

Electronic Supplementary Information (ESI)

Synthesis and Application of New CO₂-Soluble Vinyl Pivalate Hydrocarbon Stabilisers via RAFT Polymerisation

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Note ESI-1. At the time of publishing, the cost of 1Kg Krytox 157-FSL supplied by Dupont is £827 per Kg, whilst the cost of 1Kg PVPi is ~£58.

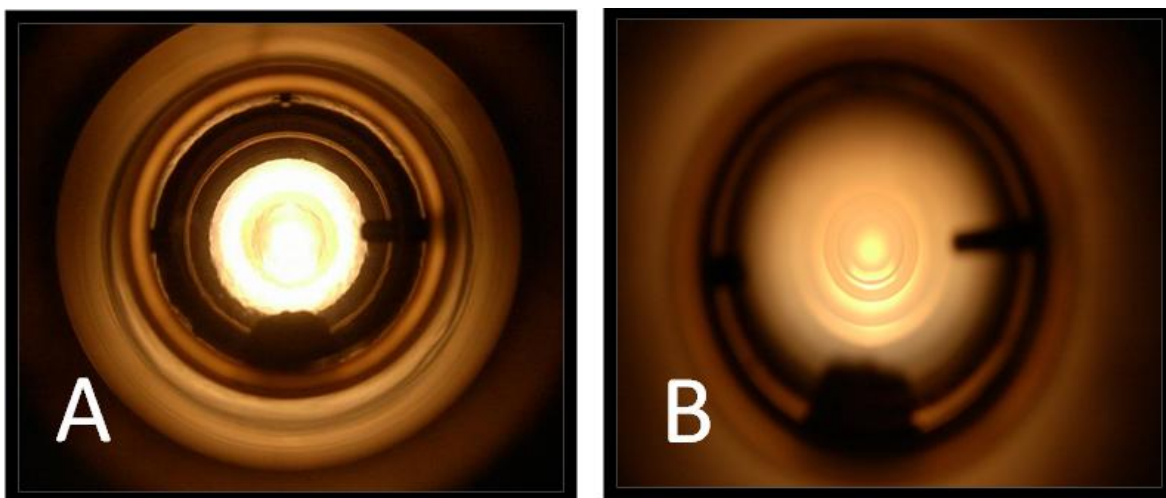


Figure ESI-1. Phase behaviour of stabiliser when completely soluble (A) and approaching the cloud point (B) indicated by presence of insoluble stabiliser material. Cloud point is measured as the pressure at which the backlight is completely obscured by precipitated stabiliser, and an average of three measurements taken.

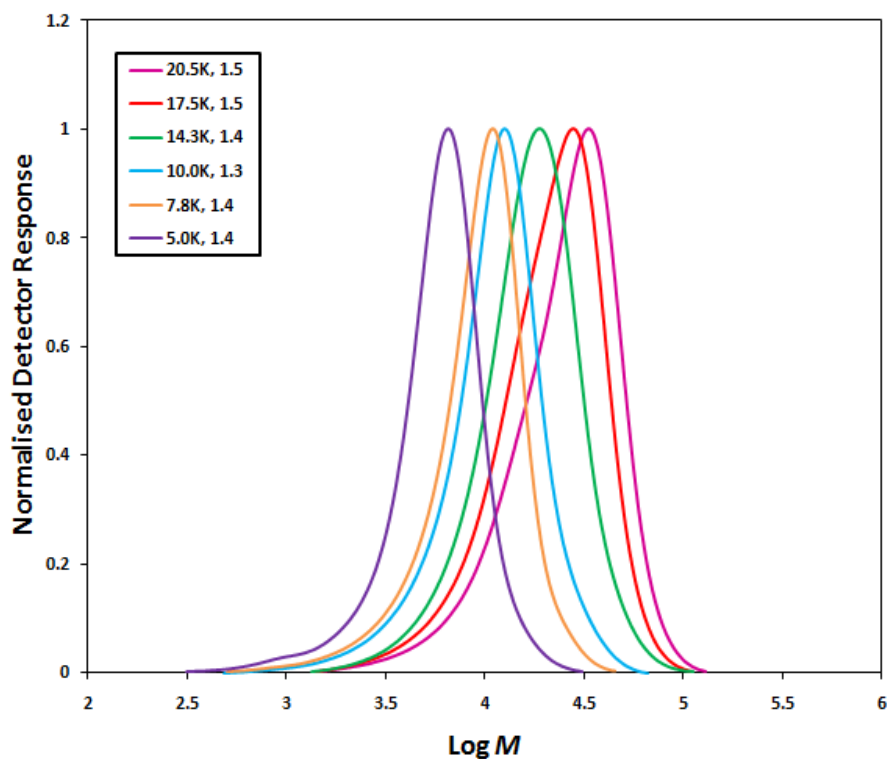


Figure ESI-2. GPC trace overlay of PVPi homopolymers of varying molecular weight. Legend shows corresponding M_n and PDI values of homopolymers as obtained from GPC with PS standards in THF.

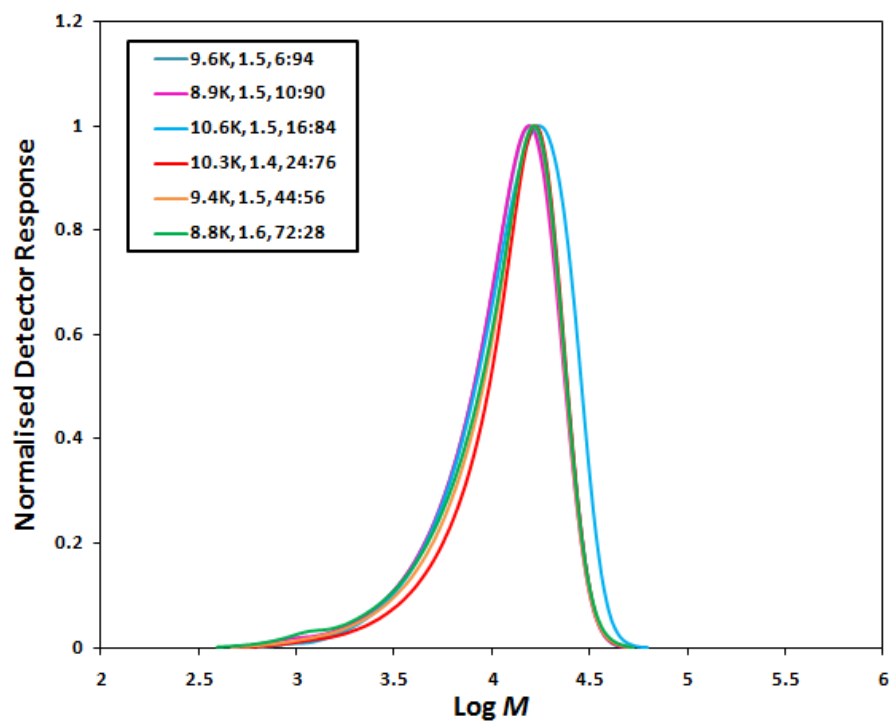


Figure ESI-3. GPC trace overlay of PVAc-s-PVPi-X copolymers of similar molecular weight and varying PVAc: PVPi ratio. Legend corresponds to: M_n , PDI, PVAc:PVPi ratio.

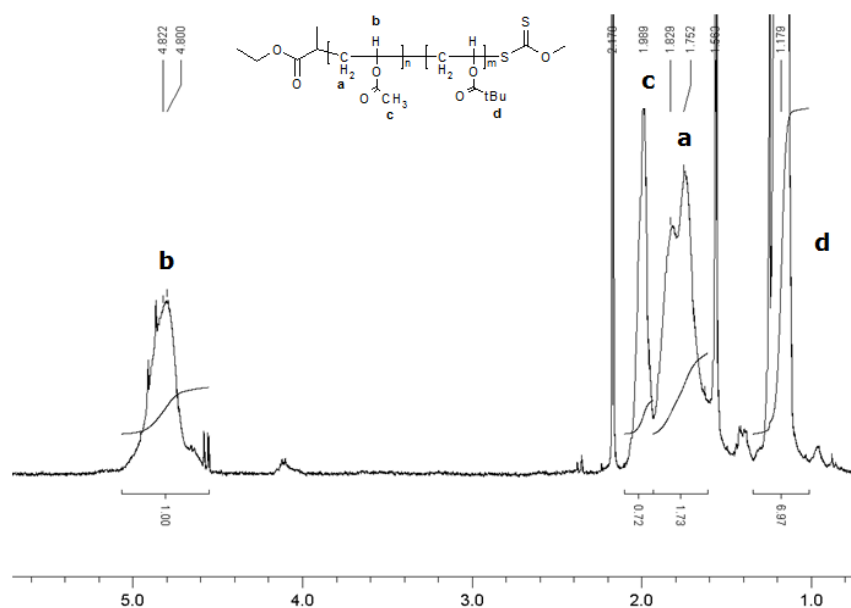


Figure ESI-4. Proton NMR in deuterated Chloroform for copolymer of PVAc and PVPi.

Monomer conversion determined from comparison of integrals of monomer (4.5-4.6 ppm) and polymer (4.8-5.0 ppm) peaks. Molar ratio of PVAc:PVPi calculated via integration of peaks c and d, relating to the CH₃ of PVAc and ^tBu of PVPi respectively.

Ratio of PVAc : PVPi = (c/3) : (d/9) = 0.72/3 : 6.97/3 = 24 : 76.

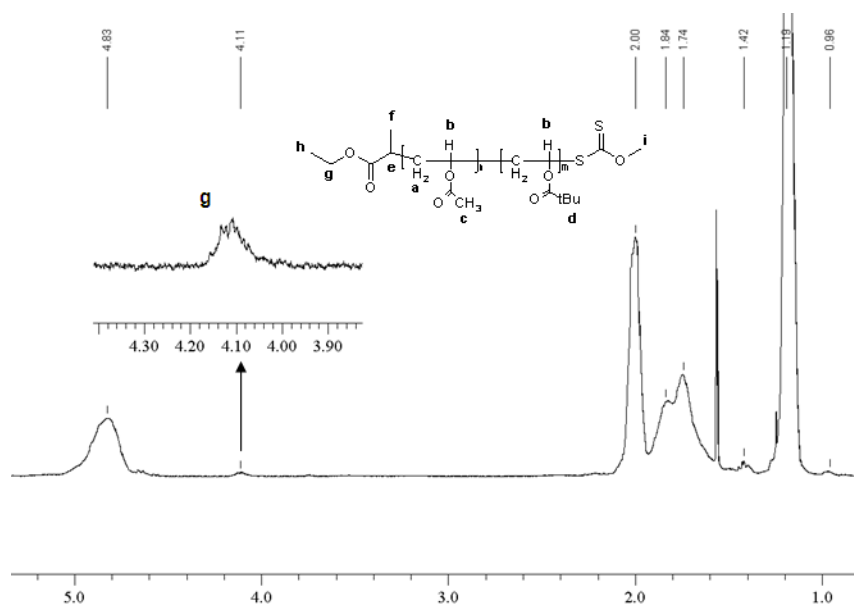


Figure ESI-5. Proton NMR of copolymer with expansion of xanthate peak used in molecular weight determination.

Table ESI-1. Molecular weights of key copolymers as determined by ^1H NMR and GPC-RI.

Polymer	M _n (NMR) (Kg/mol) ^a	M _n (GPC) (Kg/mol) ^b	PDI ^b	Ratio (PVAc:PVPi) ^a
PVAc-X	9.1	9.6	1.4	---
PVPi-X	10.0	10.0	1.3	---
	14.5	14.3	1.4	---
PVAc-s-PVPi-X	8.5	8.8	1.6	72:28
	9.0	9.4	1.5	44:56
	10.0	10.3	1.4	24:76
	10.8	10.6	1.5	16:84
	9.6	8.9	1.5	10:90
	10.8	9.6	1.5	6:94

^aRatio and M_n determined from ^1H NMR in CDCl_3 , with the assumption of one xanthate per polymer chain. Analysis via comparison of tertiary butyl group of PVPi (1.18 ppm), methyl group of PVAc (2.00 ppm), and CH_2 group of xanthate (4.11 ppm). ^bExperimental M_n and PDI obtained from GPC-RI detector using PS standards.