

Electronic Supporting Information

Precision Design of Vinyl Amine and Vinyl Alcohol-Based Copolymers via Cobalt-Mediated Radical Polymerization

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Table S1. Data used for the determination of the reactivity ratios for the CMRP of NVA and VAc.

Entry	Feed composition		Time (min)	Conv ^a (%)	Copolymer composition ^b	
	f°_{NVA}	f°_{VAc}			F_{NVA}	F_{VAc}
1	0.10	0.90	85	17	0.21	0.79
2	0.30	0.70	60	10	0.54	0.47
3	0.50	0.50	20	1	0.70	0.30
4	0.70	0.30	13	11	0.84	0.16
5	0.89	0.11	3	32 ^c	0.94	0.06

Conditions: 40 °C ; [Comonomers]/[PVAc₄-Co(acac)₂] = 700 ; comonomers/DMF = 1.4/1 m/v.^a Determined by ¹H NMR in MeOD (see Figure S1). ^b Determined by ¹H NMR in MeOD after purification of the copolymer by precipitation followed by dialysis in methanol. ^c The conversion was higher in this case due to a very fast polymerization when copolymerization with high NVA content is used. Nevertheless, as predicted by the Skeist's model, the composition drift is rather limited at this conversion and the value remains valid (see F_{cumul} in Figure 4).

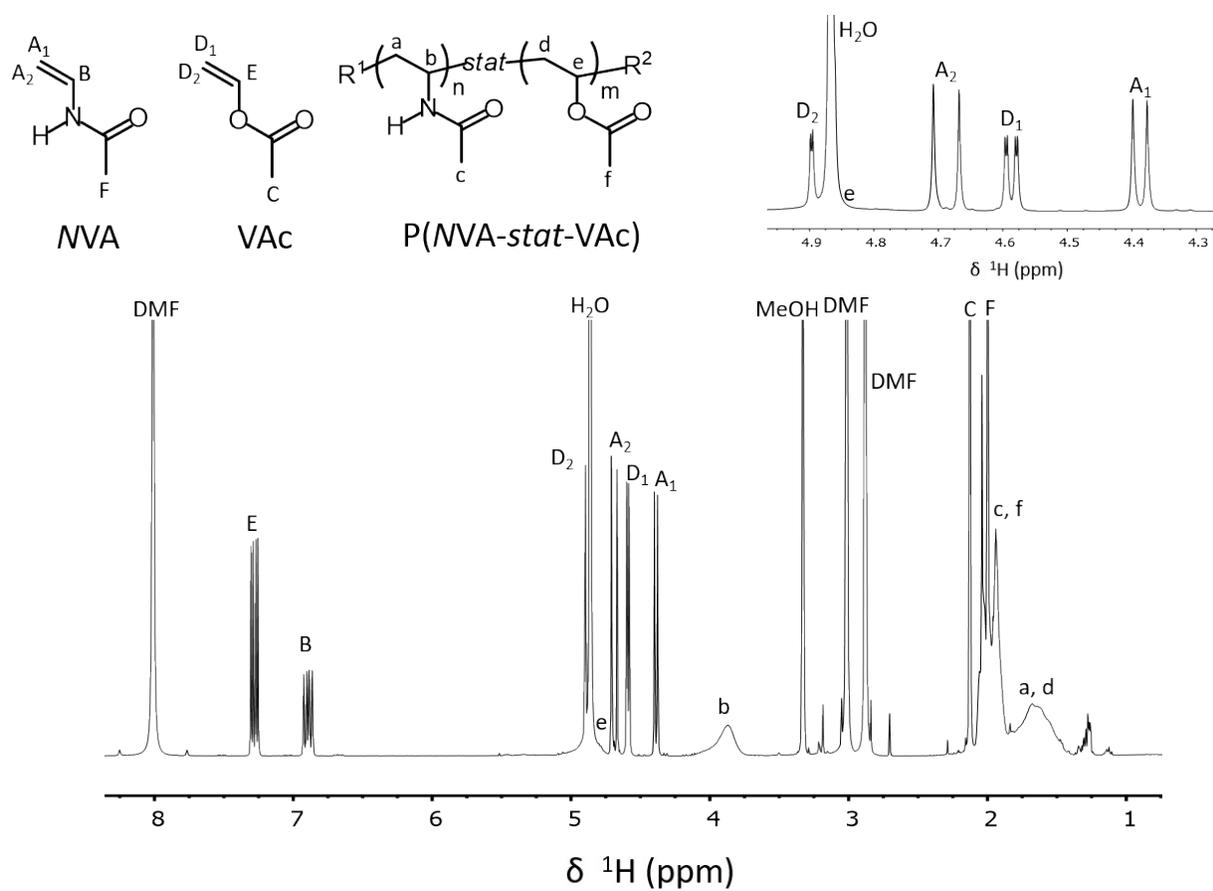


Fig S1. Typical ¹H NMR spectrum in MeOD of the reaction mixture of the cobalt-mediated radical copolymerization of NVA/VAc. Conditions: [NVA]/[VAc]/[RCo(acac)₂] = 250/250/1 ; 1 g of comonomers/mL of DMF, 40 °C, 11 h, overall conv = 47 %. Overall conversion (%) = $\frac{[[\int_{2.2-1.4 \text{ ppm}} - 3 \int_{4.6 \text{ ppm}} - 3 \int_{4.4 \text{ ppm}} \text{ ppm}]/5]}{[[\int_{2.2-1.4 \text{ ppm}} - 3 \int_{4.6 \text{ ppm}} - 3 \int_{4.4 \text{ ppm}} \text{ ppm}]/5 + \int_{4.6 \text{ ppm}} + \int_{4.4 \text{ ppm}}]} \times 100$

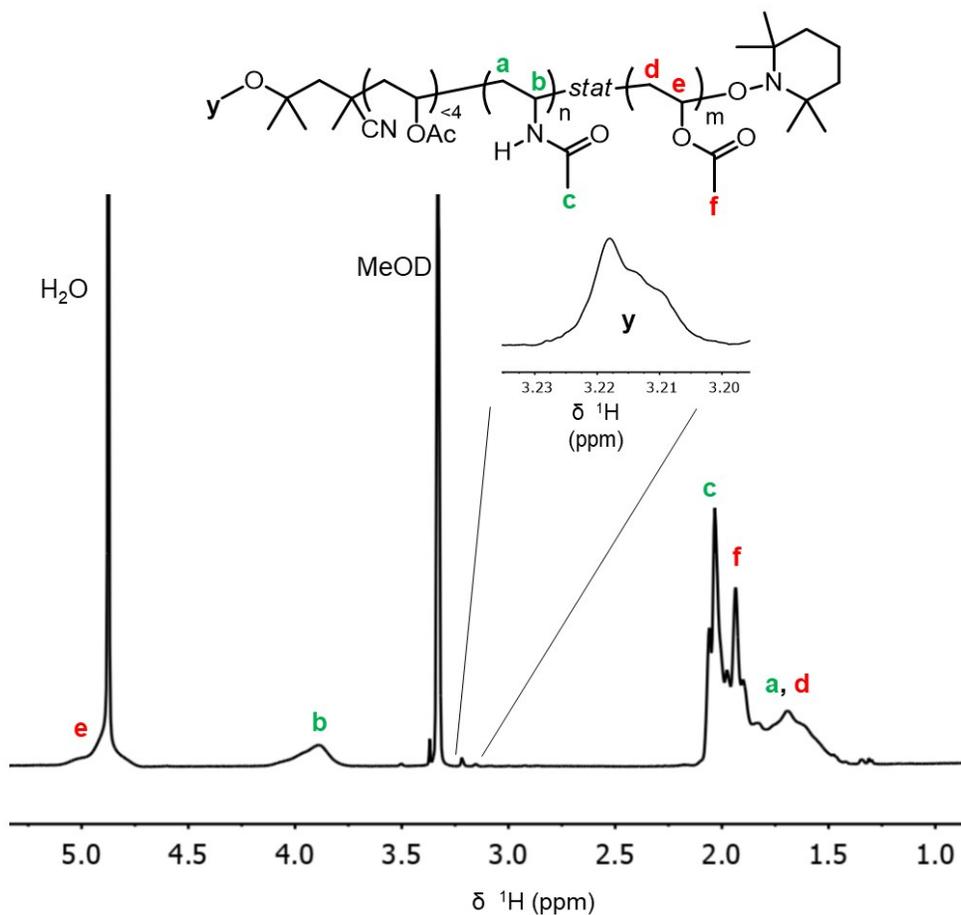


Fig S2. Typical ¹H NMR analysis of a P(NVA-co-VAc) copolymer prepared by cobalt-mediated radical copolymerization of NVA/VAc. Conditions: [NVA]/[VAc]/[RCo(acac)₂] = 150/350/1; 1 g of comonomers/mL of DMF, 40 °C, 13 h, conversion = 42 %. (See Table 1, $f^{\circ}_{NVA} = 0.3$). $F_{NVA} = 0.46$. It was determined by comparing the intensity of signal **b** at 3.8 ppm corresponding to the methine proton of the NVA units with signals between 2.3 and 1.4 ppm corresponding to the methyl and methylene groups of NVA and VAc units in the copolymer. ($F_{NVA} = \int_{4.2-3.6 \text{ ppm}} / [\int_{2.3-1.4 \text{ ppm}}/5]$)

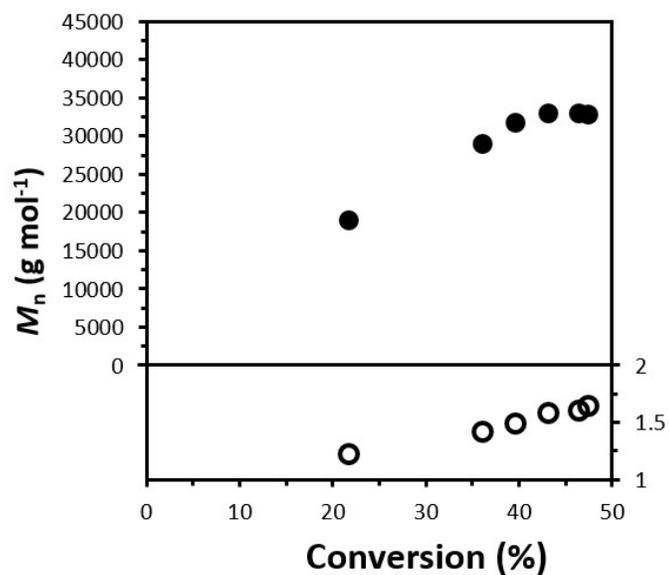


Fig S3. Dependence of the molar mass (M_n , SEC DMF CAL PS, full symbols) and dispersity (D , empty symbols) on monomer conversion (determined by ^1H NMR in MeOD) for the cobalt-mediated radical copolymerization of NVA and VAc. Conditions: $[\text{Monomer}]/[\text{R-Co}] = 500$; $[\text{NVA}]/[\text{VAc}]/[\text{PVAc}_{<4\text{-Co(acac)}_2}] = 250/250/1$; 1 g of comonomers/ mL of DMF, 40 °C. (see Table 1, $f_{\text{NVA}}^0 = 0.5$)

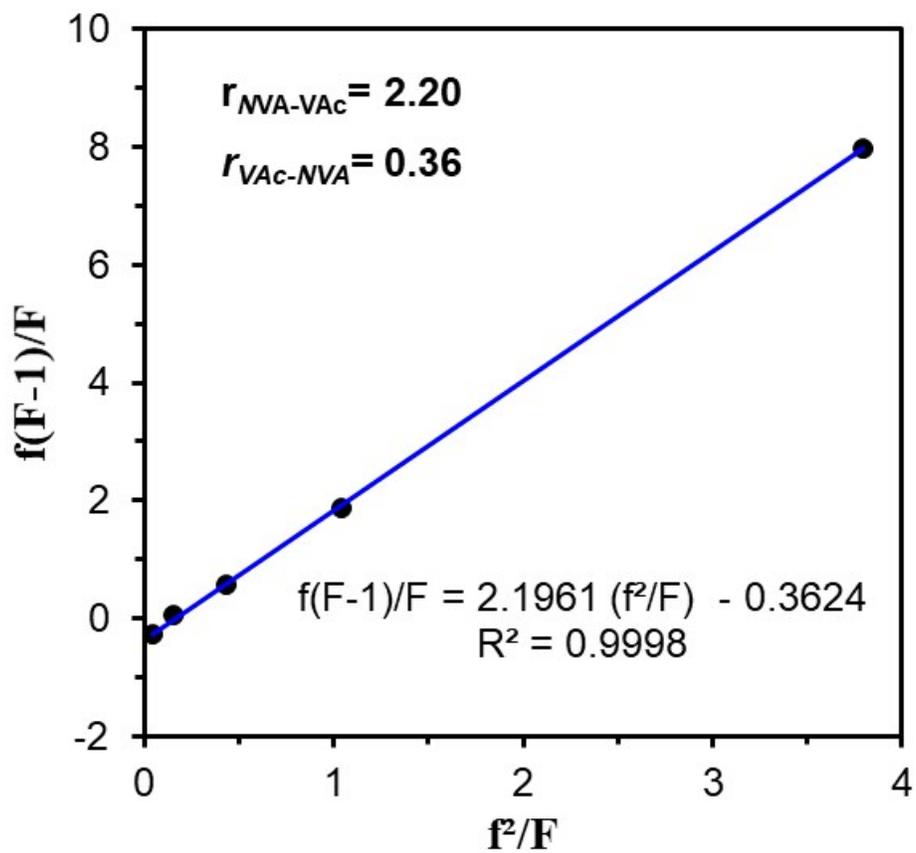


Fig S4. Fineman-Ross plot for the cobalt-mediated radical copolymerization of *NVA* and *VAc* in DMF at 40 °C in DMF. Experimental conditions and data are presented in Table S1.

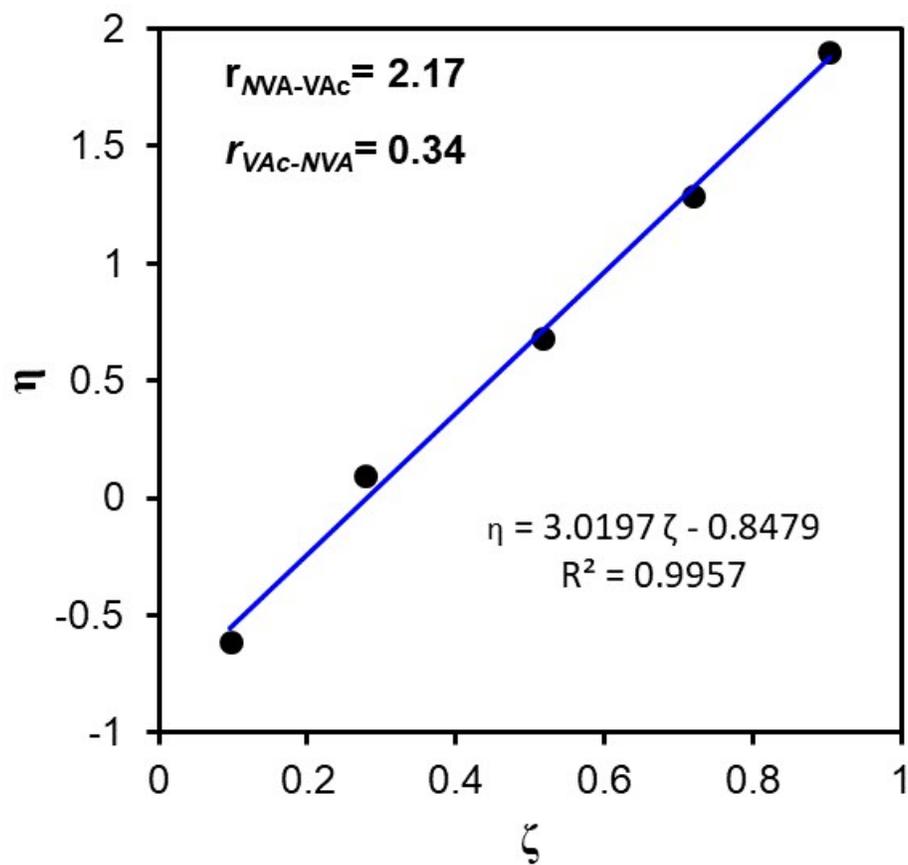


Fig S5. Kelen-Tudos plot for the cobalt-mediated radical copolymerization of NVA and VAc in DMF at 40 °C in DMF. Experimental conditions and data are presented in Table S1.

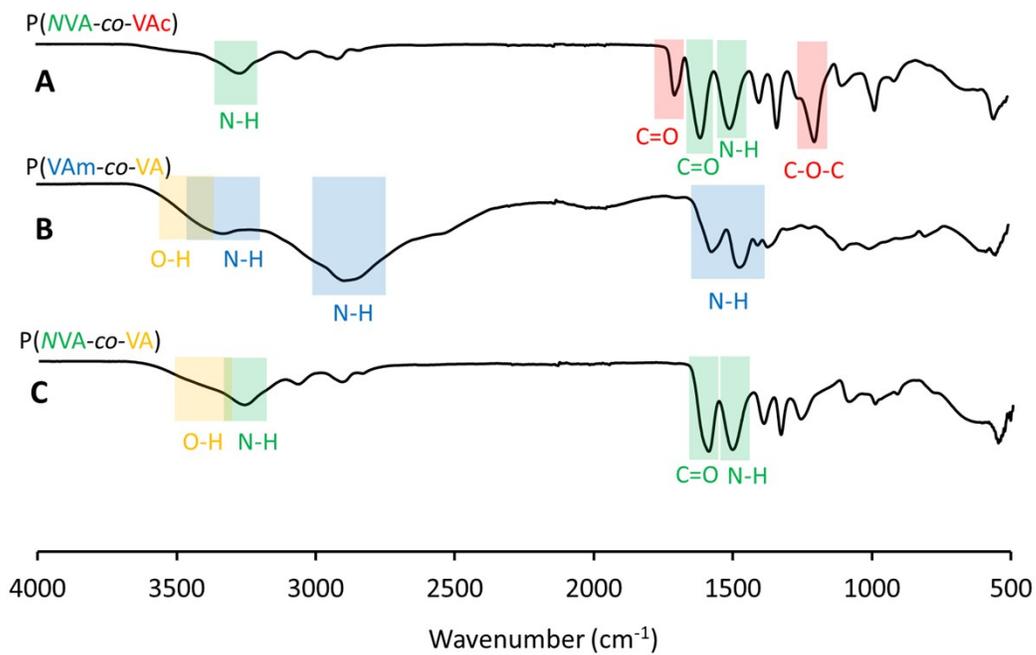


Fig S6. Infrared spectra of the P(NVA-co-VAc) copolymer (A) prepared by CMRP and the corresponding P(VAm-co-VA) (B) and P(NVA-co-VA) (C) copolymers produced via total and selective hydrolysis of (A), respectively.

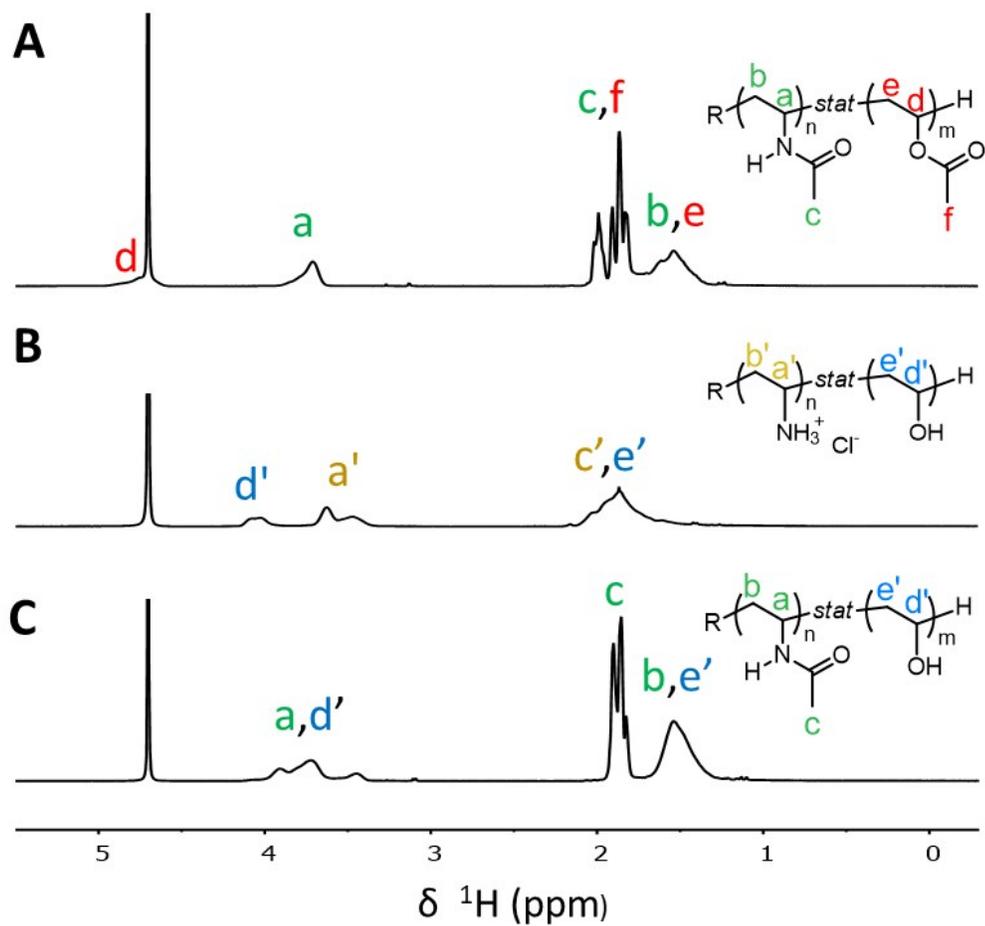


Fig S7. ^1H NMR spectra in D_2O of the P(NVA-co-VAc) copolymer (A) prepared by CMRP and the corresponding P(VAm-co-VA) (B) and P(NVA-co-VA) (C) copolymers produced via total and selective hydrolysis of (A), respectively.

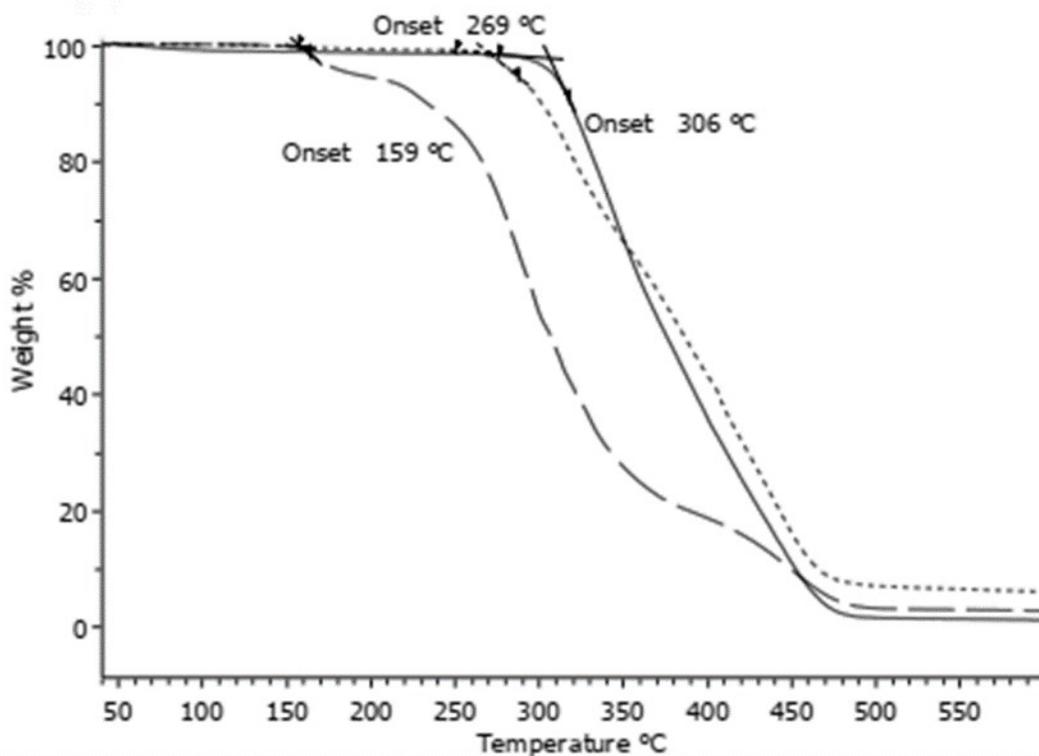


Fig S8. Thermogravimetric analysis of the P(*NVA-co-VAc*) copolymer **A** (---) prepared by CMRP and the corresponding P(*VAm-co-VA*) **B** (—) and P(*NVA-co-VA*) **C** (—) copolymers produced via total and selective hydrolysis of (**A**), respectively.

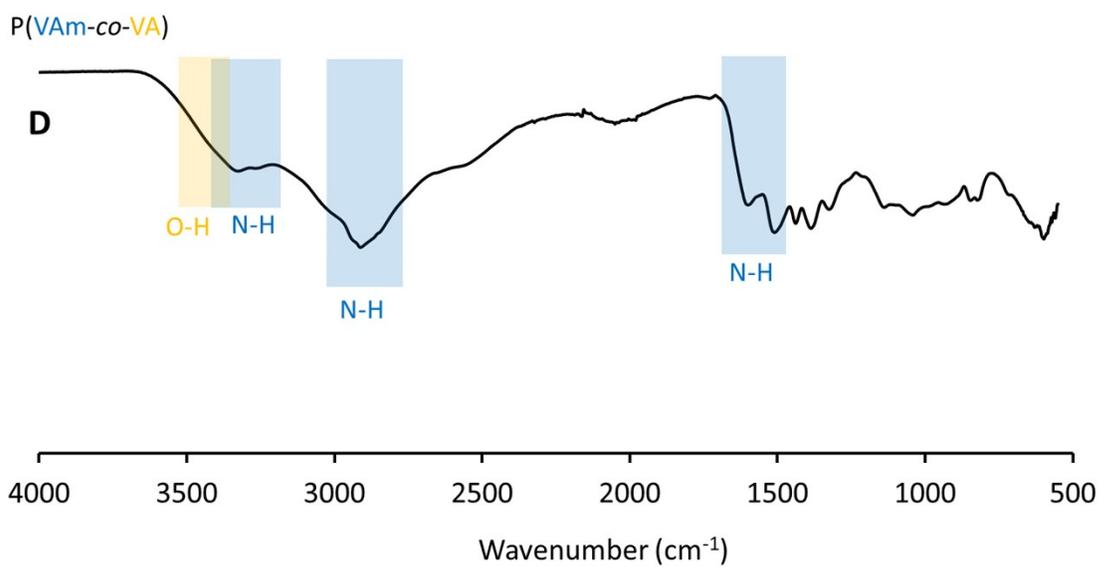


Fig S9. IR spectrum of the P(VAm-co-VA) (**D**) obtained via hydrolysis of P(NVA-co-VA) copolymer (**B**) through treatment with HCl (2N) at 120 °C for 14 h.

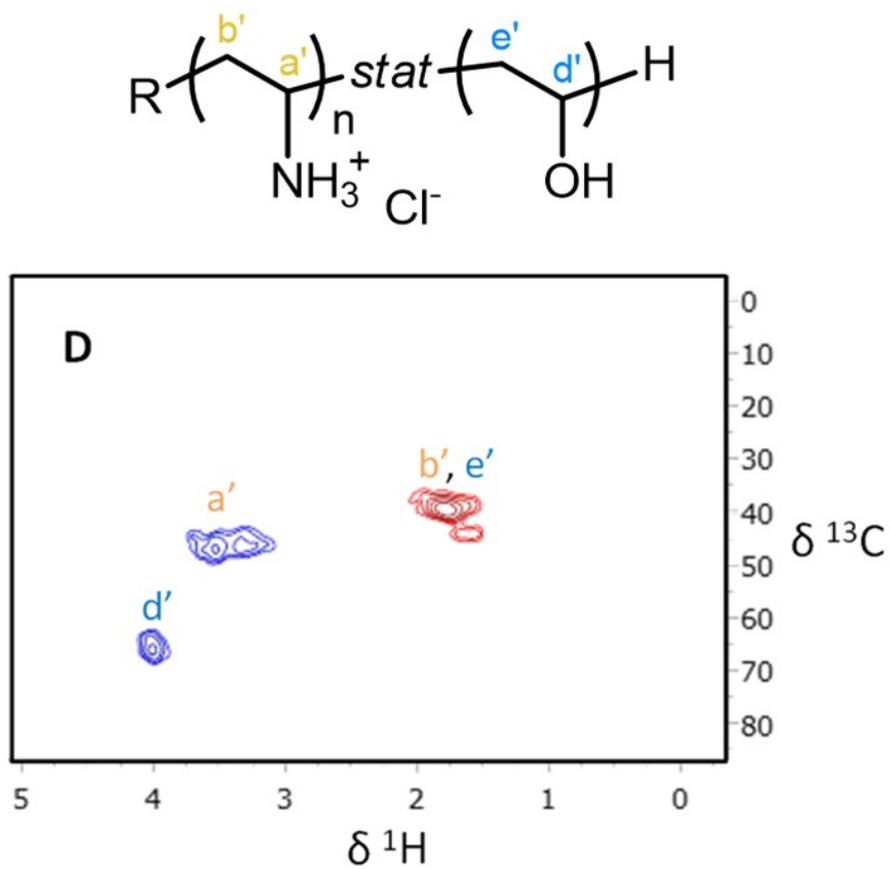


Fig S10. HSQC spectrum in D_2O of the P(VAm-co-VA) (**D**) obtained via hydrolysis of P(NVA-co-VA) copolymer (**B**) through treatment with HCl (2N) at 120 °C.