

Successful Dispersion Polymerization in Supercritical CO₂ Using Polyvinylalkylate Hydrocarbon Surfactants Synthesised and Anchored via RAFT

Hyunsuk Lee, Elaine Terry, Mengmeng Zong, Nicholas Arrowsmith, Sébastien Perrier, Kristofer J Thurecht* and Steven M Howdle*

Synthesis of PVAc by RAFT

RAFT terminated poly(vinyl alkylates) were synthesized in bulk using (S-(1-ethoxycarbonyl)ethyl) O-ethyl xanthate) as RAFT agent and azobisisobutyronitrile as initiator. Typically, the ratio of xanthate:initiator was kept at 10:1 so that almost all chains were terminated by the RAFT agent. The reaction was undertaken at 65 °C for 48 hours with stirring. The subsequent polymer was obtained by precipitating the mixture in hexane. The end-group fidelity was investigated by MALDI-TOF MS and ¹H NMR and the molecular weight characterized by GPC in THF using an RI detector and polystyrene standards.

Synthesis of PVAc by standard free radical polymerization.

PVAc was synthesised as described above, but in the absence of RAFT agent. In this case, AIBN was used as initiator and isopropanol as solvent. Different fractions of various molecular weights were separated by supercritical fluid extraction as described in a previous publication. (Tan B., Lee J., Cooper AI., *Macromolecules*, 2007, **40**, 1945-1954).

A comparison of the cloud point data scCO₂ for PVAc synthesized by the two methods is provided in Table S1. These data confirm that the RAFT terminus has only a small influence upon the solubility of the polymers in scCO₂

Table S1. Comparison of the cloud point characteristics for PVAc with different end-groups at 35 °C in sc CO₂.

End group	Cloud point / psi (MPa)	Mn / kDa	PDI
Xanthate-PVAc	5400 (37.2)	7.6	1.3
Standard PVAc	4900 (33.8)	7.0	1.5

Polymerisation of MMA using polyvinylalkylate surfactants.

Dispersion polymerization was attempted for MMA in scCO₂ using the xanthate terminated hydrocarbon surfactants. In a typical reaction, hydrocarbon surfactant (5 wt %, 420 mg) and initiator (VA-070, 1 wt%, 84 mg) were added to the autoclave and degassed by flushing with a stream of CO₂ for 10 minutes. 8.4g MMA (previously

degassed by 3 consecutive freeze-pump-thaw cycles) was added to the autoclave under a positive stream of CO₂. The reaction vessel was heated to 35 °C, pressurised to 5000 psi and stirred for 48 hours. Upon completion of the reaction period, the autoclave was vented and the resulting liquid was taken for analysis by ¹H NMR. In all cases, the recovered polymer was a liquid suggesting that insufficient stabilization (or anchoring) occurred with PMMA.

Table S2. Polymerization of MMA using PVAc-PVB block copolymer.

Entry	Conversion	Mn / kDa	PDI	Appearance
1	30	14.1	3.2	Liquid
2	42.5	14.6	2.9	Viscous liquid

Entry 1 refers to Xanthate-terminated PVAc homopolymer (Mn = 10 Da, PDI = 1.35). Entry 2 refers to xanthate-terminated PVAc-PVB copolymer (50:50, Mn = 10 kDa, PDI = 1.3)

In both of these cases the recovered PMMA polymer was a low molecular weight liquid, the conversion was poor and both factors suggest that insufficient stabilization (or anchoring) occurred with PMMA. These data are very similar to what one observes in the absence of any stabilizer for polymerizations in scCO₂

Additional SEM images of PVP particles demonstrating that when the stabilizer is effective, high yields and high MW PVP products are produced as fine free flowing solids which are comprised of discrete spherical PVP particles

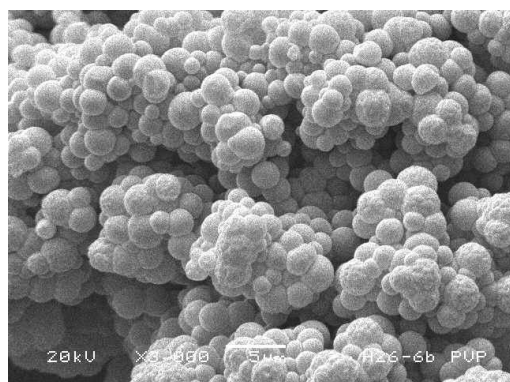


Figure S1. SEM micrograph of PVP formed using PVAc-PVB surfactant (8 kDa) in scCO₂ at 35 °C and 5000 psi (5 wt%).

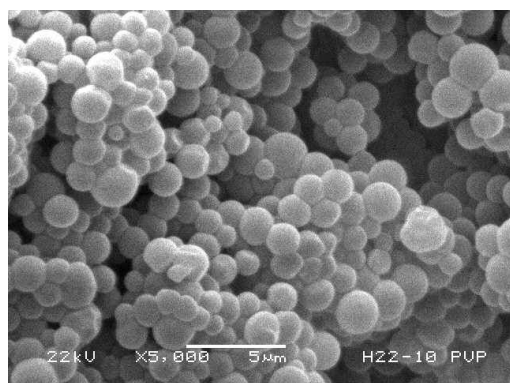


Figure S2. SEM micrograph of PVP formed using PVAc-PVB surfactant (8.5 kDa) in scCO₂ at 35 °C and 5000 psi (10 wt%)