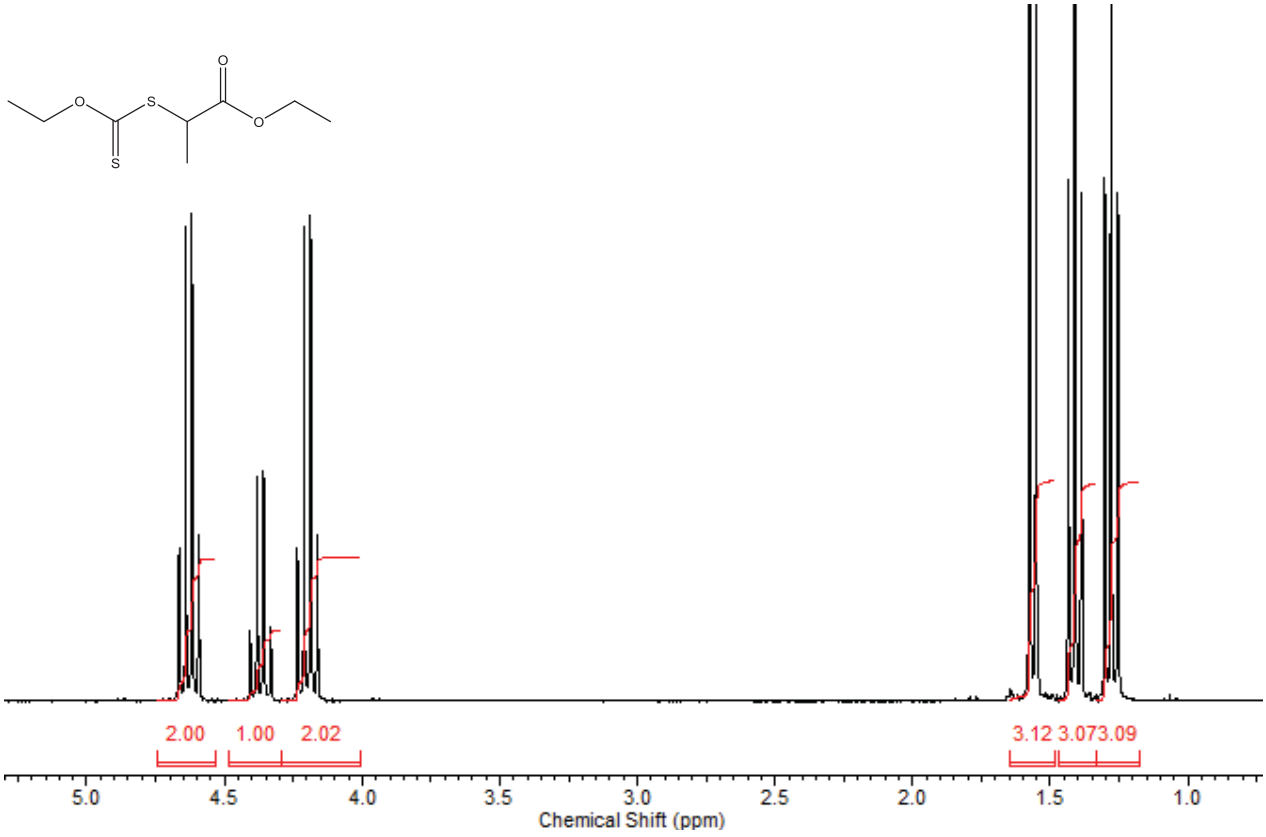
7. Supporting information

7.1. Ethyl 2-(ethoxythiocarbonylthio) propanoate synthesis

Carbon disulfide (18 g, 236.8 mmol, and 1.0 eq.) was added dropwise to a stirred solution of potassium hydroxide (13 g, 232.0 mmol, 1.0 eq.) in ethanol (100 g). After stirring for 2 hours, the solution was cooled down to 5°C, filtered and the crude product recrystallized twice from warm ethanol, affording a yellow powder. Yield: 24.2 g, 150.9 mmol, 65.0 %

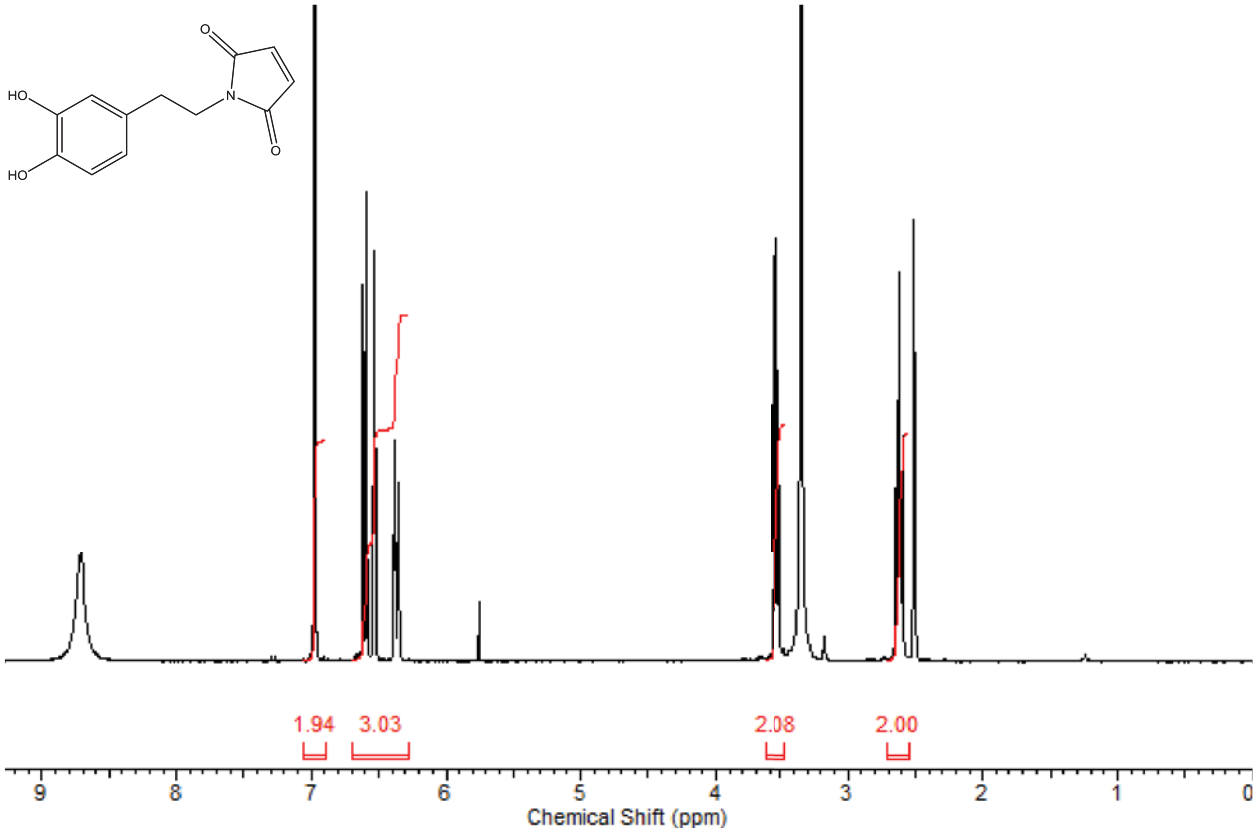
Ethyl-2-bromo propionate (10.6 g, 58.6 mmol, 1.0 eq.) in dry acetonitrile (2 mL / mmol) was cooled to 0°C and potassium ethyl xanthogenate (10 g, 62.4 mmol, 1.1 eq.) was added portionwise. The suspension was stirred at room temperature for 2 hours before the solvent was removed under reduced pressure. After re-dissolving in dichloromethane, the organic phase was washed with water and brine, dried over magnesium sulfate and concentrated. The crude product was purified via column chromatography with hexane:diethylether (19:1 to 9:1), leading to a colourless liquid. Yield: 8.1 g, 36.4 mmol, 62.1 %

7.2. Ethyl 2-(ethoxythiocarbonylthio) propanoate ^{1}H-NMR spectrum



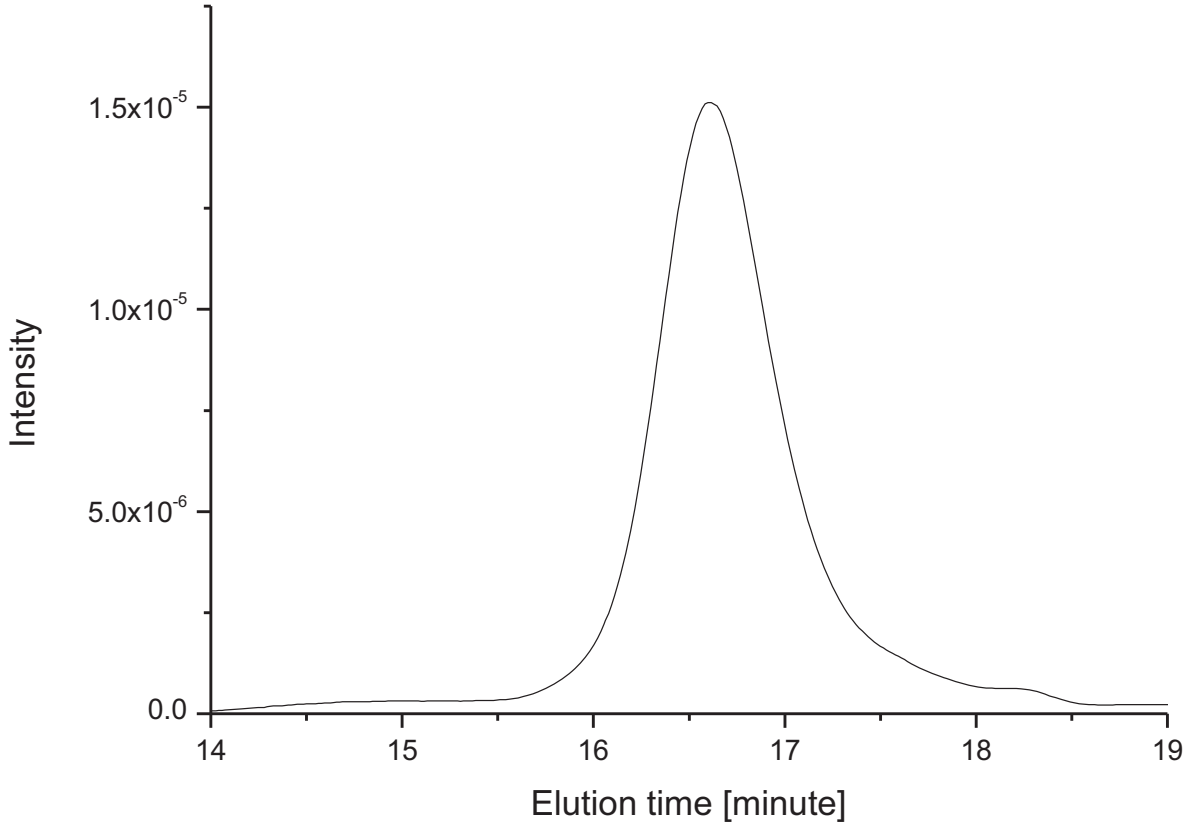
Supp. Figure 1: ^{1}H NMR (300 MHz, CHLOROFORM-d*)* δ [ppm]: 4.63 (q, *J*=7.18 Hz, 2 H), 4.37 (q, *J*=7.37 Hz, 1 H), 4.20 (q, *J*=7.18 Hz, 2 H), 1.56 (d, *J*=7.55 Hz, 3 H), 1.41 (t, *J*=7.18 Hz, 3 H), 1.28 (t, *J*=7.08 Hz, 3 H)

7.3. 1-(3,4-Dihydroxyphenethyl)-1H-pyrrole-2,5-dione ^{1}H-NMR spectrum



Supp. Figure 2: ^{1}H- NMR (300 MHz DMSO-d_6) δ [ppm]: 6.97 (s, 2H, maleimide), 6.61–6.15 (m, 3H, Ar H), 3.67–3.47 (m, 2H, CH_2N), 2.63-2.59 (m, 2H, CH_2Ar).

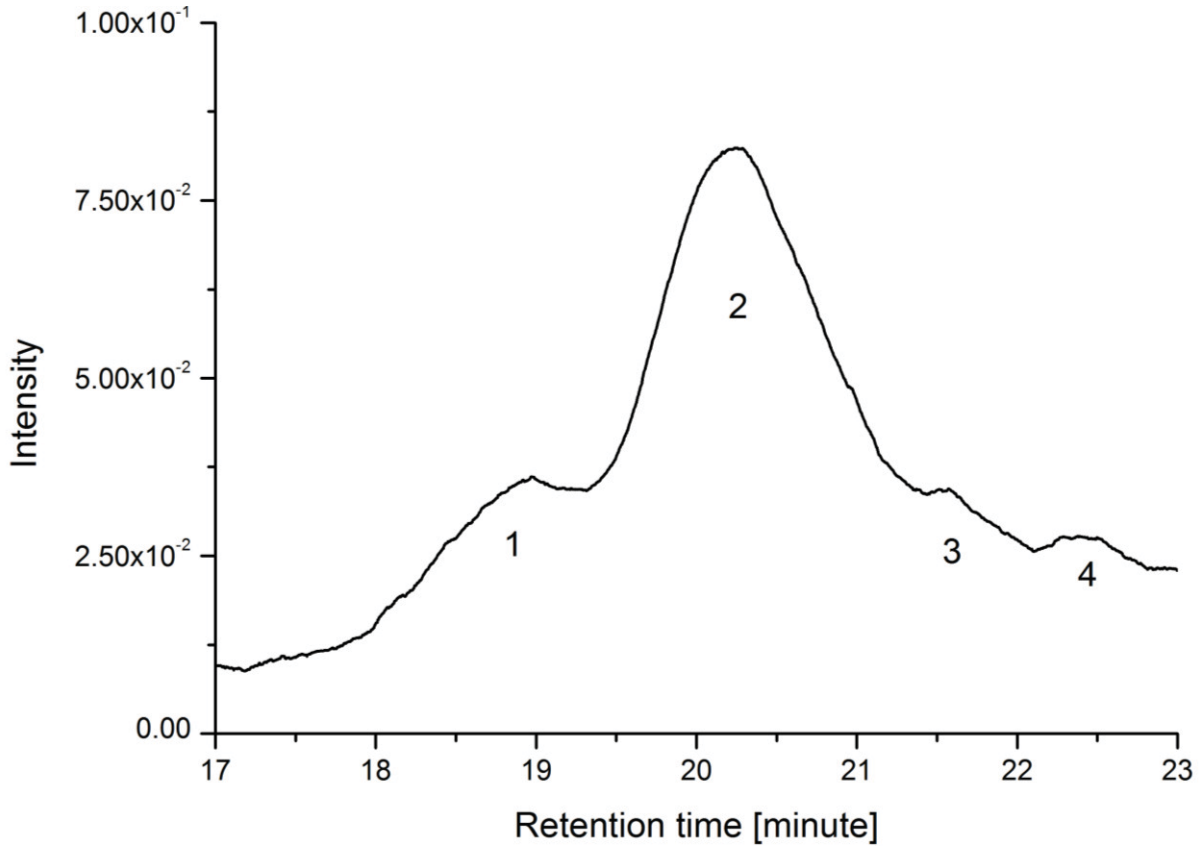
7.4. Poly(vinyl acetate) (I): GPC trace in THF



Molecular mass moment of Poly(vinyl acetate)

Mn [kDa]	2.3
Mw [kDa]	2.8
PDI	1.2

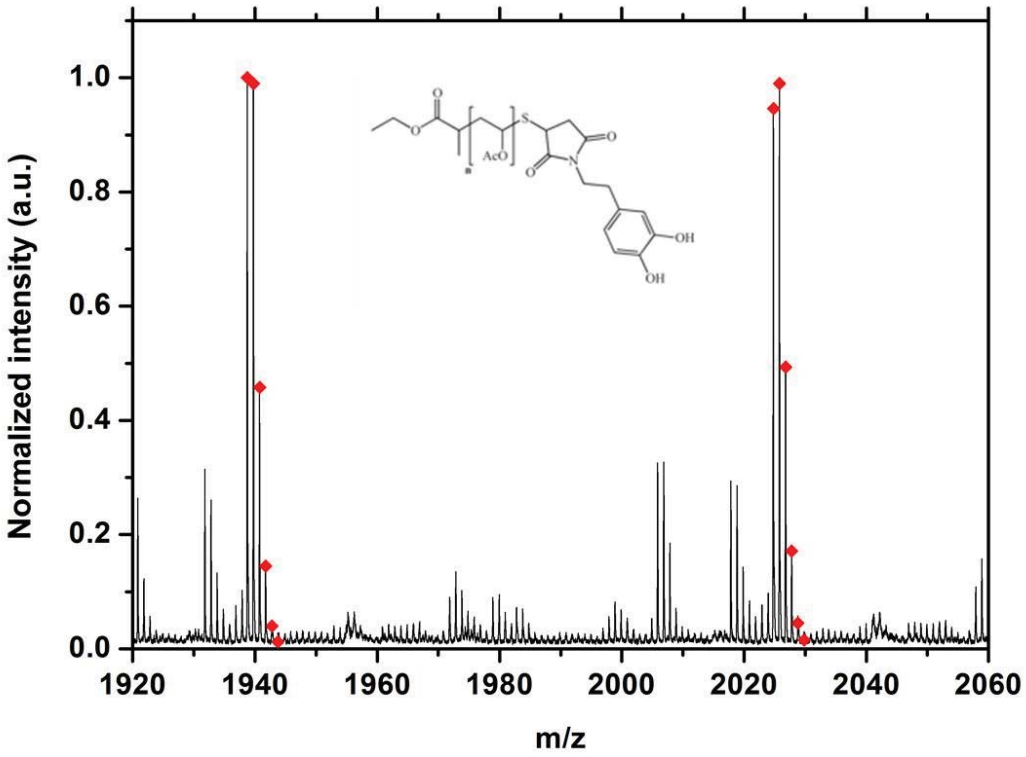
7.5. Catechol-functionalized poly(vinyl acetate) (III): GPC trace in chloroform



Molecular mass moments of catechol-functionalized poly(vinyl acetate) III

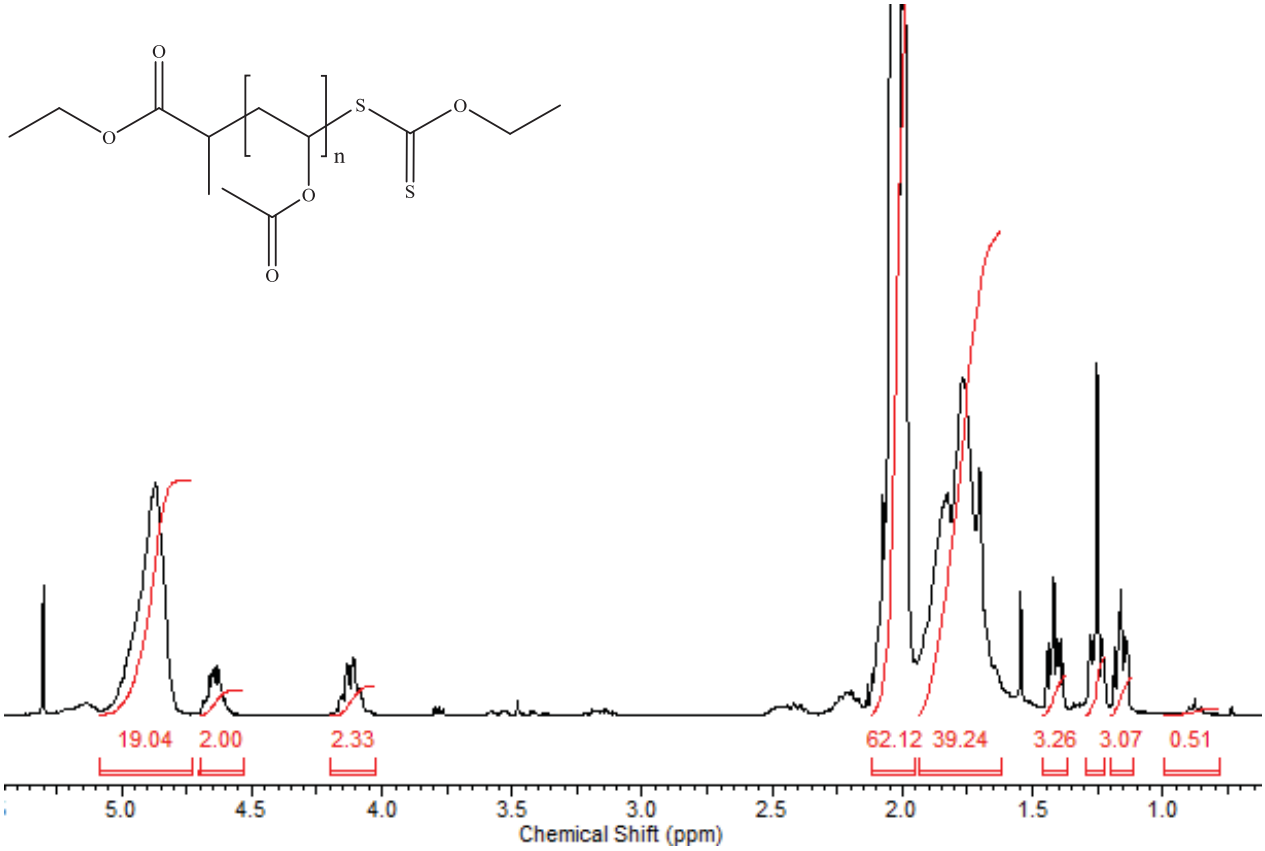
Peak *1*	Mn [kDa]	6.1
	Mw [kDa]	6.8
	PDI	1.1
Peak *2*	Mn [kDa]	1.6
	Mw [kDa]	1.9
	PDI	1.2
Peak *3*	Mn [Da]	617
	Mw [Da]	626
	PDI	1.0
Peak *4*	Mn [kDa]	381
	Mw [kDa]	391
	PDI	1.0

7.6. MALDI-ToF spectrum of Cat-PVAc



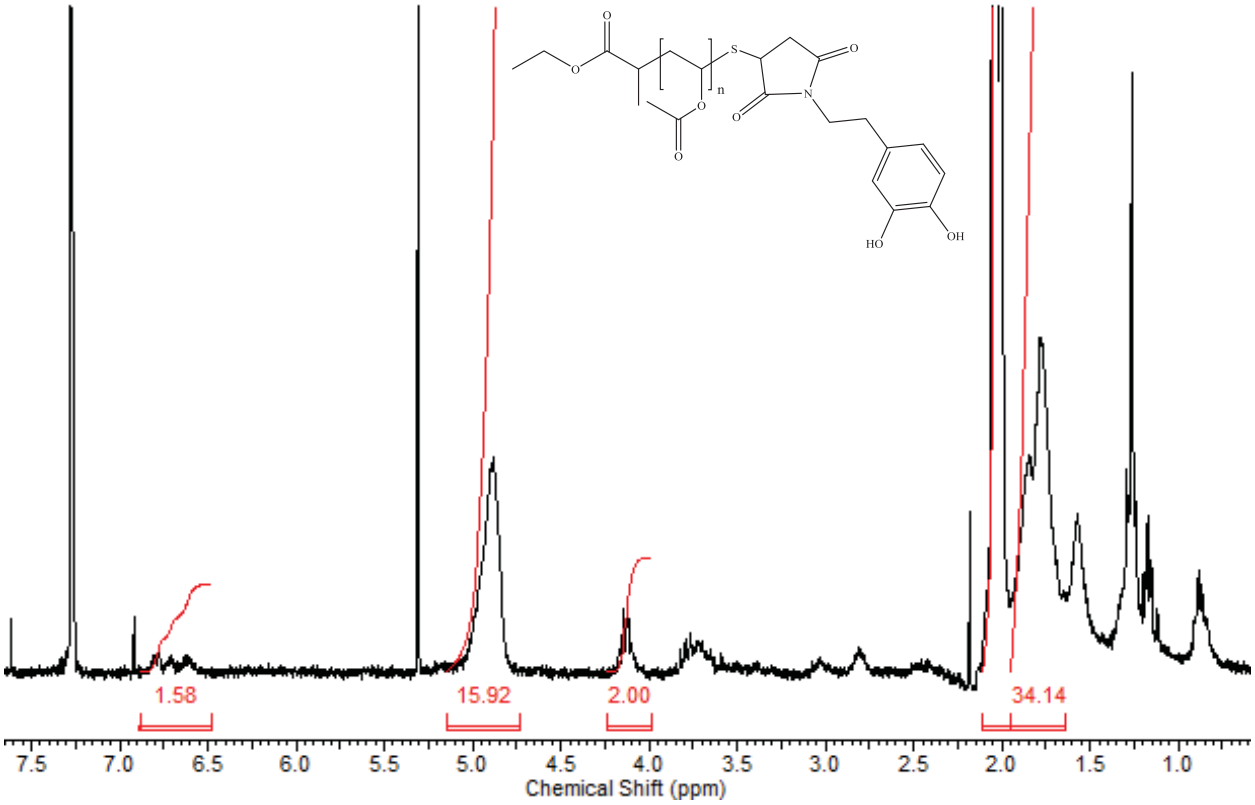
Supp. Figure 3: Zoom-in MALDI-ToF mass spectrum of Cat-PVAc, red squares depict calculated molecular weight and isotope pattern. Spacing of the all C^{12} peaks corresponds to one monomer unit (86.037 g/mol).

7.7. Poly(vinyl acetate) (I): ^{1}H-NMR spectrum



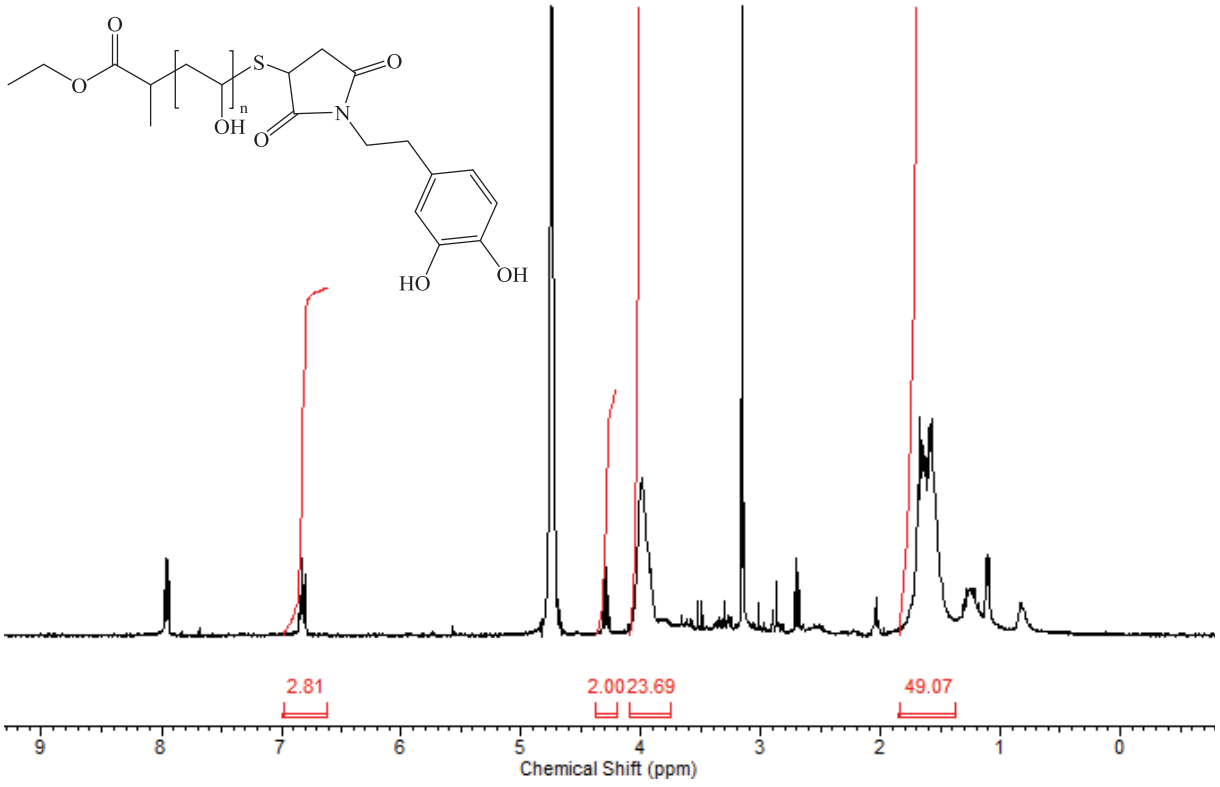
Supp. Figure 4: ^{1}H-NMR (300 MHz, CHLOROFORM-d) δ [ppm]: 4.90 (s, CH backbone), 4.70-4.55 (m, 2H, S=COC**H$_2$**CH$_3$ RAFT agent moiety), 4.20-4.10 (m, 2H, O=COC**H$_2$**CH$_3$ RAFT agent moiety), 2.15-1.95 (m, CH$_3$ backbone), 1.95-1.60 (m, CH$_2$ backbone), 1.45-1.35 (m, 3H, O=COCH$_2$C**H$_3$** RAFT agent moiety), 1.30-1.20 (m, 3H, S=COCH$_2$C**H$_3$** RAFT agent moiety), 1.20-1.10 (m, 3H, O=CCHC**H$_3$** RAFT agent moiety) 0.90-0.80 (m, H, O=CC**H**CH$_3$ RAFT agent moiety).

7.8. Catechol-functionalized poly(vinyl acetate) (III): ^{1}H-NMR spectrum



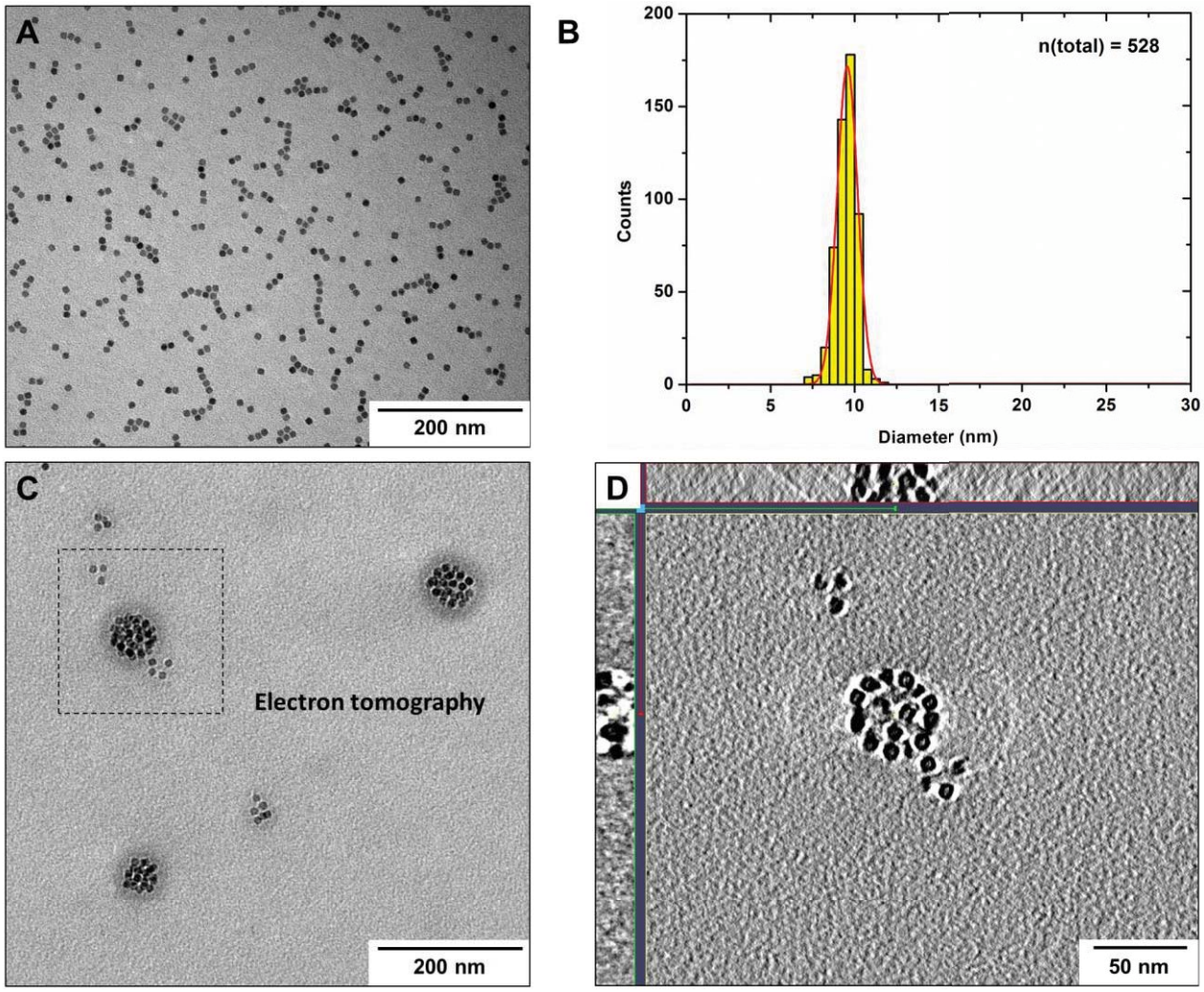
Supp. Figure 5: ^{1}H-NMR (300 MHz, CHLOROFORM-d) δ [ppm]: 6.90–6.50 (m, Ar H catechol), 4.90 (s, CH backbone), 4.20-4.10 (m, 2H, O=COC**H$_2$**CH$_3$ RAFT agent moiety), 2.15-1.95 (m, CH$_3$ backbone), 1.95-1.60 (m, CH$_2$ backbone), 1.45-1.35 (m, 3H, O=COCH$_2$C**H$_3$** RAFT agent moiety), 1.30-1.20 (m, 3H, S=COCH$_2$C**H$_3$** RAFT agent moiety), 1.20-1.10 (m, 3H, O=CCHC**H$_3$** RAFT agent moiety) 0.90-0.80 (m, H, O=CC**H**CH$_3$ RAFT agent moiety).

7.9. Catechol-functionalized poly(vinyl alcohol) (IV): ^{1}H-NMR spectrum



Supp. Figure 6: ^{1}H-NMR (300 MHz, D_2O) δ [ppm]: 6.8–6.75 (m, Ar H catechol), 4.35-4.25 (m, 2H, O=COC**H$_2$**CH$_3$ RAFT agent moiety), 4.05-3.85 (s, 22 H, CH backbone), 1.80–1.40 (m, 44 H, CH_2 backbone).

7.10. SPION characterization: Transmission electron microscopy and electron tomography



Supp. Figure 7: Oleic acid-functionalized SPIONs (A) and their size distribution (B) before ligand exchange. Micrographs of a representative cluster (C) were recorded at subsequent tilt angles, which were used to generate a tomographic reconstruction (D) of the structure.