at 290 nm and b) RI detection

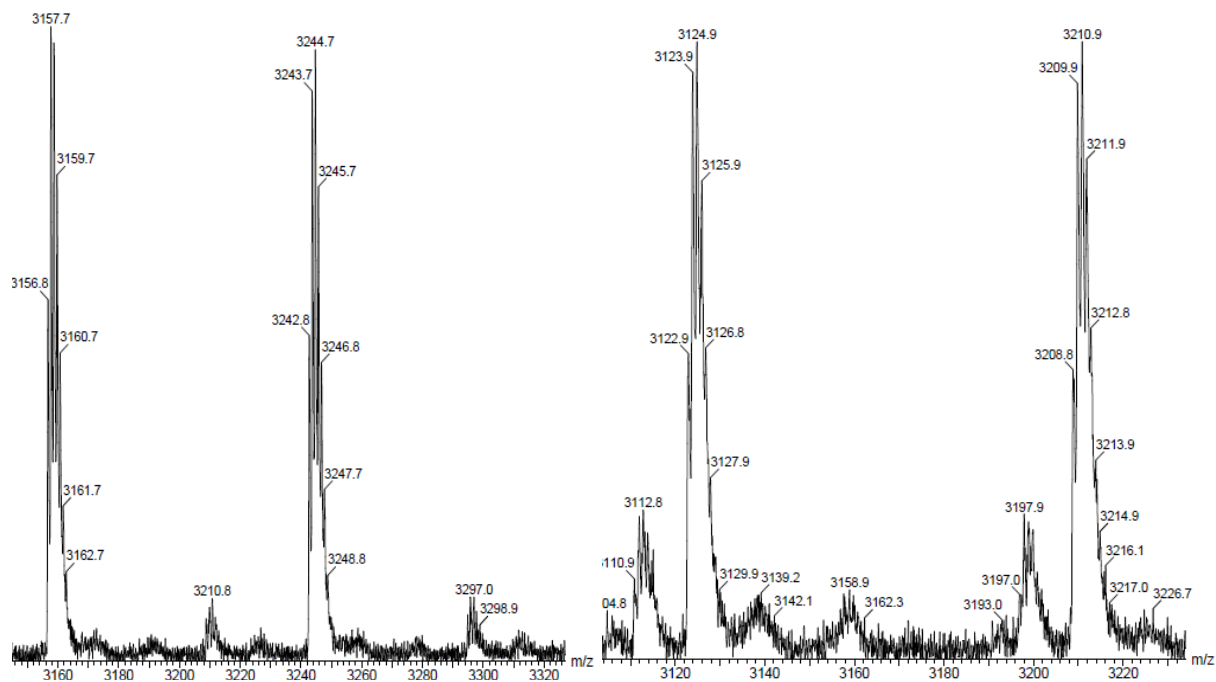


Figure S4 : Detailed views of MALDI-TOF spectra corresponding to PVAc_{4k}-Xa a) before and b) after reduction of the xanthate group (PVAc_{4k}-H)

References

- 1 Y. Kwak, A. Goto, T. Fukuda, Y. Kobayashi and S. Yamago, *Macromolecules*, 2006, **39**, 4671.
- 2 K. Martin, J. Spickermann, H. J. Rader and K. Mullen, *Rapid Commun. Mass Spectrom.*, 1996, **10**, 1471.