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Supporting information

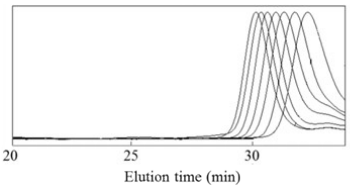
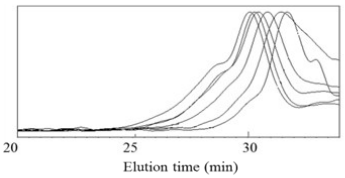
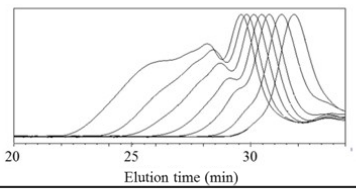
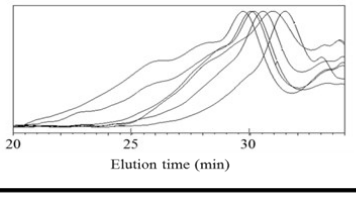
Direct One-pot Synthesis of Poly(ionic liquid) Nanogels by Cobalt-Mediated Radical Cross-linking Copolymerization in organic or aqueous media

Mathilde Weiss-Maurin,[†‡] Daniela Cordella,[†] Christine Jérôme,[†] Daniel Taton[‡]* and Christophe Detrembleur [†]*

[†]Centre of Education and Research on Macromolecules (CERM), university of Liège, Sart-Tilman B6, 4000 Liège, Belgium
[‡]Laboratoire de Chimie des Polymères Organiques (LCPO), University of Bordeaux, 16 avenue Pey Berland, 33607 Pessac Cedex, France

Supported Tables

Table S1. Kinetics data for the copolymerization of VAc with DVA bulk at 40 °C, with [VAc]/[**1**] = 60.

Entry	DVA (%mol)	Time (h)	conv (%) [a]	M_n (g/mol)[b]	M_p (g/mol) [b]	M_w/M_n [c]
1	**0**	2	12	1300	1600	1.17
		4	27	2500	2700	1.08
		5	29	3100	3300	1.07
		7	34	4100	4500	1.07
2	**2**	2	16	1700	2100	1.28
		4	23	2500	3200	1.59
		5	20	4400	4000	1.38
		7	29	5700	4700	1.50
3	**4**	2	10	1500	2000	1.31
		4	22	2300	3400	1.66
		5	26	2900	3900	1.88
		7	37	4500	5400	2.94
4	**6**	2	6	2000	2400	1.53
		4	19	3200	3900	1.69
		5	22	4500	4600	2.05
		7	26	11100	5800	3.35

[a] Determined by ^{1}H NMR in $CDCl_3$.[b] Determined by SEC in THF using PS calibration.

Table S2. Kinetics of the polymerization of vinyl acetate and its copolymerizations with divinyl adipate in ethyl acetate at 40 °C.

Entry	DVA (mol%)	time (h)	conv (%)[a]	$M_{n,}$[b] (g/mol)	M_P[b] (g/mol)	M_w/M_n[b]
1	2	8	21	-[c]	-[c]	-[c]
		24	40	2200	3400	1.4
		48	60	-[c]	-[c]	-[c]
		120	100	5500	10700	2.4
2	4	8	24	1300	1600	1.17
		24	43	2100	2600	1.4
		48	58	3800	5400	1.9
		120	100	4300	11900	2.6
3	6	8	18	-[c]	-[c]	-[c]
		24	38	2200	2900	1.5
		48	59	4700	6100	2.3
		120	100	16600	39400	2.8

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC in THF using PS calibration. [c] Not determined. Conditions: [VAc]/[**1**] = 60, [VAc] = 0.493M, x mol% DVA, 40 °C, ethyl acetate.

Table S3. Complete follow-up on kinetics data of the poly(VEtImBr-DVI) nanogels, via ^{1}H NMR and SEC in THF.

Entry	**Solvent**	%mol DVI	Time (h)	Global conv (%) [a]	$\mathbf{M_{n,}}^{b}$ **(g/mol)**	$\mathbf{M_P}^{b}$ **(g/mol)**	M_w/M_n
1	DMF	0	0.25	70	11800	16000	1.26
			1	85	13600	18100	1.24
			4	98	14800	20000	1.25
2[b]	DMF	2.9	0.25	50	- [c]	- [c]	- [c]
			1	83	- [c]	- [c]	- [c]
			4	96	- [c]	- [c]	- [c]
			8	98	- [c]	- [c]	- [c]
3[b]	DMF	4.8	0.25	42	11700	14600	1.23
			1	59	13000	14400	1.23
			4	77	12000	15200	1.24
			30	95	13500	19900	1.32
4	DMF/MeOH	0	1	33	8400	9000	1.15
			2	53	9800	13000	1.22
			4	64	12100	16500	1.22
			8	75	11900	17800	1.27
5	DMF/MeOH	2.9	0.25	14	5500	6100	1.15
			1	33	7900	8600	1.21
			4	63	11900	14300	1.29
			8	75	14600	18300	1.33
			24	85	15300	20900	1.38
6	DMF/MeOH	4.8	0.25	17	9000	9600	1.17
			1	37	13700	13800	1.24
			4	56	21400	21800	1.45
			24	81	24900	37100	1.63
7	H_2O	0	0.25	25	10100	12600	1.28
			1	40	13600	17300	1.22
			4	68	18700	25000	1.23
			8	73	20400	29700	1.30
			24	87	21300	34800	1.36
			30	87	21200	35600	1.36
8	H_2O	2.9	0.25	19	12100	14700	1.27
			1	40	12900	16300	1.26
			4	61	14900	19000	1.29
			8	72	22500	32900	1.41
			24	80	23700	39700	1.48
			30	82	28800	78300	1.59
9	H_2O	4.8	0.25	21	12500	15300	1.28
			1	36	14200	15600	1.27
			4	64	22300	28900	1.30
			8	78	26600	70700	1.42
			24	gel			

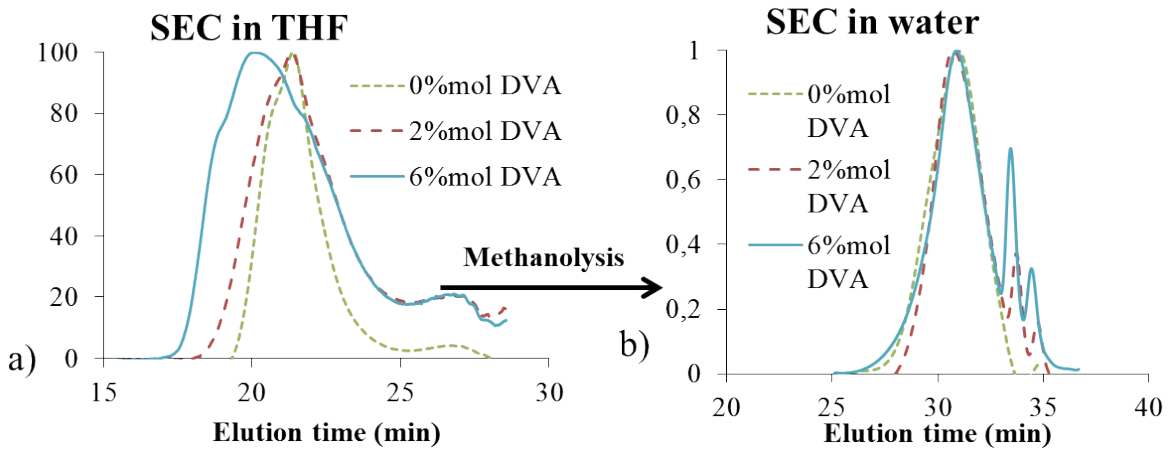
[a] Determined by ^{1}H NMR in DMSO-d6. [b] Determined by SEC in THF with $LiTf_2N$. [c] Not determined. Conditions: [VEtImBr]/[**1**] = 60, [VEtImBr] = 0.493M, xmol% DVI, 30 °C.

Table S4. Complete follow-up on kinetics data of the poly(VEtImBr-DVI) nanogels, via ^{1}H NMR and aqueous SEC.

Entry	%mol DVI	Polymerization solvent	Polymerization time (h)	Global conversion(%)[a]	M_n, aq (g/mol)[b]	M_p, aq (g/mol) [b]	M_w/M_n, aq
1	0	DMF	0.25	47	4200	5000	1.28
			1	66	6800	7700	1.37
			4	87	9000	10600	1.43
2	2.9	DMF	0.25	44	5100	4900	2.11
			1	71	6800	5900	2.18
			4	87	9600	9500	2.16
			6	90	9800	10200	2.18
3	4.8	DMF	0.25	42	- [c]	- [c]	- [c]
			1	59	- [c]	- [c]	- [c]
			4	77	- [c]	- [c]	- [c]
			30	95	- [c]	- [c]	- [c]
6	4.8	DMF/MEOH	0.25	17	2800	3700	1.74
			1	37	5800	7000	1.69
			4	56	11200	13700	2.45
			24	81	19200	26900	4.10
7	0	H_2O	0.25	25	4300	6100	2.10
			1	40	6800	9600	1.64
			4	68	10700	16500	1.64
			24	87	14800	28600	1.91
8	2.9	H_2O	0.25	19	5000	7200	2.08
			1	40	8700	11400	2.00
			4	61	15100	20800	2.42
			24	80	21600	41200	2.7
9	4.8	H_2O	0.25	21	5100	7400	2.14
			1	36	8700	10200	2.55
			4	64	17800	18500	3.45
			8	78	- [c]	- [c]	- [c]
			24	gel	- [c]	- [c]	- [c]

[a] Determined by ^{1}H NMR in DMSO-d6. [b] Determined by SEC in water (containing 0.1M NaCl and 0.1vol%TFA) [c] not determined. Conditions: [VEtImBr]/[**1**] = 60, [VEtImBr] = 0.493M, x mol% DVI, 30 °C.

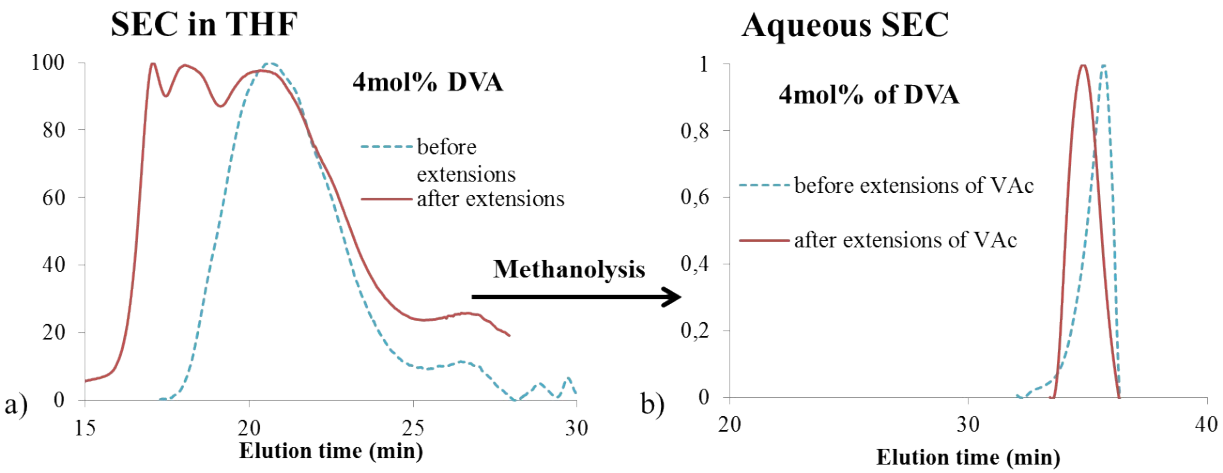
Supported Figures



c)

	Before methanolysis			After methanolysis		
mol. % DVA	$M_{n,\,SEC}$ (g/mol.)	$M_{p,\,SEC}$ (g/mol.)	M_w/M_n	$M_{n,\,SEC}$ (g/mol.)	$M_{p,\,SEC}$ (g/mol.)	M_w/M_n
0	5500	10700	2.4	8300	7400	1.2
2	4300	11900	2.6	6900	5600	1.1
6	16600	39400	2.8	6500	5100	1.6

Figure S1. a) SEC traces (in THF) of PVAc and poly(VAc-DVA) nanogels prepared with different contents of DVA before methanolysis (entries 1,2 and 4, Table 1); b) SEC traces (in water) for PVA after methanolysis of the parent PVAc and poly(VAc-DVA) nanogels; c) corresponding molecular characteristics of the different copolymer samples.

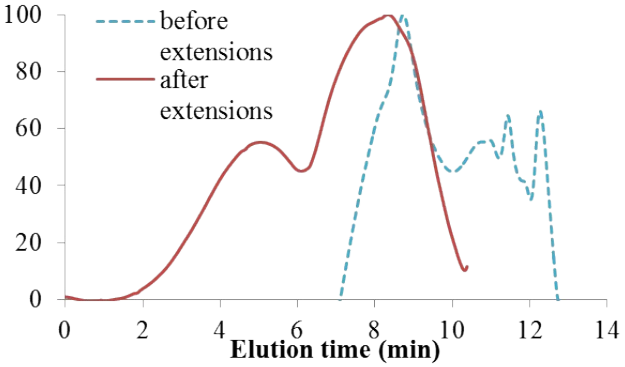


c)

	Conv. (%)	M_n (g/mol)	M_p (g/mol)	M_w/M_n
1st generation	70	10000	16000	2.1
2nd generation	30	19100	545900	8.6

Figure S2. a) SEC traces (in THF) of a chain extension polymerization on a poly(VAc-4mol% DVA) nanogel before methanolysis; b) SEC traces (in water) of primary chains of linear PVA (of the 1st and 2nd generation nanogels) after methanolysis in water; c) molecular characteristics for the 1st and 2nd generation of nanogels. Conditions: [VAc]/[**1**] = 60, [VAc] = 0.493M, 40 °C, [VAc]/[DVA] = 4, in ethyl acetate.

a)



b)

	Conv (%)[a]	$M_{n,SEC}$ (g/mol)[b]	$M_{p,SEC}$ (g/mol)[b]	M_w/M_n[b]
Before extensions	100	6100	3100	2.0
After extensions	13	39600	29900	2.6

Figure S3. a) SEC traces (in THF containing 10 mM $LiTf_2N$) of the 1st-generation poly(VAc-DVA) nanogel corresponding to Table 1, entry 3 (blue, dotted line) and the same nanogel after chain extensions with *N*-vinyl-3-ethyl imidazolium NTf_2 (red, plain line); b) macromolecular characteristics of the nanogel before and after chain extension.

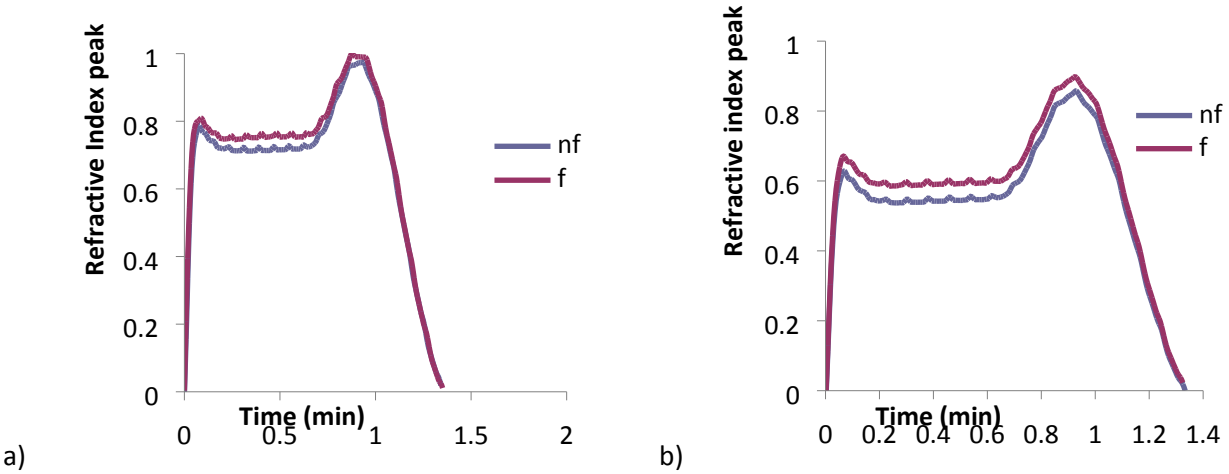


Figure S4. Intensity signal of the refractive index detector for: a) the nanogel synthesized in DMF/MeOH mixture (Table 2, entry 6) or b) the nanogel synthesized in water (Table 2, entry 9), before (nf) and after (f) filtration of the sample on a 0.2µm filter. Prior to analysis, the nanogels are solubilized in THF containing 10 mM LiTFSI at a concentration of 1 mg/mL. The very slight difference in peak area can be ascribed to the shearing of the solvent during filtration.

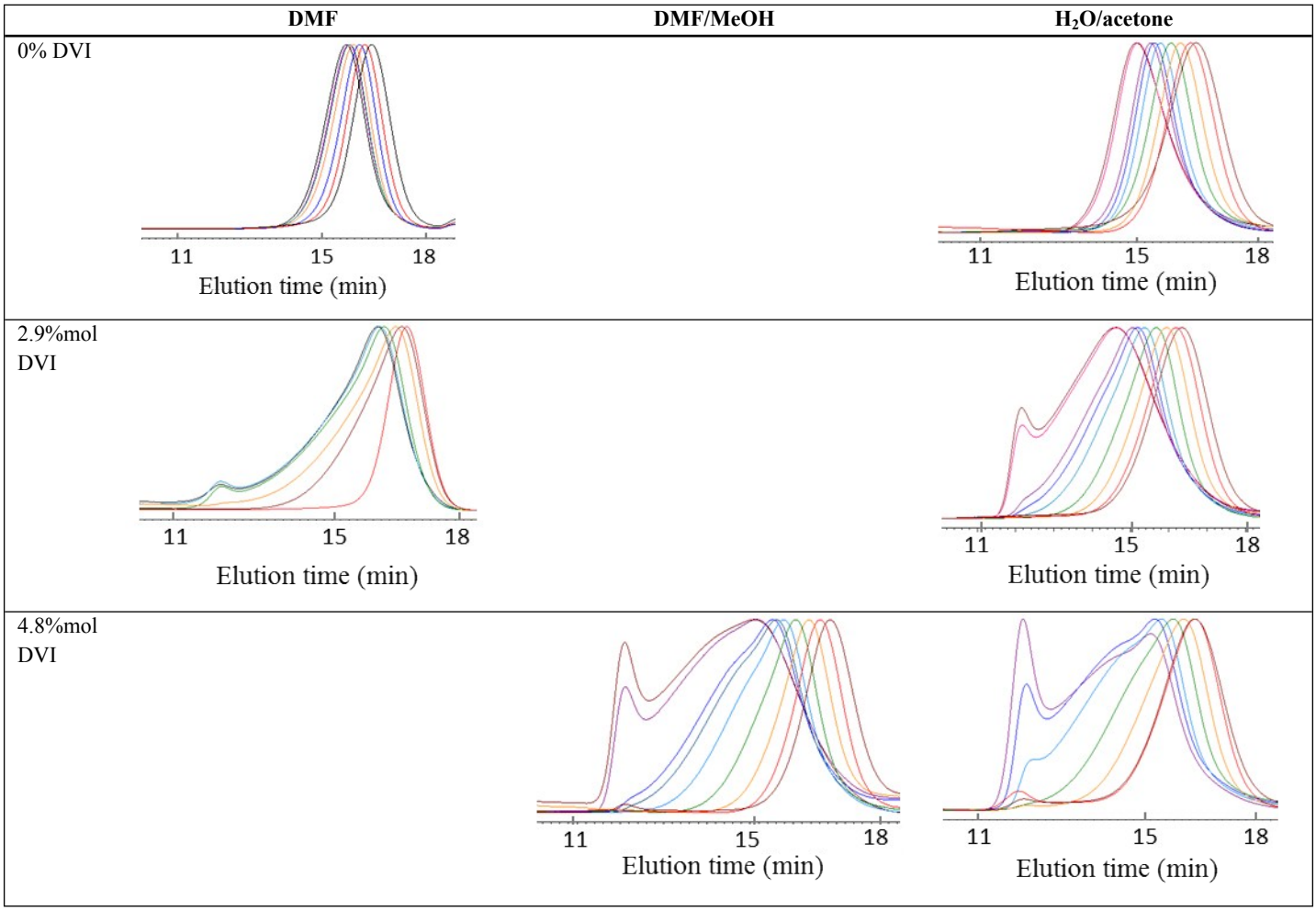


Figure S5. Aqueous SEC chromatograms for the kinetics of copolymerization of VEtImBr with DVI.