RAFT/MADIX emulsion copolymerization of vinyl acetate and *N*-vinylcaprolactam: towards waterborne physically crosslinked thermoresponsive particles

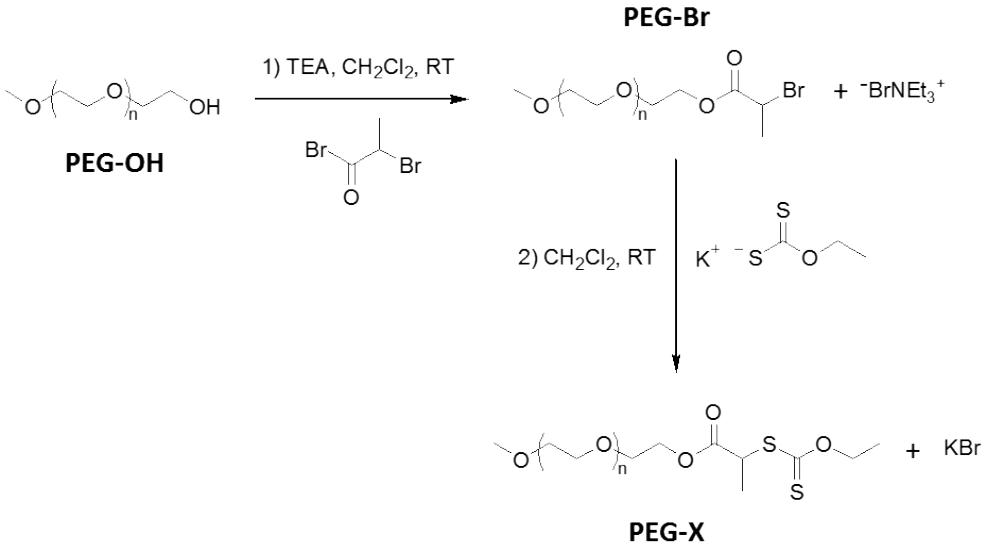
Laura Etchenausia, Abdel Khoukh, Elise Deniau Lejeune, Maud Save*

IPREM, Equipe de Physique et Chimie des Polymères, CNRS, University of Pau & Pays Adour, UMR 5254, ,2 avenue du Président Angot, Pau, F-64053, France

* Corresponding author: maud.save@univ-pau.fr

ELECTRONIC SUPPLEMENTARY INFORMATION

Electronic supplementary information (ESI) available: Preparation of PEG-X macro-chain transfer agent and ^{1}H NMR spectra; Overlay of the UV-visible (λ = 355 nm) and refractometer (RI) traces of the SEC chromatograms in THF for the PEG-X polymer; ^{1}H NMR and ^{13}C NMR spectra of the dialyzed and freeze-dried PEG-*b*-P(VAc-*co*-VCL) diblock copolymers; Pictures of the coagulum and of the dispersion recovered at the end of the emulsion copolymerization of VAc and VCL using non-reactive PEG-OH as stabilizer; Size exclusion chromatograms of PEG-X and PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer; DOSY NMR spectra of the dialyzed PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer and initial PEG-OH homopolymer; Comparison of ^{13}C NMR spectra of the VAc/VCL copolymers synthesized either by bulk polymerization or by emulsion polymerization; Transmittance at λ=500 nm versus temperature for aqueous solution of PEG-X; ^{1}H NMR spectra before and after hydrolysis of PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer; FTIR spectra before and after hydrolysis of PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer; DOSY NMR spectrum of PEG-*b*-P($VAc_{0.03}$-*co*-$VA_{0.14}$-*co*-$VCL_{0.83}$) and PEG-*b*-P($VAc_{0.05}$-*co*-$VA_{0.42}$-*co*-$VCL_{0.53}$) copolymers after hydrolysis.



Scheme 1. Preparation of PEG-X macro-chain transfer agent.

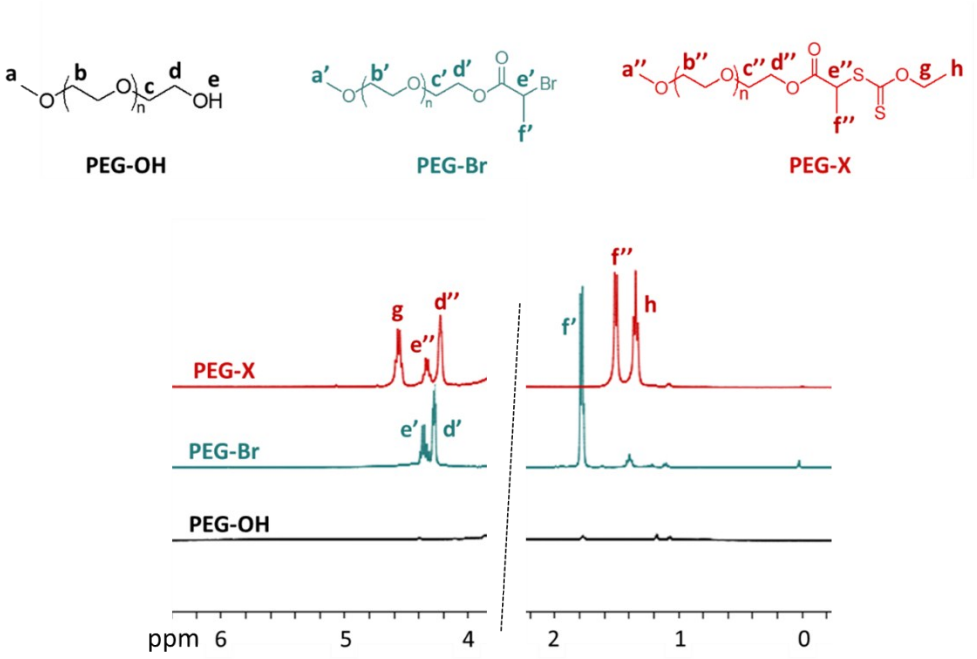


Figure S1. ^1H NMR spectra in $CDCl_3$ of the initial PEG-OH and the precipitated derivatized PEG-Br and PEG-X.

The first incorporation of the 2-bromopropionyl end-group onto PEG-OH is confirmed by the presence of the corresponding methine and methyl groups (respectively *e'* at 4.3 ppm and *f'* at 1.8 ppm in ^1H NMR (**Figure S1**)). In the second step, the appearance of new peaks characteristics of the xanthogenate end-group at 1.3 ppm (methyl protons *h* in **Figure S1**) and 4.6 ppm (methylene protons *g* in **Figure S1**), as well as the shift of the methyl protons *f'* from 1.8 ppm in PEG-Br to

1.5 ppm in PEG-X (*f''* in **Figure S1**), confirm the effective preparation of the xanthate-terminated PEG.

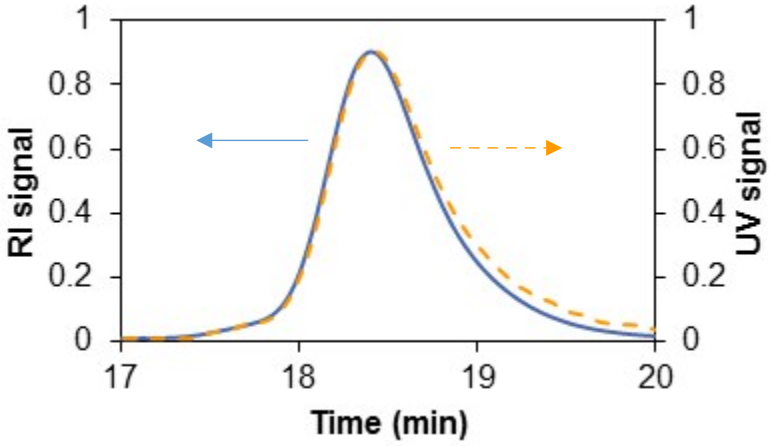
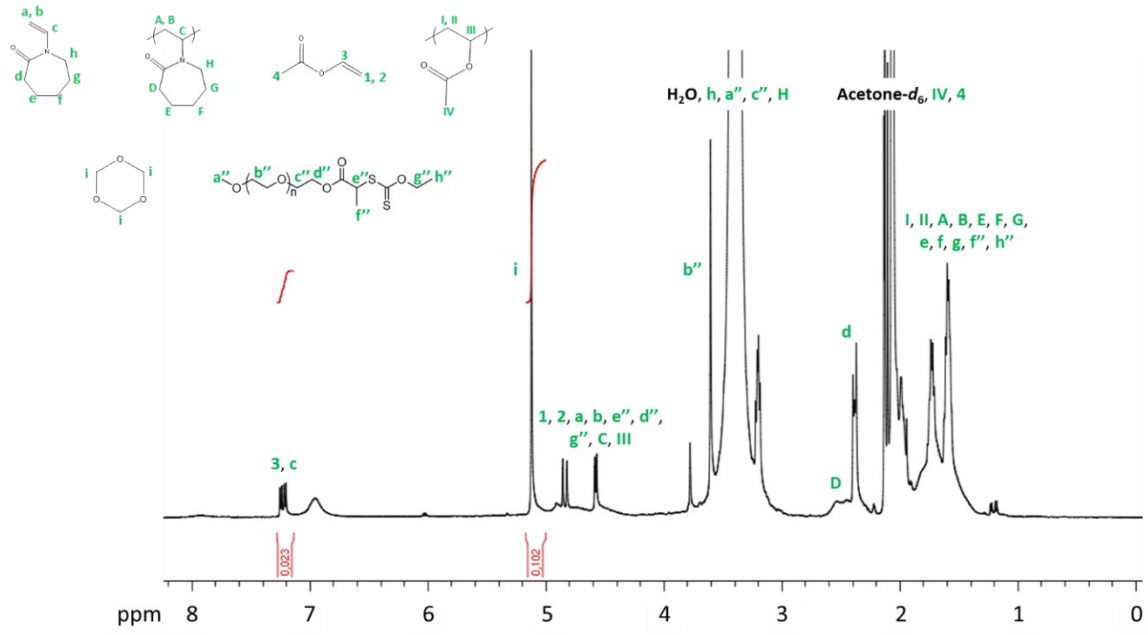


Figure S2. Overlay of the UV-visible (λ = 355 nm) and refractometer (RI) traces of the SEC chromatograms in THF for the PEG-X polymer.

(a)



(b)

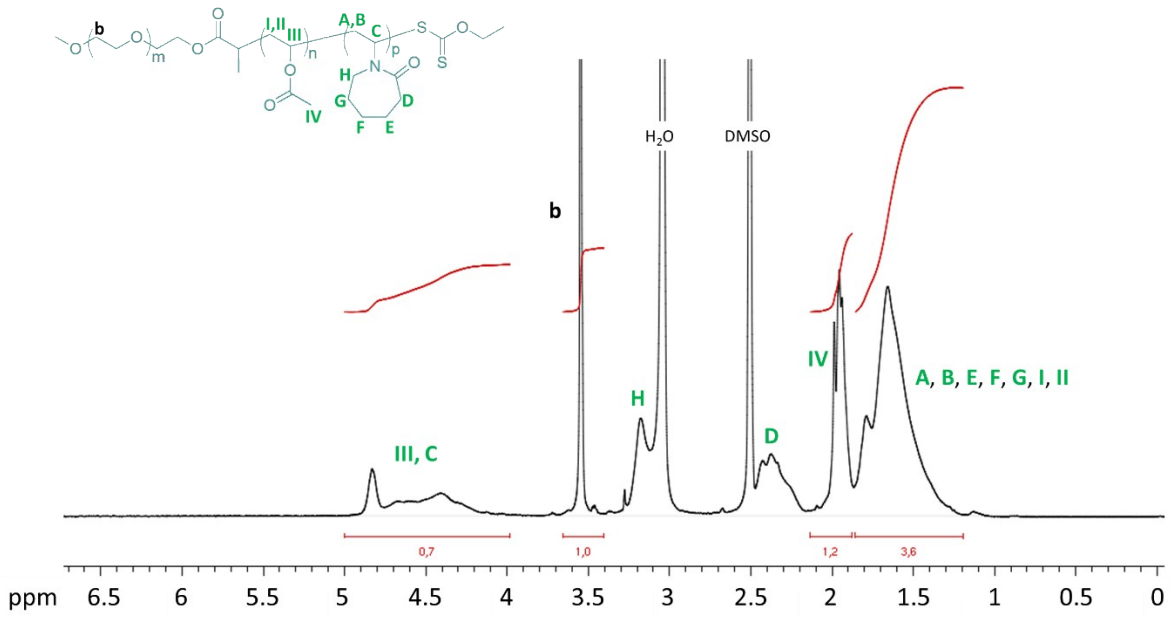


Figure S3. (a) ^{1}H NMR spectrum in acetone-d_6 of the crude solution (t = 5 h 30 min) of VAc/VCL emulsion copolymerization mediated by PEG-X for polymerization carried out with $f_{VAc,0}$ = 0.5; **(b)** ^{1}H NMR spectrum in DMSO-d_6 of the dialyzed and freeze-dried PEG-*b*-P(VAc$_{0.47}$-*co*-VCL$_{0.53}$).

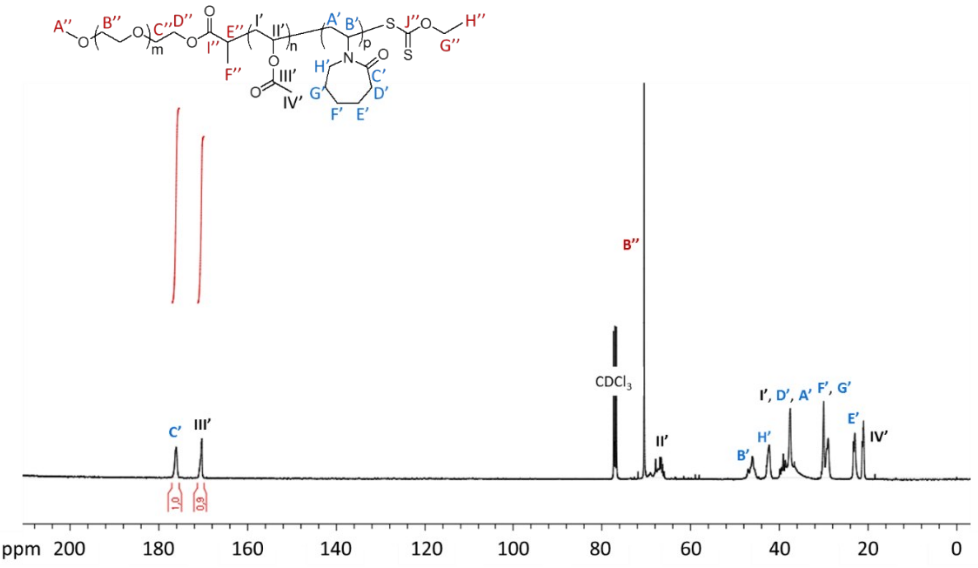


Figure S4. ^{13}C NMR spectrum in $CDCl_3$ of the dialyzed and freeze-dried PEG-*b*-P(VAc$_{0.47}$-*co*-VCL$_{0.53}$).

Figure S5. Pictures of the coagulum (left) and of the dispersion (right) recovered at the end of the emulsion copolymerization of VAc and VCL using non-reactive PEG-OH as stabilizer (expt 3 in **Table 1** of the article).

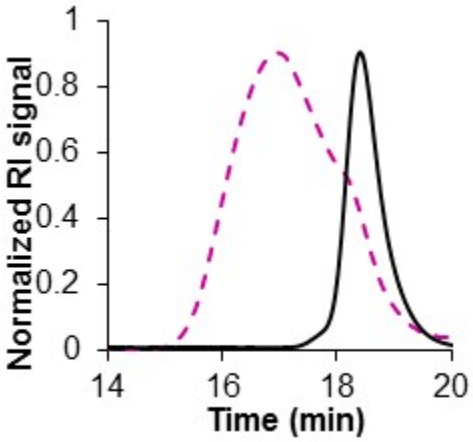
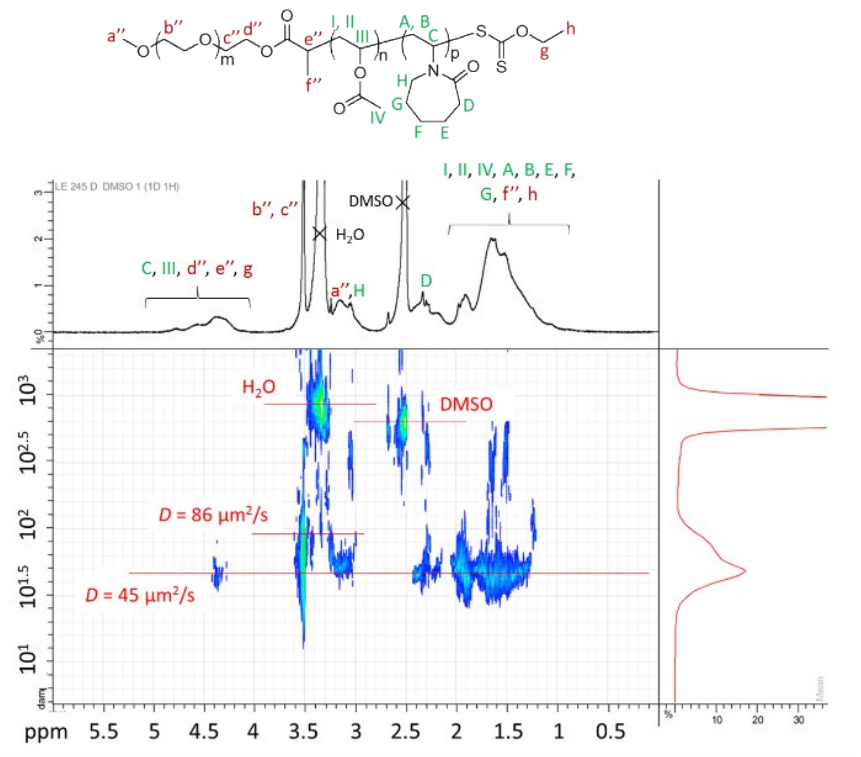


Figure S6. Size exclusion chromatograms in THF: PEG-X (full line) and PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) (expt 1 in **Table 2** of the article) copolymer synthesized by RAFT/MADIX emulsion polymerization.

(a)



(b)

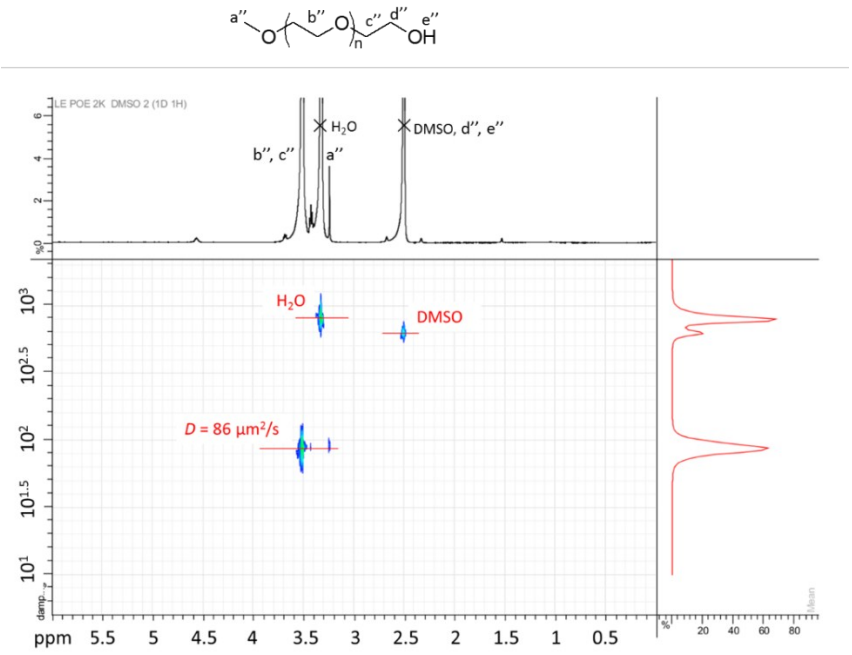
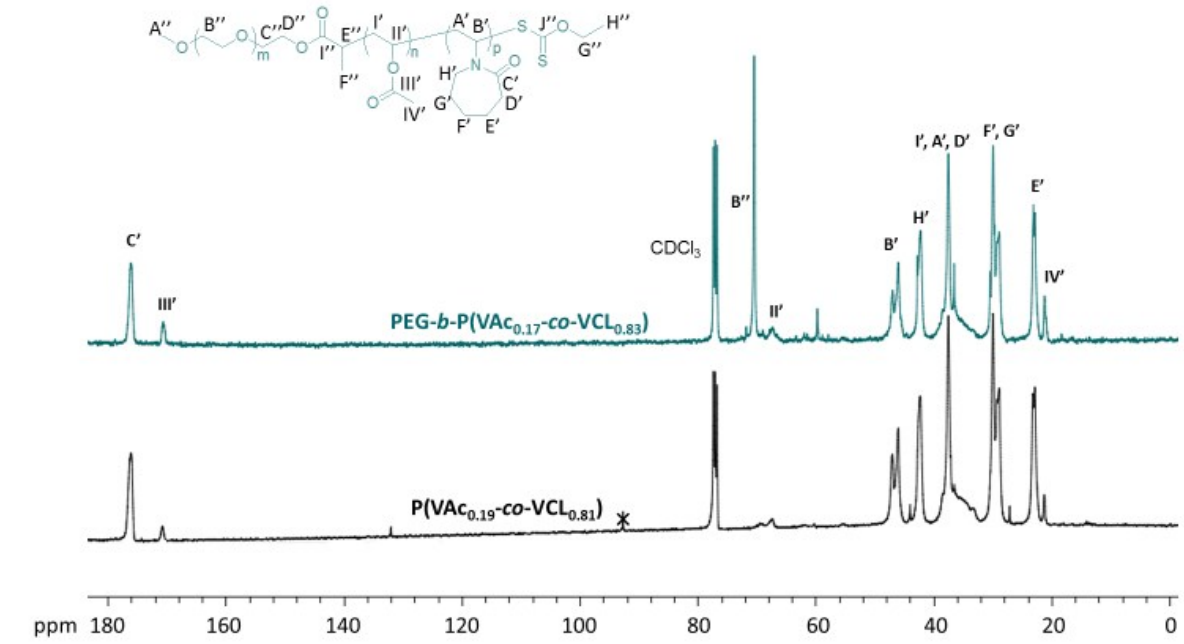


Figure S7. DOSY NMR spectra in DMSO-d_6 of: **(a)** the dialyzed PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer synthesized by RAFT/MADIX emulsion polymerization (expt 1 in **Table 2** of the article); **(b)** Initial PEG-OH homopolymer.

(A)



(B)

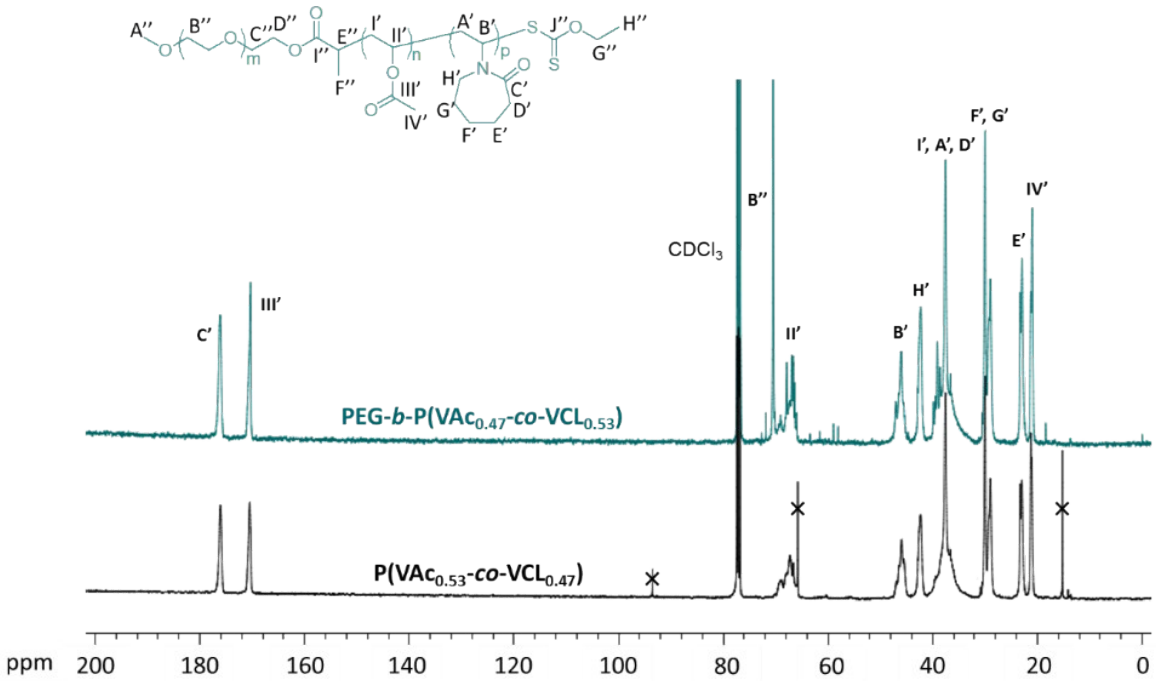


Figure S8. Comparison of ^{13}C NMR spectra in $CDCl_3$ of the VAc/VCL copolymers synthesized either by bulk polymerization (see reference 1, precipitated prior to analysis, black spectra) or by emulsion polymerization (green spectra for dialyzed and freeze-dried copolymers). (A) PEG-*b*-P($VAc_{0.47}$-*co*-$VCL_{0.53}$) (expt 2 in **Table 1**) and P($VAc_{0.53}$-*co*-$VCL_{0.47}$) (from reference 1) copolymers; (B) PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) (expt 1 in **Table 1** of the article) and P($VAc_{0.19}$-*co*-$VCL_{0.81}$) (from reference 1) copolymers. Residual trioxane (internal standard used for VAc/VCL copolymerizations) and diethyl ether (solvent of precipitation) are marked by crosses in the spectra of the copolymers synthesized in bulk.

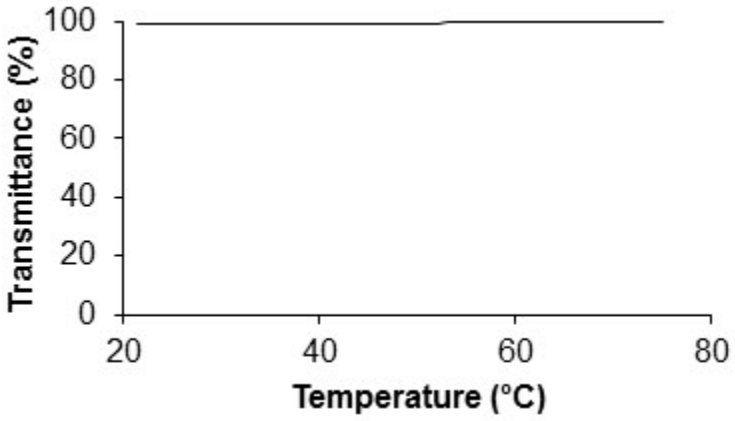


Figure S9. Transmittance at λ=500 nm versus temperature for aqueous solution of PEG-xanthate macro-chain transfer agent. Polymer concentration of 3 g.L^{-1} (Heating cycle).

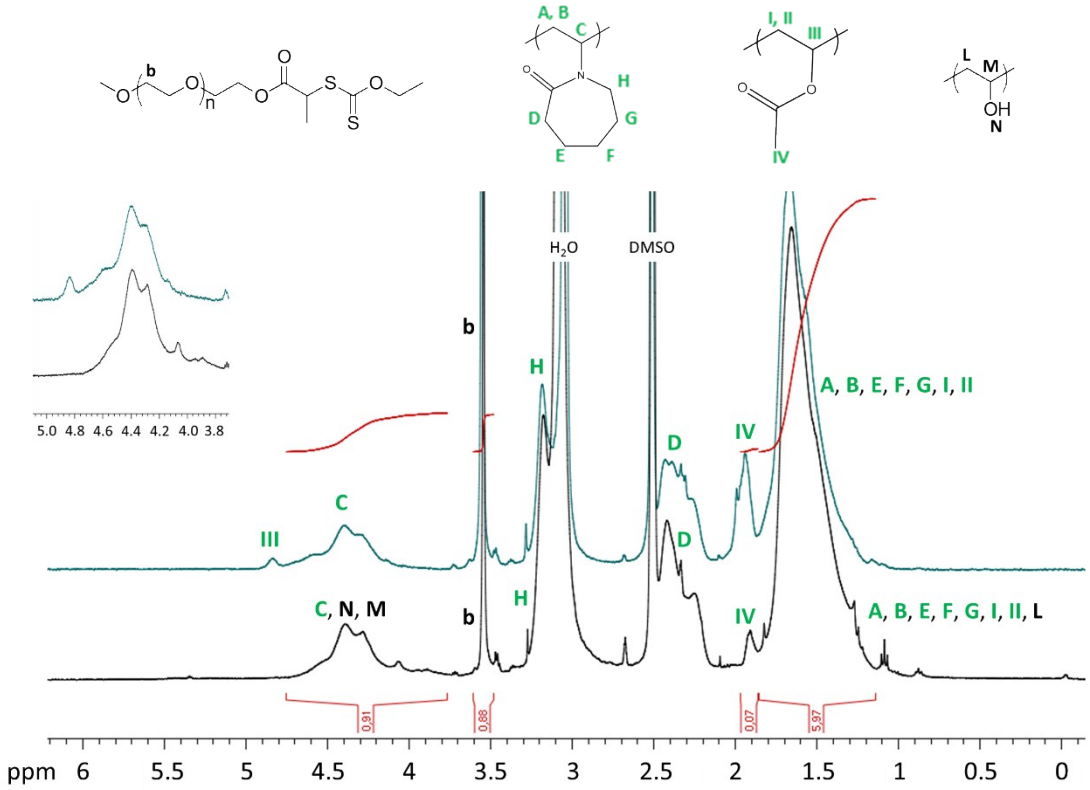


Figure S10. ^{1}H NMR spectra in DMSO-d_6 at 80°C of dialyzed (M_w cut-off: 3500 Da) and freeze-dried PEG-*b*-P(VAc$_{0.17}$-*co*-VCL$_{0.83}$) (expt 1 in **Table 1** of the article) copolymer. Blue spectrum: before hydrolysis, black spectrum: after hydrolysis.

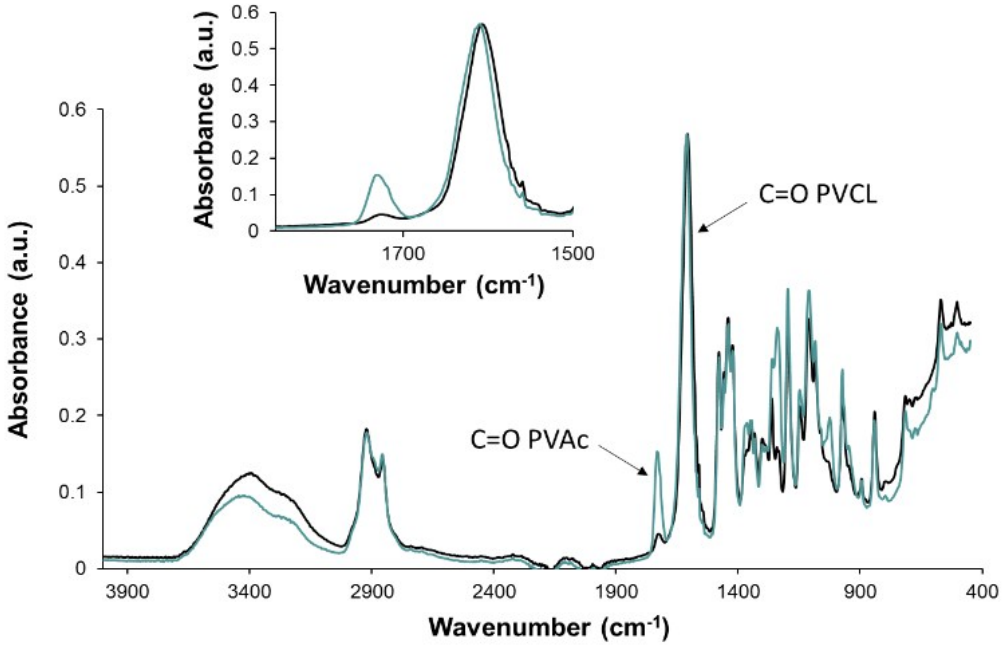
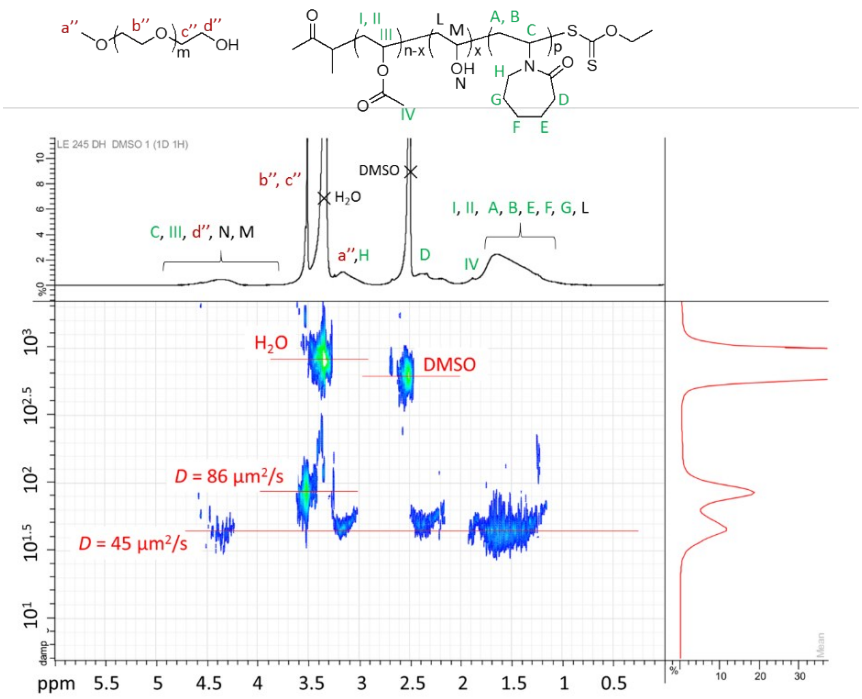


Figure S11. FTIR spectra before (blue) and after (black) hydrolysis of PEG-*b*-P($VAc_{0.17}$-*co*-$VCL_{0.83}$) copolymer.

(A)



(B)

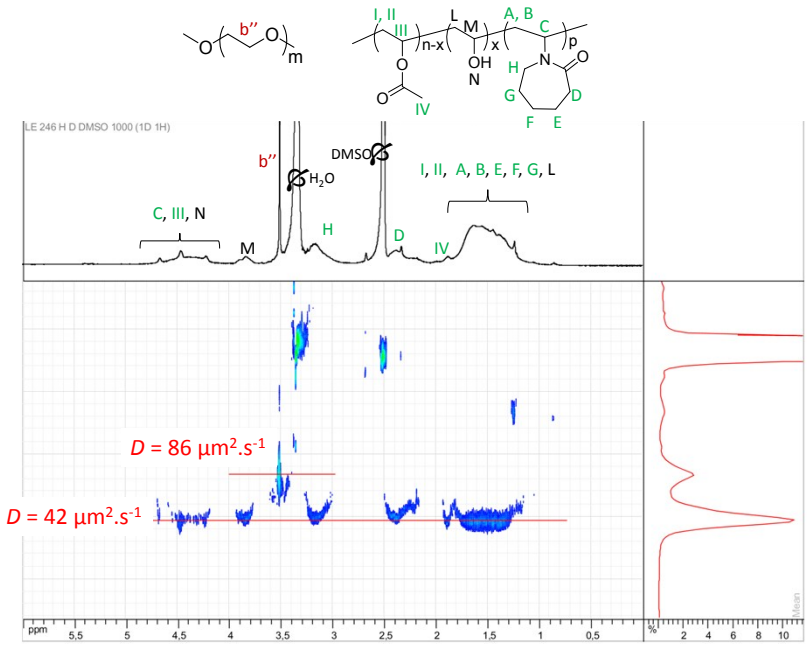


Figure S12. DOSY NMR spectrum (in DMSO-d_6) of **(A)** PEG-*b*-P(VAc$_{0.03}$-*co*-VA$_{0.14}$-*co*-VCL$_{0.83}$) and **(B)** PEG-*b*-P(VAc$_{0.05}$-*co*-VA$_{0.42}$-*co*-VCL$_{0.53}$) copolymers after hydrolysis.

Reference

1. Etchenausia, L.; Rodrigues, A. M.; Harrisson, S.; Deniau Lejeune, E.; Save, M. *Macromolecules* **2016,** 49, 6799-6809.