

Electronic Supporting Information

Far Beyond Primary Poly(vinylamine)s Through Free Radical Copolymerization and Amides Hydrolysis

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Table S1. Radical copolymerizations for the determination of the reactivity ratios.

Copolos	Feed Ratio ^a			Time (min)	Conv. (%) ^b	Copolymer composition ^c		
	f _{NVA}	f _{NMVA}	f _{VIm}			F _{NVA}	F _{NMVA}	F _{VIm}
P(NVA- <i>stat</i> -NMVA)	0.68	0.32	/	30	13	0.82	0.18	/
	0.62	0.38	/	25	11	0.78	0.22	/
	0.51	0.49	/	25	15	0.70	0.30	/
	0.41	0.58	/	30	18	0.62	0.38	/
	0.30	0.70	/	30	10	0.51	0.48	/
	0.20	0.80	/	30	14	0.41	0.59	/
	0.11	0.89	/	30	10	0.25	0.85	/
P(NVA- <i>stat</i> -VIm)	0.72	/	0.28	20	5	0.60	/	0.40
	0.49	/	0.51	20	8	0.42	/	0.58
	0.40	/	0.60	15	11	0.38	/	0.62
	0.28	/	0.72	15	18	0.28	/	0.72
	0.25	/	0.75	15	2	0.25	/	0.75
	0.16	/	0.84	20	7	0.15	/	0.85
P(NMVA- <i>stat</i> -1-VIm)	/	0.80	0.20	60	6	/	0.50	0.50
	/	0.94	0.06	180	14	/	0.79	0.21
	/	0.97	0.03	120	9	/	0.86	0.14
	/	0.86	0.14	90	17	/	0.68	0.32
	/	0.72	0.28	60	5	/	0.49	0.50
	/	0.44	0.56	45	9	/	0.25	0.75
	/	0.41	0.59	45	8	/	0.26	0.74
	/	0.28	0.72	45	18	/	0.16	0.84
	/	0.18	0.82	30	7	/	0.68	0.32

Conditions: polymerization in a MeOD/DMSO mixture (DMSO/MeOD (v/v) = 0.05), 30°C, [comonomers]₀/[V70]₀ = 50. ^a Determined by ¹H NMR of the initial feed mixture in MeOD. ^b Total monomer conversion determined by ¹H NMR in MeOD using DMSO as an internal standard. ^c Determined by ¹H NMR in MeOD after isolation of the copolymer.

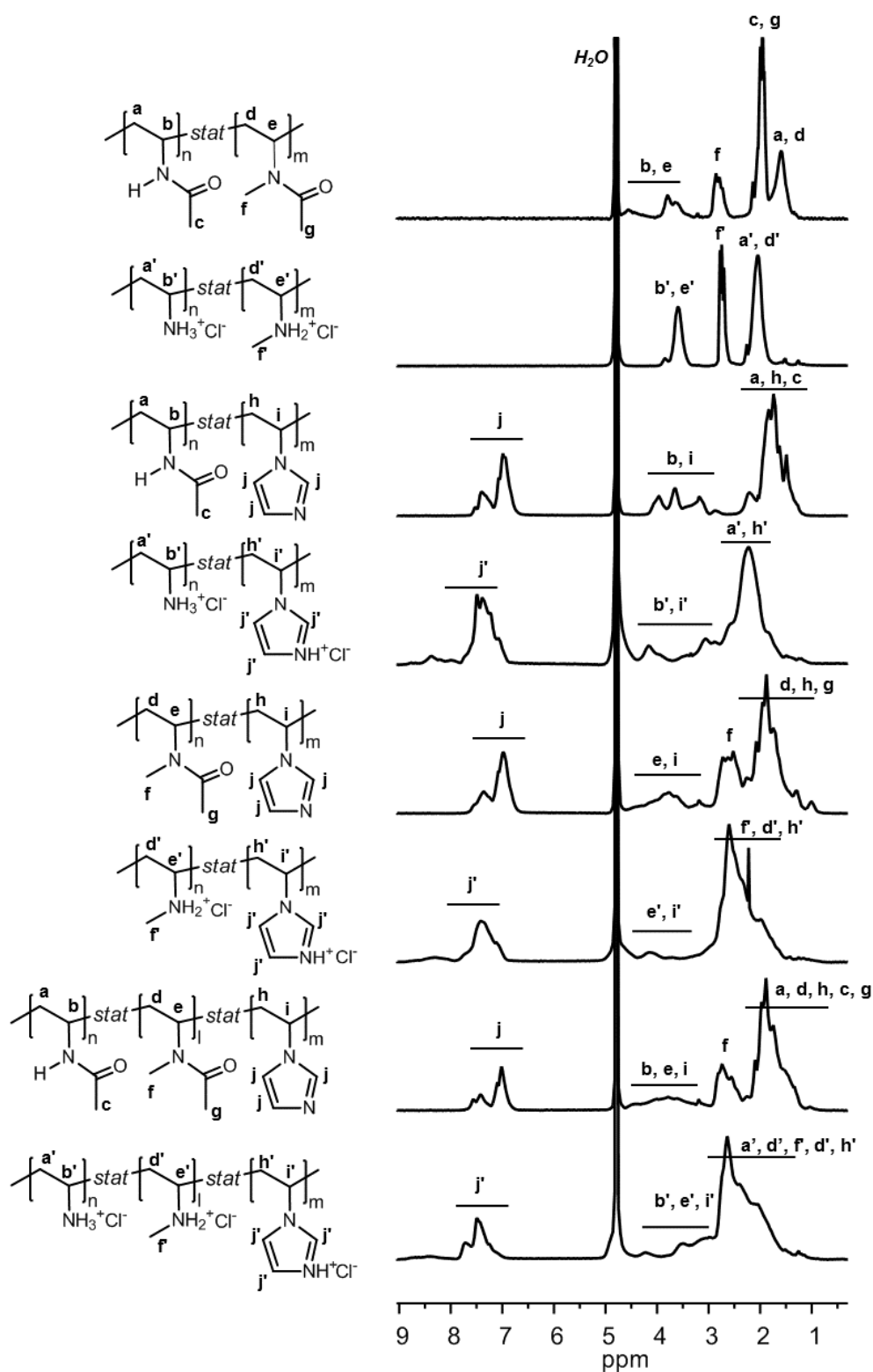


Figure S1. Overlay of the ^1H NMR spectra of poly(*N*-vinylamides)-based copolymers before and after hydrolysis with HCl 6N. Spectra were recorded at 298K in D₂O with a Bruker Avance (400 MHz) instrument.

Table S2. Determination of the reactivity ratios via the Extended Kelen-Tüdös (EKT)¹ method.

Copolymers	Feed Ratio ^a			Copolymer composition ^b			ζ_2	ζ_1	Z	G'	H'	ζ	η^c	Reactivity ratios	
	f _{NVA}	f _{NMVA}	f _{VIm}	F _{NVA}	F _{NMVA}	F _{VIm}									
P(NVA-stat-NMVA)	0.68	0.32	/	0.82	0.18	/	0.086	0.185	2.271	1.585	0.892	0.823	1.462	$r_{NVA/NMVA} = 2.142$	
	0.62	0.38	/	0.78	0.22	/	0.090	0.193	2.275	1.116	0.684	0.781	1.274		
	0.51	0.49	/	0.70	0.30	/	0.095	0.211	2.369	0.549	0.410	0.681	0.911		
	0.41	0.58	/	0.62	0.38	/	0.100	0.233	2.501	0.248	0.259	0.574	0.549		
	0.30	0.70	/	0.51	0.48	/	0.108	0.263	2.664	0.019	0.148	0.435	0.055		$r_{NMVA/NVA} = 0.316$
	0.20	0.80	/	0.41	0.59	/	0.116	0.305	2.962	-0.107	0.078	0.289	-0.395		
	0.11	0.89	/	0.25	0.85	/	0.132	0.315	2.665	-0.265	0.041	0.177	-1.134		
P(NVA-stat-VIm)	0.77	/	0.23	0.63	/	0.37	0.307	0.164	0.486	1.521	7.355	0.862	0.178	$r_{NVA/VIm} = 0.317$	
	0.72	/	0.28	0.60	/	0.40	0.284	0.165	0.541	0.984	5.243	0.817	0.153		
	0.57	/	0.43	0.47	/	0.53	0.243	0.164	0.646	-0.164	2.140	0.645	-0.049		
	0.49	/	0.51	0.42	/	0.58	0.205	0.192	0.932	-0.408	0.713	0.377	-0.215		
	0.40	/	0.60	0.38	/	0.62	0.199	0.204	1.031	-0.582	0.376	0.242	-0.374		$r_{VIm/NVA} = 0.726$
	0.28	/	0.72	0.28	/	0.72	0.225	0.172	0.741	-0.351	1.348	0.534	-0.139		
	0.25	/	0.75	0.25	/	0.75	0.2	0.199	0.990	-0.673	0.340	0.224	-0.444		
P(NMVA-stat-VIm)	0.16	/	0.84	0.15	/	0.85	0.2	0.2	0.998	-0.814	0.189	0.138	-0.596	$r_{NMVA/VIm} = 0.196$	
	/	0.86	0.14	/	0.68	0.32	0.165	0.085	0.493	-1.804	0.457	0.189	-0.748		
	/	0.72	0.28	/	0.49	0.50	0.275	0.104	0.340	-0.088	8.373	0.811	-0.009		
	/	0.60	0.40	/	0.38	0.62	0.235	0.095	0.375	-1.068	4.275	0.686	-0.171		
	/	0.44	0.56	/	0.25	0.75	0.202	0.086	0.397	-1.686	2.089	0.517	-0.417		
	/	0.41	0.59	/	0.26	0.74	0.189	0.097	0.488	-1.307	1.518	0.437	-0.376		$r_{VIm/NMVA} = 1.845$
	/	0.28	0.72	/	0.16	0.84	0.175	0.089	0.487	-1.646	0.833	0.299	-0.590		
/	0.18	0.82	/	0.68	0.32	0.275	0.104	0.340	-0.088	8.373	0.811	-0.009			

Conditions: polymerization in a MeOD/DMSO mixture (DMSO/MeOD (v/v) = 0.05), 30°C, [comonomers]₀/[V70]₀ = 50. ^a Determined by ¹H NMR of the initial feed mixture in MeOD. ^b Determined by ¹H NMR in MeOD after isolation of the copolymer. ^c Extended Kelen Tüdös (EKT) equation : $\eta = (r_1 + (r_2/\alpha)) \zeta - (r_2/\alpha)$, where $\eta = G'/(\alpha^2 + H')$; $G' = (F-1)/Z$; $H' = F/Z^2$; $Z = [\log(1-\zeta_1)]/[\log(1-\zeta_2)]$; $\zeta_1 = \zeta_2(F/f)$; $\zeta_2 = w(\mu+f)/(\mu+F)$; $\zeta = H'/(\alpha^2 + H')$; $\alpha' = (H' \max H' \min)^{1/2}$. The EKT involves parameters η and ζ , mathematical functions of the ratio of molar composition in the monomer feed ($f=f_1/f_2$) and in the copolymer ($F=F_1/F_2$). The extended method uses new parameters such as w corresponding to the percentage of weight conversion (fixed at 15%) and μ the ratio of the molecular weight of monomer 2 to monomer 1 ($\mu=M_2/M_1$). ¹ T. Kelen, F. Tüdös, B. Turcsányi and J. P. Kennedy, J. Polym. Sci. Polym. Chem. Ed., 1977, 15, 3047–3074.

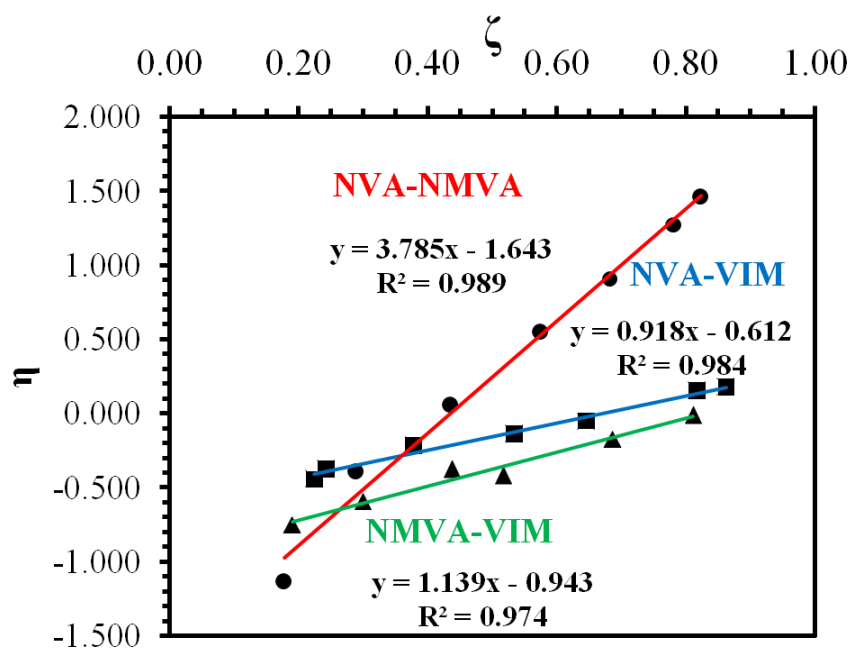


Figure S2. Extended Kelen-Tüdös plots for the copolymerization at 30 °C of N-vinylacetamide and N-methylvinylacetamide) (●), N-vinylacetamide and 1-vinylimidazole (■), N-methylvinylacetamide and 1-vinylimidazole) (▲).

Table S3. Determination of the hydrolysis level of the poly(*N*-vinylamide)-based copolymers by elementary analysis.

Entry	Molar composition of the precursor ^a			Hydrolyzed copolymer				Hydrolysis level (%)	
	F _{NVA}	F _{NMVA}	F _{VIM}	%C ^c	%N ^c	C/N _{exp} ^c	C/N _{theor.} ^{b full} hydrolysis	NVA ^d	NMVA ^e
1	1	0	0	31.115	18.810	1.814	1.716	94 ^f	/
2	0	1	0	38.945	13.410	2.904	2.574	/	81 ^g
3	0.68	0.32	0	35.260	16.645	2.118	1.990	94*	90 ^h
4	0.52	0	0.48	40.600	19.840	2.046	1.994	91 ⁱ	/
5	0	0.54	0.46	44.81	18.560	2.414	2.303	/	83 ^j
6	0.32	0.34	0.34	40.195	17.935	2.286	2.151	94*	75 ^k

Hydrolysis conditions: HCl 6N /120 °C / 64 h. ^a Determined by ¹H NMR in D₂O. ^b Determined by elementary analysis. ^c Calculated for full hydrolysis of the amides moieties. ^d NVA hydrolysis level = 100 x (1-*f*_{NVA residual}) where *f*_{NVA residual} is the molar fraction of the residual non-hydrolyzed NVA units. ^e NMVA hydrolysis level = 100 x (1-*f*_{NMVA residual}) where *f*_{NMVA residual} is the molar fraction of the residual non-hydrolyzed NMVA units. *f*_{NVA residual} and *f*_{NMVA residual} are determined based on formulas **f-k** (see below) established by taking into account the molar fraction of each comonomer in the copolymer precursor (F_{NVA}⁰, F_{NMVA}⁰ and F_{VIM}⁰) and the respective numbers of carbon and nitrogen atoms in the hydrolyzed and non-hydrolyzed monomer units. MM_C and MM_N are the molar mass of C and N, respectively. In formulas h and k, *f*_{NVA residual} is fixed at 0.06, in accordance with the hydrolysis level determined for the PNVA homopolymer, i.e. 94%.

$$f \quad f_{NVA \text{ residual}} = \frac{[MM_N \times \frac{C}{N}] - [2 \times MM_C]}{2 \times MM_C}$$

$$g \quad f_{NMVA \text{ residual}} = \frac{[MM_N \times \frac{C}{N}] - [3 \times MM_C]}{2 \times MM_C}$$

$$h \quad f_{NMVA \text{ residual}} = \frac{[MM_N \times \frac{C}{N}] - [3 \times MM_C \times F_{NMVA}^0] - [2 \times MM_C \times F_{NVA}^0 \times (f_{NVA \text{ residual}} + 1)]}{2 \times MM_C \times F_{NMVA}^0}$$

$$i \quad f_{NVA \text{ residual}} = \frac{[-MM_N \times \frac{C}{N} \times f_{NVA}^0] + [2 \times MM_N \times \frac{C}{N}] + [F_{NVA}^0 \times 3 \times MM_C] - [5 \times MM_C]}{2 \times MM_C \times F_{NVA}^0}$$

$$j \quad f_{NMVA \text{ residual}} = \frac{[2 \times MM_N \times \frac{C}{N}] - [MM_N \times \frac{C}{N}] + F_{NMVA}^0 - [5 \times MM_C] + [2 \times MM_C \times F_{NMVA}^0]}{2 \times MM_C \times F_{NMVA}^0}$$

k

$$f_{NMVA \text{ residual}} = \frac{[MM_N \times \frac{C}{N} \times (1 + F_{VIM}^0)] - [3 \times MM_C \times F_{NMVA}^0] - [2 \times MM_C \times F_{NVA}^0 \times (f_{NVA \text{ residual}} + 1)] - [5 \times MM_C \times F_{VIM}^0]}{2 \times MM_C \times F_{NMVA}^0}$$

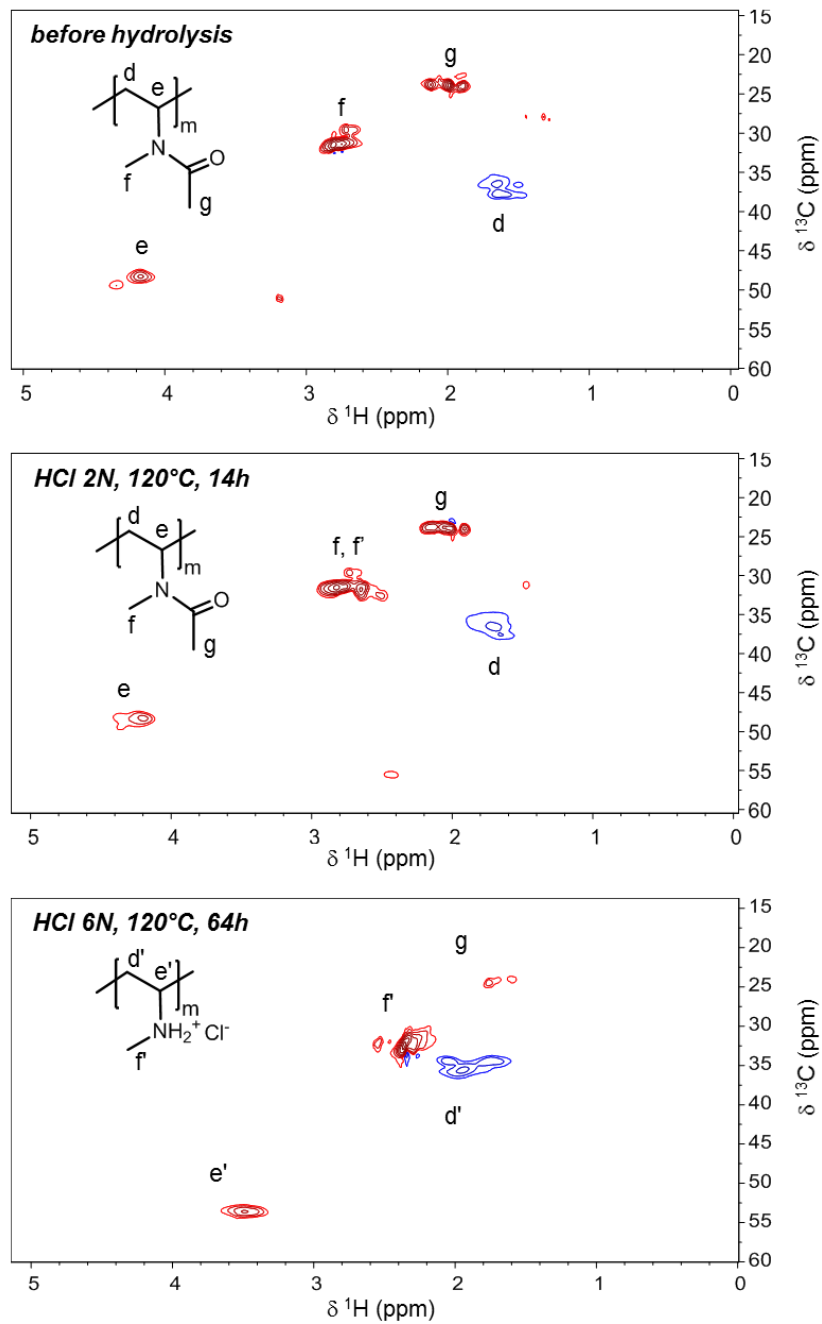


Figure S3. ^1H - ^{13}C HSQC of PNMVA before and after acidic hydrolytic treatments. Spectra were recorded at 298K in D_2O with a Bruker Avance (500 MHz) instrument.

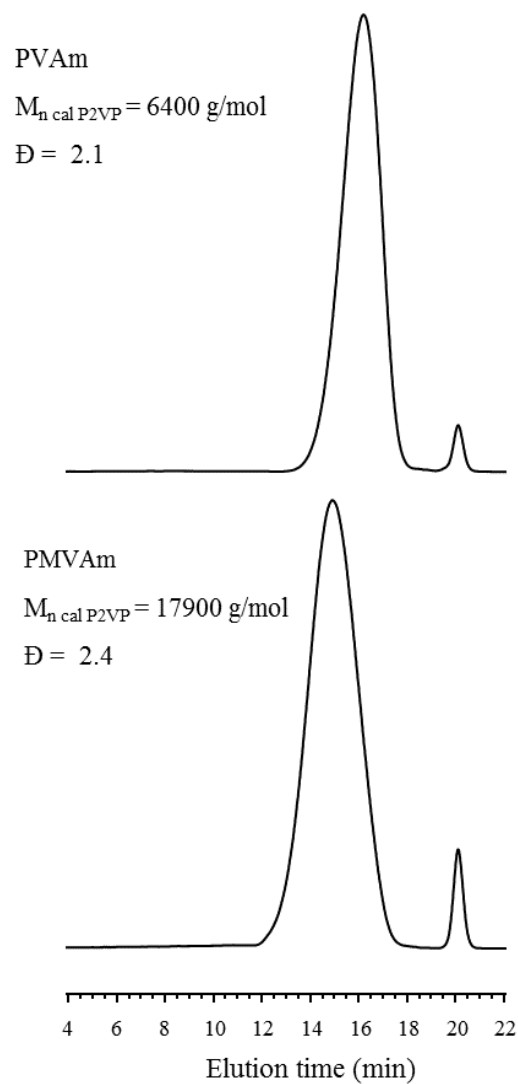


Figure S4. Aqueous size exclusion chromatograms of PVAm (upper curve) and PNMVAm (lower curve) produced by hydrolysis (HCl 6N, 120°C, 64h) of the parent PNVA and PNMVA samples, respectively. The small peak detected at higher elution time (20 minutes) corresponds to the injection peak.

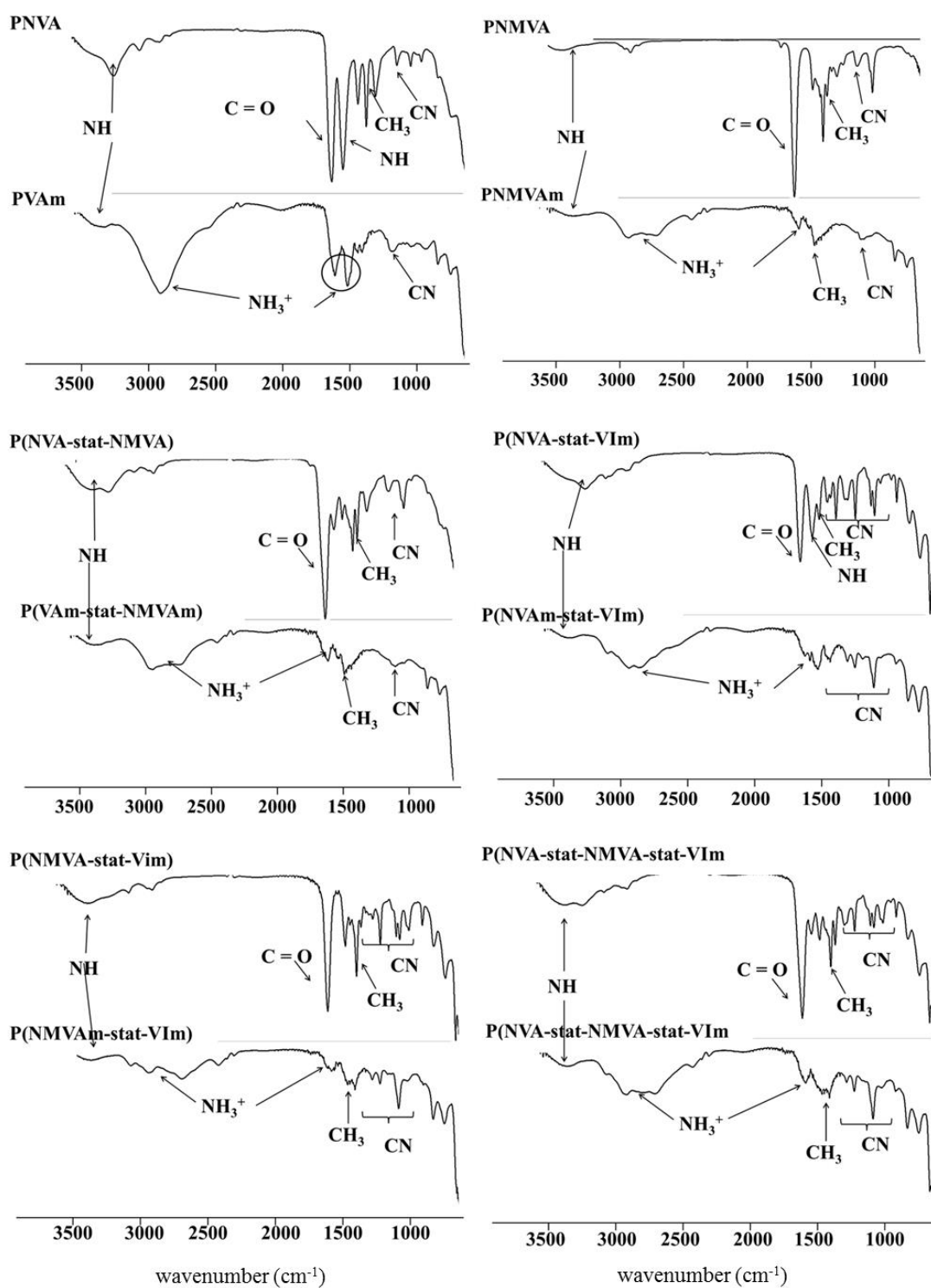


Figure S5. Overlay of the IR spectra of the copolymers before and after hydrolysis (HCl 6N, 120°C, 64h).