

Probing the Biomimetic Ice Nucleation Inhibition Activity of
Poly(vinyl alcohol) and Comparison to Synthetic and
Biological Polymers

Thomas Congdon, Bethany T. Dean, James Kasperczak-Wright, Caroline I.
Biggs, Rebecca Notman and Matthew I. Gibson*

^a Department of Chemistry,
University of Warwick,
Coventry, CV4 7AL, UK

*Corresponding author

Fax: +44 247 652 4112
m.i.gibson@warwick.ac.uk

Synthetic Procedures

Synthesis of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid.

2- (dodecylthiocarbonothioylthio)-2-methylpropanoic acid was prepared using a method similar to that already reported.¹ Dodecane thiol (4.00 g, 19.76 mmol) was added dropwise to a stirred suspension of K₃PO₄ (4.20g, 19.76 mmol) in acetone (60 mL) over 25 minutes. CS₂ (4.10 g, 53.85 mmol) was added and the solution turned bright yellow. After stirring for ten minutes 2-bromo-2-methylpropionic acid (3.00 g, 17.96 mmol) was added and a precipitation of KBr was noted. After stirring for 16 hours, the solvent was removed under reduced pressure and the residue was extracted into CH₂Cl₂ (2 x 200 mL) from 1M HCl (200 mL). The organic extracts were washed with water (200 mL) and brine (200 mL) and further dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica using an eluent comprising 75:24:1 40 – 60 °C petroleum ether: diethyl ether: acetic acid to yield a bright yellow solid (4.01 g, 61 %). ¹H NMR (500 MHz, CDCl₃) δppm: 3.22 (2H, t, J₁₂₋₁₁ = 7.55 Hz, H₁₂); 1.66 (6H, s, H₁₃); 1.60 (2H, p, J₁₁₋₁₀, 11-12 = 7.70 Hz, H₁₁); 1.31 (2H, p, J₁₀₋₉, 10-11 = 7.70 Hz, H₁₀); 1.24-1.19 (16H, m, H 2-9); 0.81 (3H, t, J₁₋₂ = 7.25 Hz, H₁). ¹³C NMR (500 MHz, CDCl₃) δppm: 220.92 (C₁₃); 177.17 (C₁₆); 55.46 (C₁₄); 37.10 (C₁₂); 31.93, 29.71, 29.64, 29.57, 29.46, 29.35, 29.12, 22.70 (C₂₋₉); 28.97 (C₁₀); 27.82 (C₁₁); 25.26 (C₁₅); 14.13 (C₁). IR cm⁻¹: 2955 (alkyl-H stretch); 1712 (C=O stretch); 1069 (S-(C=S)-S stretch)

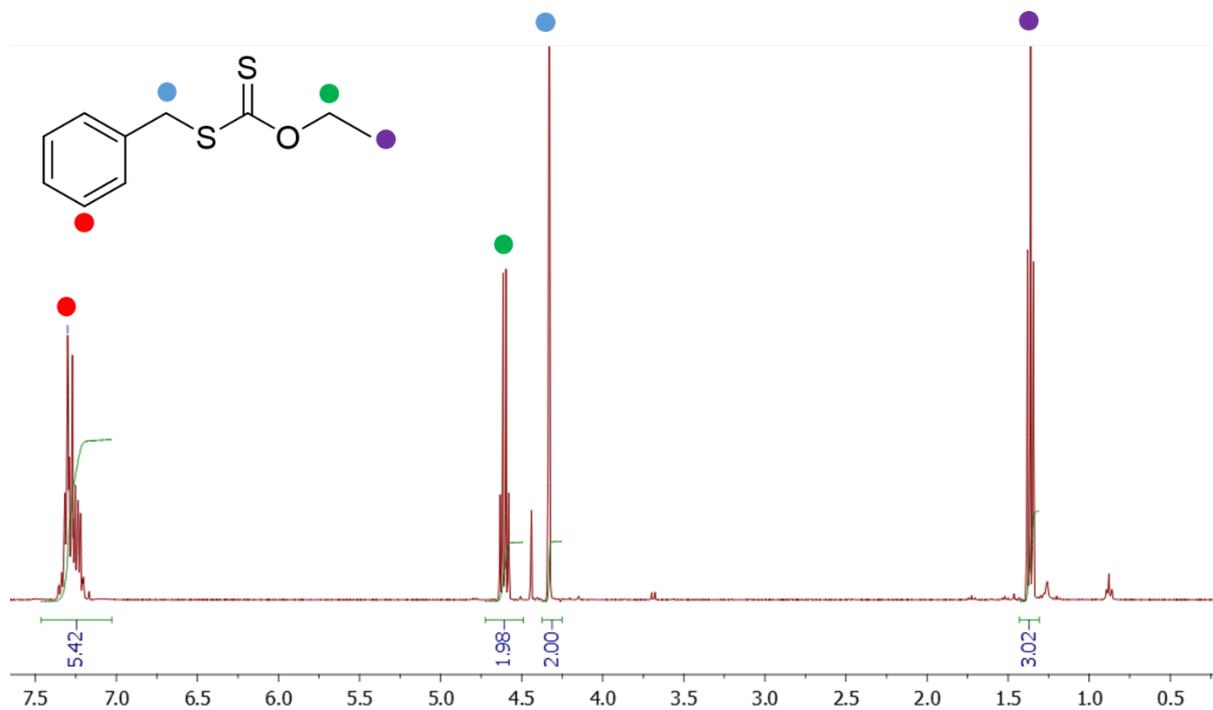


Figure S1. ^1H NMR spectrum of *O*-ethyl-S-1-phenyl carbonodithioate.

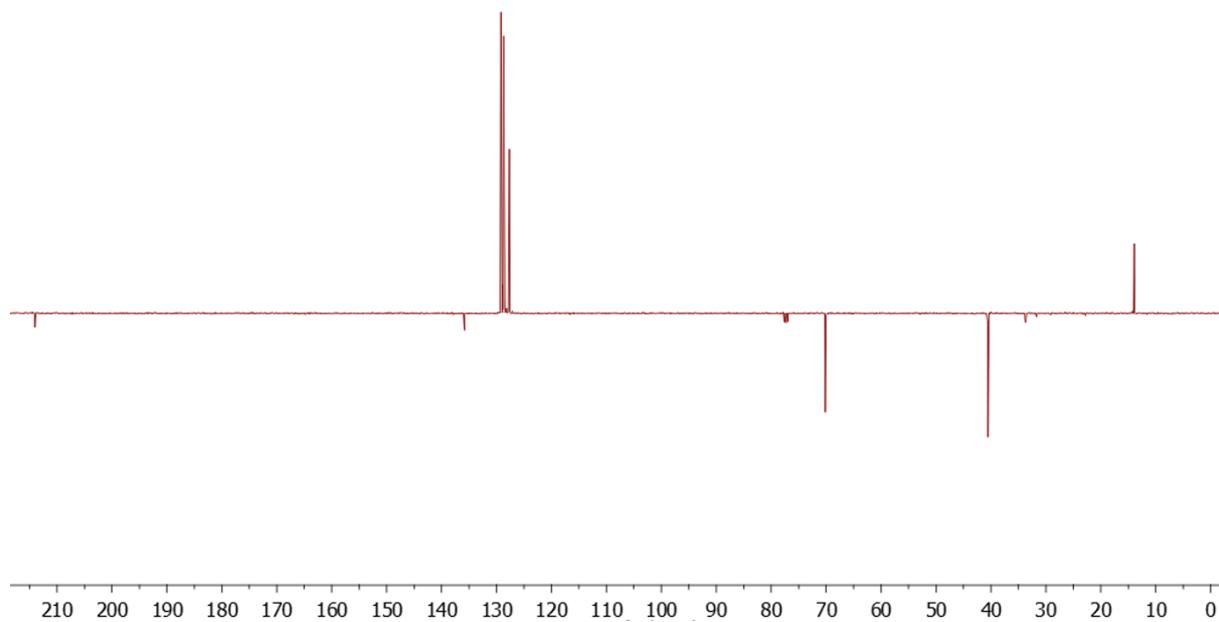


Figure S2. ^{13}C NMR spectrum of *O*-ethyl-*S*-1-phenyl carbonodithioate.

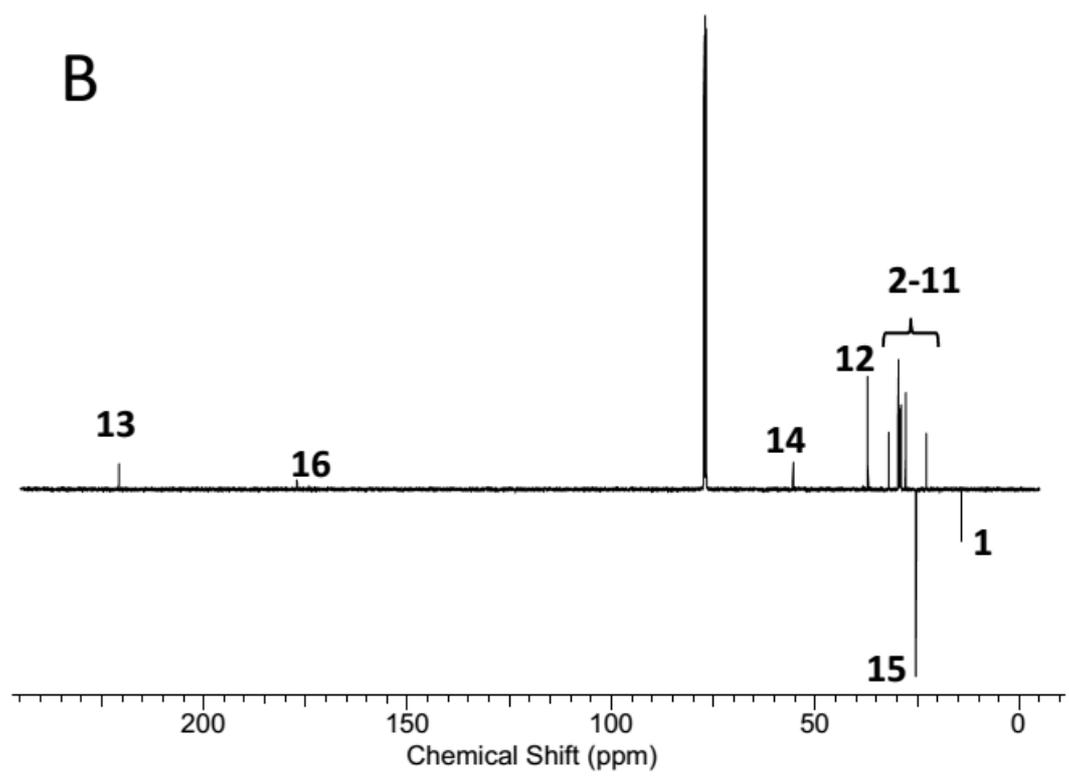
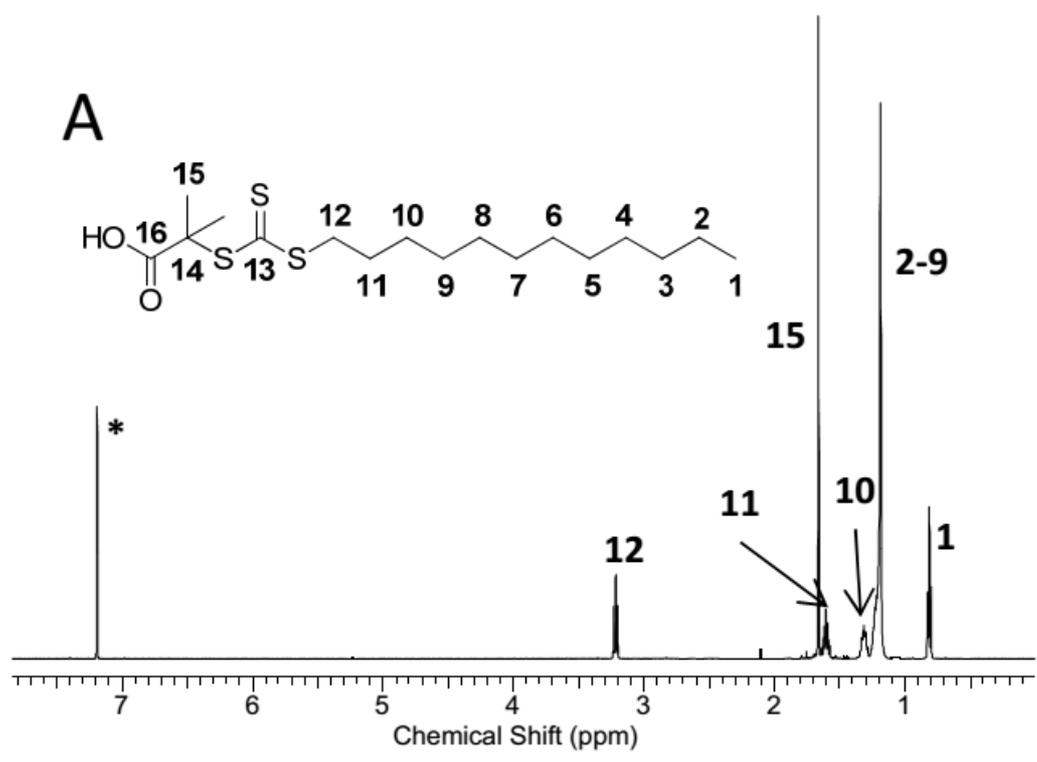


Figure S3 A) ¹H NMR and B) ¹³C NMR spectra of 2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid in CDCl₃. *=solvent.

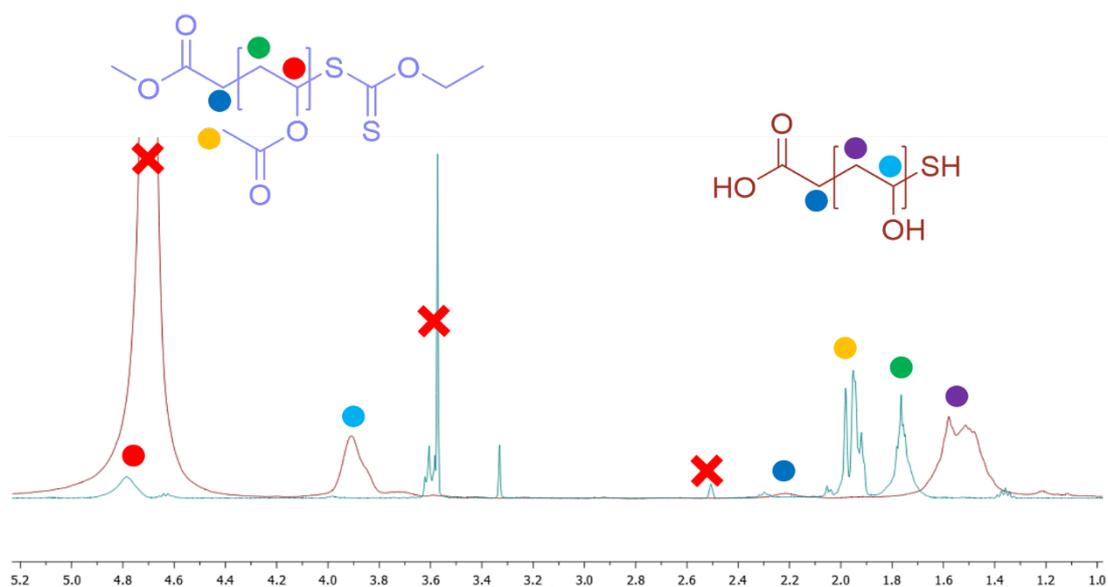


Figure S4. ¹H NMR spectra showing the conversion of PVAc (blue) to PVA (red). Residual Solvent peaks are indicated.

Differential Nucleation Plots for Commercial Polymers

Polymers were used as provided, in line with previous studies. Therefore, they may contain some impurities, and variable degrees of functionalization, hence justifying the used of well-defined polymers in this study.

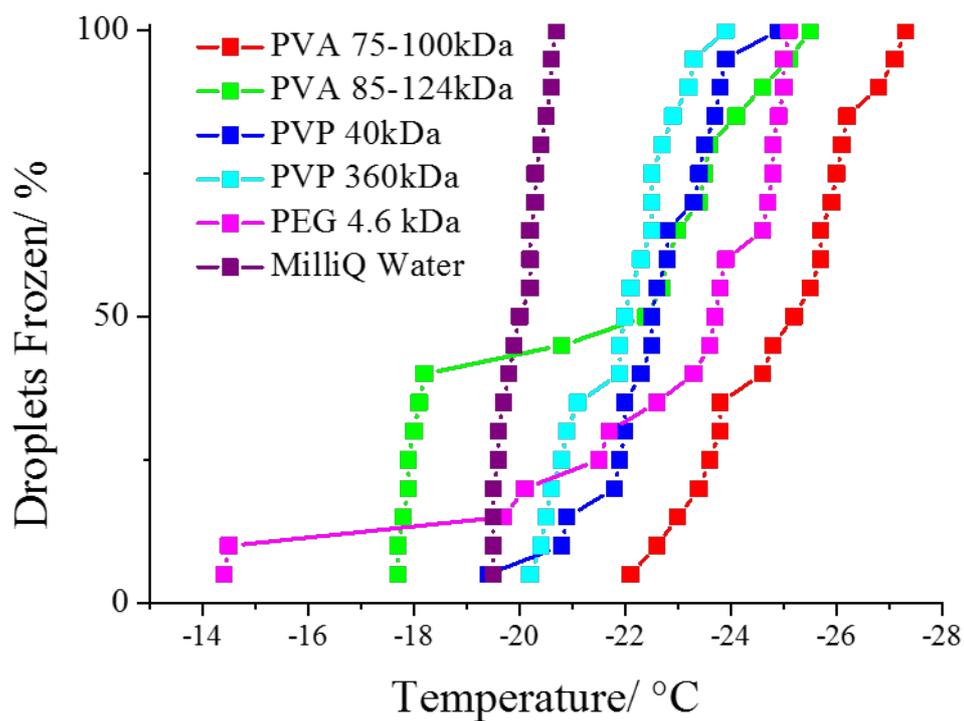


Figure S1. Multipoint freezing assay for a range of commercially available polymers and MilliQ water.