Electronic Supplementary Material (ESI) for Polymer Chemistry.

Thermoresponsive, Well-defined, Poly(Vinyl Alcohol) co-polymers.

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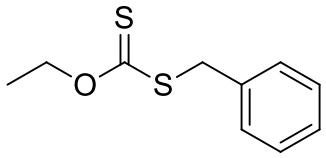
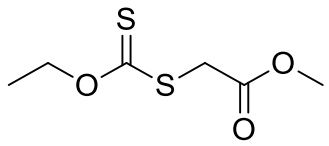
Additional Synthetic Procedures

Synthesis of CTA 1 - *O*-ethyl-*S*-1-phenyl carbonodithioate

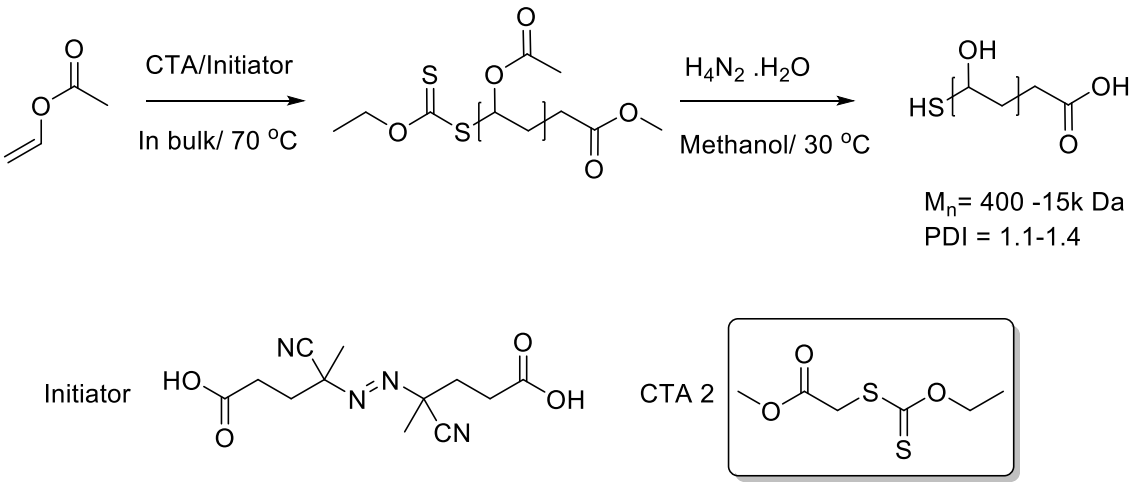


Ethanol (70 ml) was added to a round bottom flask equipped with a stir bar. Potassium Hydroxide (3.00g, 0.054 moles) added and stirred until dissolved. Carbon Disulphide (3.02 ml, 0.05 moles) added dropwise and stirred for 5 h. Benzyl Bromide (6.00 ml, 0.05 moles) added, reaction stirred at 50^{o}C for 18 h. Solution was filtered and washed with acetone, then concentrated *in vacuo*. The residue was purified on a column of silica with 99:1 Hexane:Methanol as the elutant. Yield 3.25 g 30% ^{1}H NMR ($CDCl_3$): δ = 1.36 (3H, t, J=7.2, C*H*$_3$CH$_2$), 4.33 (2H, s, SC*H*$_2$), 4.61 (2H, q, J=7.2, OC*H*$_2$CH$_3$). ^{13}C NMR ($CDCl_3$): δ = 13.91 (CH$_2$–*C*H$_3$), 40.54 (*C*H$_2$), 70.16 (*C*H$_2$CH$_3$), 127.56 (*para C*H), 128.72 (*meta C*H), 129.19 (*ortho C*H), 148.2 (*ipso* C), 212.4 (C=S).

Synthesis of CTA 2 - ethyl 2-(ethoxycarbonothioylthio)propanoate



Ethanol (70 ml) was added to a round bottom flask equipped with a stir bar. Potassium Hydroxide (11.45 g, 0.2 moles) was added and left to dissolve for 1 h. Carbon Disulphide (12.1 ml, 0.2 moles) was added dropwise, forming a yellow solution, which was left for 5 h. Methyl Bromoacetate (6.5 ml, 0.06 moles) was added dropwise and the solution left to stir overnight. The solution was filtered and washed with cold ethanol and concentrated *in vacuo*. The crude product was partition in DCM and sat. brine solution and the organic fraction concentrated *in vacuo*. The residue was washed through a column of basic alumina using pure ethyl acetate as the elutant. The fractions were concentrated *in vacuo* and then dried under vacuum. Yield 11.437 g 98%. ^{1}H NMR ($CDCl_3$): δ = 1.42 (2H, t, J=7.2, CH_3CH_2), 3.76 (3H, s, CH_3O), 3.92 (2H, d, J=7, SCH_2), 4.64 (3H, q, J=7.2, CH_3CH_2). ^{13}C NMR ($CDCl_3$): δ = 14.0 ($CH_2–CH_3$), 37.7 (CH_2), 61.0(CO_2CH_3), 70.4 ($CH_2–CH_3$), 167.7 (C=O), 212.4 (C=S).



Scheme S1. Controlled radical polymerisation and subsequent hydrolysis of vinyl acetate to PVA.

Additional Data

Infrared spectroscopy showing differences between alcohol and vinyl ester peak as a function of the degree of acetylation of the PVA/PVAc copolymers.

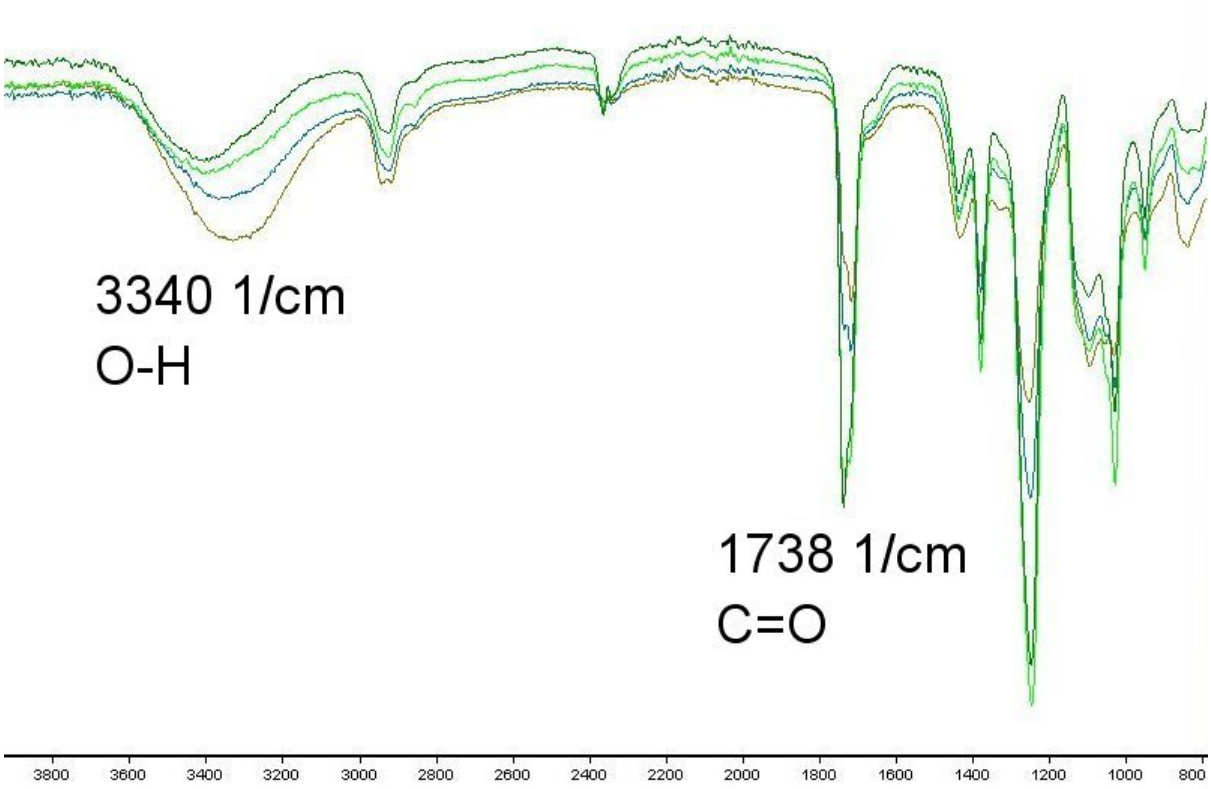


Fig S1. IR traces of partially acetylated PVA. The increasing C=O stretch at 1738 cm^{-1} corresponds to decreasing O-H stretch intensity at 3340 cm^{-1}.

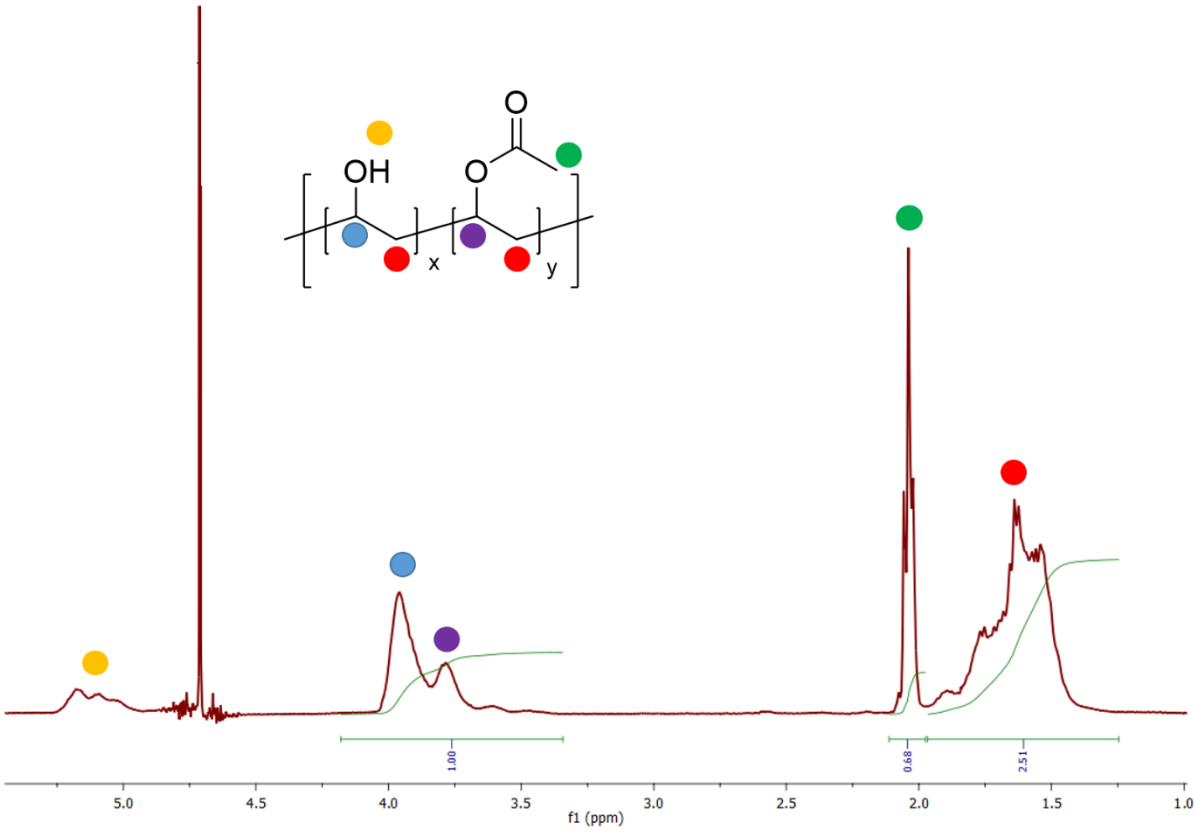


Fig S2 Representative ^{1}H NMR spectra of $\mathbf{P_{350}Ac_{0.22}}$. Degree of reacetylation determined by ^{1}H NMR, by comparing the integrals of the PVA α-H (δ = 4.00 ppm), PVAc α-H (δ = 3.82), and PVAc–CH_3 (δ = 1.74 ppm) shifts of the purified copolymer.

^{1}H NMR was used to also examine the dyad and triad peaks from methine and methylene proton shifts, in order to determine the arrangement of hydroxyl and acetate groups on the polymer, (Figure 5.4). It was necessary to determine this as previous reports have shown that this 'degree of blockiness' (whether the acetate groups are arranged at random, or in contiguous sequences) plays an important factor in many of the physical and solution properties of PVA, particularly in its use as a surfactant,[1] but also in its thermal transition temperatures.[2]

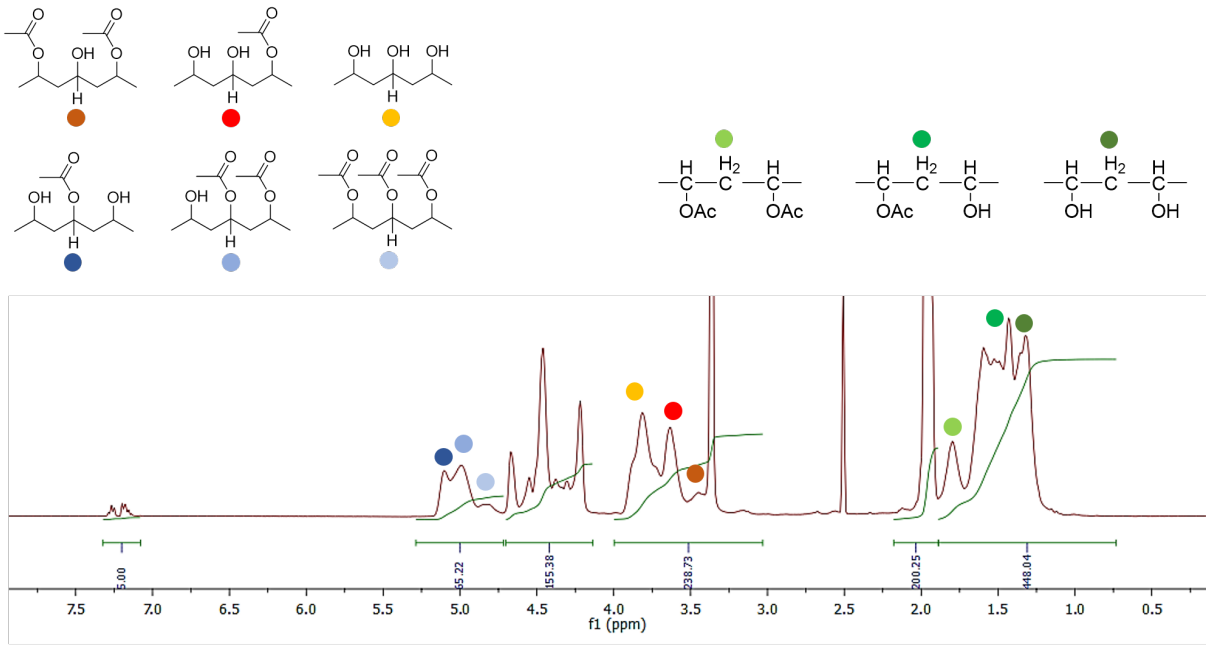


Figure S3 ^{1}H NMR of $\mathbf{P_{250}Ac_{0.25}}$ in deuterated DMSO, showing the dyads and triads from methine and methylene proton shifts.[3]

Blockiness arises during hydrolysis of acetate groups. Hydroxyl groups adjacent to acetate groups will catalyse the hydrolysis reaction, leading to blocks of hydroxyl groups if the polymer is not completely hydrolysed. It was expected that complete removal of hydroxyl groups, then reversible acid catalysed reacetylation would introduce acetate functionality randomly. Mean sequence length and the blockiness index, η can be determined by using the integrals of the methylene proton shifts, and the percentages of acetate and hydroxyl groups on the polymer, (Figure S3). Blockiness index can be defined as the percentage of alternating substituents (OH, Ac), divided by the percentages of polymer which can be blocks. $0 \leq \eta < 1$ indicates blocky distributions, $\eta = 1$ a random distribution, and $1 < \eta \leq 2$ for alternate-like polymers. A more useful graphical representation was reported by Fujiwara and Moritani,[3] (Figure S 5).

$$l_{OH} = \frac{2(OH)}{(OH, OAc)}$$

$$l_{OAc} = \frac{2(OAc)}{(OH, OAc)}$$

$$\eta = \frac{(OH, OAc)}{2(OH)(OAc)}$$

Figure S4 Equations determining mean sequence length and the blockiness index.

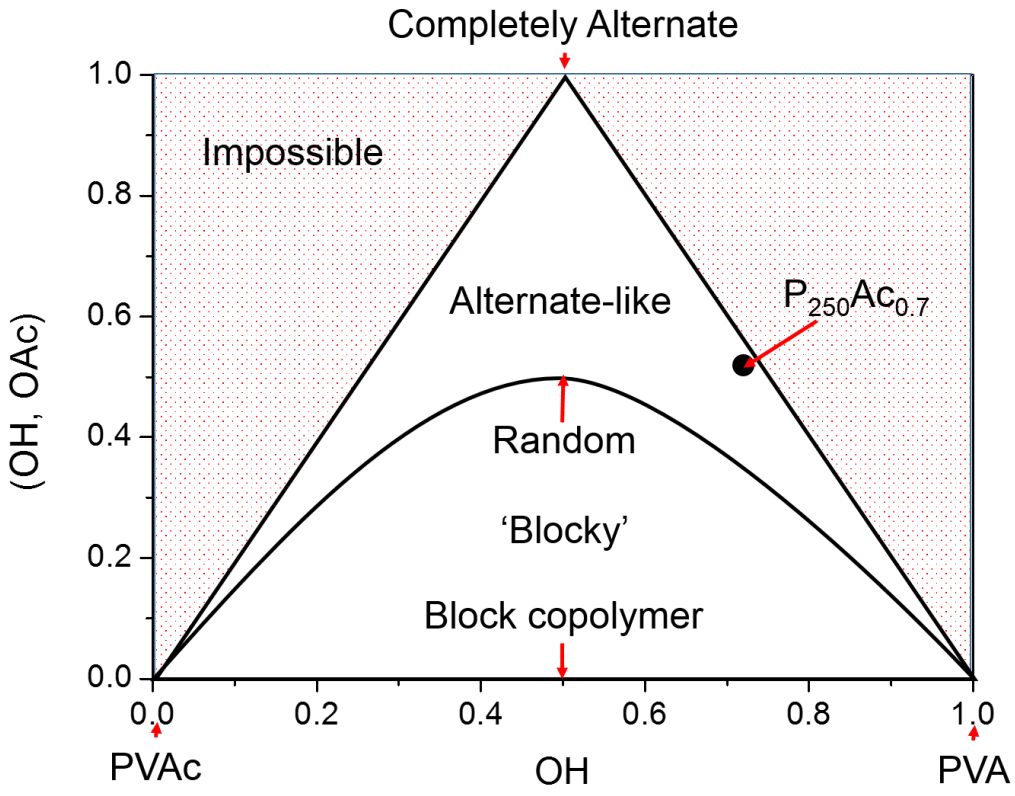


Figure S5 Graphical representation of blockiness index.

Using the above equations, for **$P_{250}Ac_{0.25}$** l_{OH} = 2.81, l_{OAc} = 1.05, and η = 1.28. For reference most PVA.PVAc copolymers prepared by hydrolysis or alcoholysis have blockiness values of η = 0.4 - 0.6. This shows that the polymer is highly alternating, and that substitution is almost statistical, with almost no blocks of acetate functionality occurring along the polymer

chain. This means that the random reacetylation reaction was highly successful, and that degree of blockiness would not be a variable factor in thermal phase transitions.

End group analysis

Due to the difficulty of using SEC to characterise PVA, and the potential side reactions that could affect chain length, $PVAc_{10}$ was prepared and characterised according to the methods used in this paper, using CTA 2 as the chain transfer agent. The polymer was then subjected to hydrazinolysis using hydrazine hydrate solution, and then treatment in 0.3 M HCl solution, mirroring the protocol used to prepare PVA.PVAc copolymers used in this study. Mass Spectroscopy was then used to examine the precise structure of the polymer at various points throughout.

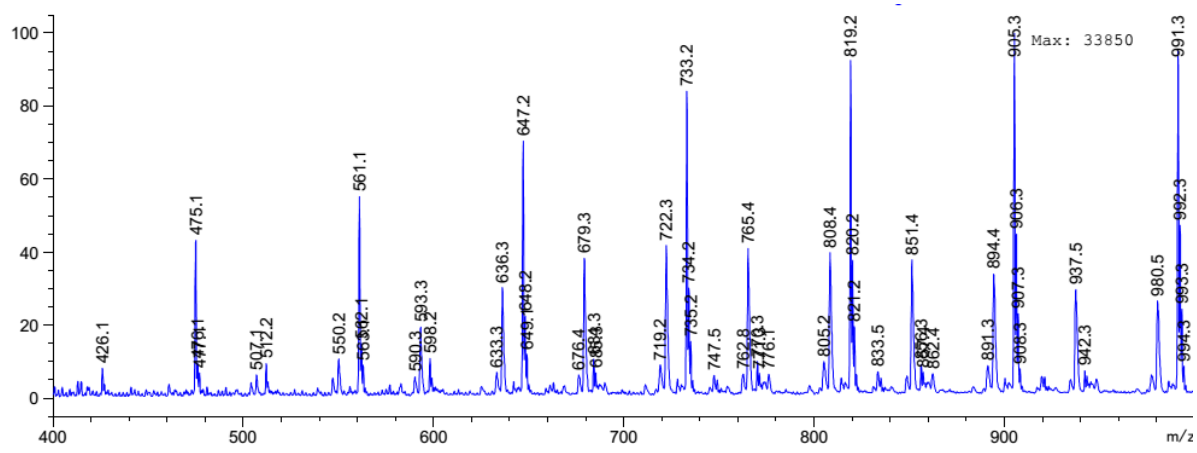


Figure S6. Mass Spectrum of $PVAc_{10}$

Figure S6 shows repeat units of 86 Da, equivalent to each vinyl acetate monomer. Each of the main peaks corresponds to the RAFT functionalised polymer.

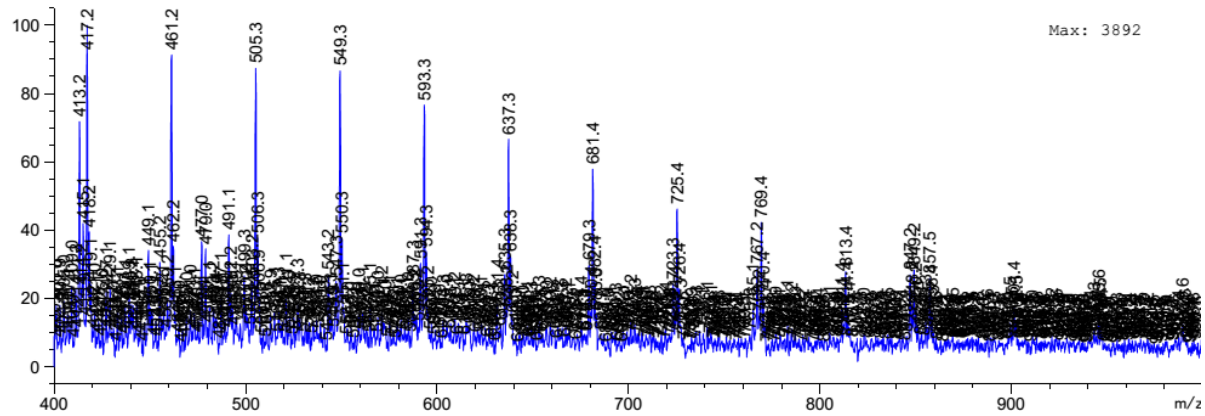


Figure S7 Mass Spectrum of PVA_{10} after hydrazinolysis

Figure S7 shows the mass spectrum of PVA_{10}. each major peak corresponds to PVA with a thiol and hydrazide end groups and a proton.

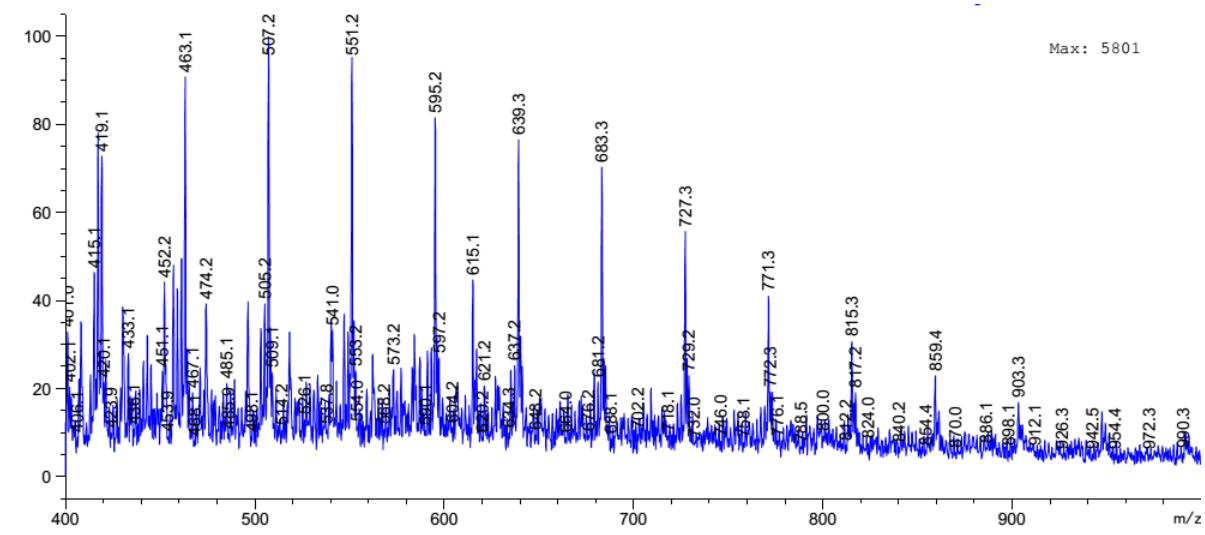


Figure S8 Mass Spectrum after 0.3M HCl treatment

Figure S8 shows the mass spectrum of PVA_{10} after 48 hours stirring in 0.3M HCl solution at 40°C. Each major peak corresponds to amide and thiol end groups and a water counter ion. It was assumed that the acid present in this sample from the reaction would have removed any sodium counterions relative intensities of these major peaks are comparable, showing that no degradation of the polymer is occurring in these conditions.

Turbidimtry curves showing the change in cloud point behaviour as a function of time for the polymers with added esterase. Samples were removed from the solution before analysis.

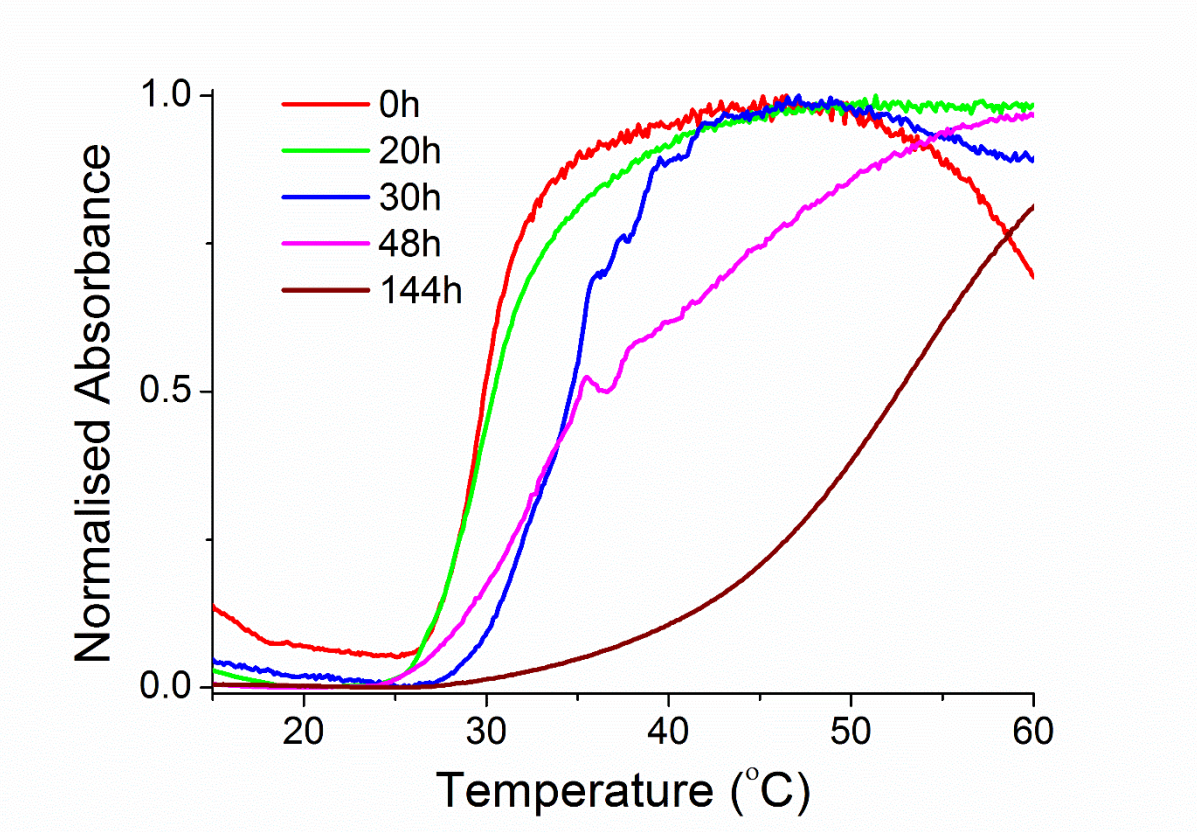


Fig S9. Turbidimetry curves showing the cloud point behaviour of $P_{350}Ac_{0.7}$ after addition of porcine liver esterase, showing increase in cloud point over time as acetate groups are enzymatically hydrolysed.

1 B. M. Budhlall, E. D. Sudol, V. L. Dimonie, A. Klein and M. S. El-Aasser, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, **39**, 3633.
2 D. Eagland and N. J. Crowther, *European Polymer Journal*, 1991, **27**, 299.
3 T. Moritani and Y. Fujiwara, *Macromolecules*, 1977, **10**, 532.