Electronic Supplementary Material (ESI) for Polymer Chemistry.

Surfactant-free emulsion polymerization of vinylidene fluoride mediated by RAFT/MADIX reactive poly(ethylene glycol) polymer chains

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Characterization of PEG-X - $M_{n,SEC}$ = 2300 g mol^{-1}

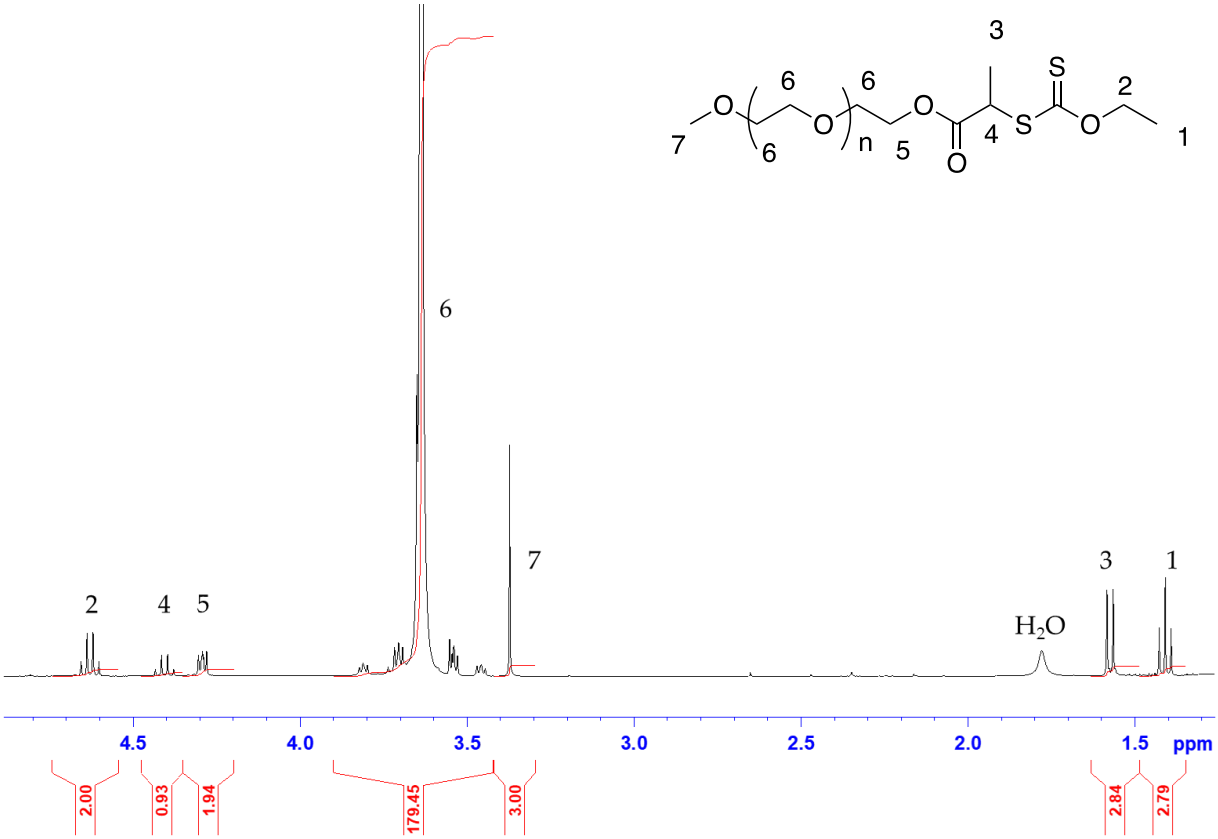

Figure S1. ^{1}H NMR spectrum of PEG-X obtained after functionalization of commercial poly(ethylene glycol) methyl ether (PEG-OH, $M_n \approx 2000$ g mol^{-1}) with a xanthate chain end (512 scans, $CDCl_3$).

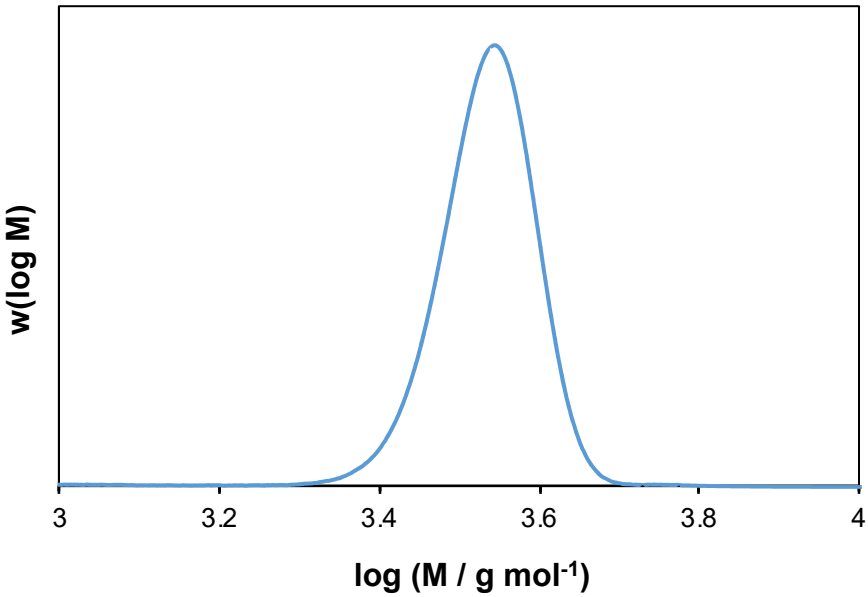

Figure S2. Molar mass distribution of PEG-X ($M_{n,SEC}$ = 2300 g mol^{-1}) by SEC analysis in THF. PS standards are used for the calibration.

Characterization of PEG-X - $M_{n,SEC}$ = 1300 g mol^{-1}

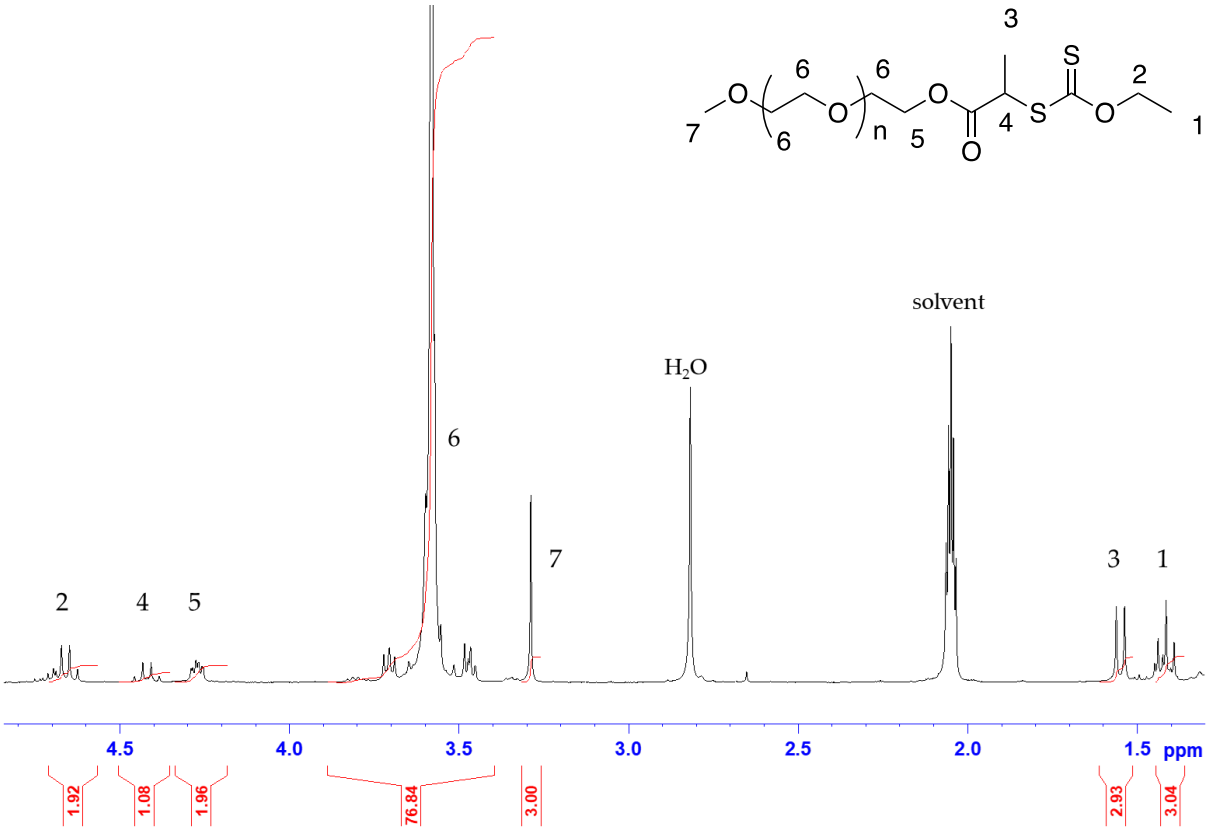

Figure S3. ^{1}H NMR spectrum of PEG-X obtained after functionalization of commercial poly(ethylene glycol) methyl ether (PEG-OH, $M_n \approx 750$ g mol^{-1}) with a xanthate chain end (512 scans, $CDCl_3$).

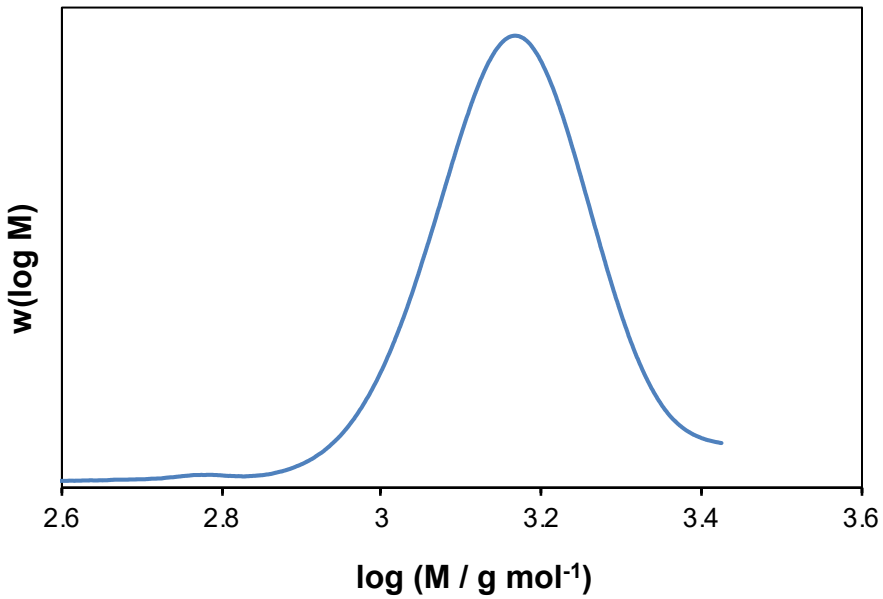

Figure S4. Molar mass distribution of PEG-X ($M_{n,SEC}$ = 1300 g mol^{-1}) by SEC analysis in THF. PS standards are used for the calibration.

Characterization of X-PEG-X - $M_{n,SEC}$ = 3420 g mol^{-1}

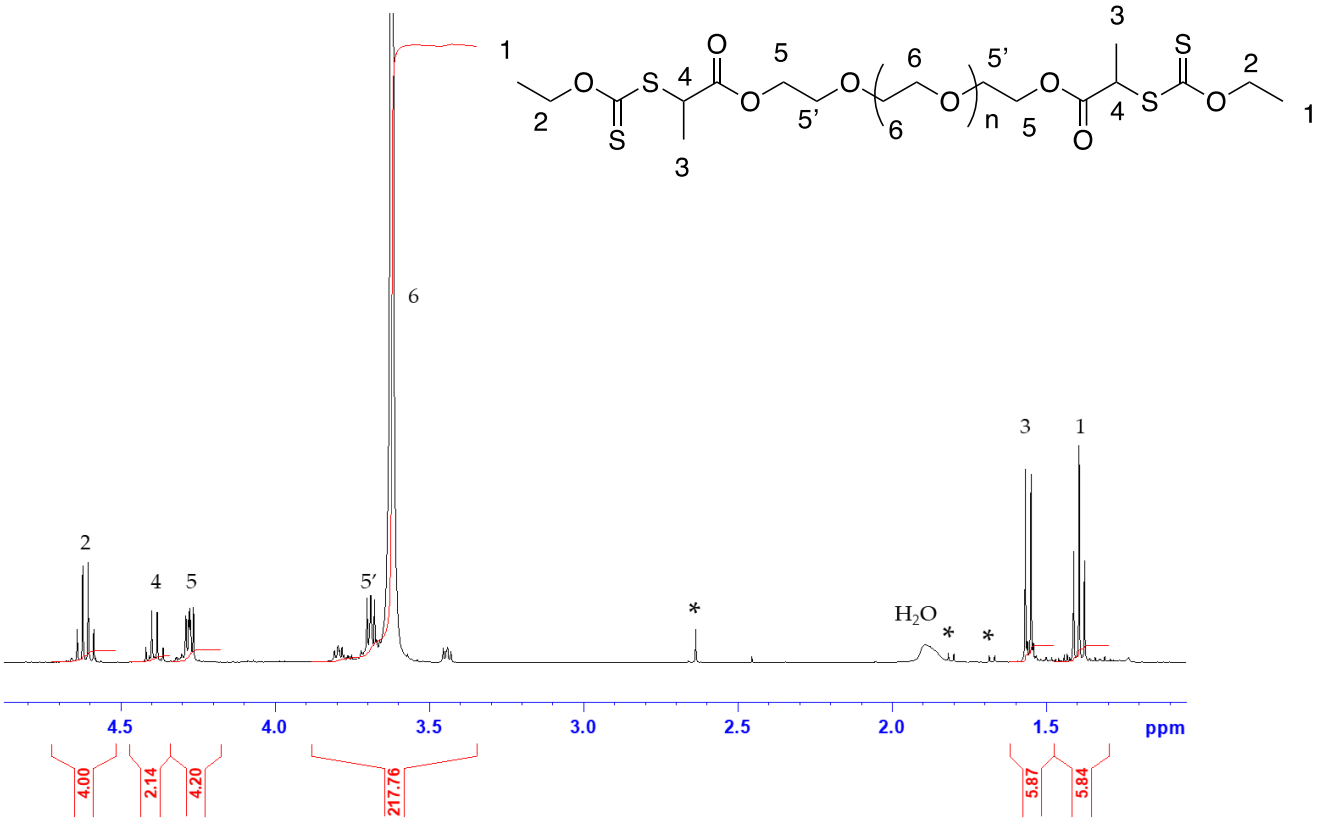

Figure S5. ^{1}H NMR spectrum of X-PEG-X obtained after functionalization of commercial α,ω-dihydroxy poly(ethylene glycol) (HO-PEG-OH, $M_n \approx 2050$ g mol^{-1}) with xanthate chain ends (512 scans, $CDCl_3$). Starred peaks correspond to solvent impurities.

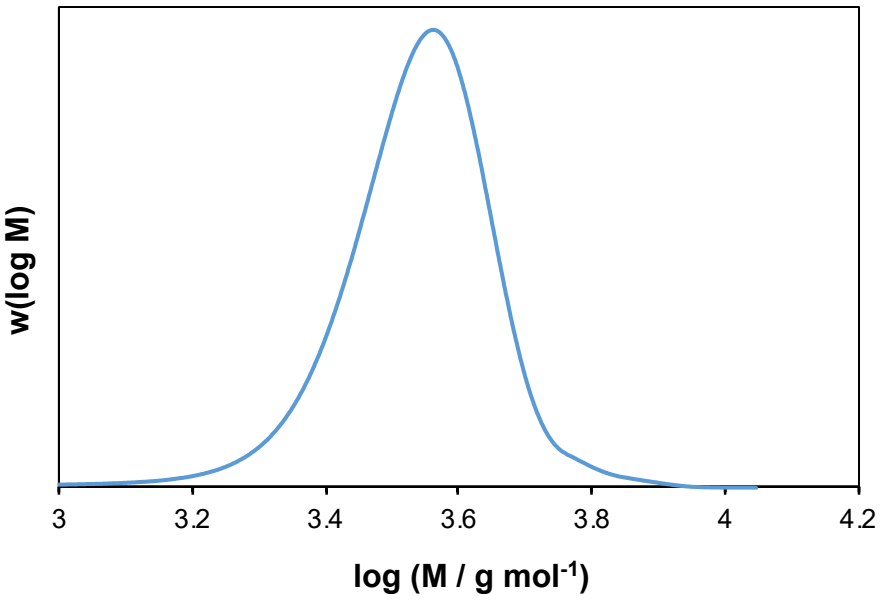

Figure S6. Molar mass distribution of X-PEG-X ($M_{n,SEC}$ = 3420 g mol^{-1}) by SEC analysis in THF. PS standards are used for the calibration.

Kinetic studies performed with PEG-OH and PEG-X

As one can see in Figure S7, both kinetics show a steady polymerization rate, slightly lower in the case of PEG-X, probably as a result of a slightly lower KPS/PEG ratio (2.5 *vs* 2.2). This confirms that the snapshot we provided is indeed a good indication of the kinetics.

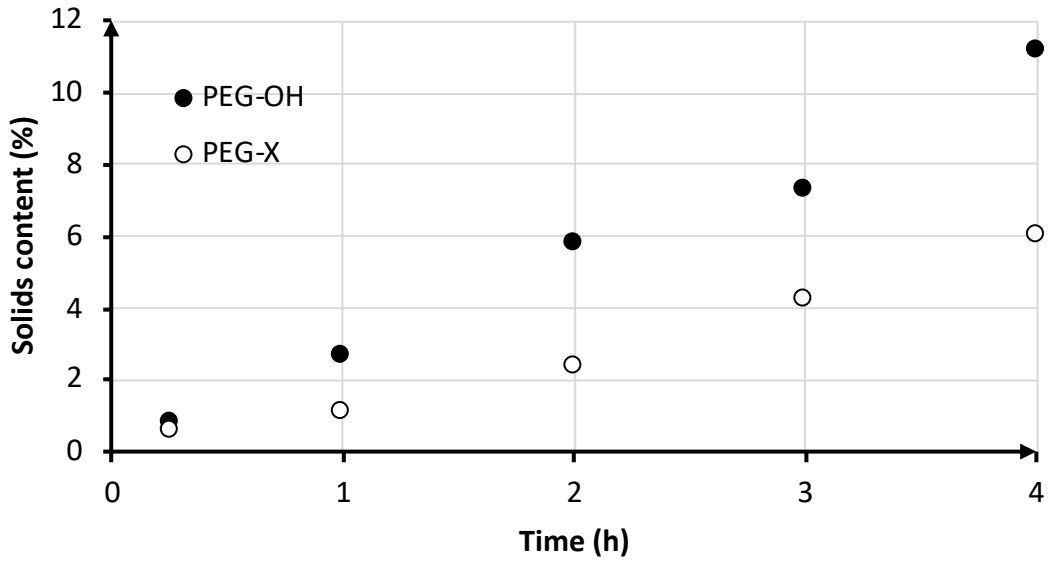

Figure S7. Evolution of the solids content *versus* time for the kinetic studies conducted with PEG-OH (black circles) and PEG-X (open circles) with n = 44. T = 80 °C; P = 30 bar. The same molar amounts of PEG were used in the 2 studies ($n_{PEG\text{-}OH} = n_{PEG\text{-}X}$), corresponding to the following weight ratios: KPS/PEG-OH = 2.5; KPS/PEG-X = 2.2. Please note that each point corresponds to one experiment, and that the experiment at 4 h for PEG-OH is L01 in Table 1.

Calibration curves used for the surface tension measurements

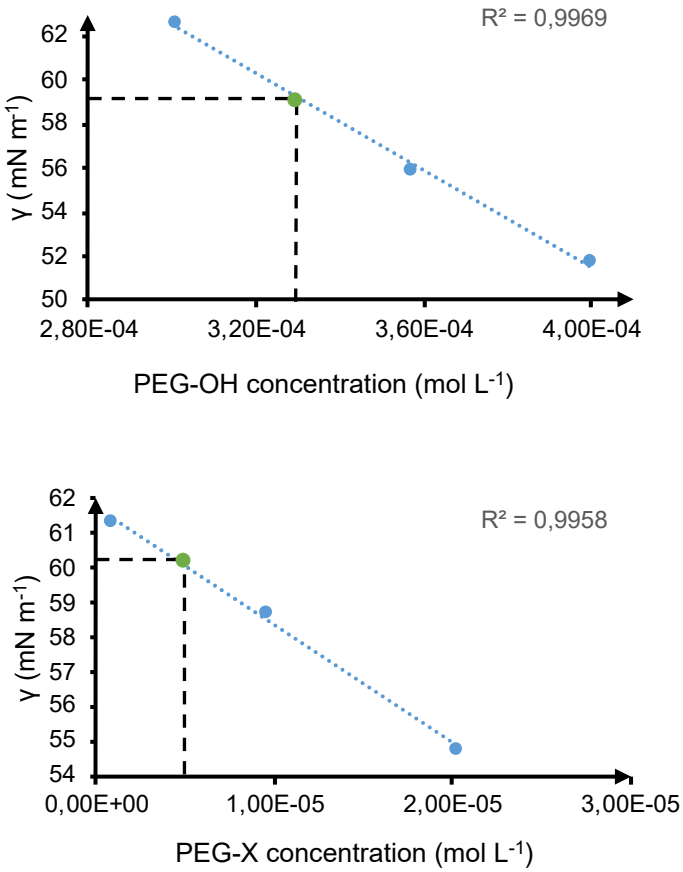

Figure S8. Calibration curves for surface tension measurements made on selected PEG-OH and PEG-X solutions in water (full blue cicles) and surface tension measurement for L01 and L03 (full green circle).

Thermal properties of PVDF

Table S1. Thermal properties of the PVDF polymers obtained by emulsion polymerization of VDF performed with various-PEG based macromolecules

Exp.[a]	Stabilizer		KPS/ Stabilizer[b]	SC [c] (%)	T_c (°C)[d]	T_m (°C)[d]	X_c (%)[d]
	Name	*n*[a]					
L01	PEG-OH	44	2.5	11.2	130	168	44.9
L02	-	-	-	7.8	-	-	-
L03	PEG-X	44	2.5	10.4	130	169	44.6
L04	PEG-SH	44	2.5	8.1	130	170	48.6
L05	PEG-X	44	1.25	2.4	125	154	30.6
L06			5	14.4	130	167	49.3
L07	PEG-X	15	2.5	10.4	129	168	48.1
L08			6.7	15.9	129	165	44.7
L09	X-PEG-X	44	2.5	8.5	132	169	46.4
L10	PEG-OH	44	2.5	7.6	123	167	47.7
L11	PEG-X	44	2.5	6.8	131	168	41.4

[a] See Table 1 for detailed experimental conditions and latex characterization. [b] Weight ratio; [c] Solids content taking into account all the non-volatile species (including stabilizer and PVDF). [d] Determined by DSC after the second heating.