Electronic Supplementary Information (ESI)

Effects of Poly(Vinyl Pivalate)-based Stabiliser Architecture on CO_2-Solubility and Stabilising Ability in Dispersion Polymerisation of N-Vinyl Pyrrolidone

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Table ESI-1. Synthesis Data for Statistical and Block Copolymer Stabilisers of Varying Ratio and Molecular Weight.

Polymer	M:R:I[a]	PVAc Block A (M_n, PDI)[a]	$M_{n,th}$ (Kg/mol)	$M_{n,expt}$ (Kg/mol)[a]	PDI[a]	Feed Ratio	Expt. Ratio[b]	Conv. (%)[b]	T_g (°C)[c]
PVAc-*s*-PVPi-X	109:1:0.1	-	11.6	12.1	1.46	25:75	24:76	89	40.7
	124:1:0.1	-	11.1	11.6	1.40	60:40	51:49	85	50.2
	140:1:0.1	-	12.7	11.7	1.38	80:20	74:26	94	61.7
PVAc-*b*-PVPi-X	69:1:0.1	2.2K, 1.20	9.1	12.3	1.54	25:75	27:73	83	36.2, 70.3
	53:1:0.1	4.2K, 1.27	8.3	11.9	1.45	50:50	46:54	75	39.8, 66.1
	33:1:0.1	7.7K, 1.33	9.8	11.8	1.52	75:25	70:30	82	41.6, 67.5
	25:1:0.1	2.2K, 1.20	4.8	6.7	1.31	50:50	46:54	79	37.0, 53.4
	47:1:0.1	4.5K, 1.24	7.9	10.2	1.45	50:50	51:49	75	39.3, 64.1
	78:1:0.1	7.0K, 1.25	12.6	15.8	1.52	50:50	47:53	74	41.0, 72.5

Polymerisation conditions: Statistical copolymers synthesised *via* bulk polymerisation at 65 °C for ~4 h, and block copolymers synthesised *via* solution polymerisation in dry toluene (5 mL) at 65 °C for 24 h. [a]Experimental M_n and PDI obtained from GPC-RI detector using THF eluent and PS standards. [b]Conversion and PVAc:PVPi ratio determined from ^{1}H NMR in $CDCl_3$. Ratios correspond to PVAc:PVPi composition. [c]T_g obtained from DSC analysis. Reactivity ratio of VAc and VPi is 0.79 and 0.96 respectively as obtained from the literature.

Table ESI-2. Dispersion Polymerisation using Free Radical Copolymer Stabiliser.

Stabiliser	Stabiliser Details (M_n, PDI, ratio)	Cloud Point (bar)[a]	PNVP Yield (%)[b]	PNVP Appearance
PVAc-*s*-PVPi-FRP	10.0K, 2.05, 29:71	252.1	53	Hard Solid
PVAc-*s*-PVPi-X	10.3K, 1.44, 24:76	144.8	86	Powder

Polymerisation conditions: $scCO_2$ polymerisation at 35 °C for 48 hours with V-70 initiator. [a]Cloud point pressure determined at 35 °C using variable volume view cell. [b]Yield determined gravimetrically.

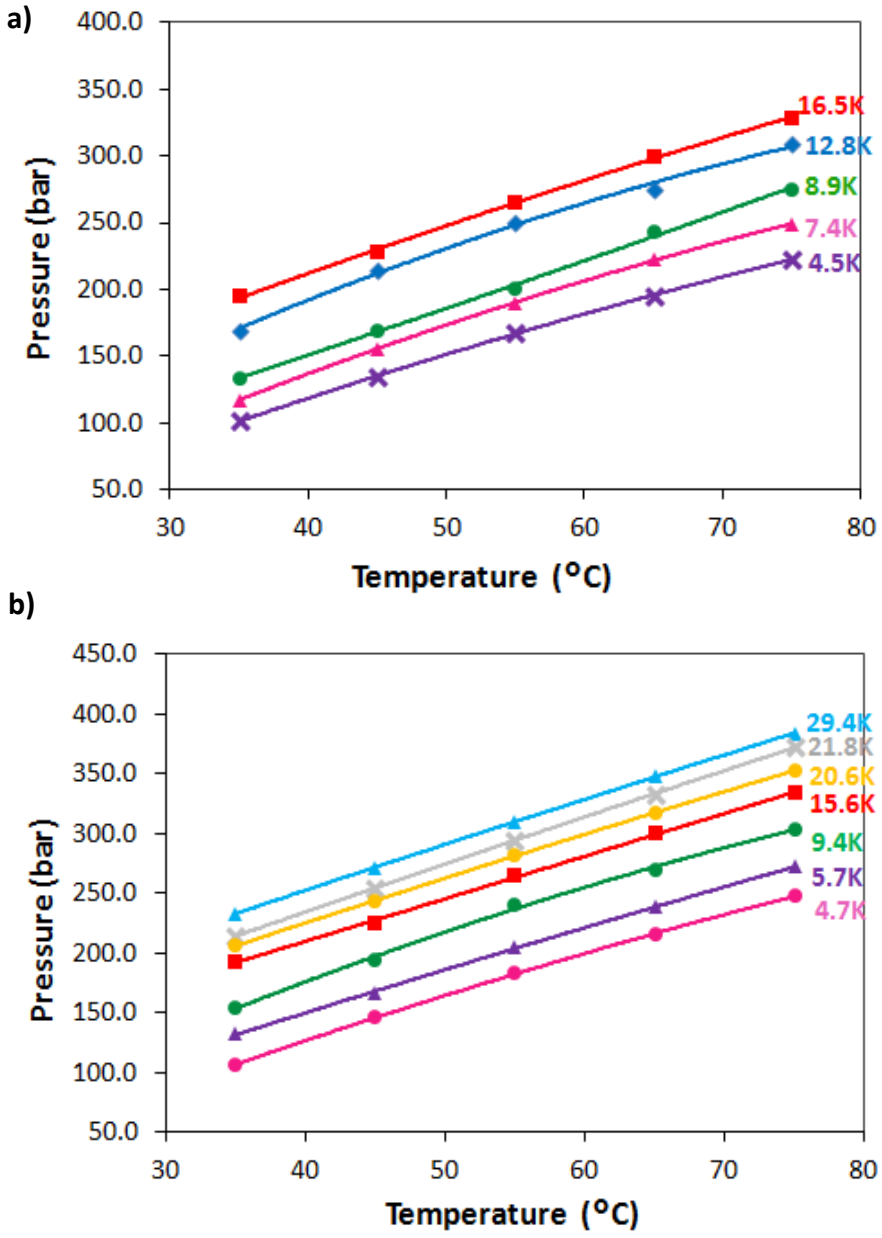


Figure ESI-1. Cloud Point curves of statistical copolymers of varying molecular weight with monomer feed ratio a) 10:90 and b) 50:50. Measurements taken in CO_2, with 15 wt % NVP w.r.t CO_2 and 5 wt % statistical copolymer w.r.t monomer.

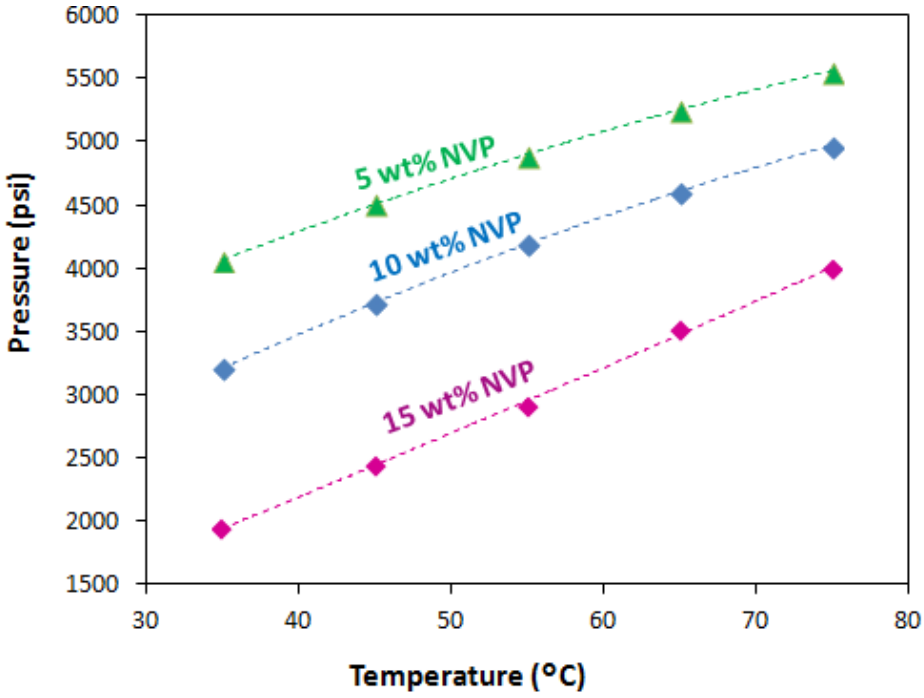


Figure ESI-2. PVAc-*s*-PVPi-X (8.9K, 1.53, 10:90) at varying NVP concentration, 20 g CO_2 and 0.15 g stabiliser.

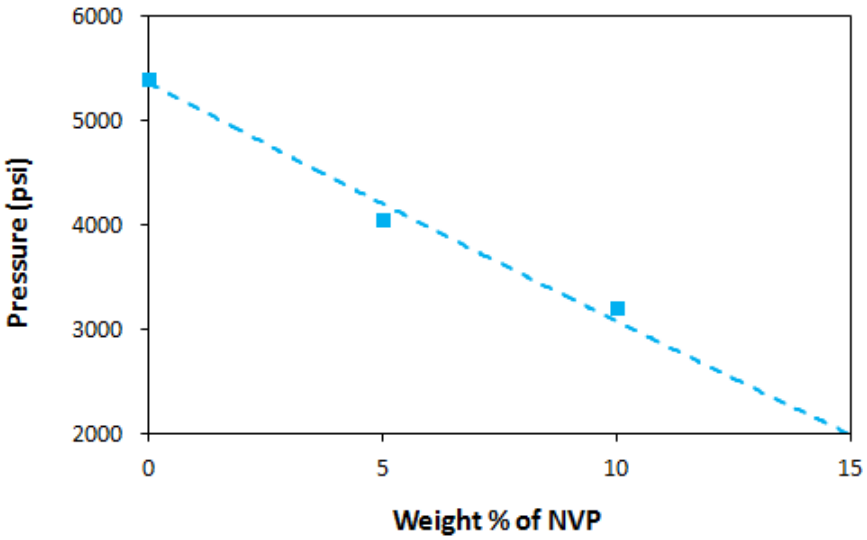


Figure ESI-3. Comparison of cloud points at 35 °C for 10:90 PVAc:PVPi-X stabiliser at varying NVP weight percentages.

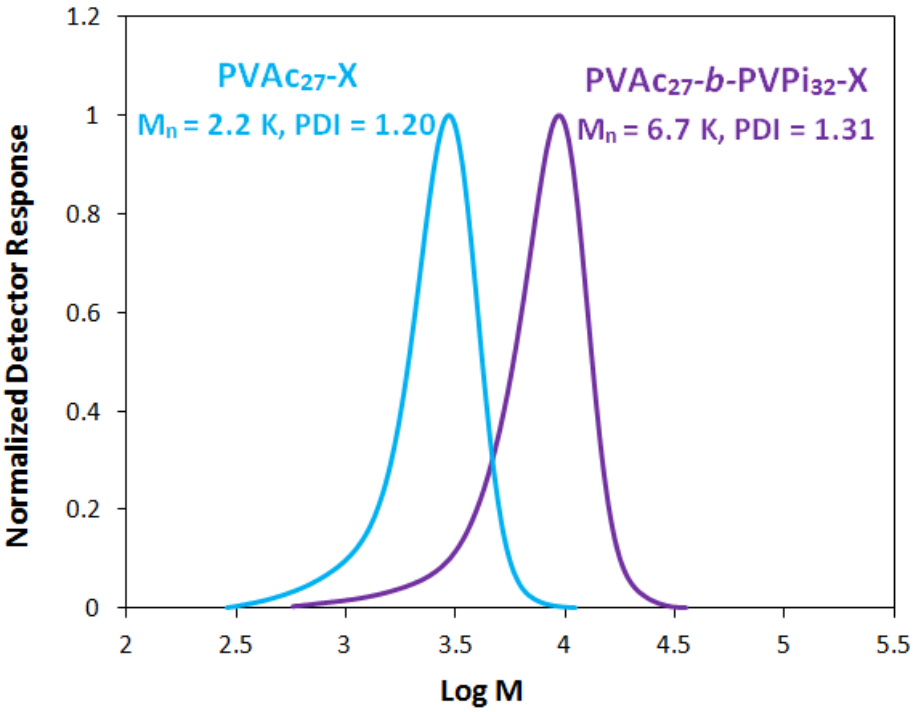


Figure ESI-4. Characteristic block copolymer GPC trace, showing initial PVAc-X block, followed by chain extension to yield PVAc-*b*-PVPi-X block copolymer structure.

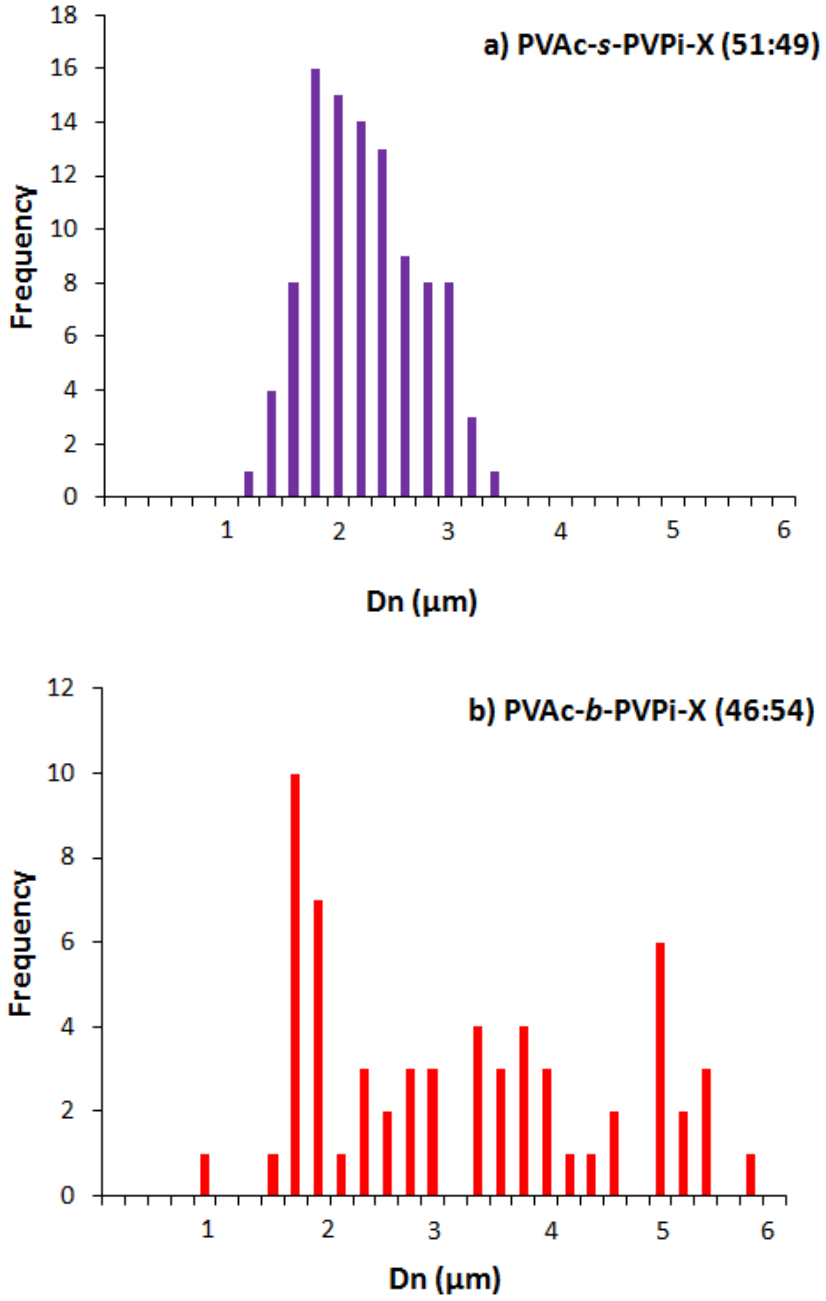


Figure ESI-5. Histogram of PNVP particle diameters synthesized by dispersion polymerisation in $scCO_2$ using block and statistical copolymers of comparable molecular weight (~12.0 K) and 50:50 PVAc:PVPi composition, comparing ~100 particles from SEM images. Results obtained from data in Table 1, entries 2 and 5.

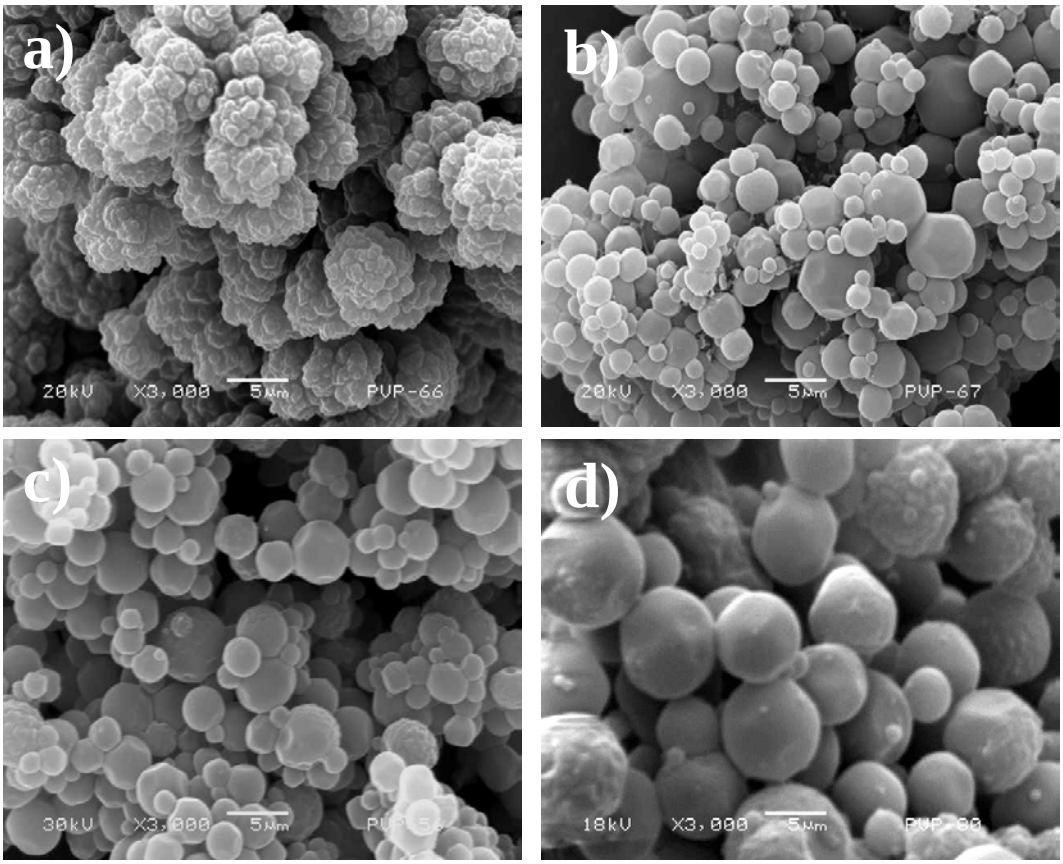
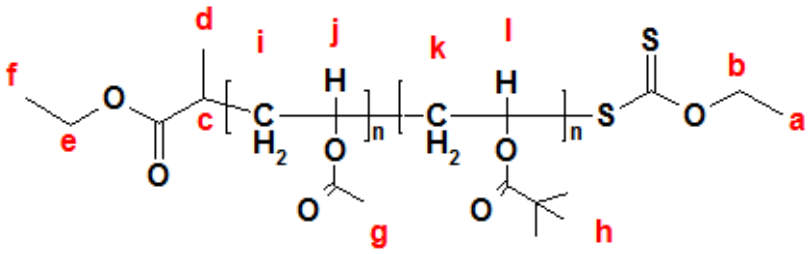
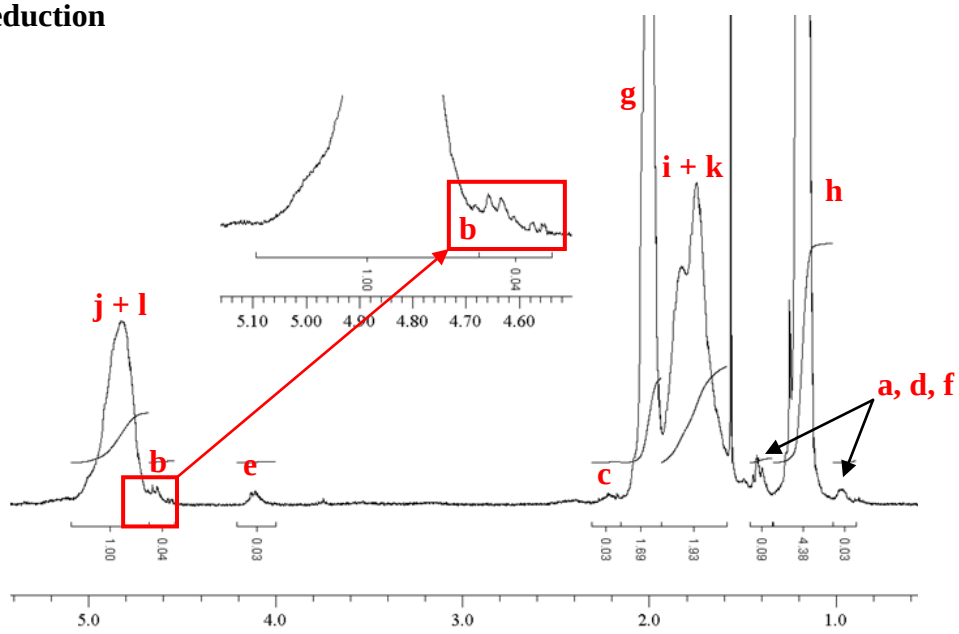


Figure ESI-6. Comparison of PNVP products using block copolymer stabilisers of varying molecular weight. (a) 6.7K; (b) 10.2K; (c) 11.9K; (d) 15.7K. Data taken from Table ES1-1, entries 5, 7, 8, 9.



(a) Before Reduction



(b) After Reduction

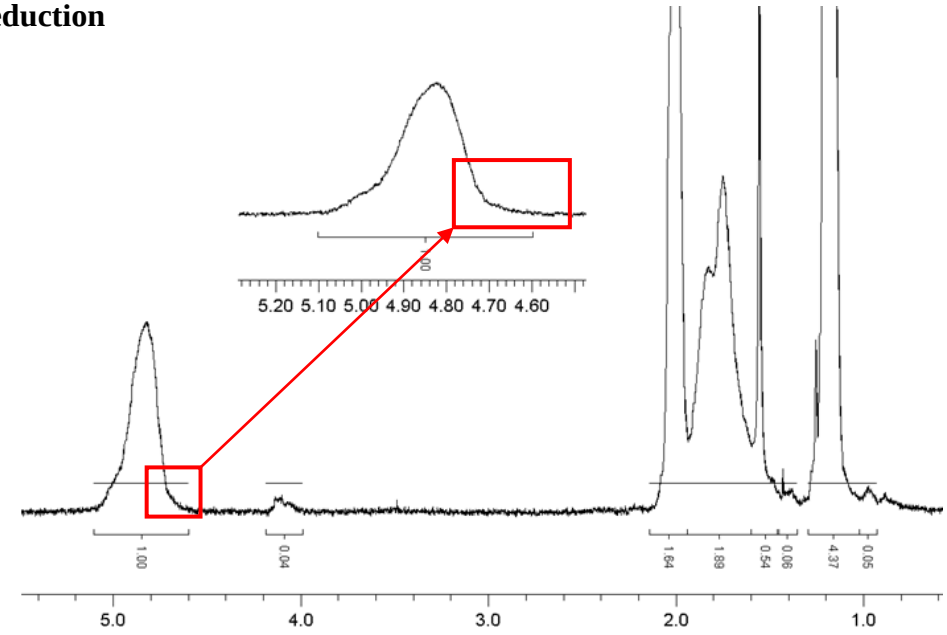


Figure ESI-7. ^{1}H NMR of stabiliser (a) prior to and (b) after reduction. Peaks corresponding to xanthate end-group are completely removed after reduction, resulting in a polymer with a C-H end group.

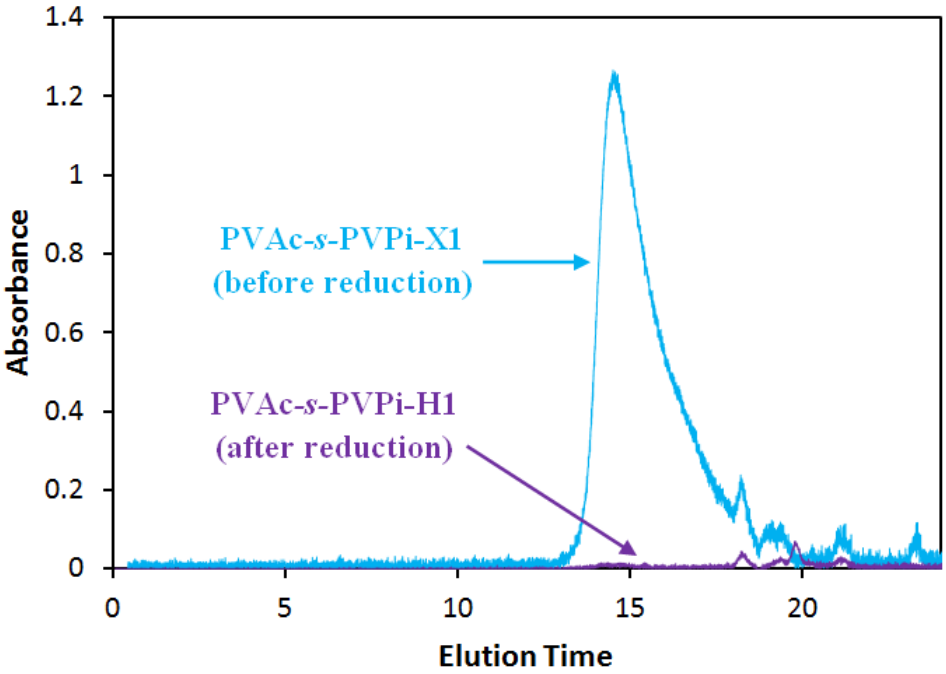


Figure ESI-8. GPC-UV analysis employed for determination of the removal of the xanthate group from the polymer. After reduction, the characteristic thiocarbonylthio absorbance is diminished, evidence that the reduction was successful. Characteristic sulfur absorbance is present at 254 nm prior to reduction (blue) and absent in trace after radical-induced reduction (purple).

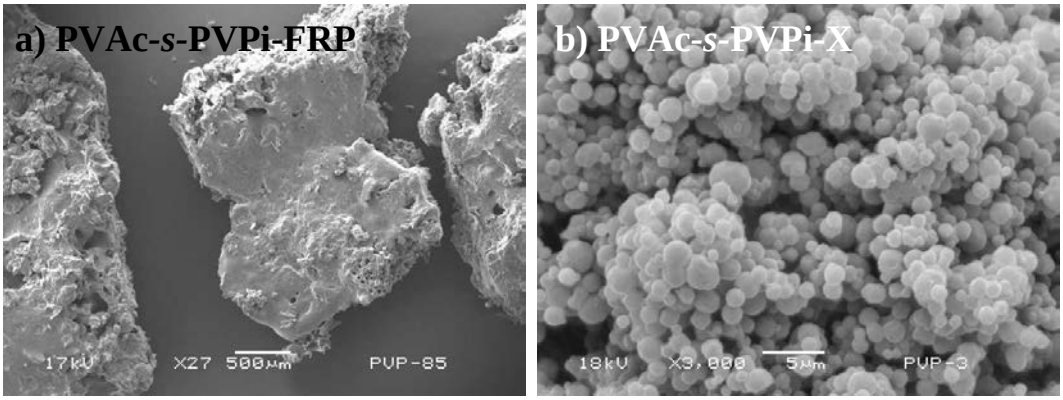


Figure ESI-9. Comparison of PNVP products obtained from dispersion polymerisation using PVAc-*s*-PVPi-FRP copolymer synthesised by free radical polymerisation and PVAc-*s*-PVPi-X copolymer synthesised by RAFT polymerisation. (a) PVAc-*s*-PVPi 10.0 kg/mol, 2.05, 29:71; (b) PVAc-*s*-PVPi-X 10.3 kg/mol, 1.44, 24:76. The free radical copolymer, PVAc-*s*-PVPi, is unsuccessful in producing a dispersion polymerisation, and a highly agglomerated, irregular mass of PNVP is produced using this as a stabiliser. This is in distinct contrast to the polymerisation employing the RAFT synthesised copolymer, in which a high yielding PNVP powder with spherical microparticle formation is obtained.

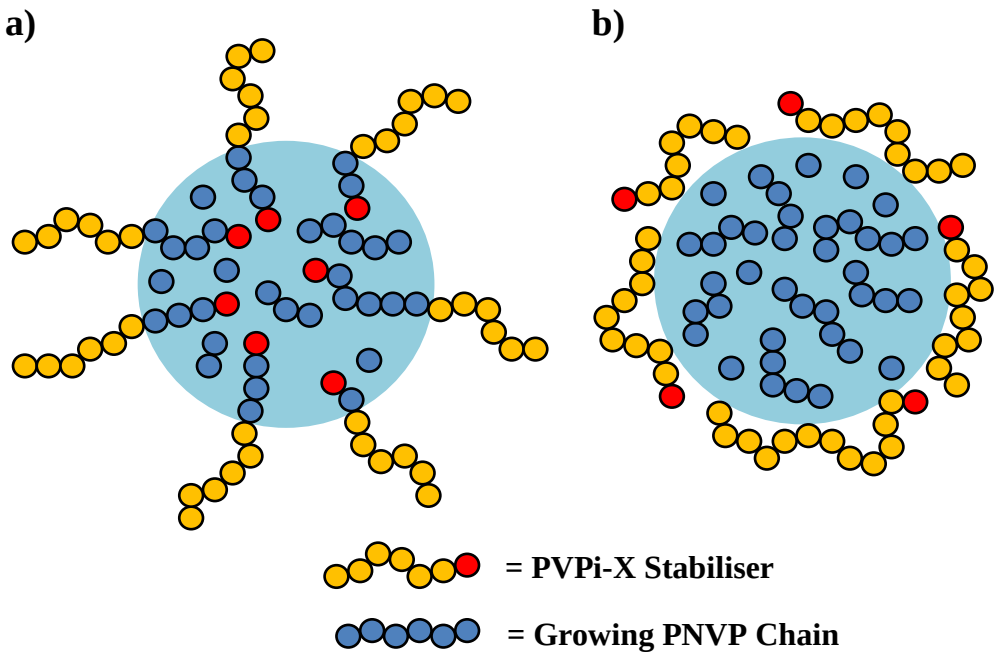


Figure ESI-10. Two possible modes of anchoring via the PVPi-based stabilisers: a) Chemical anchor mechanism involving RAFT polymerisation of the growing PNVP chains This will lead to the formation of a block copolymer consisting of the hydrocarbon stabiliser grafted to the PNVP chain, and terminated with the RAFT agent. The xanthate terminated growing PNVP chains will associate and form primary particles. Additional polymerisation will continue within the monomer-swollen particles, leading to high molecular weight PNVP products; b) Physical anchor mechanism in which the stabiliser physically adsorbs to the surface of the growing polymer particle.