

ACCESSORY PUBLICATION

Molecular weight and tacticity of oligoacrylates by  
capillary electrophoresis – mass spectrometry

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## Synthesis of the oligoacrylates<sup>1</sup>

The 2-[(Butylsulfanyl)carbonothioyl]sulfanylpropanoic acid (RAFT agent, 1equiv, 3.31 g,  $1.39 \times 10^{-2}$  mol) was reacted with different amount of acrylic acid (n equiv. between 2 and 7) in the presence of initiator (0.1 equiv, V-501, 0.389 g,  $1.39 \times 10^{-3}$  mol) in 10 mL of 1,4-dioxane. All the reactants were added to a round-bottom flask. This was capped with a rubber septum and stirred to dissolve the RAFT agent. The flask was deoxygenated by bubbling nitrogen through the solution. The flask was then immersed in an oil bath at 60 °C, and the polymerization allowed to proceed for 2 h. The oligomers were recovered by evaporation of the solvent.

## **Quantification of the RAFT agent, DP of one and DP of two using CE UV**

The amount of unreacted RAFT agent, DP of one and DP of two is important to understand the kinetics of RAFT polymerization. All the quantifications performed in this work are given in Table S1. The corresponding averages and standard deviations are given in Table 1 (main text).

Sample	RAFT mol%	DP1 mol%	DP2 mol%	Buffer	capillary
AA2	51.4	31.3	NR	LB500	bare fused silica <sup>1</sup>
	59.8	25.5	9.9	Amm150	bare fused silica <sup>1</sup>
	59.1	25.9	10.1	Amm150	bare fused silica <sup>1</sup>
	48.4	29.2	14.1	LB50	C18 coated <sup>2</sup>
	48.7	28.6	3.8	LB500M10	bare fused silica <sup>2</sup>
AA3	17.1	20.2	17.2	Amm150	bare fused silica <sup>3</sup>
	15.8	23.8	20.5	Amm150	bare fused silica <sup>3</sup>
	12.4	16.9	16.9	Amm150	bare fused silica <sup>3</sup>
AA5	8.9	14.5	15.7	LB1000	bare fused silica <sup>4</sup>
	9.7	15.1	16.0	LB1000	bare fused silica <sup>4</sup>
	8.8	14.3	15.3	LB200	bare fused silica <sup>4</sup>
	8.6	13.7	NR	LB200	bare fused silica <sup>4</sup>
	8.7	13.7	NR	LB200	bare fused silica <sup>4</sup>

	8.8	14.0	NR	LB300	bare fused silica <sup>4</sup>
	8.8	14.2	NR	LB300	bare fused silica <sup>4</sup>
	9.4	14.3	15.6	NB<200	bare fused silica <sup>4</sup>
	9.2	14.3	15.4	NB<200	bare fused silica <sup>4</sup>
	9.3	14.3	NR	LB500	bare fused silica <sup>4</sup>
	9.4	14.1	NR	LB500	bare fused silica <sup>4</sup>
	9.1	13.8	NR	LB500M10	bare fused silica <sup>2</sup>
	9.7	14.9	15.1	LB200	bare fused 1 m long <sup>2</sup>
	8.6	13.6	15.3	LB100	bare fused silica <sup>2</sup>
	8.5	13.7	15.2	LB100	C18 coated <sup>2</sup>
	8.8	14.1	14.7	LB50	C18 coated <sup>2</sup>
AA7	0.7	1.5	2.3	KB40	bare fused silica <sup>1</sup>
	0.6	1.4	NR	LB500	bare fused silica <sup>1</sup>
	0.5	1.4	NR	LB50	C18 coated <sup>2</sup>
	0.4	NR	NR	LB500M10	bare fused silica <sup>2</sup>
	0.4	1.7	2.3	Amm150	bare fused silica <sup>3</sup>
AA15	0.0	0.1	NR	LB500	bare fused silica <sup>4</sup>
	0.0	0.2	NR	LB50	C18 coated <sup>2</sup>

Table S-1: quantification using CE with UV detection at 290 nm. NR stands for “non resolved”, LB for lithium borate, NB for sodium borate and KB for potassium borate. The number following the buffer name is the concentration of borate in mM. The exponent after the capillary type corresponds to the piece of equipment used chronologically: four different Agilent CE have been used by three different operators.

#### CE ESI-MS of oligoacrylates AA3 and AA4

The ESI-MS electropherogram and MS spectra after CE separation are given and discussed in the main text in the case of the oligoacrylate AA2. Similar spectra (with the same experimental

conditions) are obtained in the case of AA3 and AA4 and are given below together with the corresponding MS electropherograms.

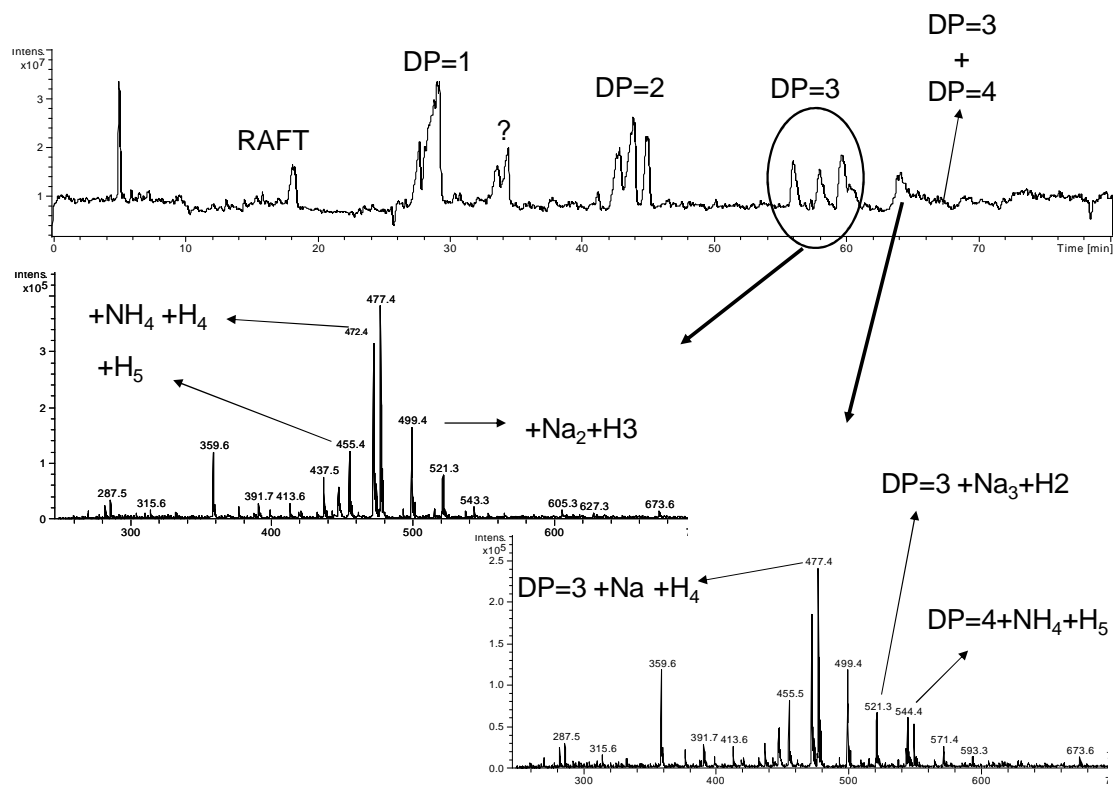
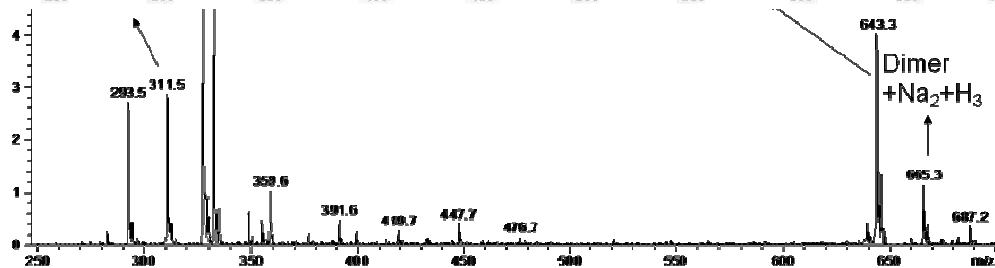
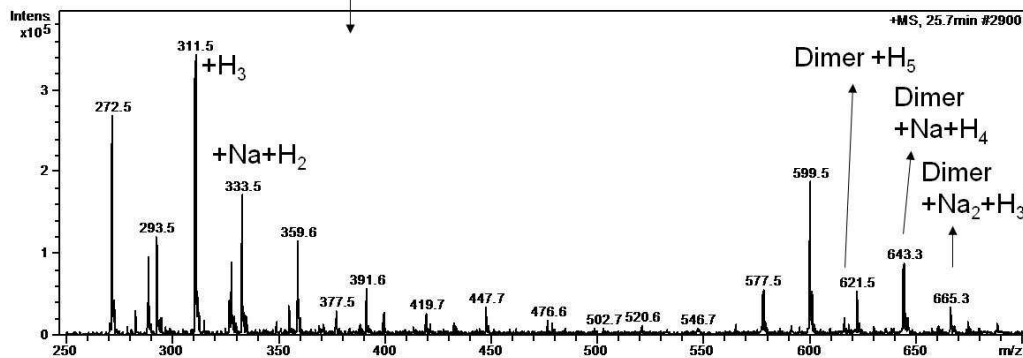
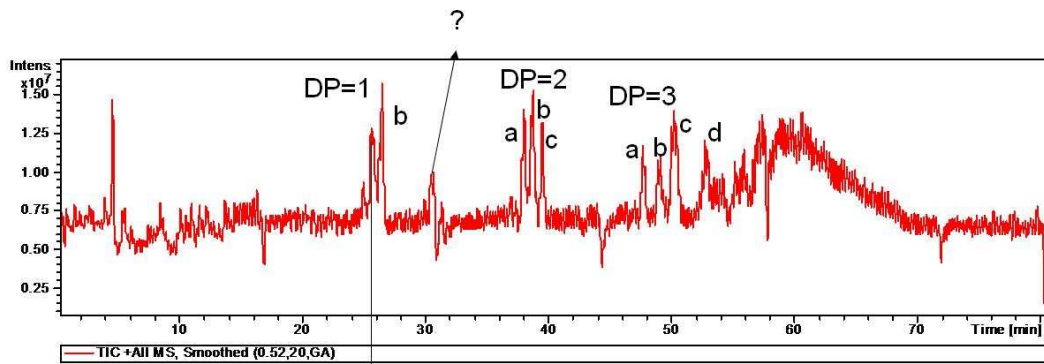
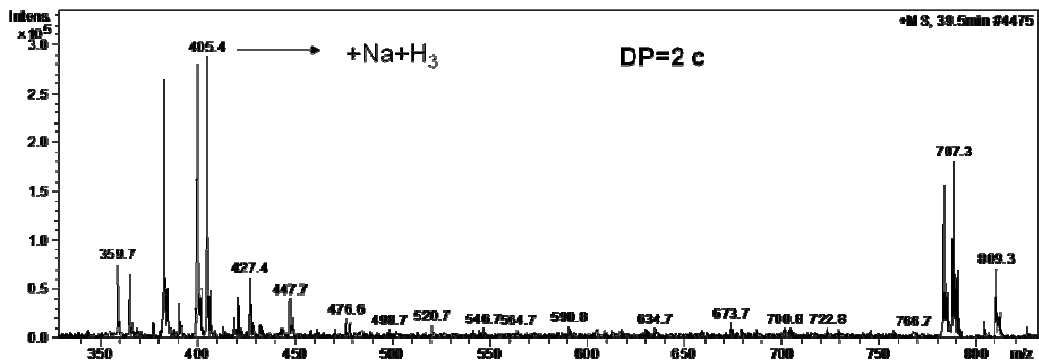
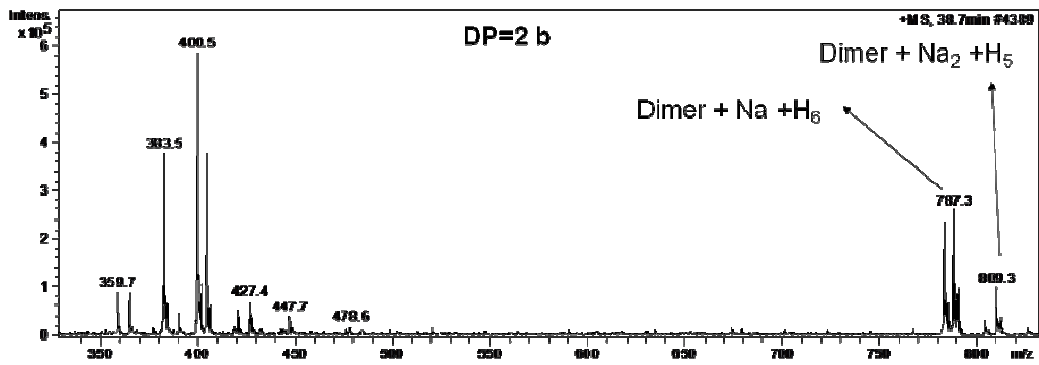
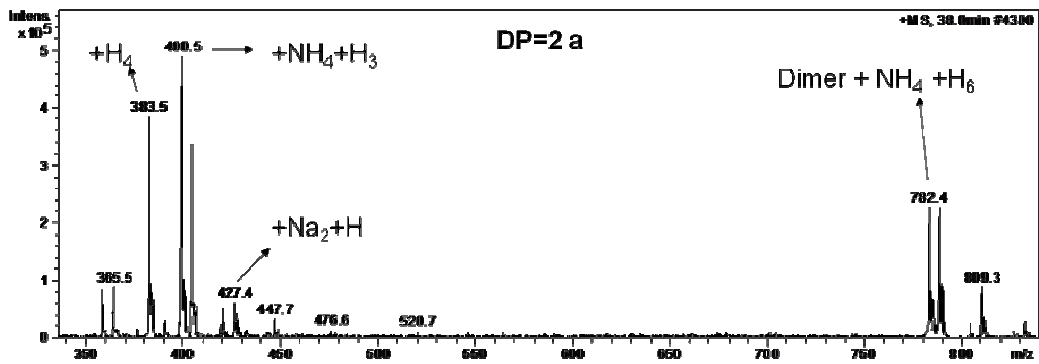


Figure S1: MS electropherogram (top) and some average mass spectra (bottom) for the peaks corresponding to the DP of three (and four) for the sample AA3.





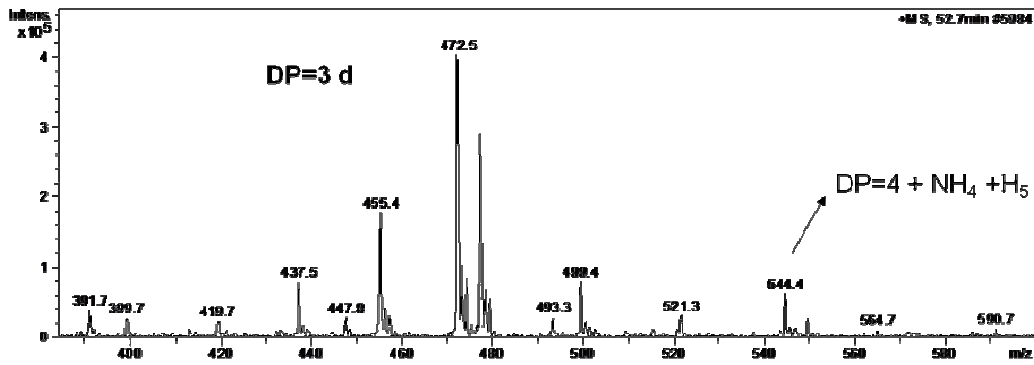
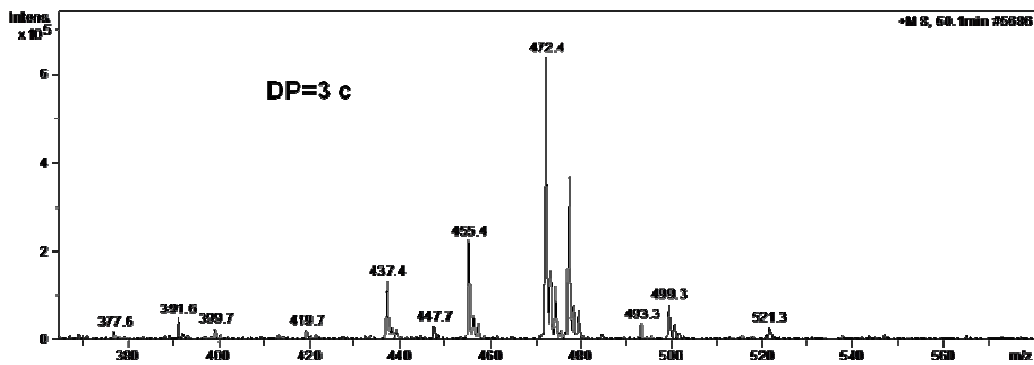
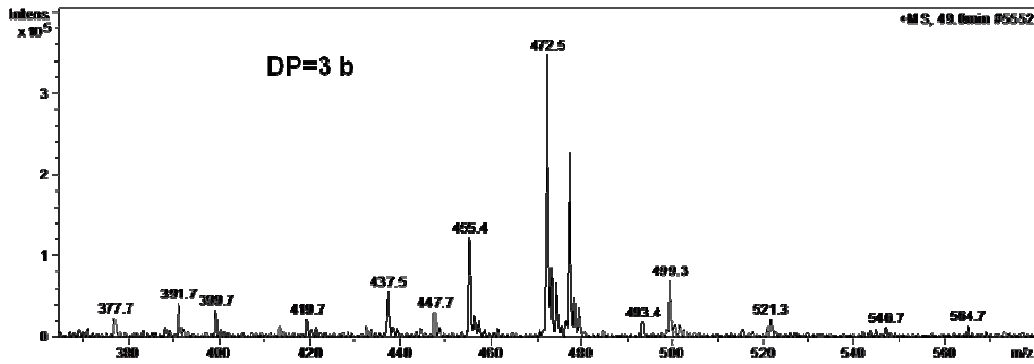
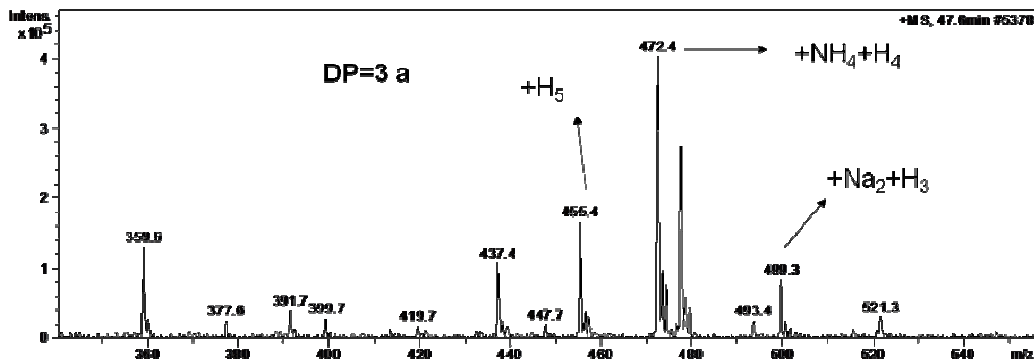




Figure S2: MS electropherogram (top, red line) and some average mass spectra (bottom, black lines) for the peaks corresponding to the DP of 1; 2 and 3 for the sample AA4.

## **<sup>1</sup>H and <sup>13</sup>C solution-state NMR of oligo(acrylic acid)**

Samples AA2, AA4, AA7 and AA15 were dissolved in D<sub>2</sub>O at ca 130, 130, 165 and 160 mg·mL<sup>-1</sup> respectively. NMR spectra were recorded at 25°C on a Bruker Avance spectrometer operating at 500 MHz Larmor frequency for <sup>1</sup>H, using a BBO probe (unless otherwise specified). Quantitative <sup>1</sup>H NMR spectra of samples AA2 and AA4 were recorded using a TXI5z probe, with 20 s relaxation delay and 128 transients. <sup>1</sup>H NMR spectra of samples AA7 and AA15 were recorded with 2 s relaxation delay and 32 transients. <sup>13</sup>C NMR spectra of the 4 samples were recorded with a 45° flip angle, 2 s relaxation delay and 18000 to 33000 transients.

For poly(acrylic acid), the tacticity is determined on <sup>1</sup>H NMR spectra using the CH<sub>2</sub> signal around 1.6-2.1 ppm.<sup>2</sup> For DP higher than two, the signal at ca 1.75 ppm are the CH<sub>2</sub> groups of all acrylic acid units except the one next to the Z end group (see Figure S3). For sample AA2, containing predominantly the oligomer with DP of two, the signal at ca 1.75 ppm originates solely from the CH<sub>2</sub> group between the I end and the next monomer unit. For other oligoAA, with increasing DP, the relative intensity decreases. Thus the exact chemical shifts observed in our sample are 2.28 (m), 2.07 (r) and 1.93 (m) ppm (Figure S4). Note a shift compared to literature values, due to differences in temperature and pH. According to CE (figure 5 of the main text), for an atactic sample of DP 2, the relative proportions of m, r, and m would be 3, 3, 2 or 2, 3, 3. This is in agreement with observed intensities (within experimental error, mostly due to signals not being fully resolved).

Tacticity can also be determined for poly(acrylic acid) on <sup>13</sup>C NMR spectra using the CH and CH<sub>2</sub> signals at ca 44 and 37 ppm respectively.<sup>2</sup> However, in the case of short oligomers, the spectra are too complex to draw any conclusion (see Figures S5 for spectra and Figure S6 for calculated chemical shifts).

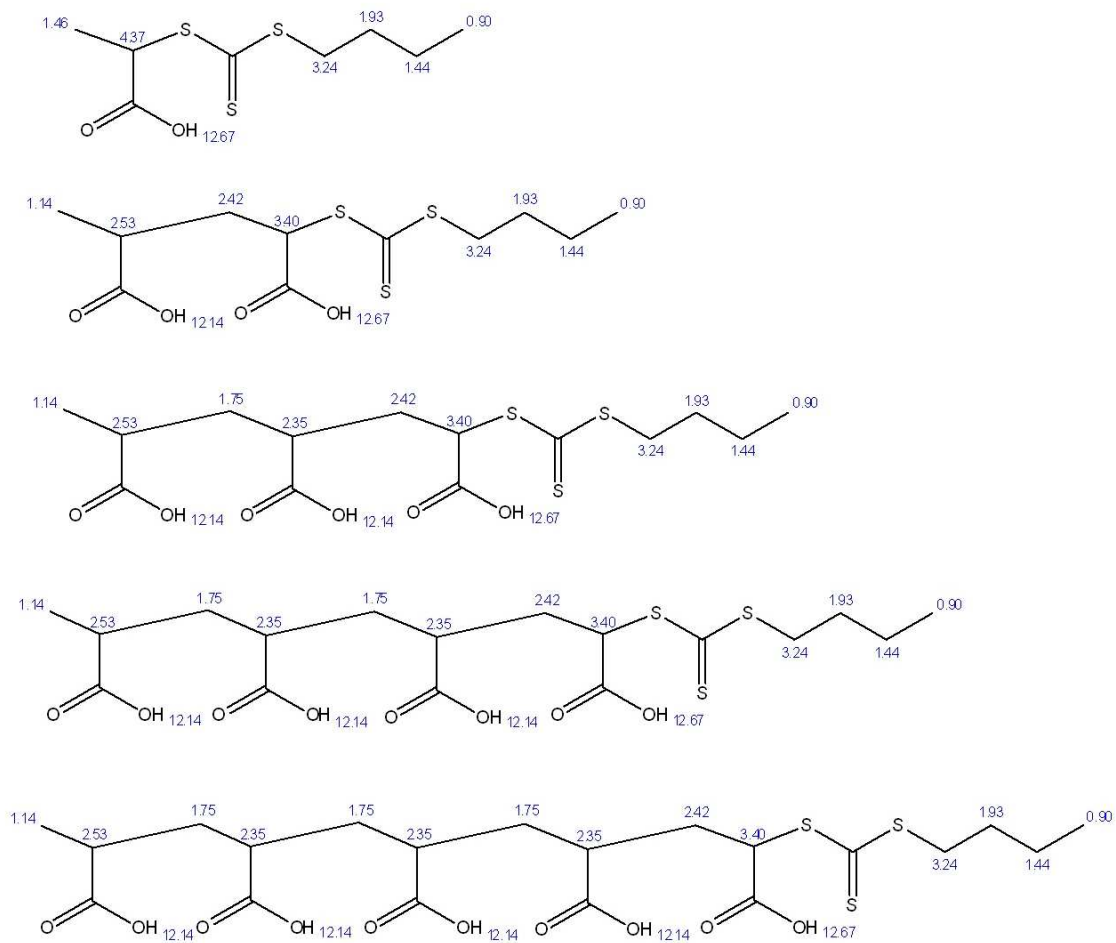


Figure S3: expected  $^1\text{H}$  NMR chemical shifts for short oligo(acrylic acid). Calculations done with the ChemBioDraw Ultra 11.0.1 software (CambridgeSoft Inc.).

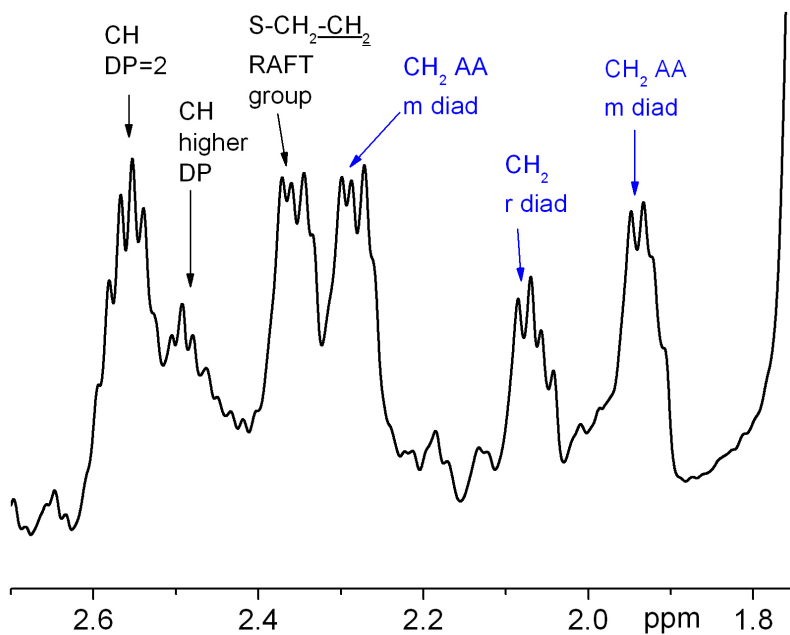


Figure S4: <sup>1</sup>H NMR spectrum of sample AA2, zoom on region of interest for determination of tacticity.

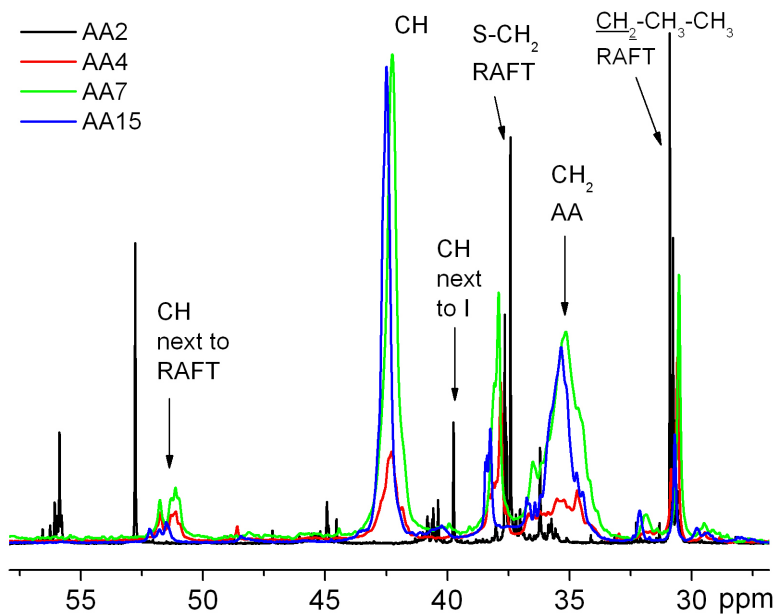


Figure S5: <sup>13</sup>C NMR spectra of samples AA2, AA4, AA7 and AA15, zoom on region of interest for determination of tacticity.

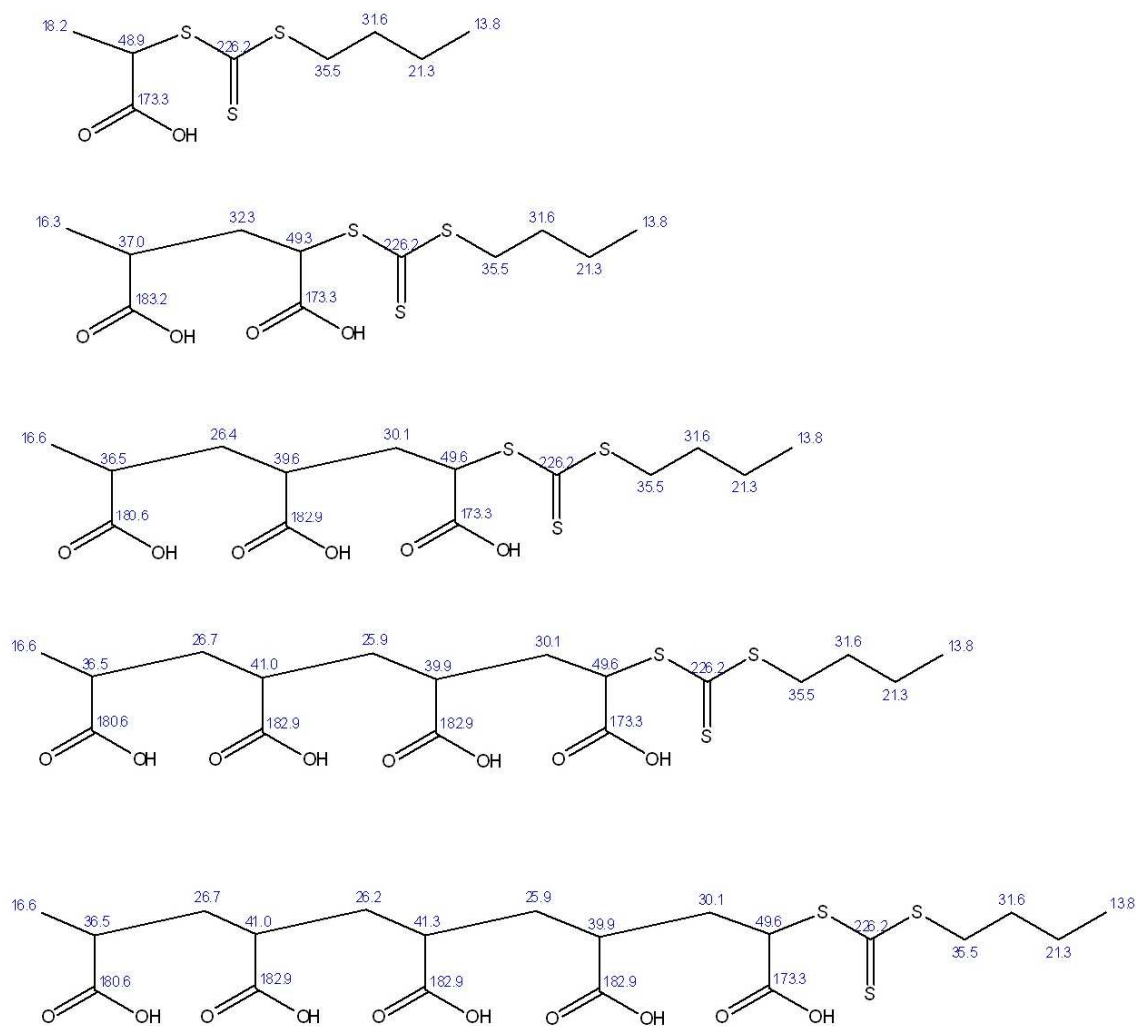


Figure S6: expected  $^{13}\text{C}$  NMR chemical shifts for short oligo(acrylic acid). Calculations done with the ChemBioDraw Ultra 11.0.1 software (CambridgeSoft Inc.).

## CE separation of one oligomethacrylate

Oligo(methacrylic acid) has been synthesized using RAFT and characterized by THF double-detection SEC.<sup>3</sup> CE in the same conditions as oligoacrylates lead to a separation with even more peaks as seen on Figure S7. The attribution on Figure S7 to DP of one (MAA1), two (MAA2), three (MAA3) and four (MAA4) is based on ESI-MS detection using the same instrument and conditions as for the oligoacrylates. The MS electropherogram is shown on Figure S8. The peaks at 10 min correspond to the electro-osmotic flow (EOF). The massif between 15 and 19 min corresponds mainly to the RAFT agent as seen on the MS spectrum displayed on Figure S9. The massif between 26 and 29 min correspond to DP of one (Figure S10). The massif between 35 and 39 min corresponds to DP of two (Figure S11). The numerous following peaks correspond to incompletely resolved peaks corresponding at the same time to some isobars and to increasing DP (Figure S12).

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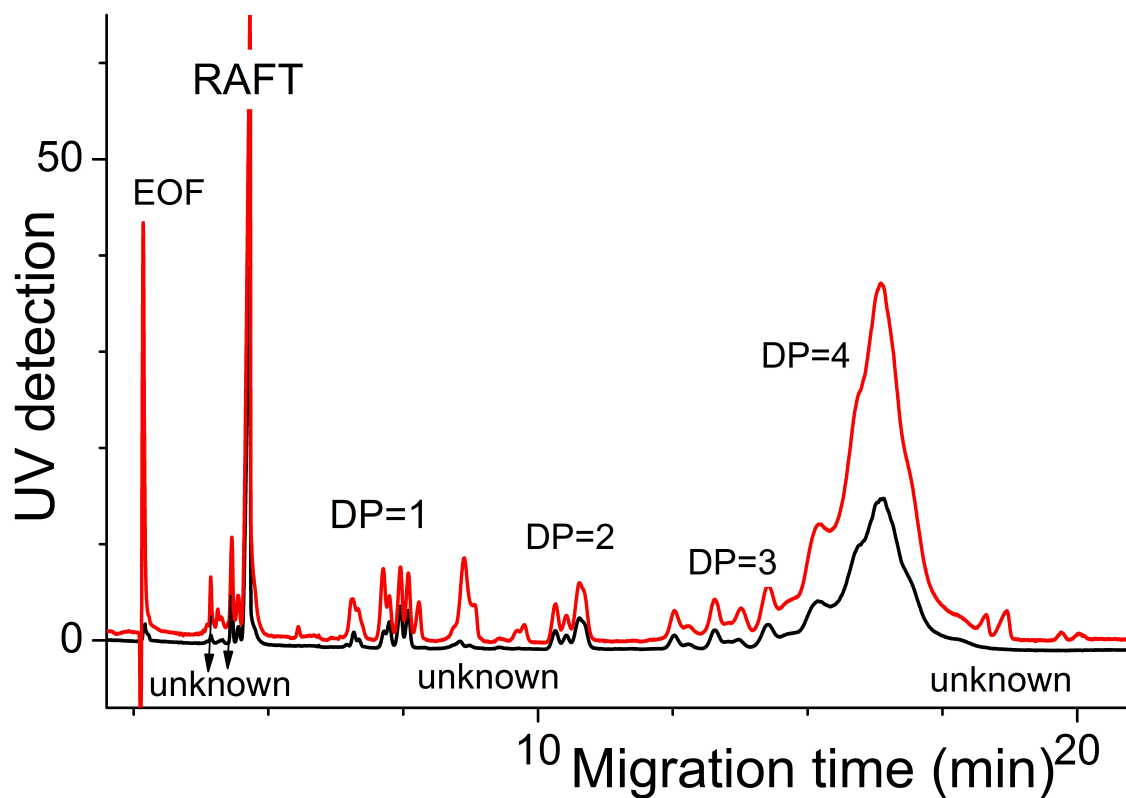
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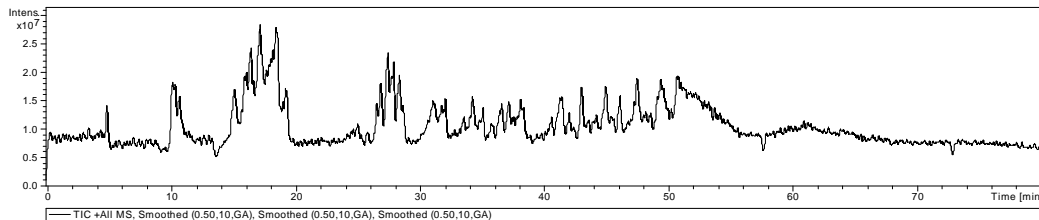
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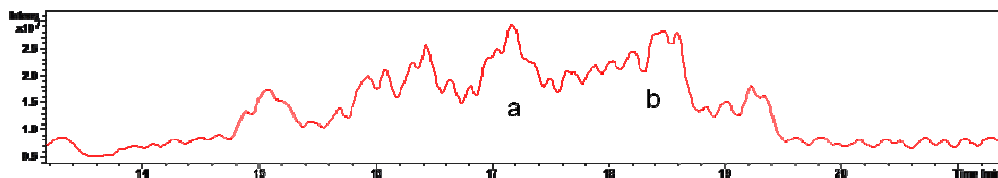
Figure S7: Separation of oligomethacrylate using CE with UV detection at 200 nm (red) and 290 nm (blue).



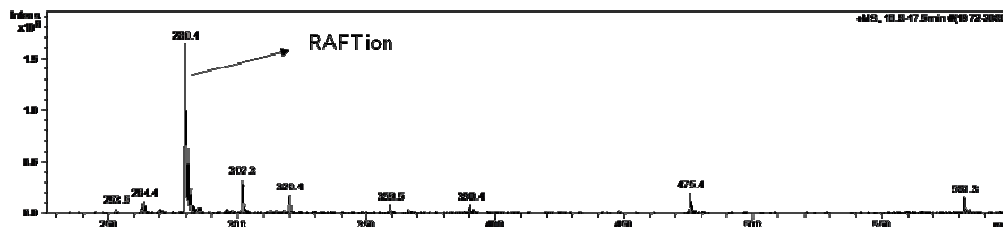
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Figure S8: Separation of oligomethacrylate using CE with ESI-MS detection.

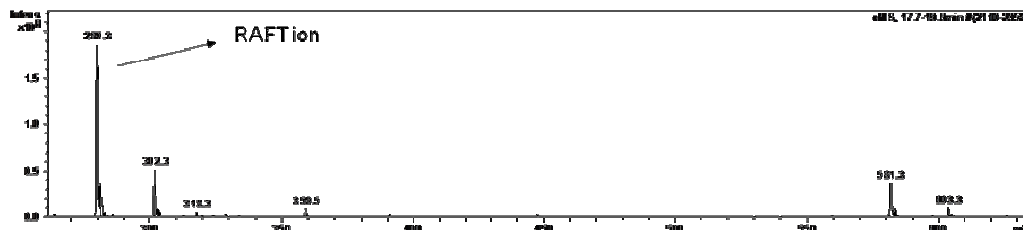
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a average mass spectrum from 16.8 min to 17.5 min



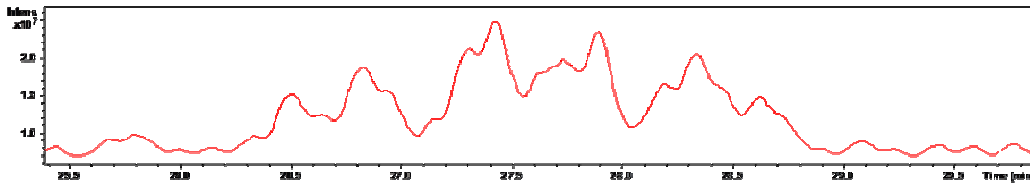
b average mass spectrum from 17.7 min to 19.6 min



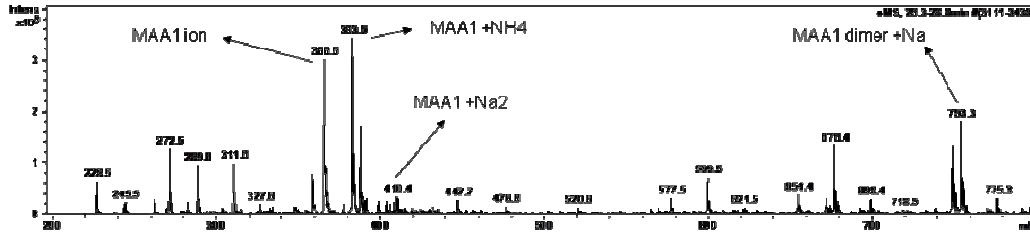
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Figure S9: Zoom on the MS electropherogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectra (middle and bottom, a and b)

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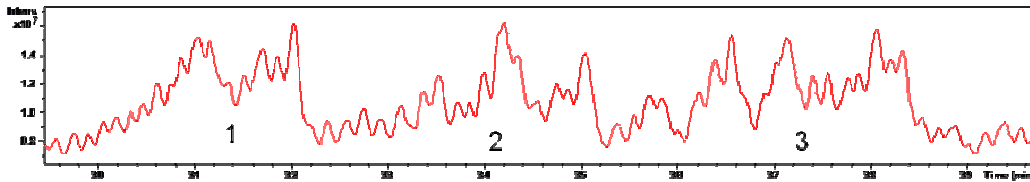
average mass spectrum from 26.3 min to 28.8 min



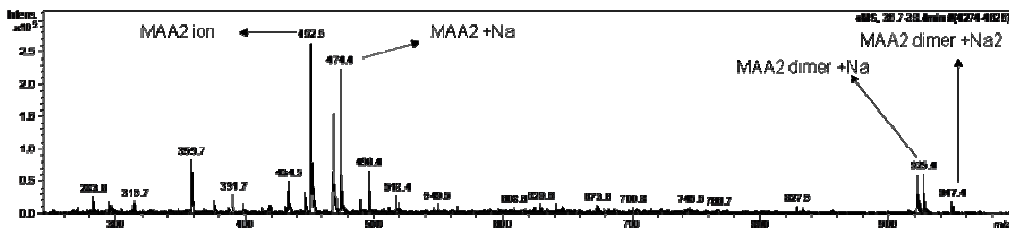
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Figure S10: Zoom on the MS chromatogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectrum (bottom)



3 average mass spectrum from 35.7 min to 38.4 min

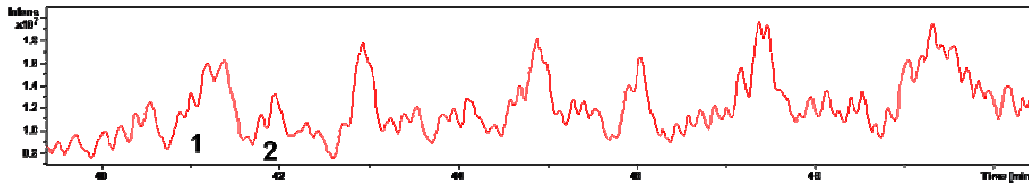


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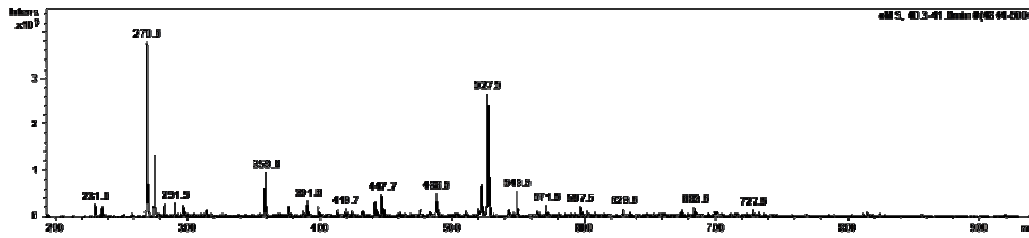
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Figure S11: Zoom on the MS chromatogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectrum (bottom)

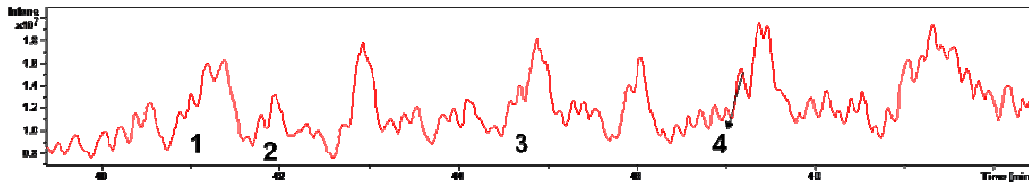
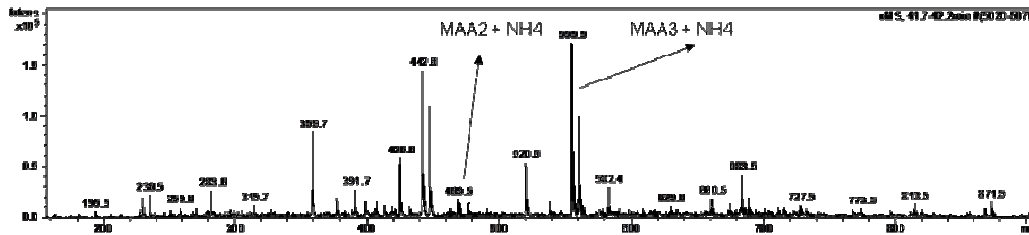




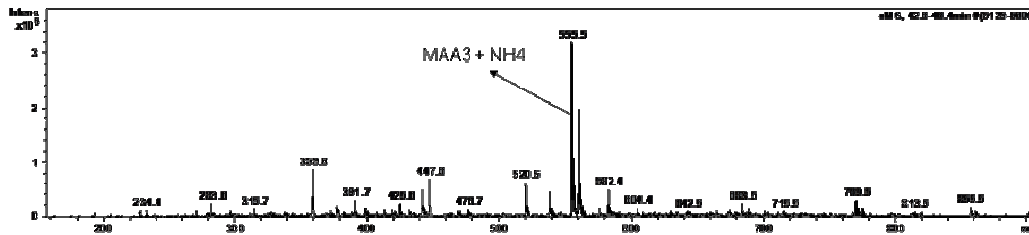
1 average mass spectrum from 40.3 min to 41.6 min



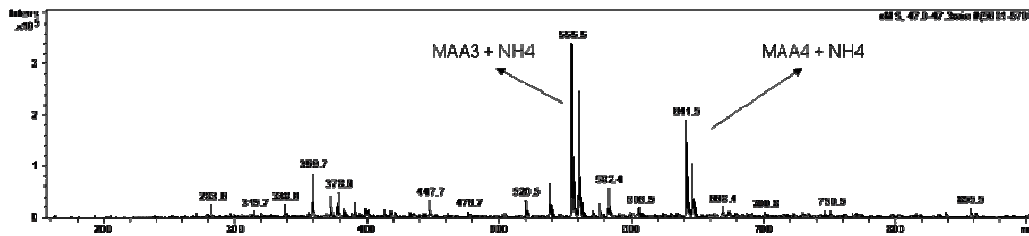
2 average mass spectrum from 41.7 min to 42.2 min

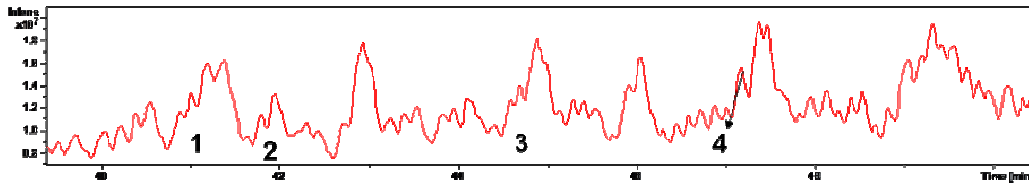


3 average mass spectrum from 42.6 min to 46.4 min

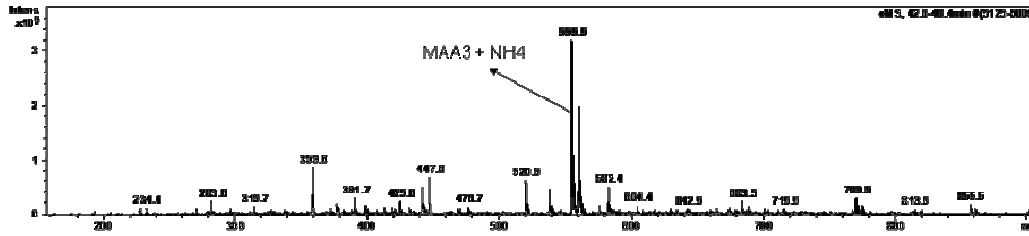


4 average mass spectrum from 47.0 min to 47.3 min

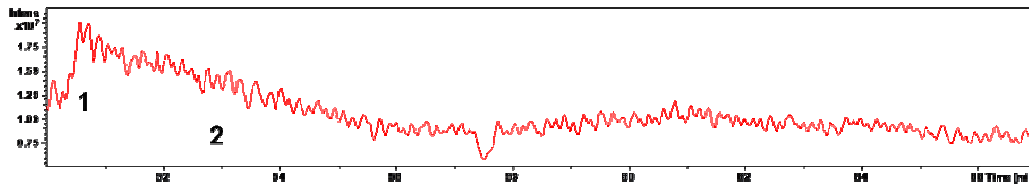
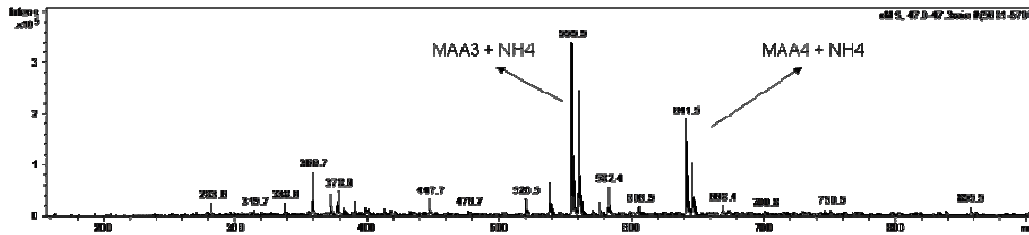




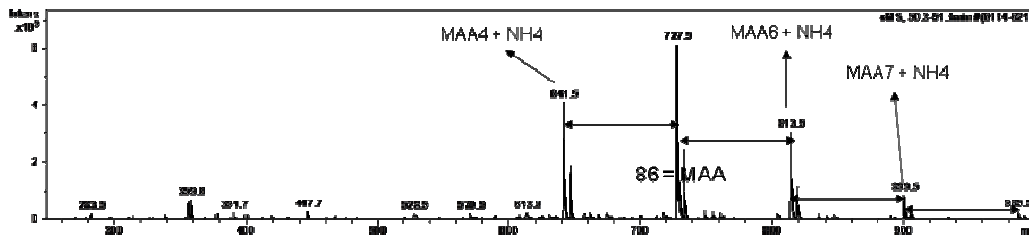
3 average mass spectrum from 42.6 min to 46.4 min



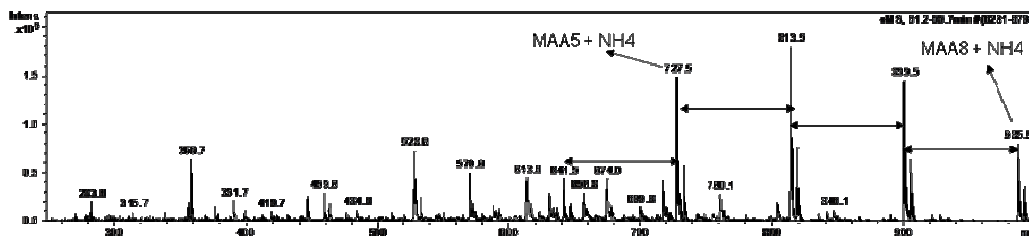
4 average mass spectrum from 47.0 min to 47.3 min

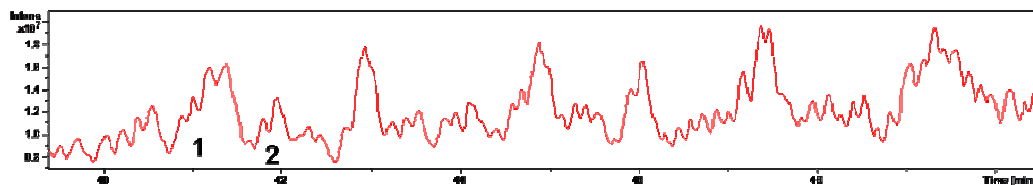


1 average mass spectrum from 50.3 min to 51.1 min

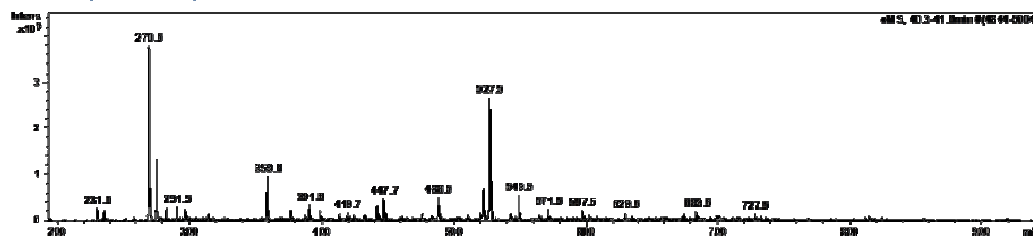


2 average mass spectrum from 51.2 min to 55.7 min





1 average mass spectrum from 40.3 min to 41.6 min



2 average mass spectrum from 41.7 min to 42.2 min

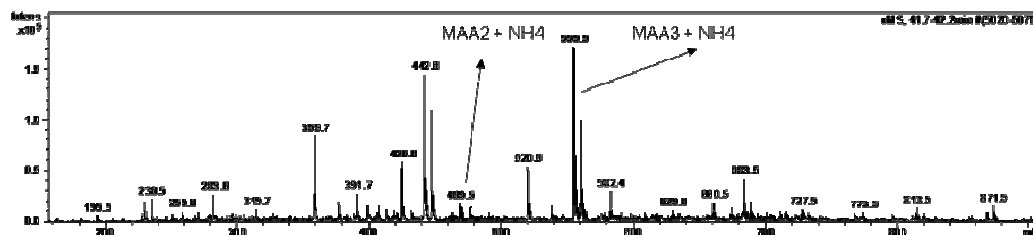


Figure S12: Zooms on the MS chromatogram corresponding to figure S7 (red lines) and corresponding ESI-MS spectra (corresponding black line below each zoom)

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[1] Castignolles P, Gaborieau M, Hilder E, Sprong E, Ferguson CJ, Gilbert RG. First separation of oligo(acrylic acid) by capillary electrophoresis. *Macromolecular Rapid Communications*. **2006**, 27, 42-6.

[2] Spevacek J, Suchoparek M, Al-Alawi S. Characterization of the stereochemical structure of poly(acrylic acid) by one-dimensional and 2-dimensional C-13-H-1 nuclear-magnetic-resonance spectra. *Polymer*. **1995**, 36(21), 4125-30.

[3] Hosseini Nejad E, Castignolles P, Gilbert RG, Guillaneuf Y. Synthesis of methacrylate derivatives oligomers by dithiobenzoate-RAFT-mediated polymerization. *J Polym Sci Polym Chem*. **2008**, 46(6), 2277-89.