

Electronic Supplementary Information

Reversible Deactivation Radical (Co)Polymerization of Dimethyl Methylene Oxazolidinone towards Responsive Vicinal Aminoalcohol-Containing Copolymers.

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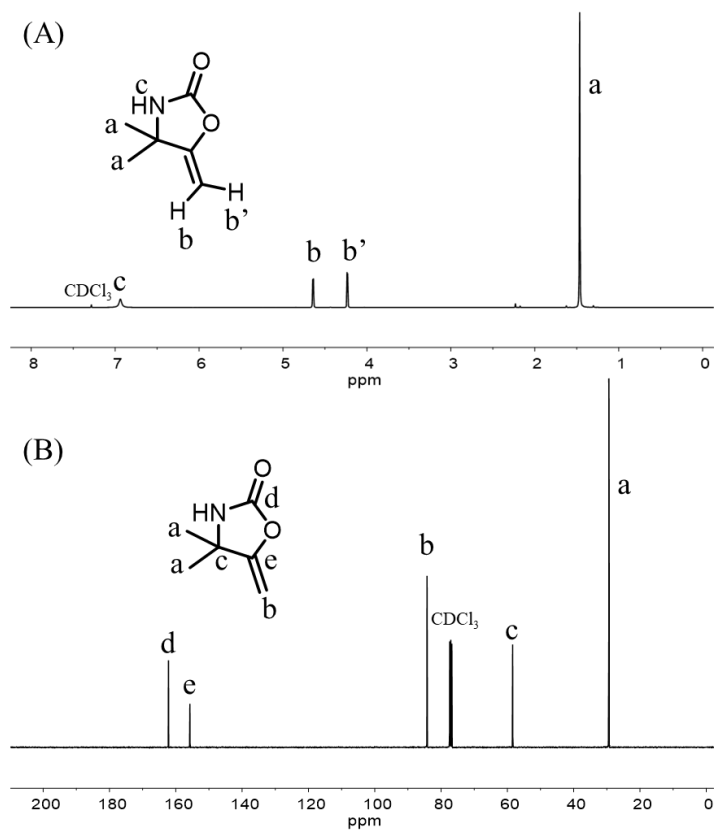


Figure S1. ¹H NMR (A) and ¹³C NMR (B) spectra of 4,4-dimethyl-5-methyleneoxazolidin-2-one (DMOX) in CDCl₃.

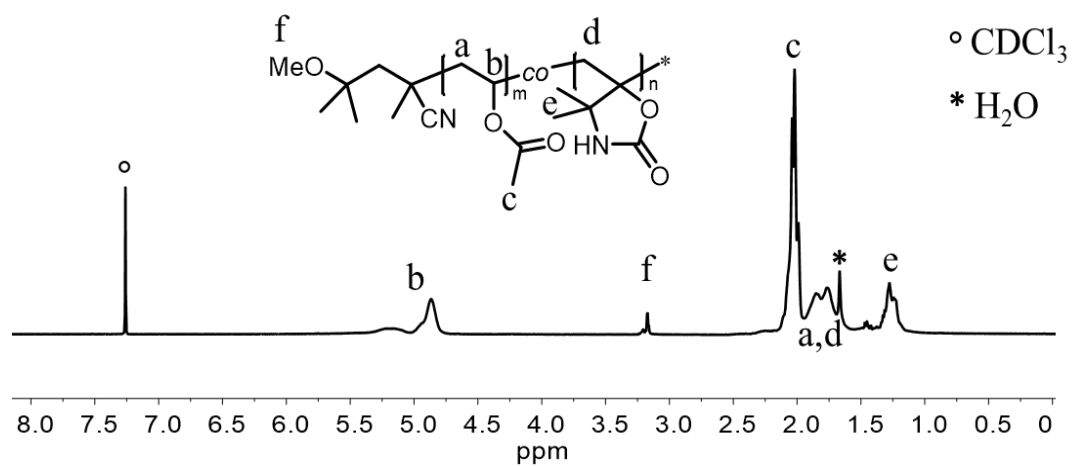


Figure S2. ^1H NMR of P(DMOx-co-VAc) ($F_{\text{DMOx}} = 0.08$; entry 3 Table 2) in CDCl_3 .

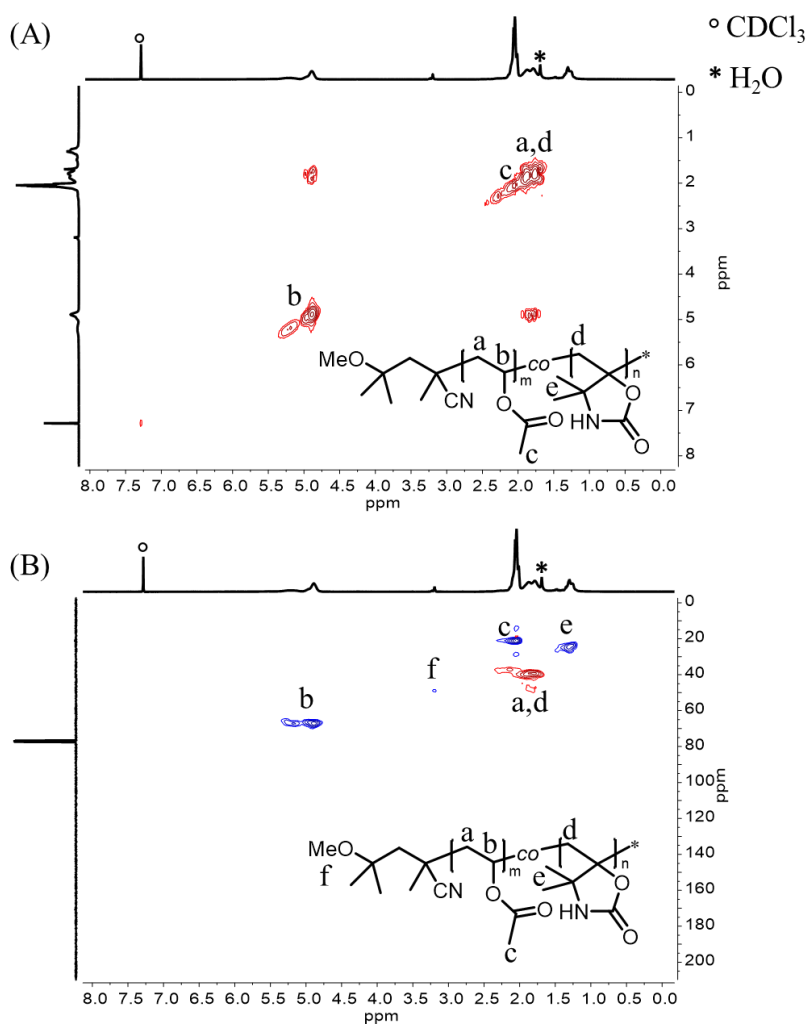


Figure S3. COSY (A) and HSQC (B) spectra in CDCl_3 of P(DMOx-co-VAc) ($F_{\text{DMOX}} = 0.08$) prepared by conventional radical polymerization with V70 as initiator (Table 2, entry 3).

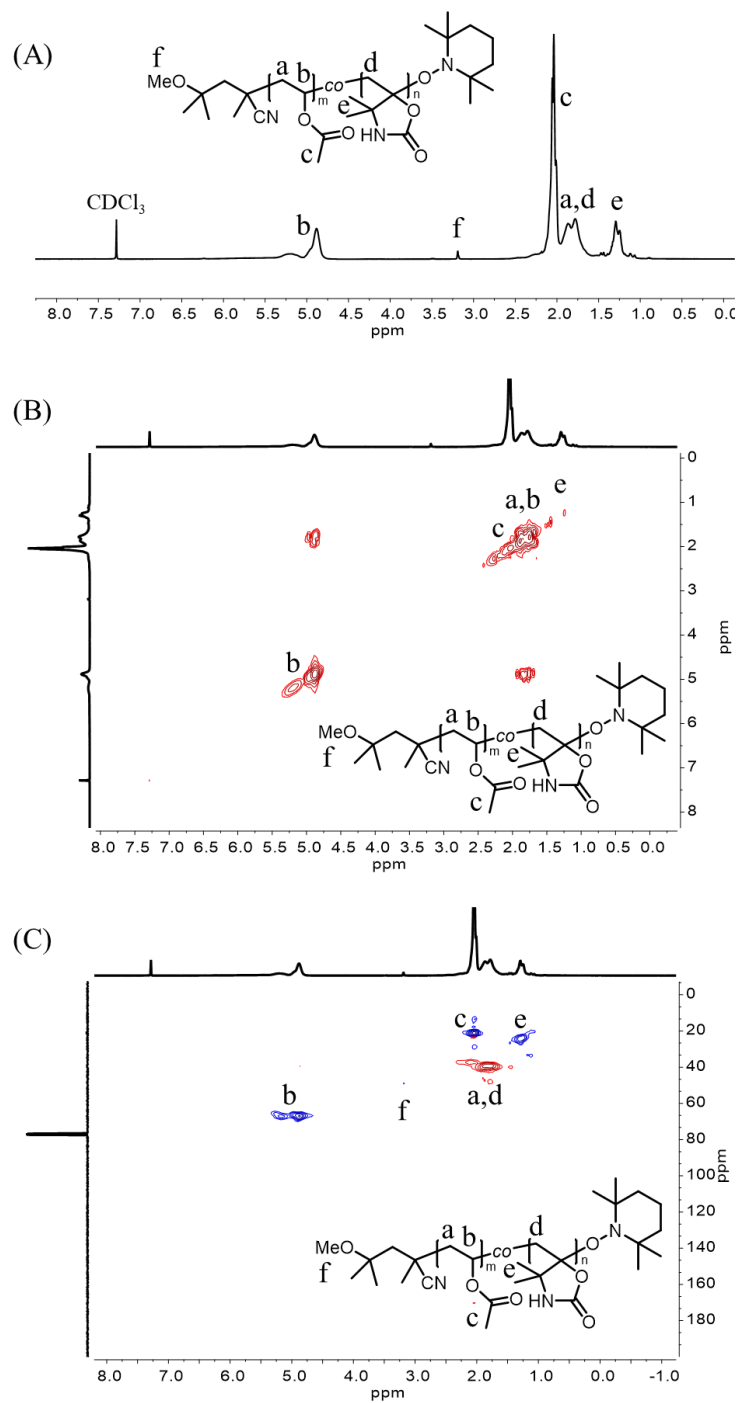


Figure S4. ^1H NMR (A), COSY (B) and HSQC (C) spectra in CDCl_3 of the P(DMOx-co-VAc) ($F_{\text{DMOx}} = 0.10$) prepared by OMRP (Table 3, entry 1).

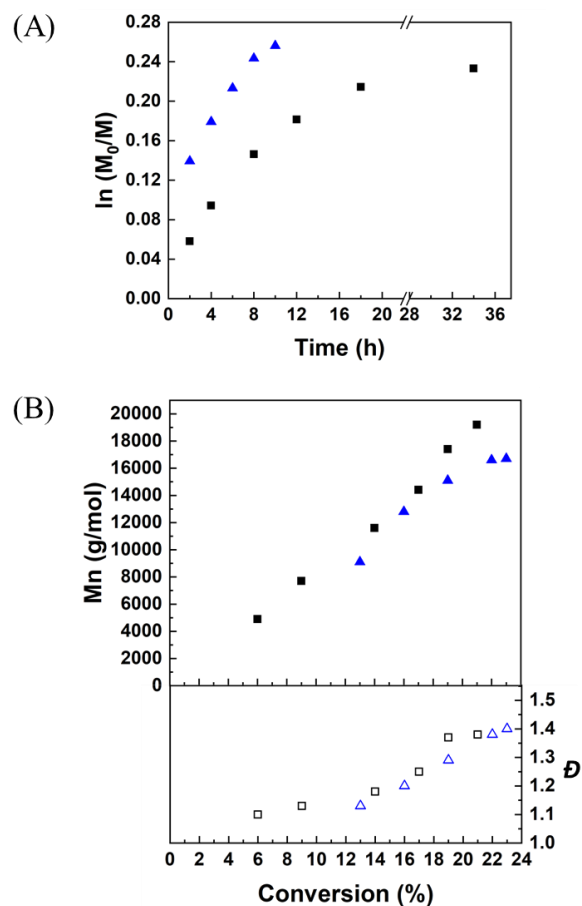


Figure S5. (A) Time dependence of $\ln[M]_0/[M]$ and (B) evolution of M_n (full symbols) and \mathcal{D} (hollow symbols) on the total monomer conversion for the OMRP ($f_{\text{DMOx}}^{\circ} = 0.4$, $[\text{DMOx}]/[\text{VAc}]/[\text{RCo}] = 200/300/1$) at 40 °C (■) and 50 °C (▲).

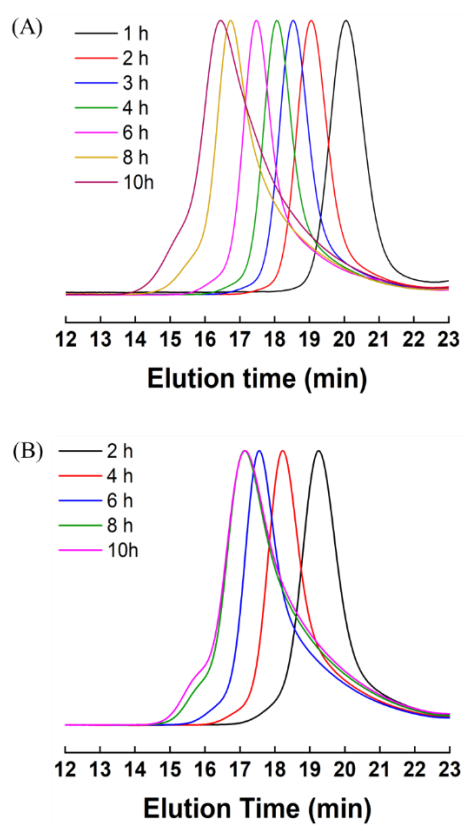


Figure S6. Overlay of SEC traces for the OMRP of DMOx and VAc performed at 50 °C with f_{DMOx} equal to (A) 0.2 and (B) 0.4 (Table 3, entries 3 and 4).

Table S1. Data used for the determination of the reactivity ratios for the OMRP of DMOx and VAc at 40 °C.

Entry	Feed composition		Time (h)	Conv. ^a (%)	$F_{\text{DMOx}}^{\text{b}}$
	f°_{DMOx}	f°_{VAc}			
1	0.19	0.81	2	12	0.12
2	0.31	0.69	2	10	0.19
3	0.47	0.53	2	8	0.26
4	0.51	0.49	2	7	0.29
5	0.59	0.41	3	5	0.31

Conditions: bulk polymerization, 40 °C, $[\text{comonomers}]_0/[\text{RCO}]_0 = 500/1$, ^a total monomer conversion determined by ¹H NMR in CDCl₃. ^b Determined by ¹H NMR in CDCl₃ after purification of the copolymers.

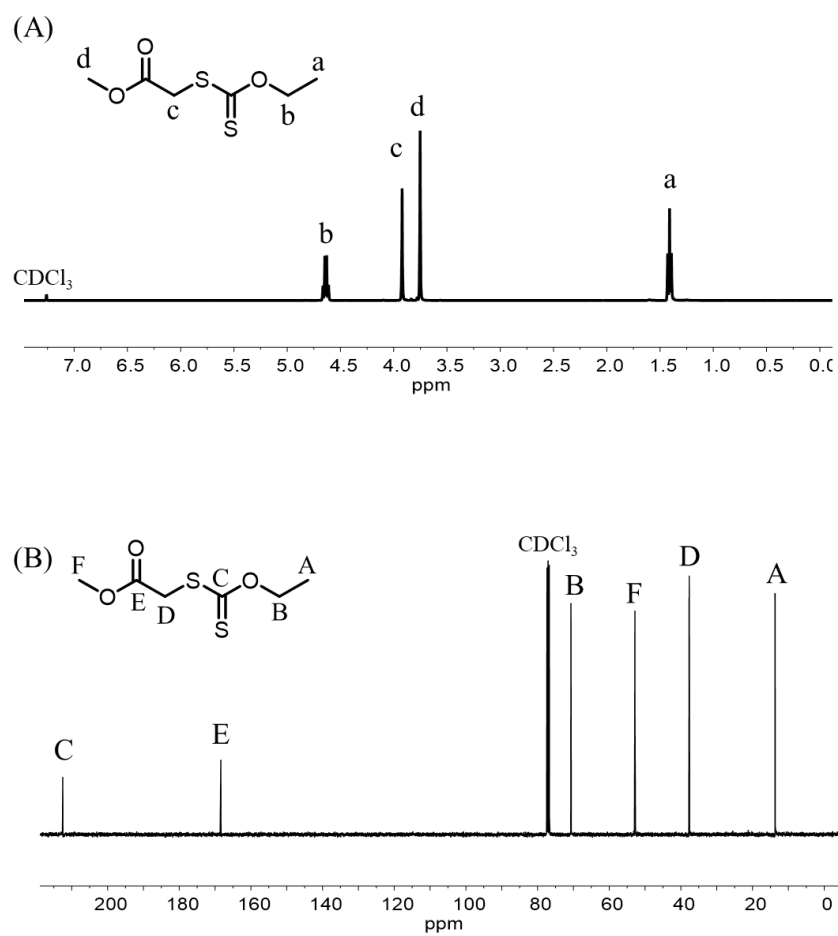


Figure S7. ^1H NMR (A) and ^{13}C NMR (B) spectra of methyl (ethoxycarbonothioyl)sulfanyl acetate in CDCl_3 .

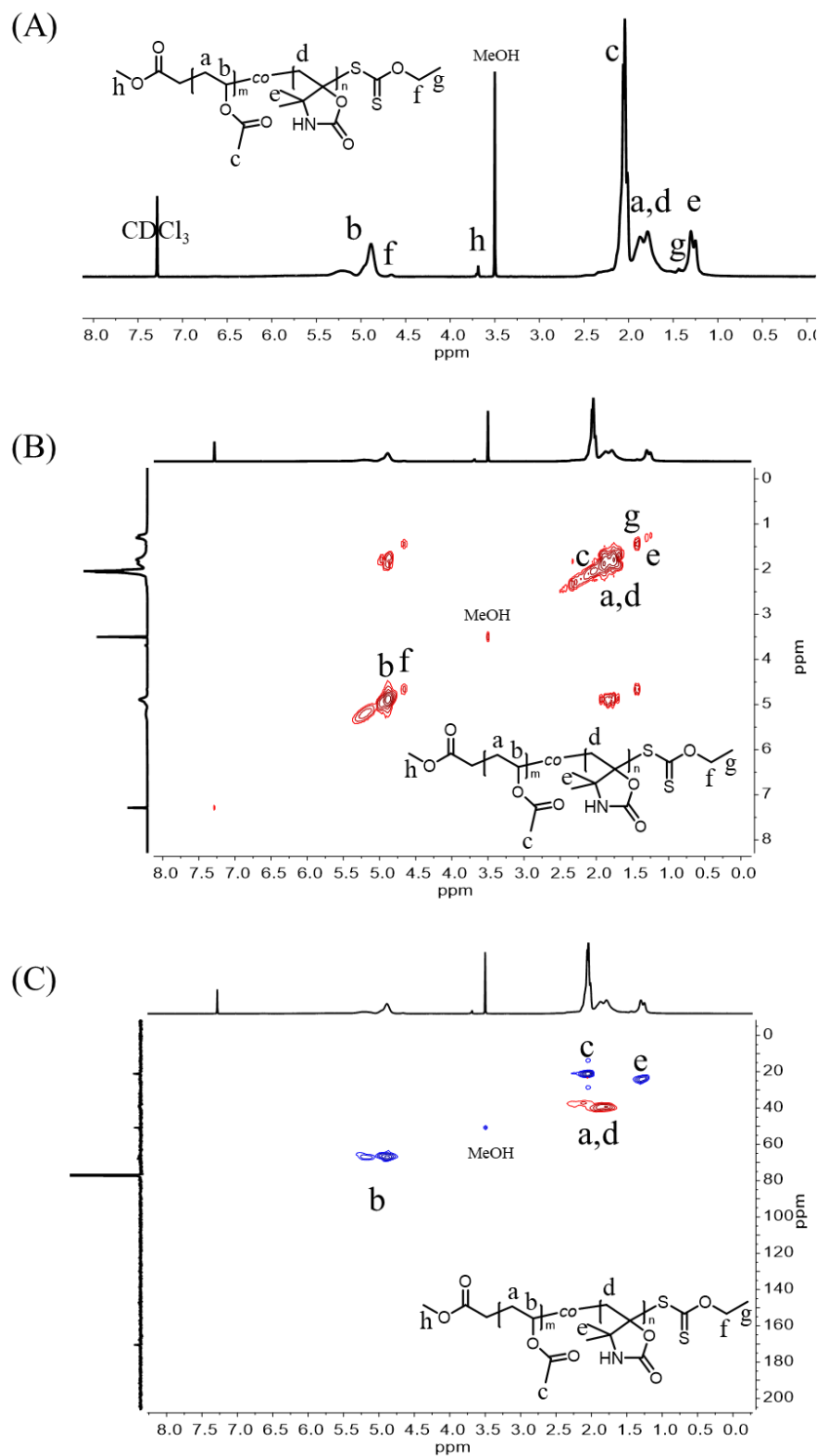


Figure S8. ^1H NMR (A), COSY (B) and HSQC (C) spectra in CDCl_3 of the P(DMOx-co-VAc) ($F_{\text{DMOx}} = 0.12$) prepared by RAFT (Table 4, entry 2).

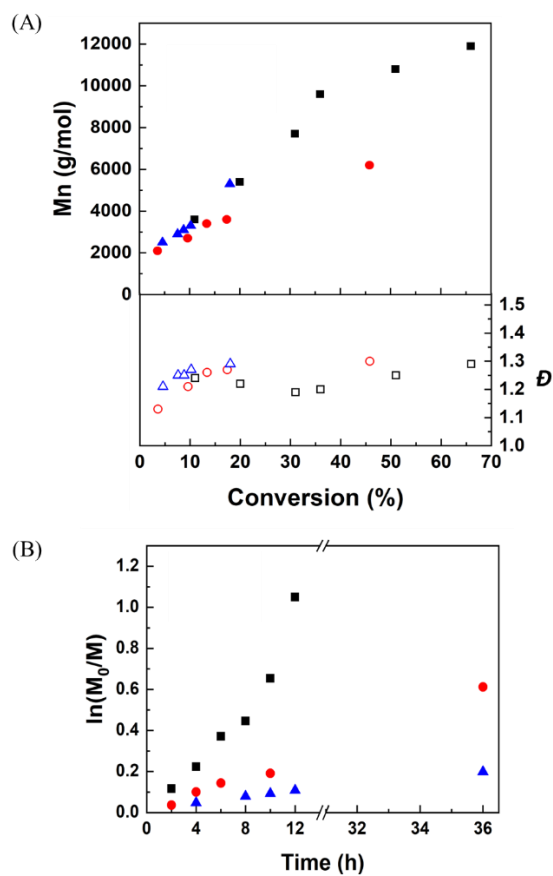


Figure S9. (A) The total monomer conversion dependence of M_n (full symbols) and \bar{D} (hollow symbols) and (B) Time dependence of $\ln[M]_0/[M]$ for the RAFT of DMOx and VAc ($[\text{comonomers}]/[\text{Xanthate}]/[\text{AIBN}] = 150/1/0.2$) with different initial rate: $f_{\text{DMOx}}^0 = 0.2$ (■), 0.4 (●), 0.6 (▲).

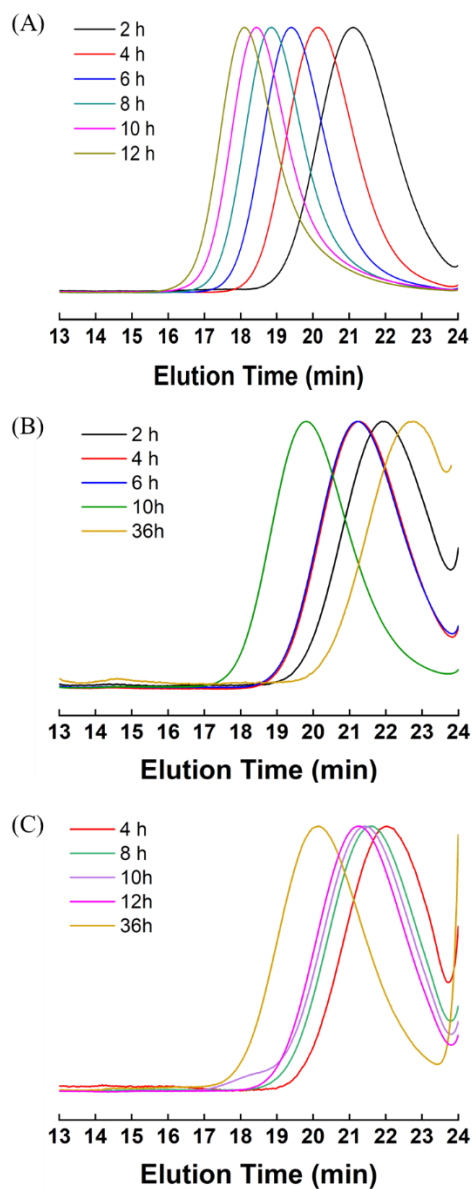


Figure S10. Overlay of SEC chromatograms for the RAFT of DMOx/VAc using (A) $[\text{DMOx}]_0/[\text{VAc}]_0/[\text{xanthate}]_0/[\text{AIBN}]_0 = 30/120/1/0.2$ (Table 4, entry 2), (B) $[\text{DMOx}]_0/[\text{VAc}]_0/[\text{xanthate}]_0/[\text{AIBN}]_0 = 60/90/1/0.2$ (Table 4, entry 3), (C) $[\text{DMOx}]_0/[\text{VAc}]_0/[\text{xanthate}]_0/[\text{AIBN}]_0 = 90/60/1/0.2$ (Table 4, entry 4).

Table S2. Data used for the determination of the reactivity ratios for the RAFT of DMOx and VAc at 65 °C.

Entry	Feed composition		Time (h)	Conv. ^a (%)	$F_{\text{DMOx}}^{\text{b}}$
	f°_{DMOx}	f°_{VAc}			
1	0.12	0.88	1	5	0.06
2	0.23	0.77	2	6	0.12
3	0.36	0.64	3	6	0.20
4	0.49	0.51	3	8	0.28
5	0.60	0.40	4	6	0.39

Conditions: bulk polymerization, 65 °C, [comonomers]/[Xanthate]/[AIBN] = 150/1/0.2, ^a total monomer conversion determined by ¹H NMR in CDCl₃. ^b Determined by ¹H NMR in CDCl₃ after purification of the copolymers.

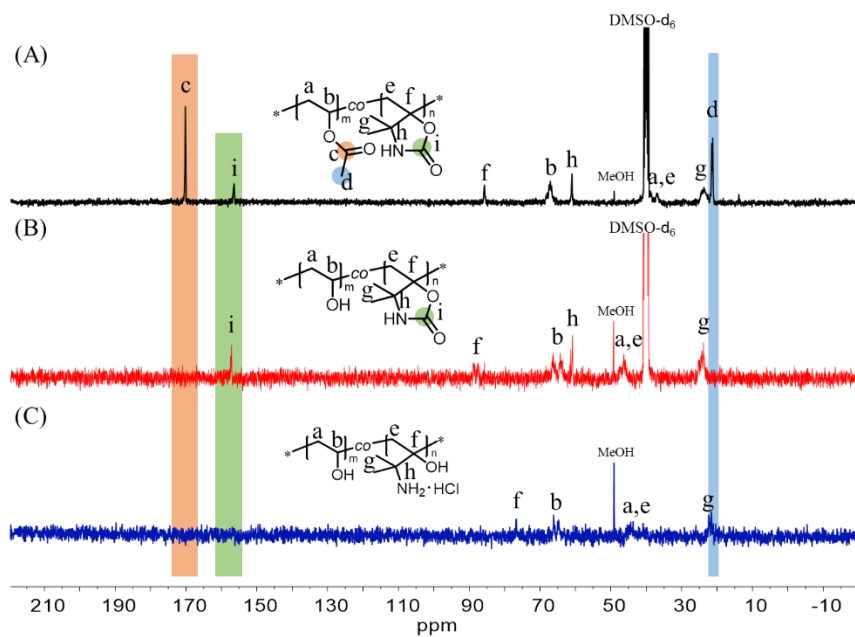


Figure S11. Overlay of ^{13}C NMR spectra of (A) P(DMOx-co-VAc) (M_n : 10000 g/mol, $F_{\text{DMOX}} = 0.24$) in DMSO- d_6 , (B) P(DMOx-co-VA) in DMSO- d_6 and (C) P(AMBO-co-VA) in D_2O .

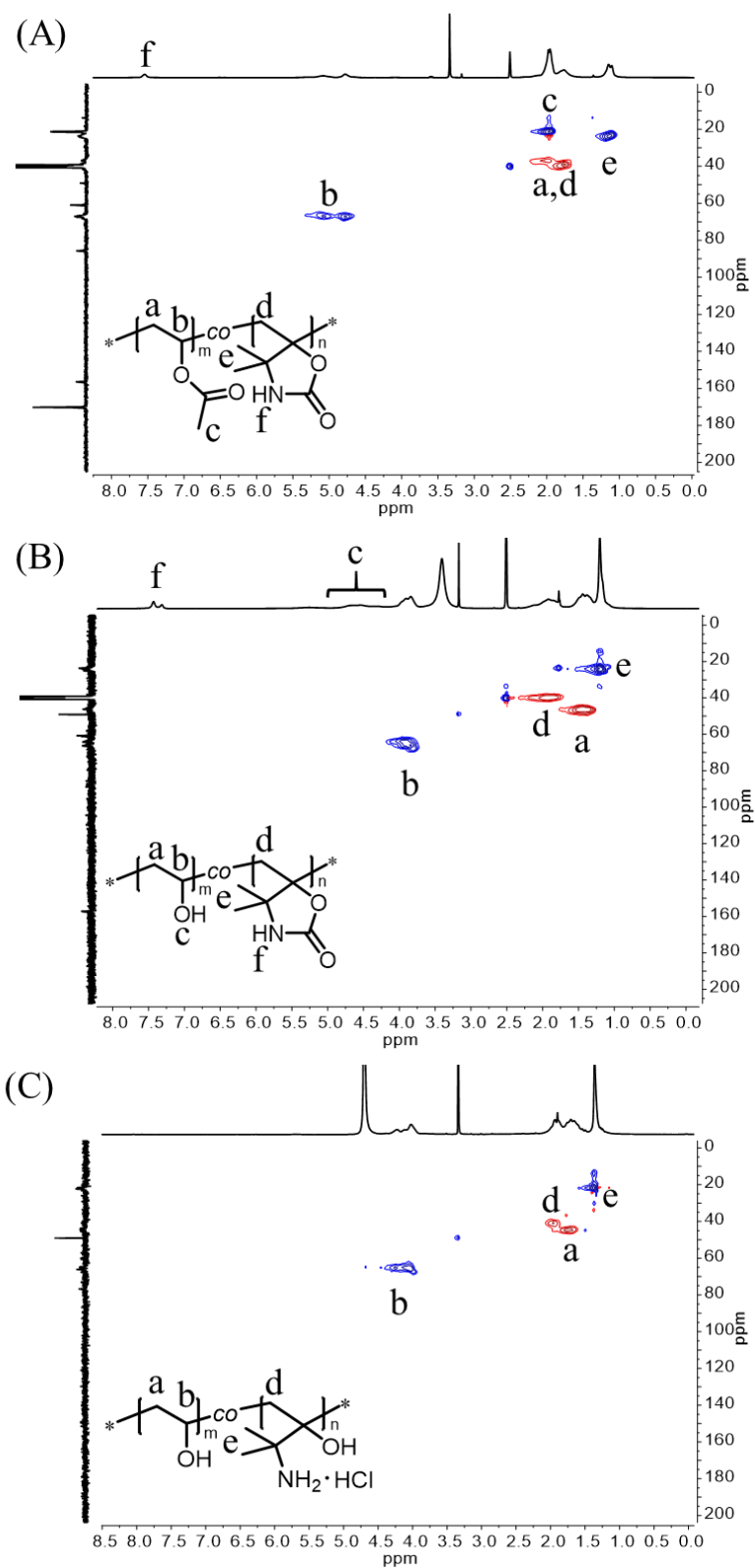


Figure S12. HSQC spectra of (A) P(DMOx-co-VAc) in DMSO-d₆, (B) P(DMOx-co-VA) in DMSO-d₆ and (C) P(AMBO-co-VA) in D₂O.

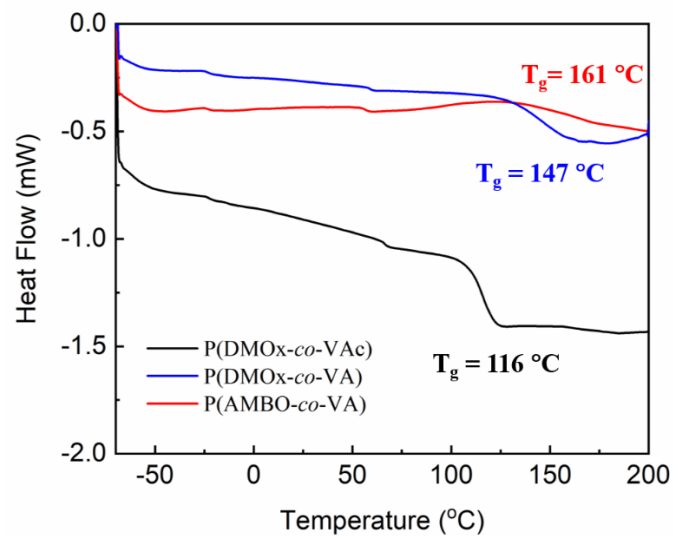


Figure S13. Differential scanning calorimetry (DSC) analyses of P(DMOx-co-VAc) (M_n : 10000 g/mol, $F_{\text{DMOx}} = 0.24$) and the corresponding P(DMOx-co-VA) and P(AMBO-co-VA).