

Supplementary Information:

Merging CO₂-Based Building Blocks with Cobalt-Mediated Radical Polymerisation for the Synthesis of Functional Poly(vinyl alcohols)

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Table S1. Copolymerisations of DMMDO and VAc at 40 °C using R-Co(acac)₂

Entry	$f_{\text{VAc}}^{\theta}/f_{\text{DMMDO}}^{\theta}$ ^a	Time (h)	VAc conv. ^a (%)	DMMDO conv. ^a (%)	Total conv. ^a (%)	Comp. ($F_{\text{VAc}}/F_{\text{DMMDO}}$) ^b	$M_{n,theo}$ ^c (g.mol ⁻¹)	$M_{n,SEC}$ ^d (g.mol ⁻¹)	M_w/M_n ^d
1	1/0	23	83	-	83	1/0	29,200	29,300	1.30
2	0/1	23	-	0	0	-	-	-	-
3	0.94/0.06	2	4	3	4		2,000	2,200	1.11
		4	8	4	8		3,400	3,500	1.09
		6	14	5	13		5,300	4,900	1.08
		8	18	10	18		6,800	6,200	1.09
		23	51	30	50	0.89/0.11	18,100	19,300	1.36
4	0.88/0.12	2	6	1	6		2,500	2,700	1.11
		4	9	2	8		3,500	4,500	1.09
		6	14	3	13		5,100	6,500	1.08
		8	21	5	19		7,300	8,700	1.09
		23	51	56	52	0.87/0.13	19,500	24,800	1.32
5	0.75/0.25	2	6	3	5		2,600	3,100	1.09
		4	9	2	7		3,200	5,200	1.08
		6	15	6	13		5,300	7,500	1.10
		25	46	43	45	0.83/0.16	18,000	19,800	1.37
6	0.66/0.34	2	1	1	1		1,000	2,700	1.11
		4	7	2	5		2,600	4,000	1.10
		6	12	2	9		3,800	5,300	1.10
		23	31	8	23		9,100	11,900	1.28
		25	38	13	30	0.78/0.22	11,500	13,600	1.29
7	0.60/0.40	2	2	1	2		n.d.	1,300	1.28
		4	4	1	3		n.d.	2,100	1.13
		6	4	1	3		n.d.	2,700	1.12
		23	6	3	5		n.d.	5,500	1.31
		29	7	3	5	0.60/0.40	n.d.	6,200	1.35
8	0.26/0.74	24	3	0	2		n.d.	5,700	1.54
		48	3	0	2	-	n.d.	6,200	1.66
9 ^e	0.57/0.43	29	16	34	26	0.69/0.31	10,800	15,200	1.33
10	0.78/0.22	25	25	48	43	0.81/0.19	17,000	18,400	1.29
11 ^f	0.85/0.15	6	45	26	42	0.86/0.16	4,400	3,900	1.10
12	0.78/0.22	25	41	26	38	0.77/0.23	14,600	15,700	1.36

Conditions: bulk, M/R-Co(acac)₂ = 400/1, magnetic stirring at 500 r.p.m. ^aDetermined by ¹H-NMR spectroscopy. ^bComposition of the copolymer determined by ¹H-NMR spectroscopy. ^c $M_{n,theo} = M_w^{init} + (\text{Conv}_{\text{DMMDO}} \times M_w^{\text{DMMDO}} + \text{Conv}_{\text{VAc}} \times M_w^{\text{VAc}}) + M_w^{\text{TEMPO}}$ ^dDetermined by size exclusion chromatography (SEC) in THF using PS standard. ^eAddition of H₂O, R-Co(acac)₂/H₂O = 1/20. ^fConditions: bulk, M/R-Co = 100, magnetic stirring at 500 r.p.m. n.d. = not determined

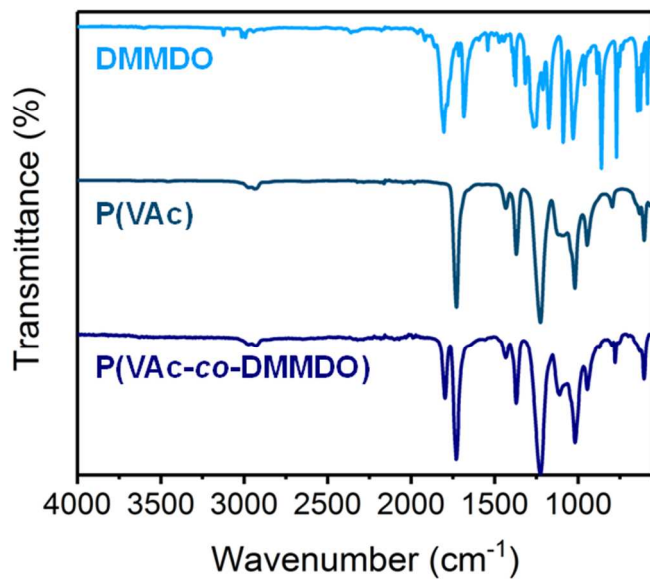


Figure S1. FT-IR spectra of DMMDO, PVAc (Entry 1, Table 1), P(VAc-co-DMMDO) at 43% conversion containing 16 mol% DMMDO (Entry 5, Table 1).

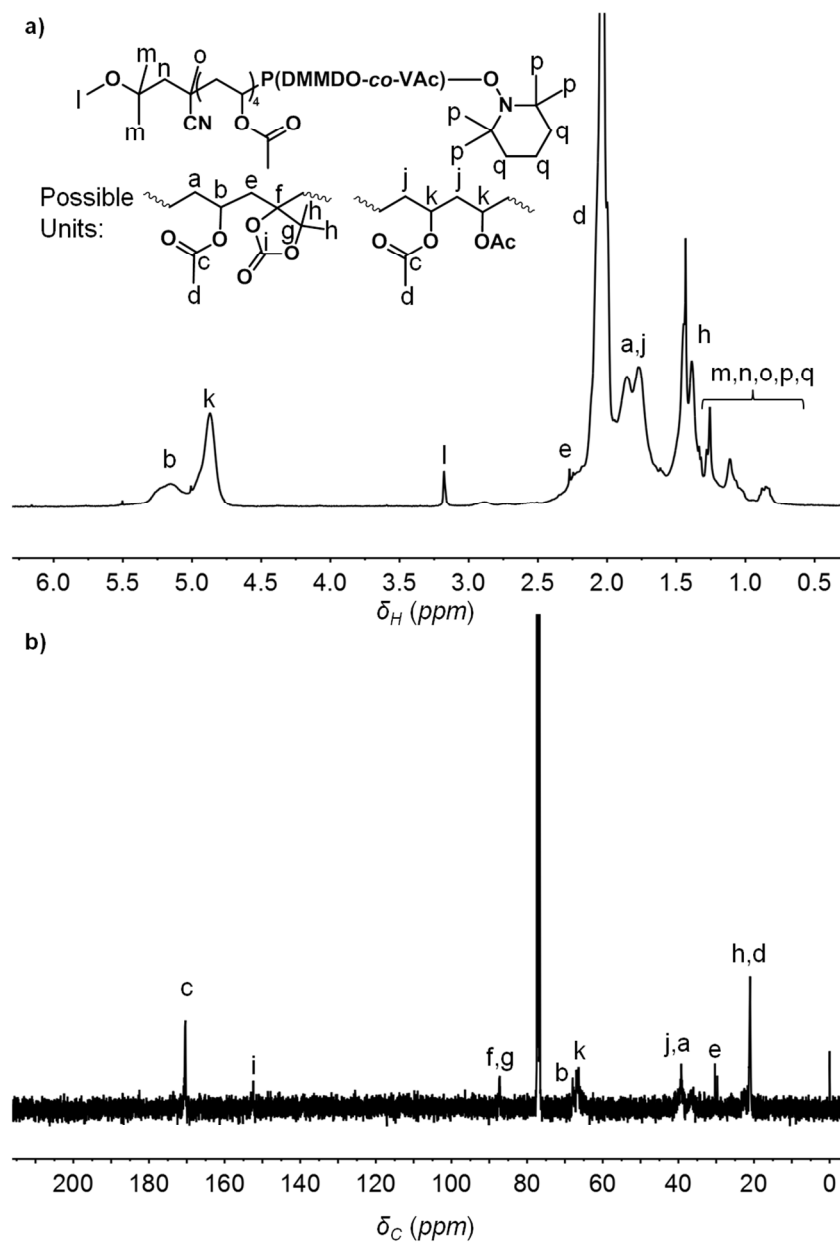


Figure S2. a) ^1H -NMR spectrum and b) ^{13}C -NMR spectrum of a copolymer at 21% conversion containing 23 mol% DMMDO prepared by CMRP at 90 °C. NMR spectra taken in CDCl_3 on a 400 MHz spectrometer.

Table S2. Polymerisations of DMMDO and VAc by free radical polymerisation (Entries 1-11) and by cobalt-mediated radical polymerisation (Entries 11-14) at 40 °C to determine the reactivity ratios of the monomers.

Entry	f_{VAc}^0 / f_{DMMDO}^0 ^a	Time (h)	VAc conv. ^a (%)	DMMDO conv. (%)	Total conv. ^a (%)	Comp. (F_{VAc}/F_{DMMDO}) ^b	M_n SEC ^c (g.mol ⁻¹)	M_w/M_n ^c
1	0.89/0.11	1	3	2	3	0.90/0.10	25,300	2.70
2	0.79/0.21	4	5	2	4	0.85/0.15	21,100	1.75
3	0.70/0.30	4	5	1	4	0.79/0.21	18,500	1.62
4	0.69/0.31	6	2	2	2	0.76/0.24	16,800	1.93
5	0.60/0.40	9.5	2	2	2	0.69/0.31	11,200	1.76
6	0.53/0.47	30	3	2	3	0.70/0.30	12,100	1.92
7	0.50/0.50	20	4	0	2	0.68/0.32	10,200	1.97
8	0.42/0.58	42	1	1	1	0.66/0.34	10,400	1.71
9	0.29/0.71	62	0	1	1	0.56/0.44	5,500	1.74
10	0.28/0.72	62	1	0	0	0.54/0.46	6,300	1.73
11 ^d	0.08/0.92	-	-	-	-	-	-	-
12	0.89/0.11	2	11	3	11	0.87/0.13	4,800	1.08
13	0.68/0.32	8	17	4	13	0.76/0.24	8,100	1.13
14	0.60/0.40	29	7	3	5	0.60/0.40	6,200	1.35

Conditions: Entries 1-11: 40°C, bulk, M/V-70 = 200 (as two radicals are formed from one molecule of V-70), magnetic stirring at 500 r.p.m. Entries 12-14: 40°C, bulk, M/R-Co(acac)₂ = 400, magnetic stirring at 500 r.p.m. ^aDetermined using ¹H-NMR spectroscopy ^bComposition of the copolymer determined by ¹H-NMR spectroscopy. ^cDetermined using size exclusion chromatography in THF using PS standard. ^dNo precipitate/polymer observable after >250 hours.

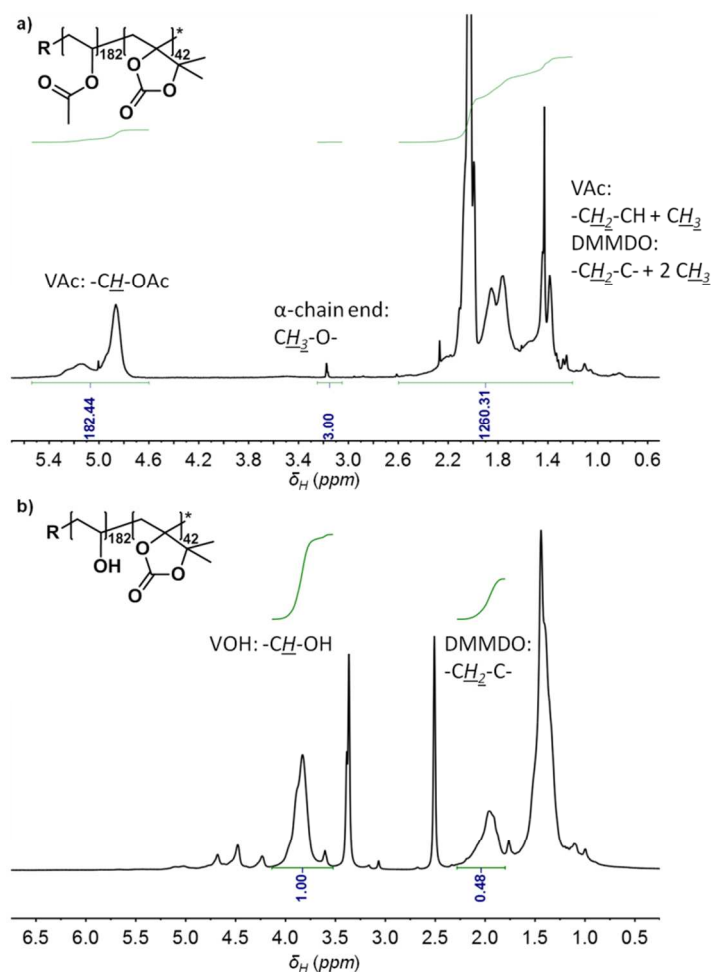


Figure S3. $^1\text{H-NMR}$ spectra of a) $\text{P}(\text{VAc}_{182}\text{-co-DMMDO}_{42})$ (Entry 10 Table S1) and b) $\text{P}(\text{VOH}_{182}\text{-co-DMMDO}_{42})$ recorded in CDCl_3 and $\text{DMSO-}d_6$, respectively, on a 400 MHz spectrometer..

Table S3. PVAc and $\text{P}(\text{VAc-co-DMMDO})$ prepared by CMRP with similar DPs for the comparison of solubility.

Entry	$f_{\text{VAc}}^{\theta}/f_{\text{DMMDO}}^{\theta}$ ^a	Time (h)	Total conv. ^a (%)	Comp. ($F_{\text{VAc}}/F_{\text{DMMDO}}$) ^b	DP (VAc/DMMDO) ^a	$M_{n,theo}$ ^c (g.mol ⁻¹)	M_n SEC ^d (g.mol ⁻¹)	M_w/M_n ^d
1	1/0	8	31	1/0	134/0	11,500	12,800	1.10
2	0.72/0.28	21	24	0.82/0.18	108/24	9,800	11,800	1.25

Conditions: bulk, $M/R\text{-Co}(\text{acac})_2 = 400/1$, magnetic stirring at 500 r.p.m. ^a Determined by $^1\text{H-NMR}$ spectroscopy. ^b Composition of the copolymer determined by $^1\text{H-NMR}$ spectroscopy. ^c $M_{n,theo} = M_w \text{ init} + (\text{Conv}_{\text{DMMDO}} \times M_w \text{ DMMDO} + \text{Conv}_{\text{VAc}} \times M_w \text{ VAc}) + M_w \text{ TEMPO}$ ^d Determined by size exclusion chromatography (SEC) in THF using PS standard.

Table S4. Solubility of PVOH₁₃₄ compared with P(VOH₁₀₈-*co*-BD₂₄) at different concentrations (Entries 1 and 2, Table S3)

	Concentration (g/L)					
	1	10	25	50	150	375
PVOH soluble at (°C)	50	60	60	80	80 (only partially soluble)	-
P(VOH- <i>co</i> -BD) soluble at (°C)	20	20	20	20	20	30

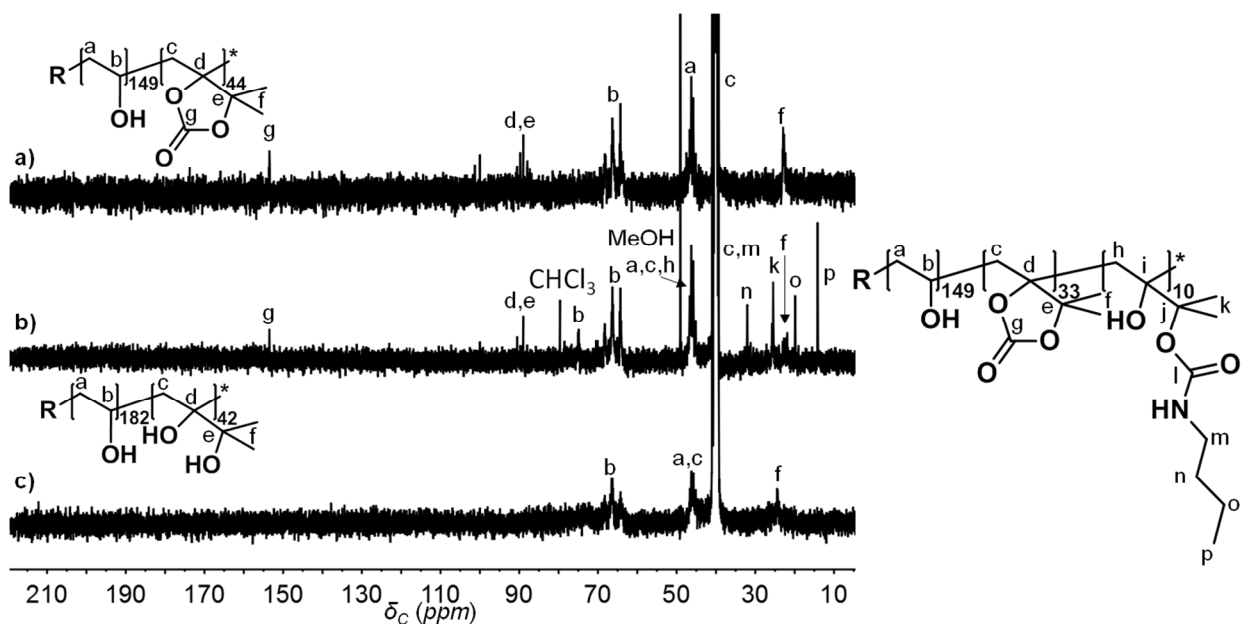


Figure S4. ¹³C-NMR spectra of a) P(VOH₁₄₉-*co*-DMMDO₄₄), b) P(VOH₁₄₉-*co*-DMMDO₃₃-*co*-HU₁₀) functionalised using dry n-butylamine and c) P(VOH₁₈₂-*co*-BD₄₂); all spectra are recorded in DMSO-*d*₆ on a 400 MHz spectrometer.

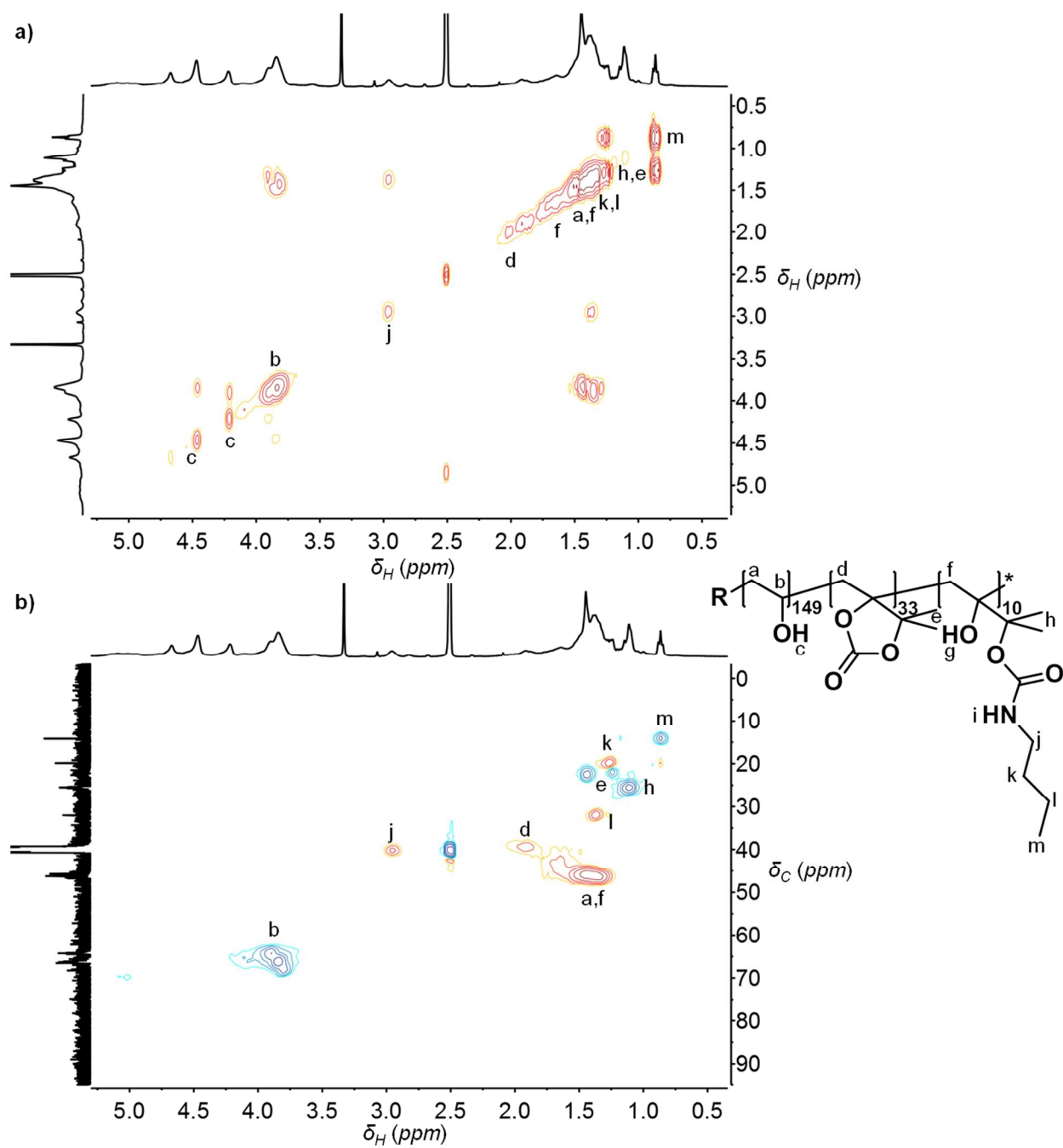


Figure S5. a) COSY and b) HSQC spectra of P(VOH₁₄₉-co-DMMDO₃₃-co-HU₁₀) functionalised using dry n-butylamine; recorded in DMSO-*d*₆ on a 400 MHz spectrometer.

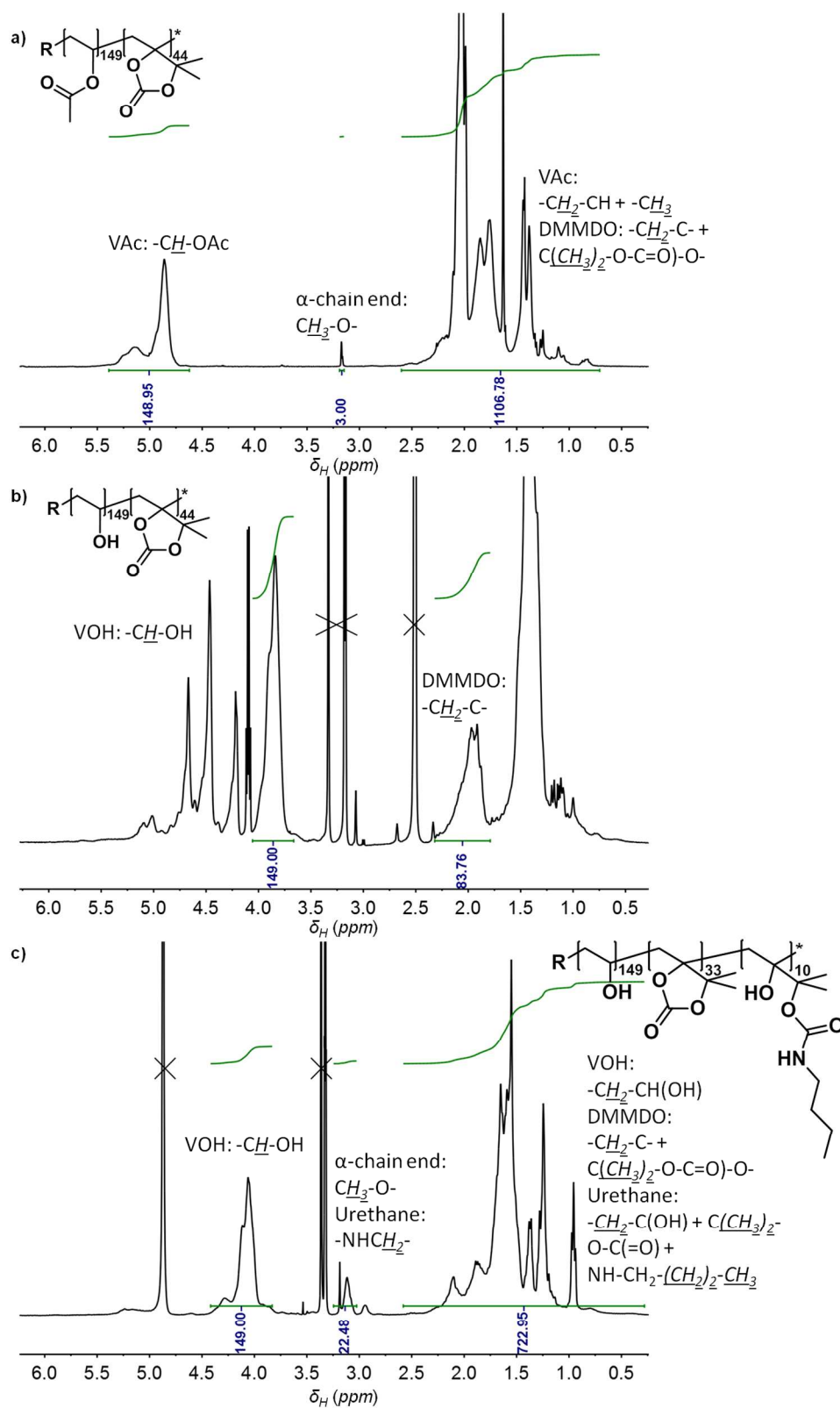


Figure S6. ^1H -NMR spectra of a) P(VAc₁₄₉-co-DMMDO₄₄) recorded in CDCl₃ b) P(VOH₁₄₉-co-DMMDO₄₄) recorded in DMSO-*d*₆ and c) P(VOH₁₄₉-co-DMMDO₃₃-co-HU₁₀) functionalised using dry n-butylamine, recorded in MeOD-*d*₄. All spectra recorded on a 400 MHz spectrometer.

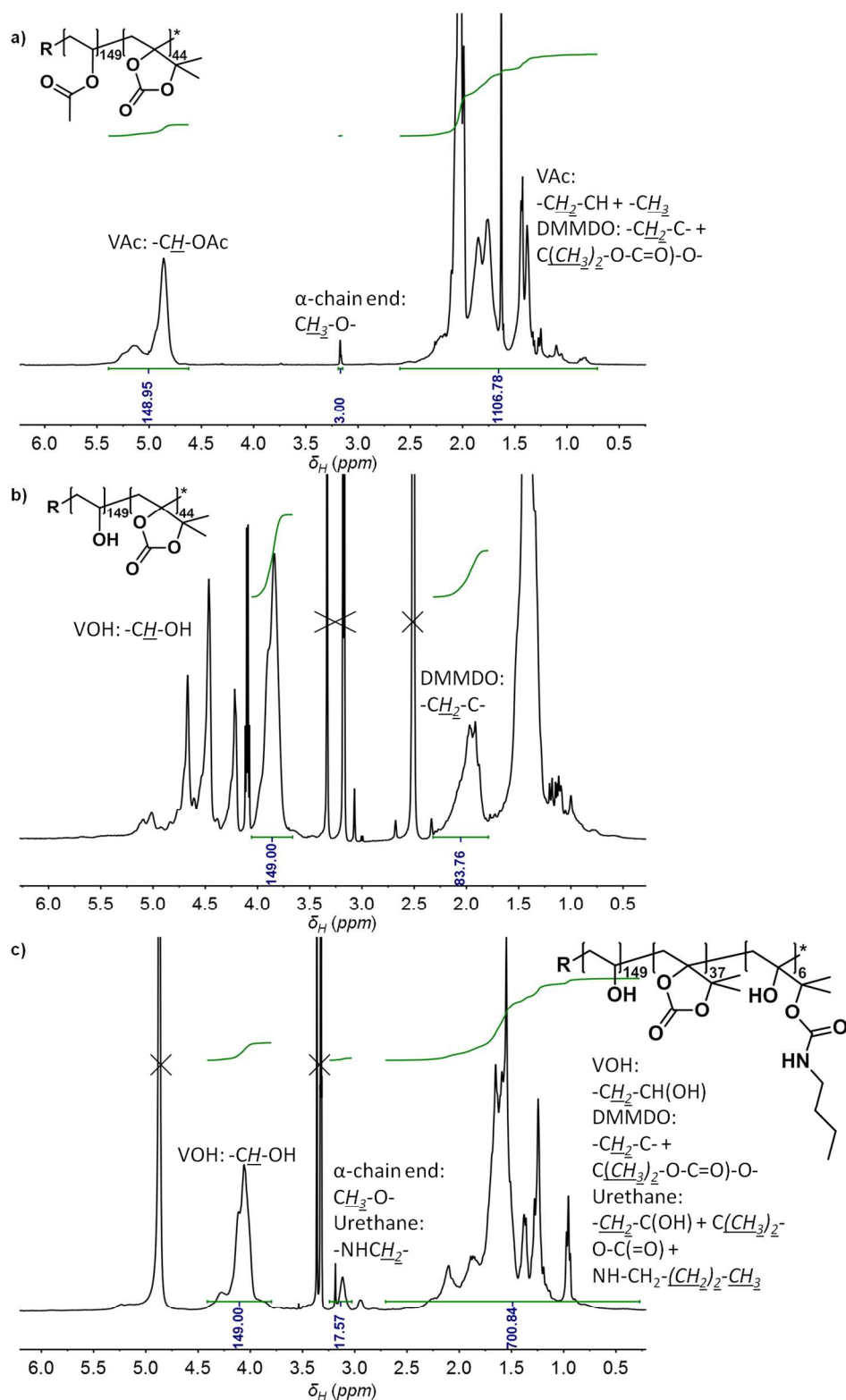


Figure S7. ^1H -NMR spectra of a) $\text{P}(\text{VAc}_{149}\text{-co-DMMDO}_{44})$ recorded in CDCl_3 , b) $\text{P}(\text{VOH}_{149}\text{-co-DMMDO}_{44})$ recorded in $\text{DMSO-}d_6$ and c) $\text{P}(\text{VOH}_{149}\text{-co-DMMDO}_{36}\text{-co-HU}_7)$ functionalised using wet *n*-butylamine recorded in $\text{MeOD-}d_4$. All spectra are recorded on a 400 MHz spectrometer.

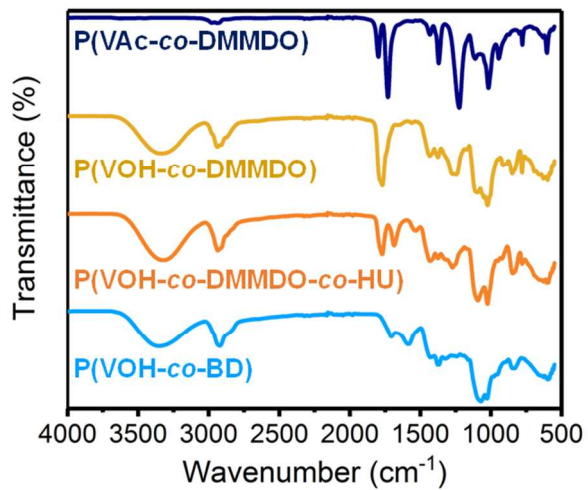


Figure S8. FT-IR spectra of P(VAc₁₄₉-co-DMMDO₄₄), P(VOH₁₄₉-co-DMMDO₄₄), P(VOH₁₄₉-co-DMMDO₃₆-co-HU₇) functionalised using wet n-butylamine and P(VOH₁₈₂-co-BD₄₂)