Supporting information for

EFFECT OF COPOLYMER COMPOSITION OF RAFT / MADIX-DERIVED *N*-VINYLCAPROLACTAM / *N*-VINYLPYRROLIDONE STATISTICAL COPOLYMERS ON THEIR THERMORESPONSIVE BEHAVIOR AND HYDROGEL PROPERTIES

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CONTENT

A. DETAILED PROCEDURE FOR THE SYNTHESIS OF VP/VCL STATISTICAL COPOLYMERS BY RAFT/MADIX COPOLYMERIZATION

Synthesis of P(VP/VCL)$_{10k}$. In a Schlenk tube are added VCL, VP, and a dioxane solution containing both X1 and AIBN (detailed quantities are reported in the table below). The reaction mixture is then degassed by four freeze-pump-thaw cycles, put under argon and heated at 65°C for 20h in an oil bath. The reaction mixture is then cooled down with liquid nitrogen to stop the polymerization. A sample is withdrawn and analyzed by ^{1}H NMR to access conversion of both VCL and VP, while the remaining solution is precipitated in diethyl ether. The precipitated polymer is filtered off, dried under vacuum and analyzed by SEC-RI-MALS in THF to determine $M_{n\ MALS}$ and dispersity.

Mn targeted (g/mol)	Composition		VCL		VP		Xanthate X1 and AIBN solution in dioxane
	VCL (wt%)	VP (wt%)	m (g)	n (mol)	m (g)	n (mol)	[34mg of AIBN +231,5mg of xanthate X1 in 20,6g of dioxane]
10000 g/mol	100	0	2,062	0,01481428	0	0	4,183
	90	10	1,854	0,01331992	0,208	0,00187151	4,182
	75	25	1,549	0,01112867	0,516	0,00464279	4,179

Synthesis of P(VP/VCL)$_{20k}$. In a Schlenk tube are added VCL, VP, X1 and a dioxane solution containing AIBN (detailed quantities are reported in the table below). The reaction mixture is then degassed by four freeze-pump-thaw cycles, put under argon and heated at 65°C for 20h in an oil bath. The reaction mixture is then cooled down with liquid nitrogen to stop the polymerization. A sample is withdrawn and analyzed by ^{1}H NMR to access conversion of both VCL and VP, while the remaining solution is precipitated in diethyl ether. The precipitated polymer is filtered off, dried under vacuum and analyzed by SEC-RI-MALS in THF and DMF-LiBr to determine $M_{n\ MALS}$ and dispersity.

Mn targeted (g/mol)	Composition		VCL		VP		Xanthate X1		AIBN solution in dioxane (g)
	VCL (wt%)	VP (wt%)	m (g)	n (mol)	m (g)	n (mol)	m (g)	n (mol)	[34mg of AIBN in 20,6g of dioxane]
20000	100	0	2,085	0,0150	0	0,0000	2,18E-02	1,05E-04	4,121
	90	10	1,853	0,0133	0,214	0,0019	2,36E-02	1,13E-04	4,133
	75	25	1,535	0,0110	0,521	0,0047	2,36E-02	1,13E-04	4,124
	60	40	1,240	0,0089	0,832	0,0075	2,28E-02	1,09E-04	4,133
	25	75	0,519	0,0037	1,549	0,0139	2,37E-02	1,14E-04	4,134
	10	90	0,212	0,0015	1,854	0,0167	2,36E-02	1,13E-04	4,120

Synthesis of P(VP/VCL)$_{60k}$. In a Schlenk tube are added VCL, VP, and a dioxane solution containing both X1 and AIBN (detailed quantities are reported in the table below). The reaction mixture is then degassed by four freeze-pump-thaw cycles, put under argon and heated at 65°C for 20h in an oil bath. The reaction mixture is then cooled down with liquid nitrogen to stop the polymerization. A sample is withdrawn and analyzed by ^{1}H NMR to access conversion of both VCL and VP, while the remaining solution is precipitated in diethyl ether. The precipitated polymer is filtered off, dried under vacuum and analyzed by SEC-RI-MALS in THF and DMF-LiBr to determine $M_{n\ MALS}$ and dispersity.

Mn targeted (g/mol)	Composition		VCL		VP		AIBN+xanthate X1 solution in dioxane
	VCL (wt%)	VP (wt%)	m (g)	n (mol)	m (g)	n (mol)	[34mg of AIBN + 36,1mg of xanthate X1 in 20,6g of dioxane]
60000	100	0	2,065	0,0148		0	4,300
	90	10	1,854	0,0133	0,21	0,00189	4,133
	75	25	1,553	0,0112	0,524	0,00471	4,132
	50	50	1,031	0,0074	1,037	0,00933	4,151
	25	75	0,524	0,0038	1,549	0,01394	4,149
	10	90	0,206	0,0015	1,855	0,01669	4,374

B. CHARACTERIZATION OF POLYMERS

B.1. Determination of the VP and VCL conversion and of the polymer composition

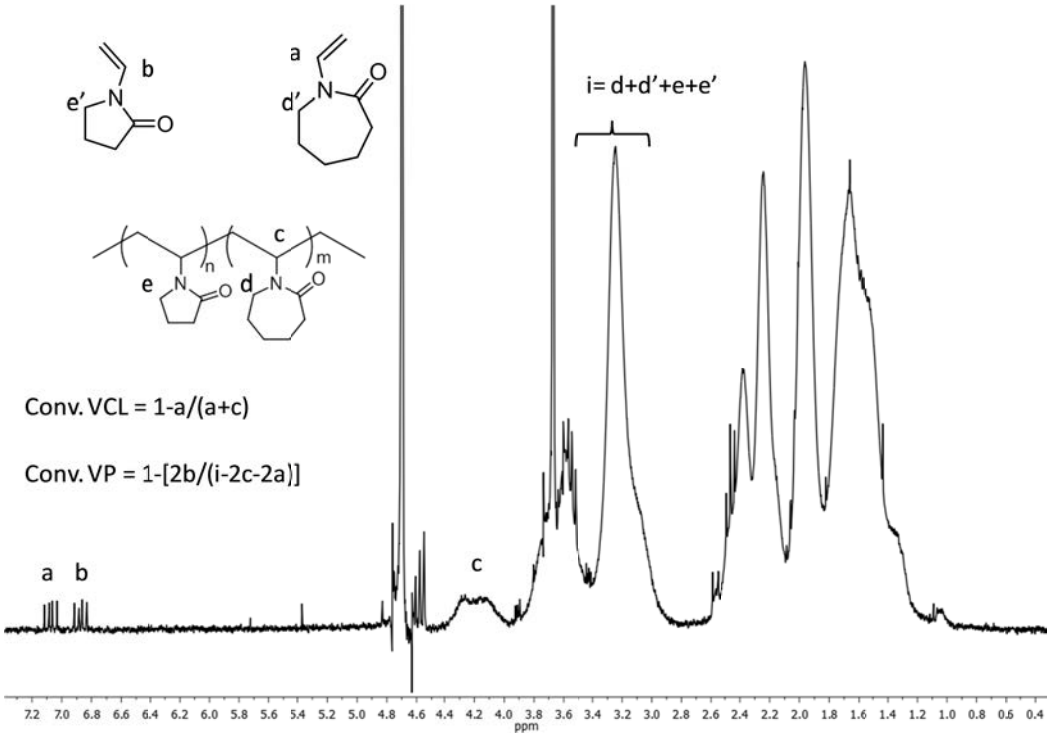


Figure SI1. Determination of the VP and VCL conversion by ^{1}H NMR from the crude polymerization.

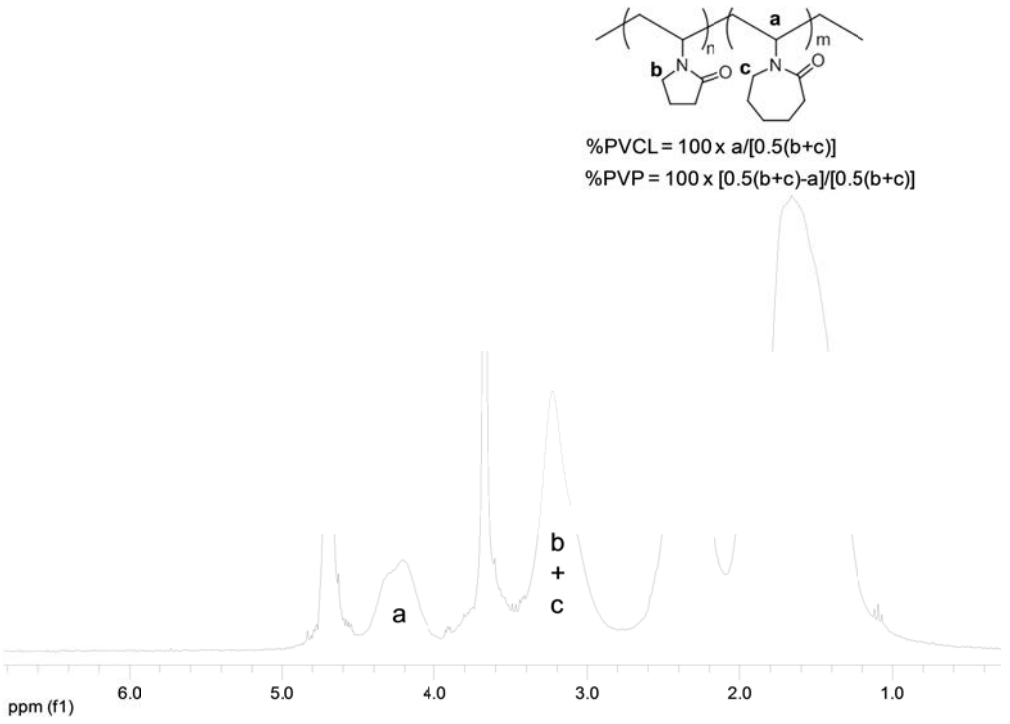


Figure SI2. Determination of the composition in V**P** and VCL on a precipitated P(VCL/VP) copolymer from^{1}H NMR.

B.2. Comparison between experimental and calculated cumulated copolymer composition.

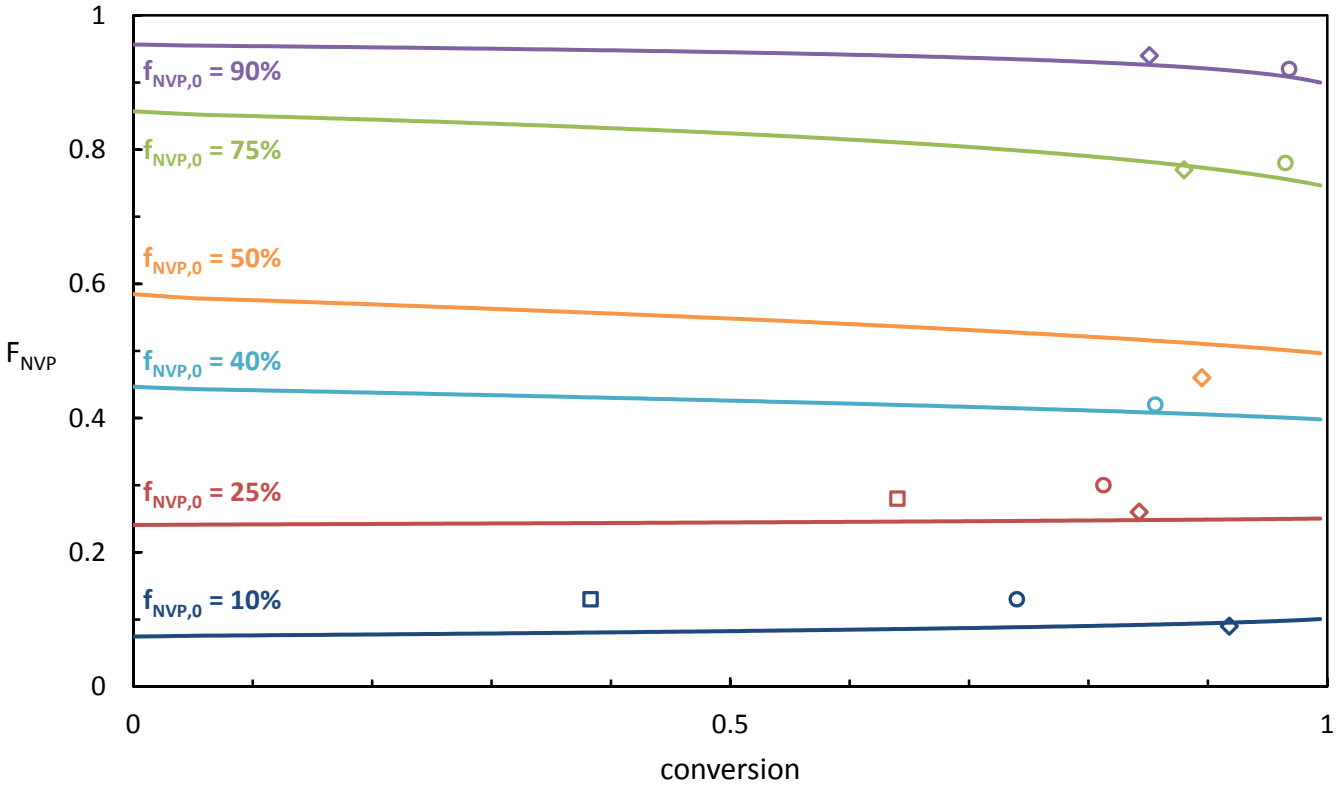


Figure SI3. Comparison of measured NVP content (F_{NVP}) with calculated NVP content (lines) for initial NVP compositions ($f_{NVP,0}$) of 10 to 90%. Squares: targeted M_n of 10,000 g/mol; circles: targeted M_n of 20,000 g/mol; diamonds: targeted M_n of 60,000 g/mol. Expected NVP content was calculated using the Skeist equation [Meyer, V. E. and Lowry, G. G. Integral and differential binary copolymerization equations. *J. Polym. Sci. A Gen. Pap.***1965**, *3*, 2843–2851] with reactivity ratios for NVP and VCL of 2.8 and 1.7, respectively.

B.3. Size exclusion chromatography

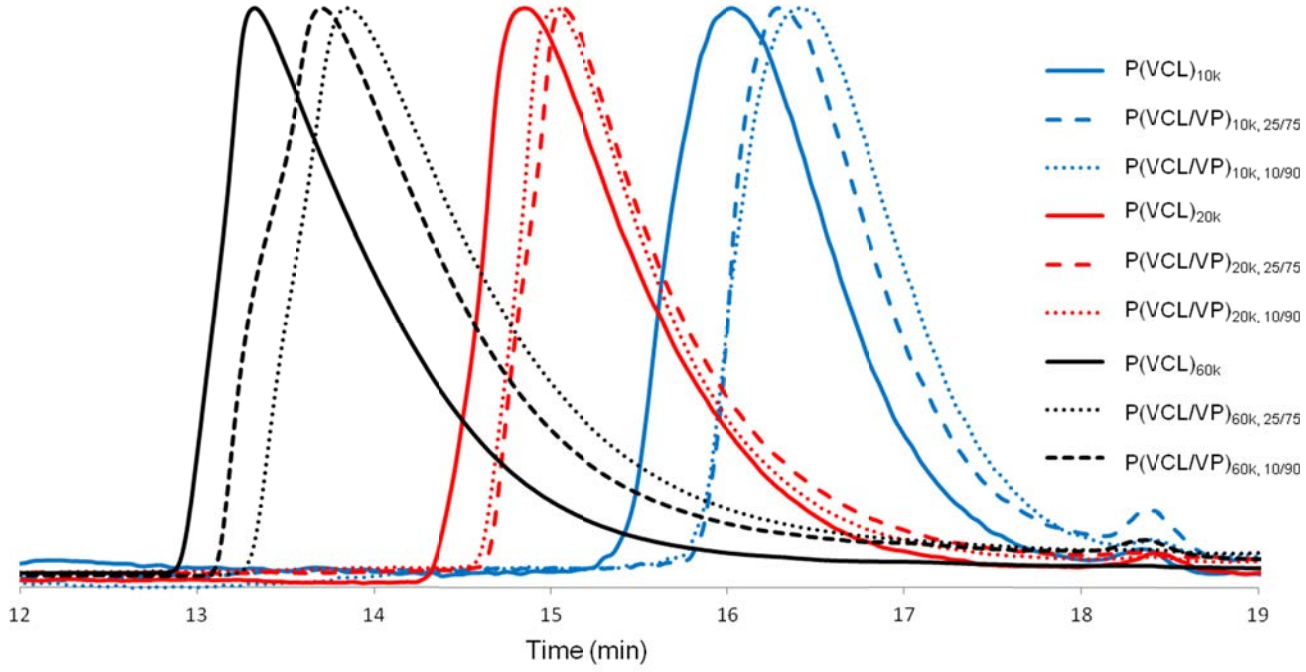


Figure SI4. Superposition of SEC-MALS traces for P(VCL/VP) of different molar masses and compositions in THF (1mL/min).

C. CHARACTERIZATION OF POLYMER PROPERTIES IN SOLUTION

C.1. Determination of cloud point temperature.

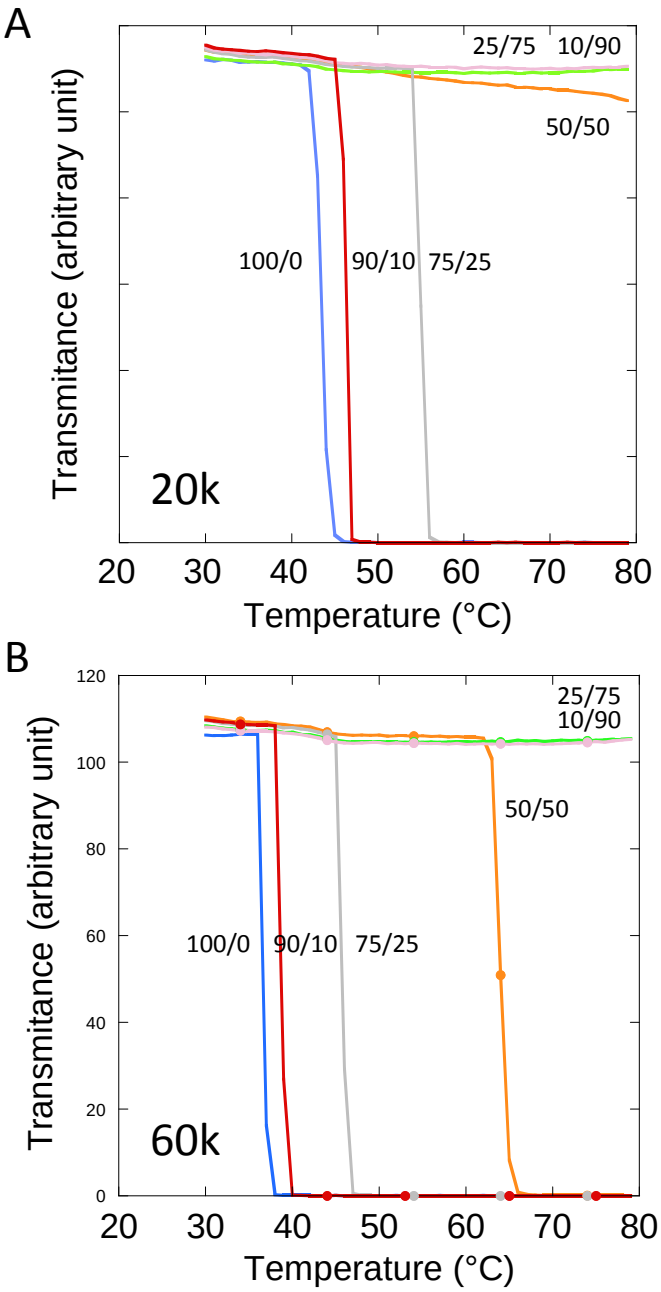


Figure SI5. Transmittance monitored at 500 nm as a function of temperature for $P(VCL/VP)_{20k \text{ and } 60k}$ statistical copolymers in 0.5 wt % aqueous solution with different molar fractions of VP. Cloud points were obtained from the inflection points of these curves.

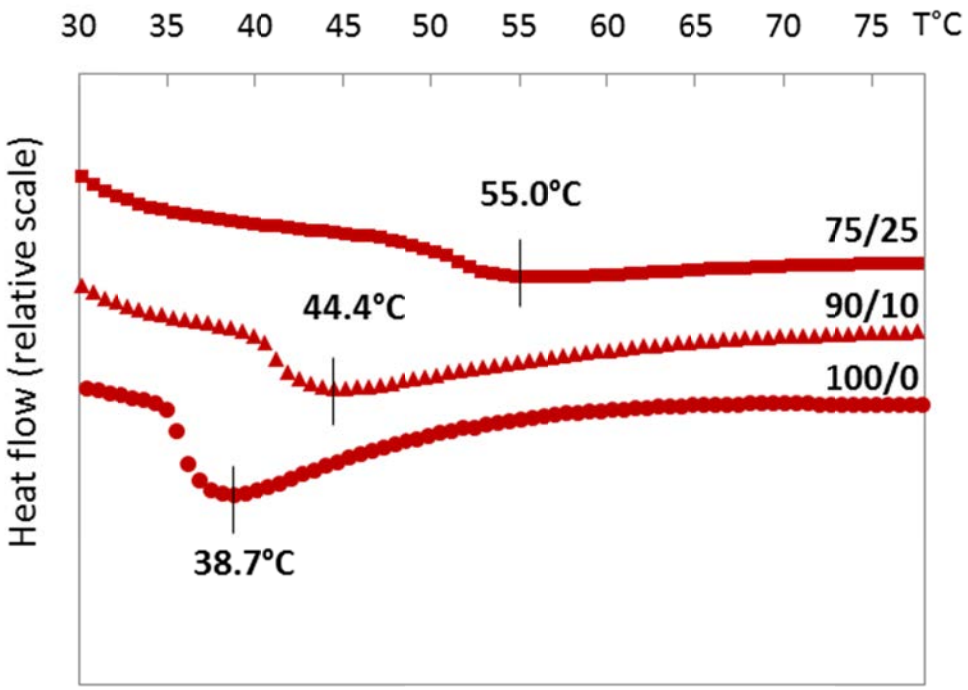


Figure SI6. Thermograms for 20 wt % aqueous solution with heating rate at 3°C / min for 100 / 0, 90 / 10, and 75 / 25 copolymers.

C.2. Correlation between polymer composition and the variation of enthalpy measured during transition phenomenon.

Table S1. Theoretical number fraction of dimer, trimer, tetramer… for a given composition of VCL/VP statistical copolymers (a stated for VCL monomer units and b for VP monomer units).

THEORETICAL VALUES		**VP content (molar ratio)**						
		0	**10**	**25**	**40**	**50**	**75**	**90**
dimer	**aa**	1	0.81	0.5625	0.36	0.25	0.0625	0.01
	ab ou ba	0	0.18	0.375	0.48	0.5	0.375	0.18
	bb	0	0.01	0.0625	0.16	0.25	0.5625	0.81
trimer	**aaa**	1	0.729	0.421875	0.216	0. 125	0.015625	0.001
	aab ou baa	0	0.162	0.28125	0.288	0.25	0.09375	0.018
	bab	0	0.009	0.046875	0.096	0.125	0.140625	0.081
	aba	0	0.081	0.140625	0.144	0.125	0.046875	0.009
	abb ou bba	0	0.018	0.09375	0.192	0.25	0.28125	0.162
	bbb	0	0.001	0.015625	0.064	0.125	0.421875	0.729
tetramer	**aaaa**	1	0.6561	0.31640625	0.1296	0.0625	0.00390625	0.0001
pentamer	**aaaaa**	1	0.59049	0.23730469	0.07776	0.03125	0.00097656	0.00001
hexamer	**aaaaaa**	1	0.531441	0.17797852	0.046656	0.015625	0.00024414	0.000001
EXPERIMENTAL VALUES	**ΔH** (at a given VP content) **/ ΔH** (measured for VP content =0% i.e for PVCL homopolymer)							
10k		1	0.57	0.29	0	0	0	0
20k		1	0.53	0.26	0.10	0	0	0
60k		1	0.66	0.40	/	0.07	0	0

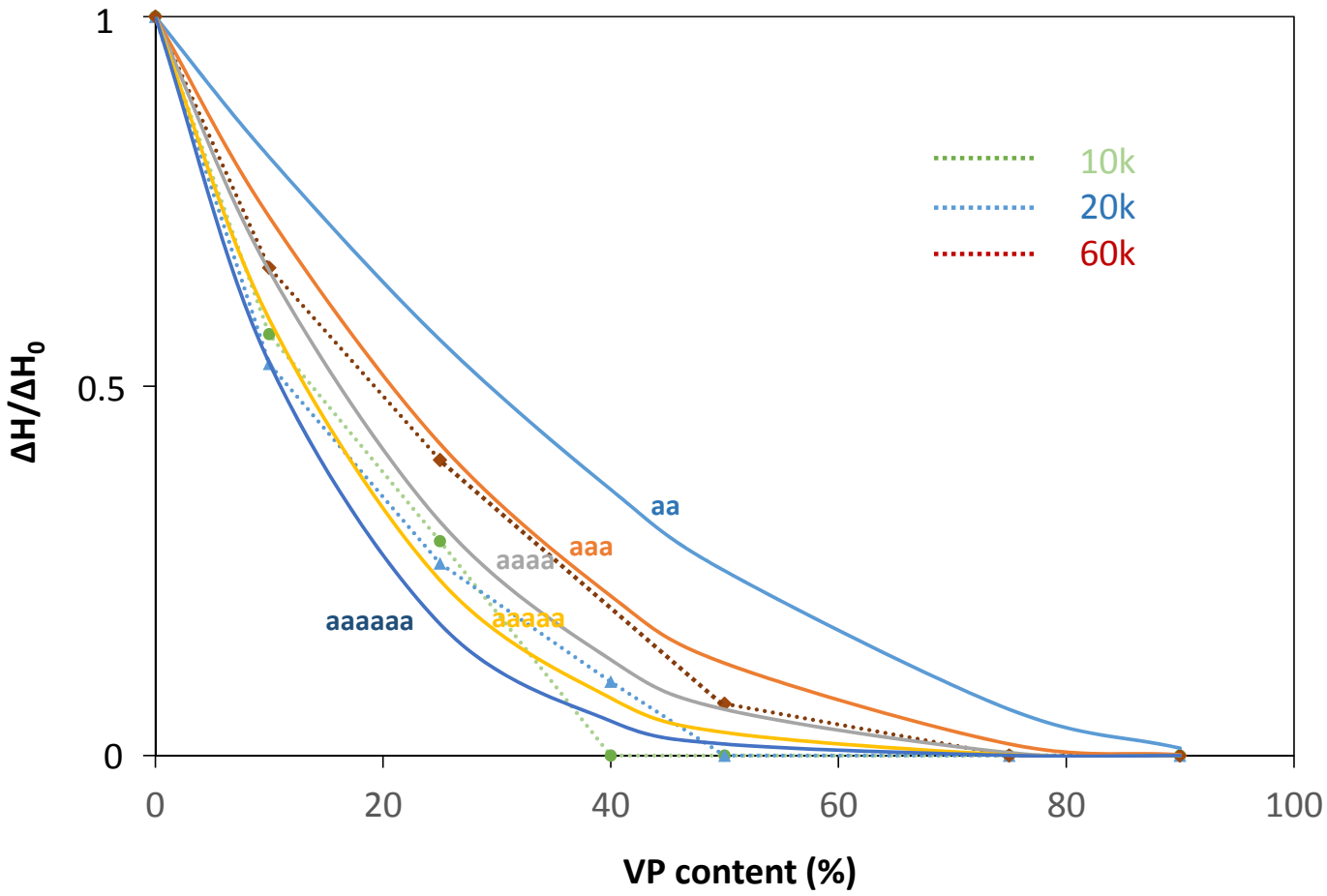


Figure SI7. Evolution of $\Delta H/\Delta H_0$ as a function of PVP content for P(VCL-*stat*-VP)$_{60k}$ copolymer in 2 wt % aqueous solution as a function of VP molar fraction and comparison with the calculated variation assuming that specific sequences were involved in the dehydration process. ΔH_0 is the ΔH value measured for VP content =0% i.e: VCL homopolymer.

As can be seen in Figure SI5 and Table SI1:

- Whereas the experimental evolution of $\Delta H/\Delta H_0$ as a function of VP content is found almost similar for statistical polymer of average molecular weight of 10000 and 20000 g/mol, the one observed for statistical polymer of average molecular weight of 60000 g/mol differs significantly.
- The filled line represents the expected evolution of $\Delta H/\Delta H_0$ considering that the main responsible factor governing its evolution is the interactions of water molecules with part of the molecules (by neglecting the effect of interactions between different polymers as well as entropic factors. Clearly the experimental points cannot be fitted by considering the involvement of short specific sequences (unimer, diad, triad… of VCL units or mix of VCL and VP units). Moreover no clear and common correlation was evidenced for the three different masses between the observed decrease of $\Delta H/\Delta H_0$ and the evolution calculated from the involvement of longer sequences (or combination of them).

This suggests in addition to results presented in Figure SI6 and the ones reported in literature for PVCL (main text) that the whole macromolecule is involved in the hydration/dehydration phenomenon in addition to the entropic contribution.

C.3. Evolution of ΔH as a function of polymer concentration.

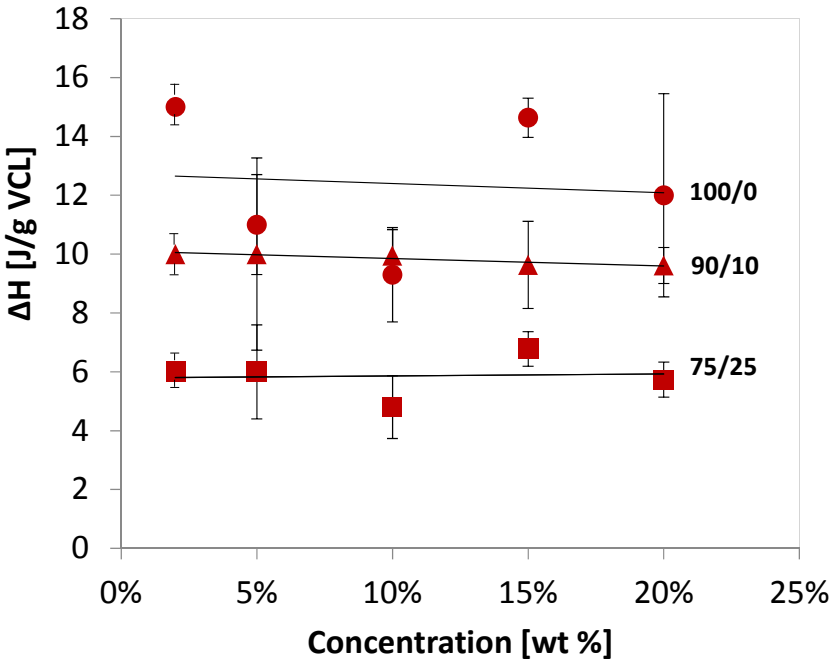


Figure SI8. Evolution of ΔH per gram of VCL as a function of polymer concentration for P(VCL-stat-VP)$_{60k}$ copolymers (100/0, 90/10 and 75/25). Each point is an average of 4 values obtained on heating at 5, 4, 3, 2 °C / min.of cloud point temperature. For 90/10 and 75/25 statistical copolymers, no significant variation of ΔH values was found in the range of concentration studied (Student test, $p<0.05$). For 100/0 PVCL homopolymer, a more pronounced variation around the average value is observed but no clear tendency is observed.

C.4. Effect of ionic strength on cloud point temperature.

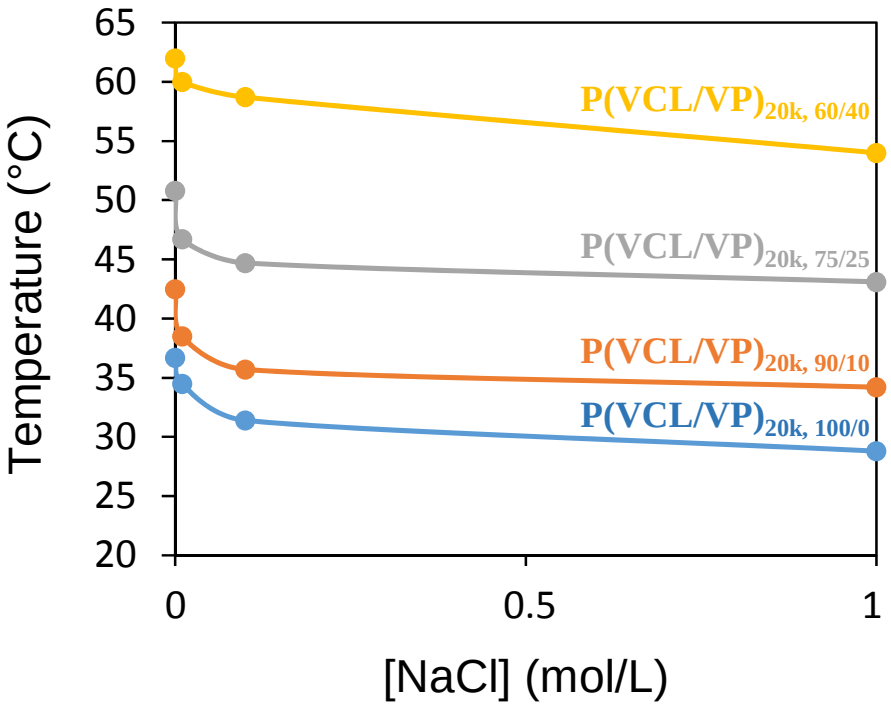


Figure SI9. Evolution of cloud point temperature for 2.5 wt % aqueous solutions as a function of NaCl concentration for statistical $P(VCL/VP)_{20k}$ copolymers, VCL/VP content: 100/0, 90/10, 75/25 and 60/40.

D. CHARACTERIZATION OF HYDROGELS

D.1. Sol-gel transition.

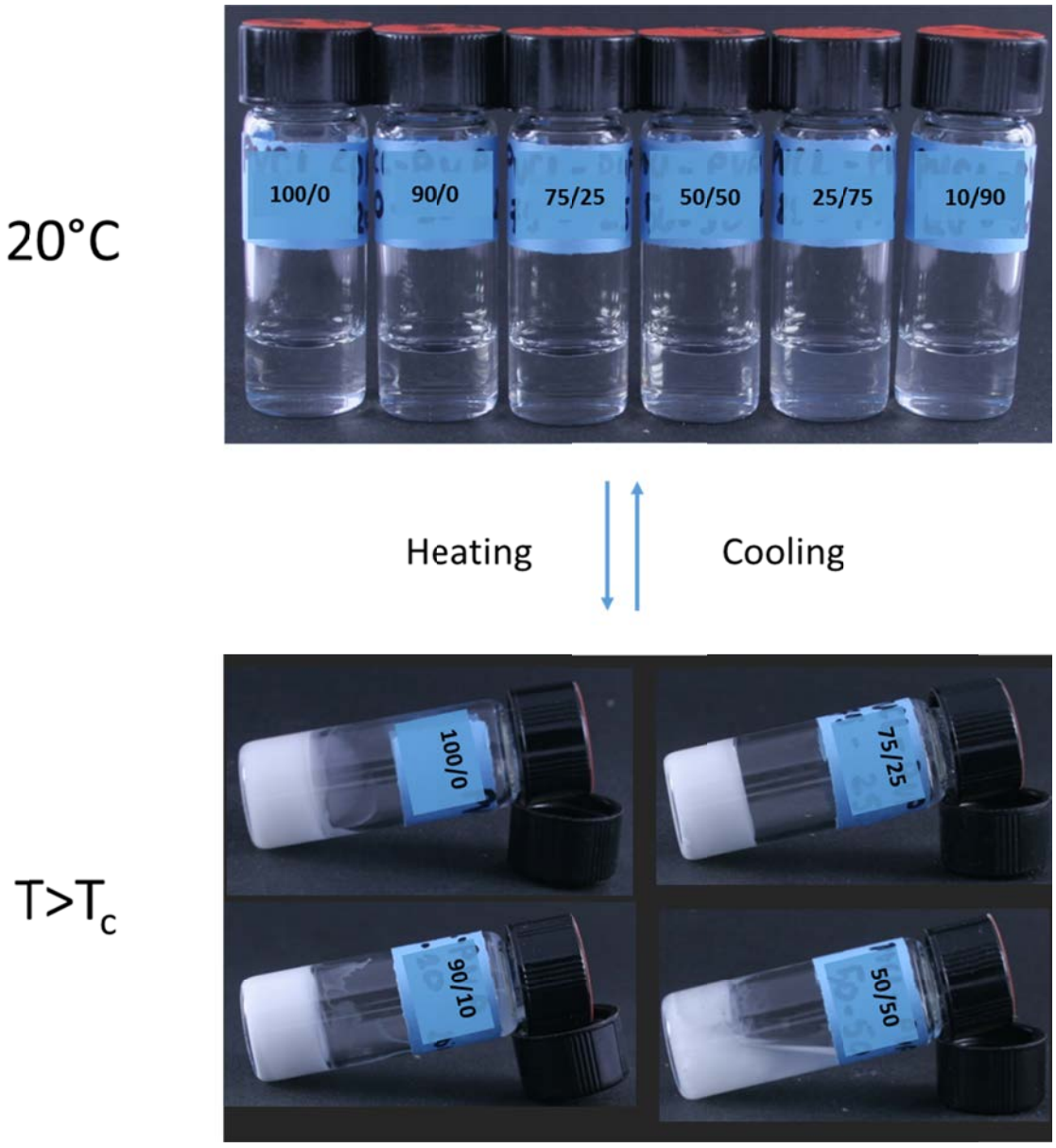


Figure SI10. Gelation properties of 20 wt % solutions of l P(VCL-*stat*-VP) with different compositions (i.e. 100/0, 90/10, 75/25, 50/50, 25/75 and 10/90) with an average M_n of 60000 g·mol^{-1}. For the two compositions 25/75 and 10/90, no transition occured when heating.

D.2. Rheological behavior.

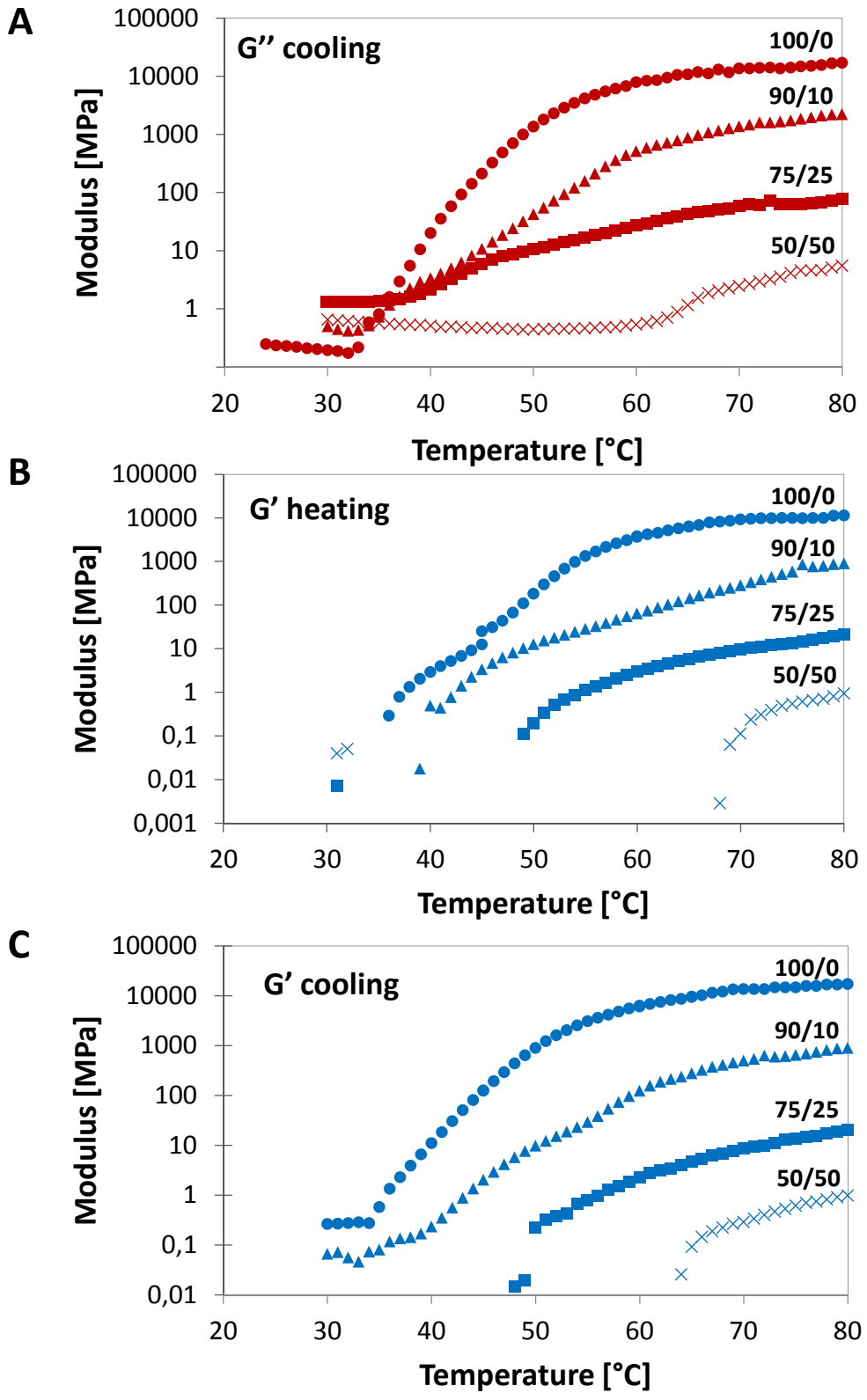


Figure SI11. Temperature – dependent elastic G' and viscous G'' moduli for 20 wt % aqueous solution with heating or cooling rate at 1°C / min for 100 / 0, 90 / 10, 75 / 25 and 50 / 50 copolymers: A) G'' on cooling B) G' on heating C) G' on cooling.

D.3. Cryo-SEM

Samples for Cryo SEM were prepared as follows: one drop of the sample was preheated to undergo gel transition just before being frozen in nitrogen slush at -220°C. The frozen sample was transferred under vacuum in the cryo-fracture apparatus chamber where it was fractured at -145°C.

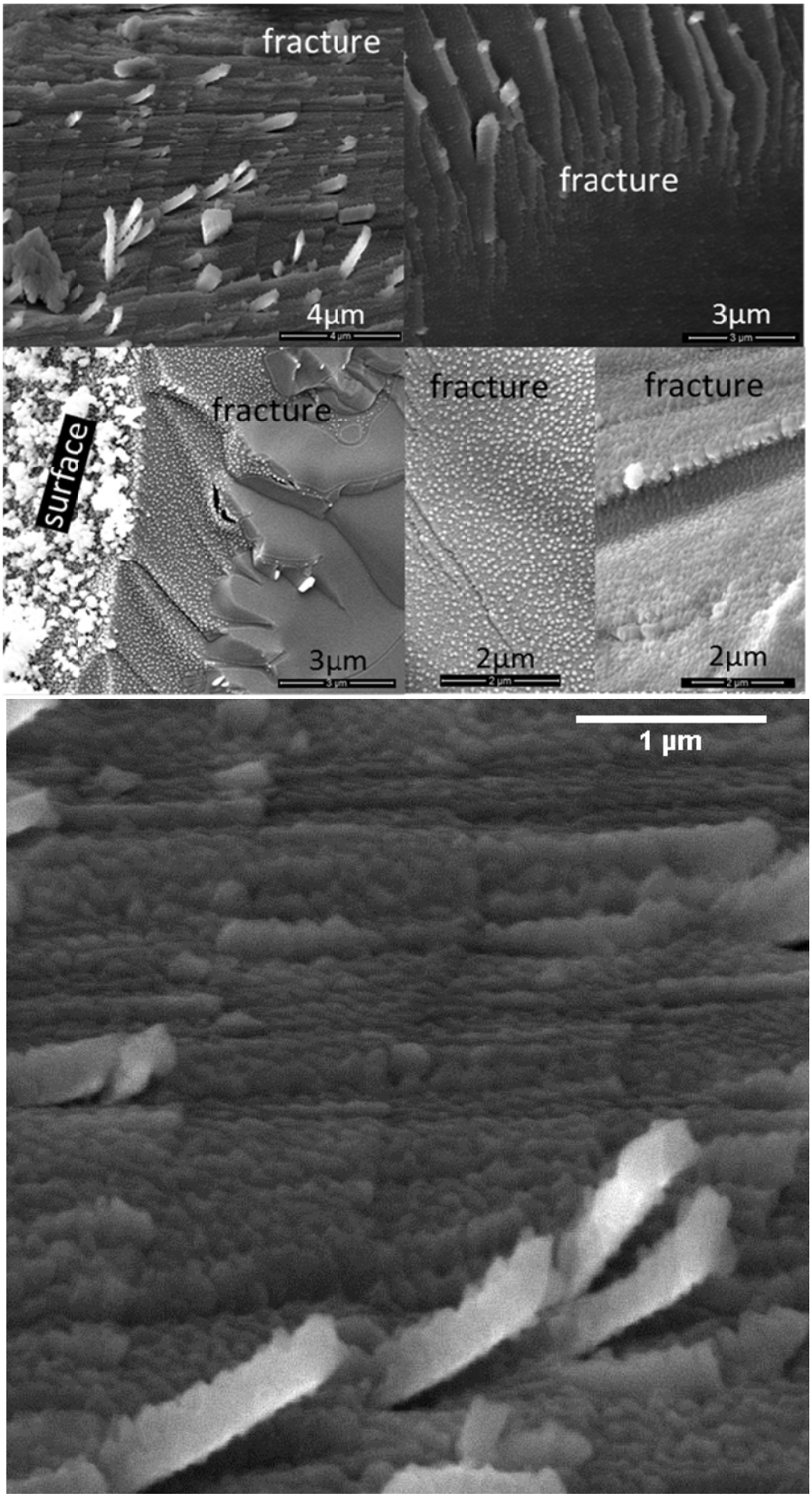


Figure SI12. Cryo-SEM images of hydrogel obtained from 20 wt % P(VCL/VP)60k, 100/0 solution.

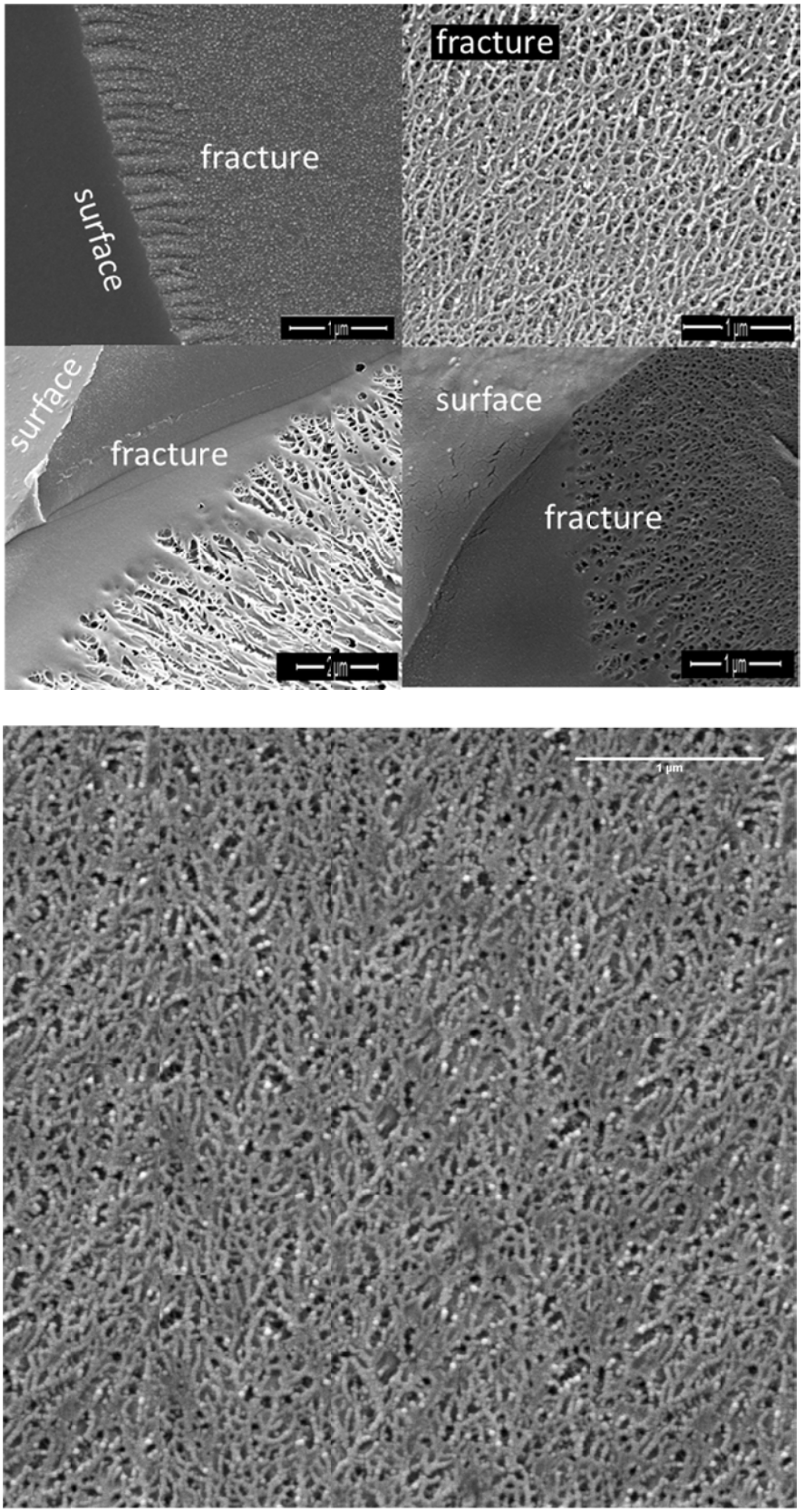
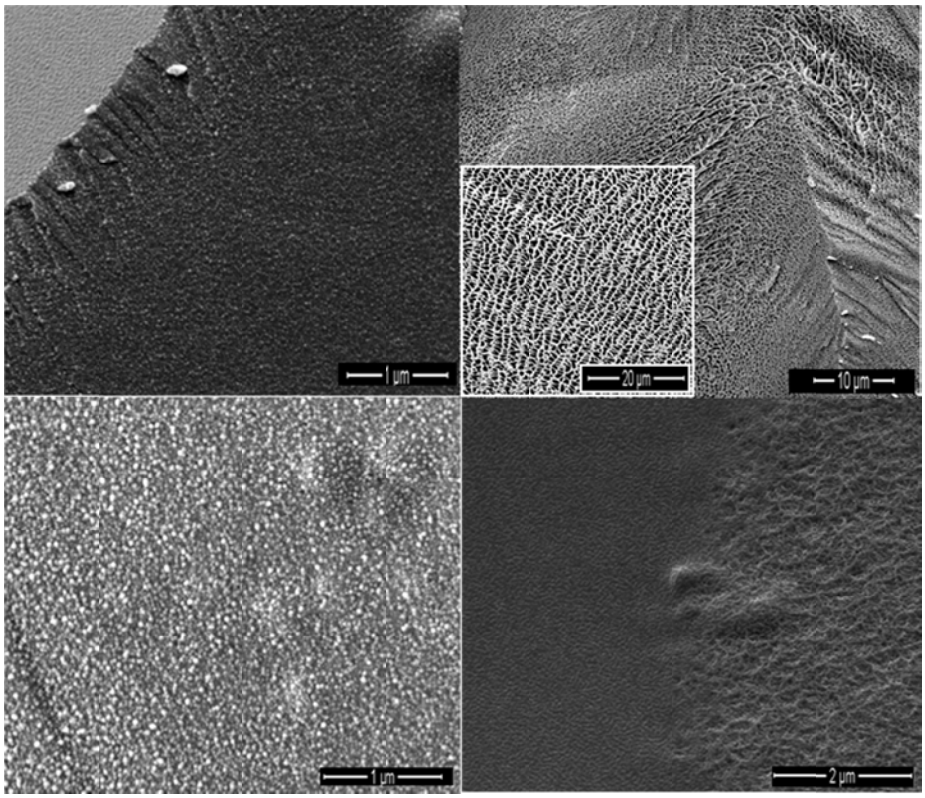


Figure SI13. Cryo-SEM images of hydrogel obtained from 20 wt % P(VCL/VP)60k, 90/10 solution.



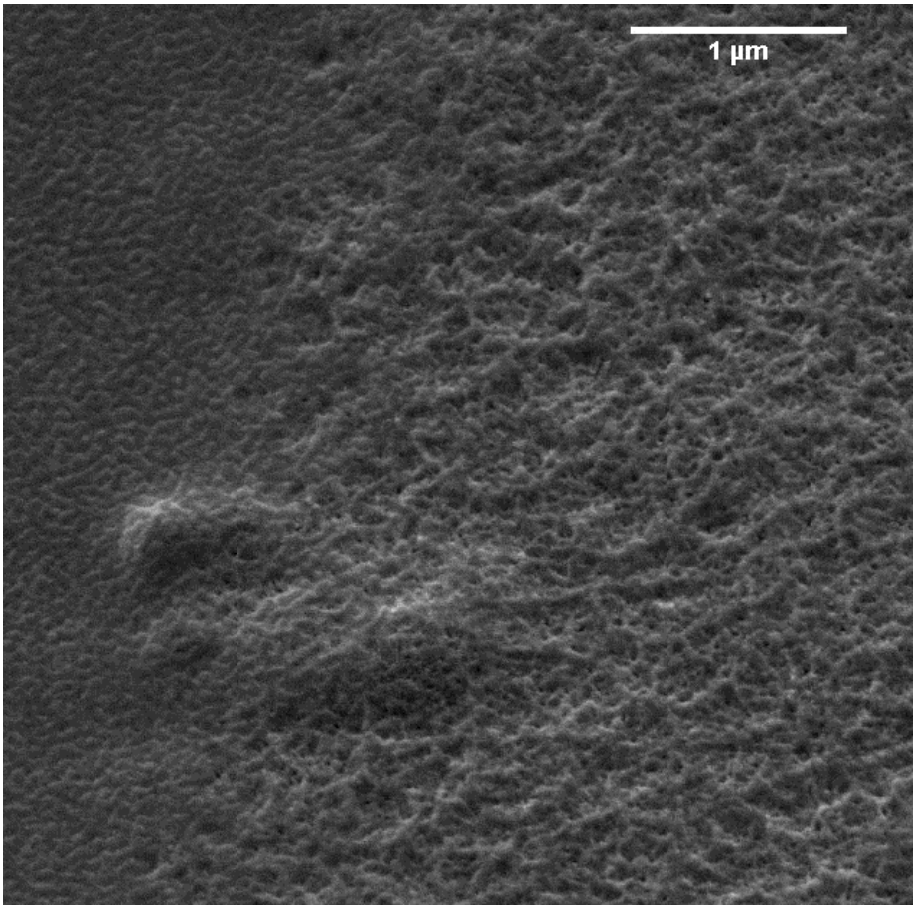


Figure SI14. Cryo-SEM images of hydrogel obtained from 20 wt % P(VCL/VP)60k, 75/25 solution.