

Electronic Supplementary Information

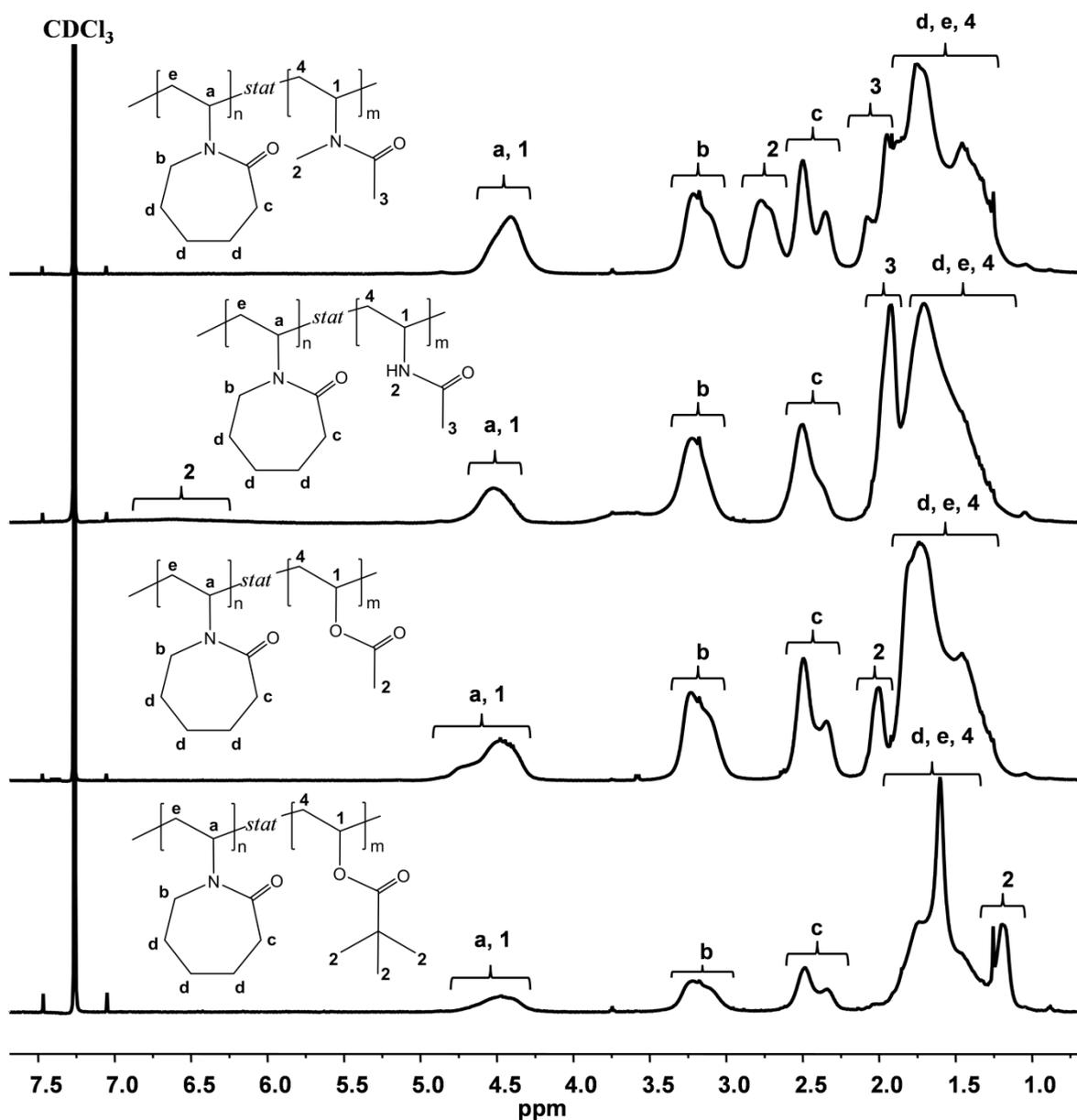


Figure S1. Overlay of the ^1H NMR spectra (CDCl₃ at 25 °C) of some representative NVCL-based statistical copolymers prepared by CMRP.

Table S1. Phase transition temperatures of the *NVCL*-based statistical copolymers in aqueous solutions (1 g/L) measured by turbidimetry upon heating and cooling (1 °C/min).

M	In copolymer		T_{CP} upon heating (°C)	T_{CP} upon cooling (°C)
	(mol%)			
	M	<i>NVCL</i>		
<i>NMVA</i>	10	90	43.3	41.0
	19	81	50.6	48.2
	29	71	57.0	54.9
	37	63	66.9	64.8
<i>NVA</i>	9	91	42.2	39.3
	22	78	47.5	44.7
	24	76	49.3	46.8
	32	68	53.7	50.9
	45	55	63.5	60.5
	57	43	80.7	78.5
<i>VAc</i>	11	89	35.9	33.5
	15	85	35.0	32.9
	27	73	30.6	28.5
	31	69	27.1	25.0
	40	60	22.2	20.2
	45	55	19.4	17.4
<i>VPi</i>	7	93	32.6	30.6
	10	90	29.8	27.5
	14	86	27.1	24.6
	23	77	20.8	17.7

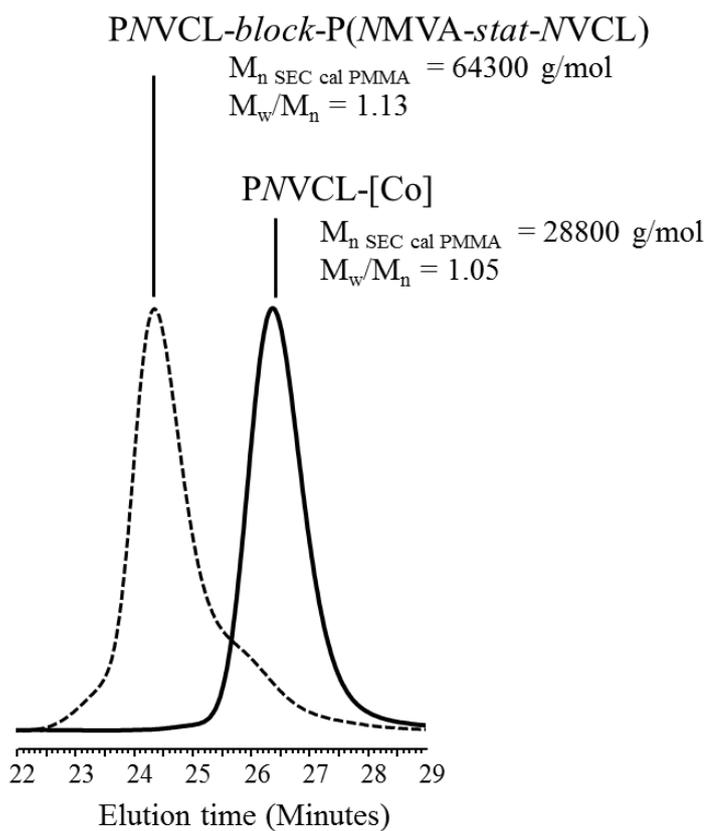


Figure S2. SEC chromatograms in DMF/LiBr (calibration PMMA) for the statistical copolymerization of NVCL and NMVA (40/60:NVCL/NMVA) initiated in bulk at 40 °C from a PNVCCL-Co(acac)₂ macroinitiator.

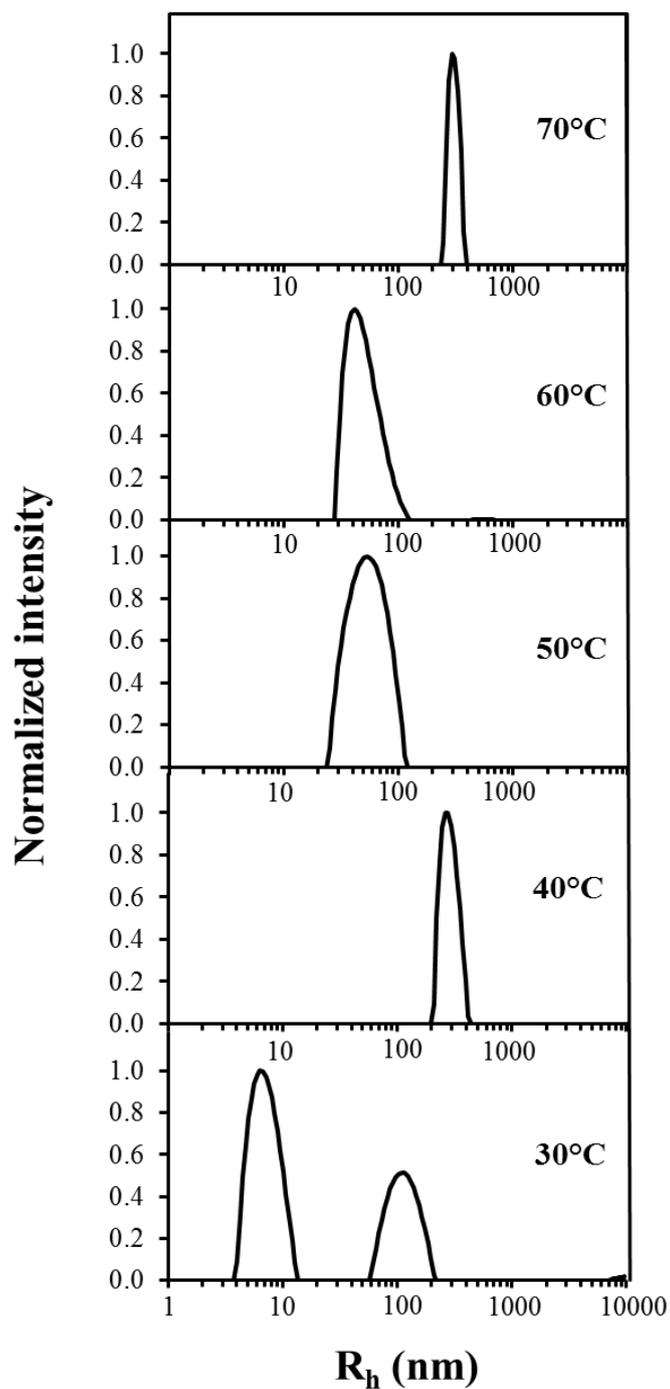


Figure S3. CONTIN size distribution of the $\text{PMVCL}_{315}\text{-block-P}(\text{NMVA}_{215}\text{-stat-NVCL}_{143})$ copolymer in water (1 g/L) at various temperatures. At 30°C, the sample mainly consists in free chains. Indeed, the population at 100 nm is absent from the number distribution graph.

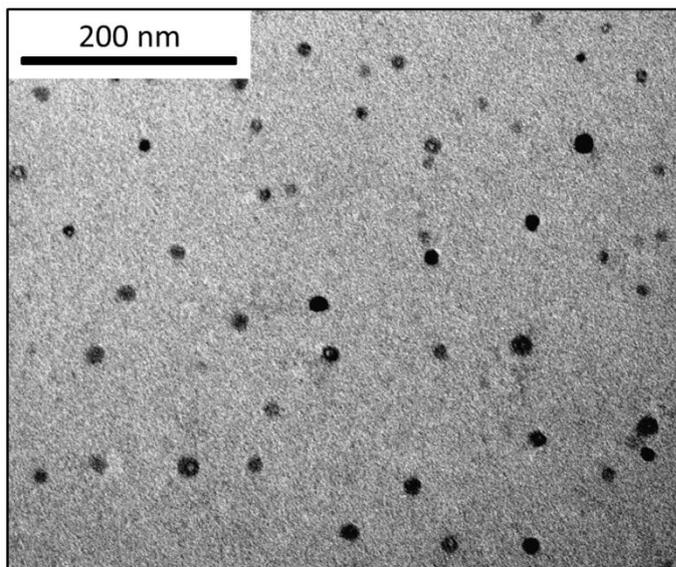


Figure S4. Transition electron microscopy image after spin-coating deposition on a copper grid with formvar of a drop of the $P(NVCL_{315}\text{-}block\text{-}P(NMVA_{215}\text{-}stat\text{-}NVCL_{143}))$ (NMVA content in the second block = 60 mol%) aqueous solution (1 g/L) thermostated at 60 °C.

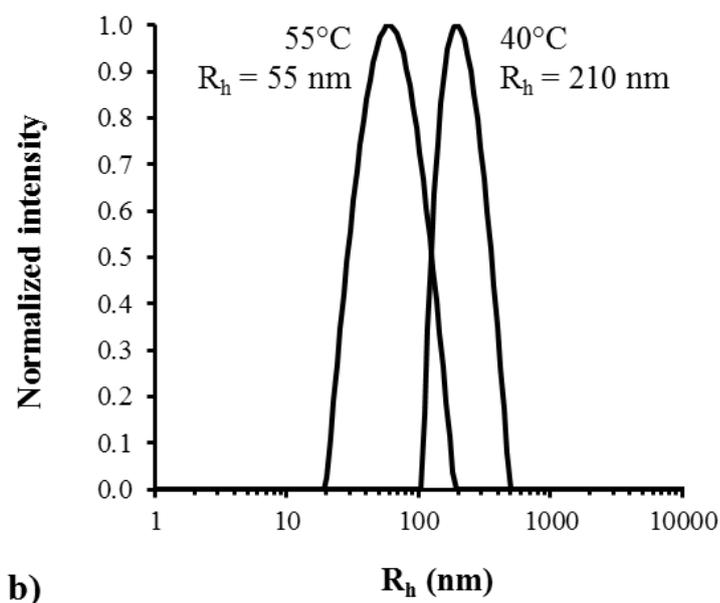
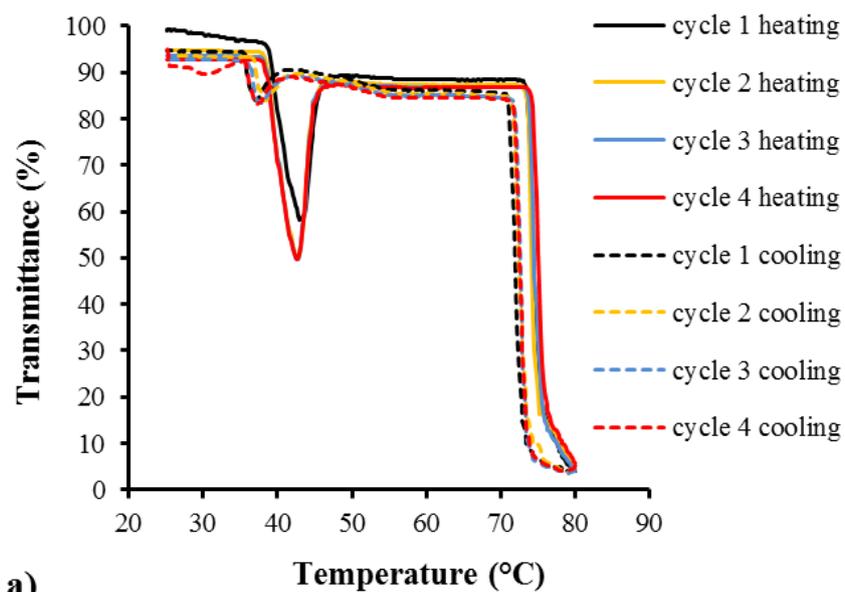


Figure S5. Repeated heating-cooling cycles for the $PMVCL_{315}$ -*block*- $P(NMVA_{215}$ -*stat*- $NVCL_{143})$ in water (1 g/L). (a) Transmittance curves recorded at a heating and cooling rate of 1 °C/min. (b) CONTIN size distribution of the copolymer during the second cycle at 40°C and 50°C.

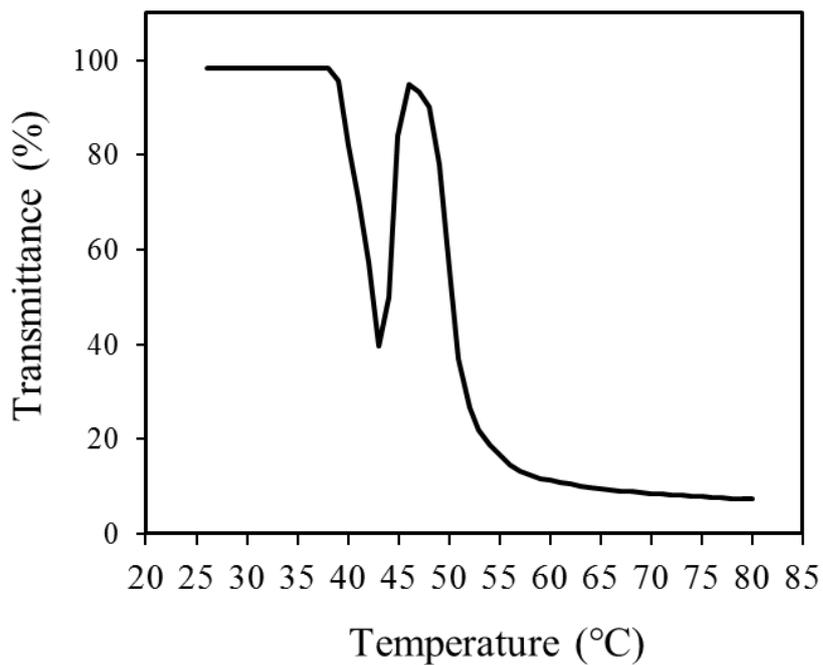


Figure S6. Transmittance curve for the PNVCL_{252} -*block*- $\text{P}(\text{NMVA}_{85}$ -*stat*- $\text{NVCL}_{127})$ (M_n $M_{\text{ALLS}} = 56000$ g/mol, $M_w/M_n = 1.13$) aqueous solution (1 g/L) recorded at a heating rate of 1 °C/min.