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

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Abstract

Oligo(acrylic acid) efficiently stabilizes polymeric particles, especially particles produced by RAFT (as hydrophilic block of an amphiphilic copolymer). Capillary electrophoresis (CE) has a far higher resolution power to separate these oligomers than the commonly used size-exclusion chromatography (SEC). Coupling CE to electrospray ionization mass spectrometric (ESI-MS) detection unravels the separation mechanism. CE separates these oligomers not only according to their degree of polymerisation, but also according to their tacticity in agreement with NMR. This will bring insight into the role of these oligomers as stabilizers in emulsion polymerisation and to the mechanism of the RAFT polymerisation with respect to degree of polymerisation and tacticity.

Keywords:

Acrylics, Methacrylics, Oligomers, Tacticity, Molecular Weight, Separation, Capillary Electrophoresis, Mass Spectrometry

Introduction

Hydrophilic polymers are a key material in an increasing number of applications from the paint and coating industry to medicine or fuel-cell membranes. Charged polymers, polyelectrolytes, have a fascinating ability to interact with their environment. Short polyelectrolyte chains, oligoelectrolytes, are used to stabilize emulsions^[1] and play a key role in paint and coating,^[2-4] controlled mineralization^[5-7] and other applications^[8]. This article proposes new and advanced characterization of these oligoelectrolytes.

Polymer science relies heavily on size exclusion chromatography (SEC, also known as gel permeation chromatography, GPC) for separation and characterization. SEC is highly repeatable, widely available and detection is continuously improving.^[9-10] However, SEC usually relies on calibration,

which may induce artefacts^[11] and relies on the validity of Mark-Houwink-Sakurada parameters.^[12-13] Light scattering detection can lead to other types of artifacts related to signal-to-noise ratios.^[14] Band broadening is also significant,^[15-16] the size-exclusion mechanism leading to universal calibration^[17-18] may not be dominant and anomalous elution can occur.^[19] Even when universal calibration is valid, separation in terms of molecular weights can be incomplete, e.g. in the case of branched polymers.^[13, 20-21] Due to these different factors, SEC suffers generally from poor reproducibility, especially for aqueous SEC.^[22-24] In the case of poly(acrylic acid), there is an additional controversy arising from significantly different molecular weights determined by aqueous SEC and organic SEC.^[25] In the case of natural polymers, ion-pair liquid chromatography is used as well as SEC.^[26] The aim of this work was thus to investigate complementary separation methods to characterize oligoelectrolytes, especially the challenging oligoacrylates.

Capillary electrophoresis (CE) is one of the methods of choice for separation of some natural polymers, such as DNA and proteins.^[27] Its application to synthetic polymers has been successful, but is currently limited, especially in its simplest mode, free solution CE.^[28] Separation of synthetic oligoelectrolytes has been demonstrated in the case of oligo(styrene sulfonate)^[29-30] and oligo(*N*-phenylaniline)^[31] by the group of Cottet, in the case of oligoacrylates by ourselves^[32] and in the case of oligoguanidines^[33]. The latter compares ion-pair liquid chromatography and CE, while we compared SEC and CE. As would be expected, the resolution of CE is higher than that of SEC, but the mechanism of separation is complex: charge, and hydrodynamic as well as electrostatic interactions each play a role.^[34] No direct determination of molecular weights after CE separation of oligoelectrolytes has ever been performed. In this current study we used electrospray ionization mass spectrometric (ESI-MS) detection to understand the high quality separation we previously communicated on oligoacrylates.^[32] The aim of this paper is first to reveal the separation mechanism. This then allows us to discuss the potential of CE for the determination of molecular weights and also tacticity of oligoacrylates. We then discuss the potential of the method to study stability of emulsions, RAFT polymerisation etc.

Results

The oligoacrylates were characterized by CE, but also by direct infusion ESI-MS. The samples are named AA x for oligo(Acrylic Acid), whose directly infused ESI-MS spectrum exhibit a maximum at a degree of polymerisation of x . Separation of the samples AA2, AA5 and AA7, also studied here, were previously presented using CE with borate buffers. Non-volatile buffer salts such as borate are not compatible with online ESI-MS and thus ammonium acetate has been used as an alternative buffer system in this work. Using buffers based on ammonium acetate leads to the same separation selectivity with equivalent resolution as the borate buffers (data not shown). Injection of RAFT agent separately allowed us to identify the peak corresponding to the remaining RAFT agent in the oligoacrylates as well as the degree of polymerisation (DP) of one.^[32] This separation was obtained using borate buffers; the same interpretation is valid in ammonium acetate as shown in Figure 1 using UV detection. Coupling with ESI-MS has then been used to further identify the peaks.

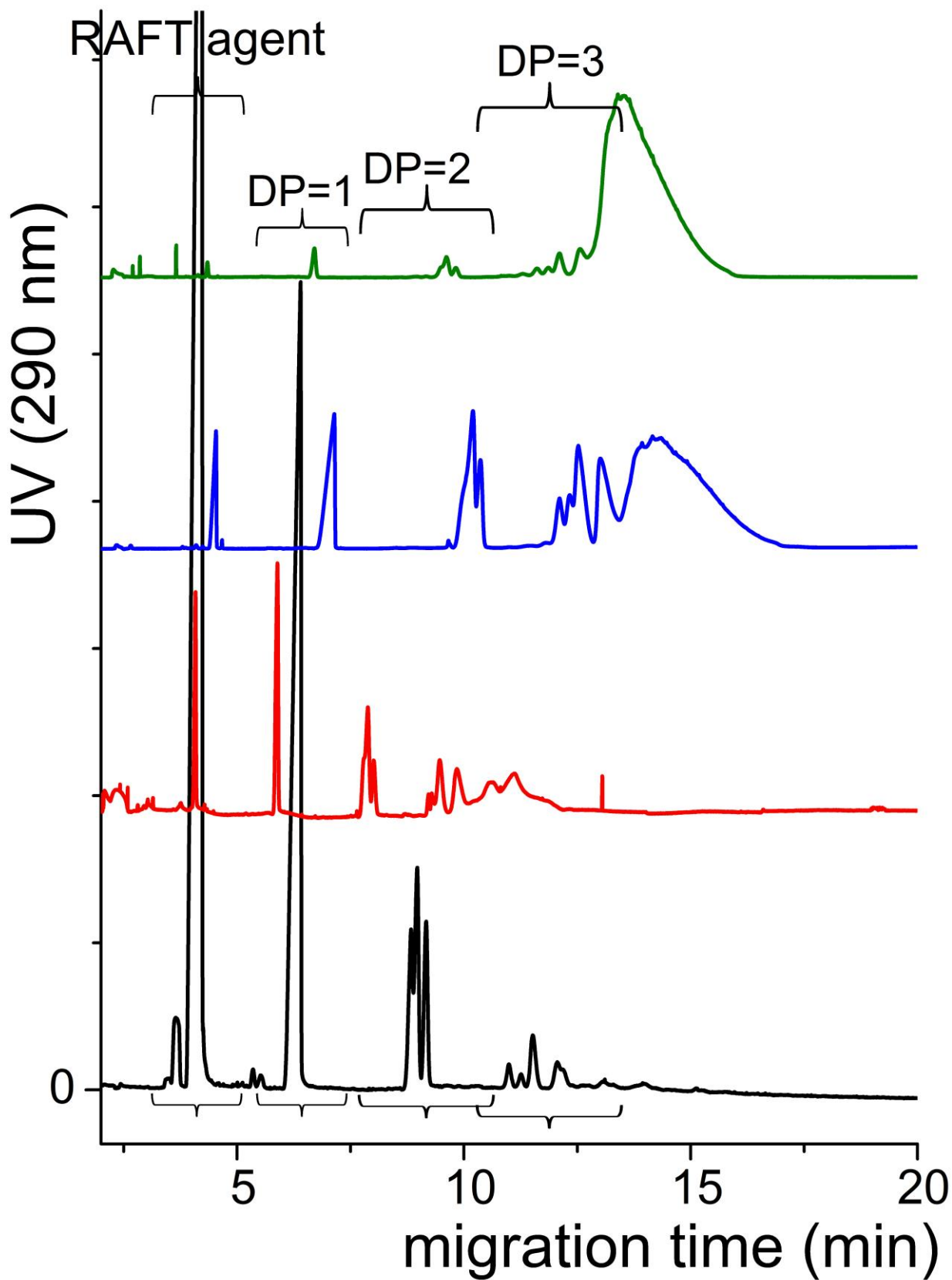


Figure 1: Separation by capillary electrophoresis (fused silica capillary, 40 cm total length and 31.5 cm effective length) in ammonium acetate buffer (150 mM) of (from bottom to top) AA2 (black), AA3 (red), AA4 (blue) and AA7 (green); the electropherograms have been normalised according to the total

area and then translated vertically to allow visual comparison. Detection is by UV at 290 nm (absorption by the RAFT moiety^[32]).

Figure 2 shows the MS response (total ion count) obtained after CE separation in ammonium acetate for AA2. It is qualitatively similar to the electropherogram obtained using UV detection, but the relative intensities are different. This is not unexpected since the intensity for the MS detection is biased due to differences in ionization efficiency for each species. ESI-MS is used for identification in this case by considering the MS spectrum corresponding to each peak, while quantification is performed using the UV response (see discussion). Using this approach, the first peak was confirmed by the ESI-MS spectrum to correspond to the RAFT agent (Figure 2, top insert). The second peak is identified as degree of polymerisation of one (Figure 2, bottom insert). Then three peaks migrate closely. Their ESI-MS spectra are very similar and reveal that they correspond to molecules which have the same molecular weights (Figure 3) and correspond to a degree of polymerisation of two. Then a large number of peaks are not completely resolved. In the case of sample AA2 (and not AA3 and above), this large number of peaks however, correspond to only four peaks, which are resolved. Again these four peaks correspond to isobaric molecules (Figure 4) corresponding to a degree of polymerisation of three. The same identification is obtained with the other oligoacrylate samples (see Supporting Information Figure S1 and S2 for samples AA3 and AA4 respectively). The large number of separated species compared to SEC is explained by the ability of CE to separate isomers in the oligoacrylates, due to the superior resolution that can be achieved with this technique.

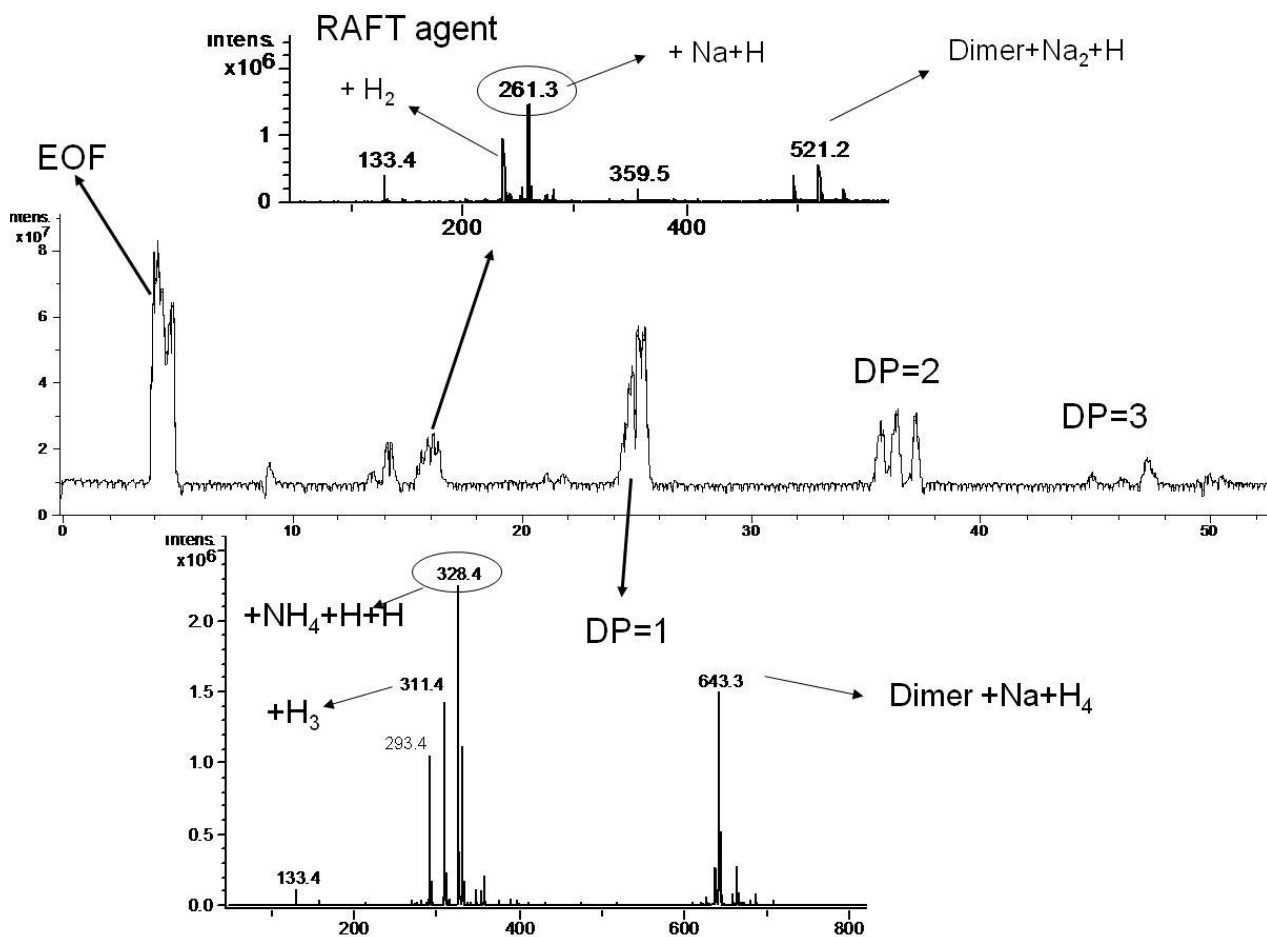


Figure 2: CE-MS electropherogram and corresponding mass spectra summed across each peak for the peaks corresponding to the RAFT agent and DP of one; sample AA2 is injected here electrokinetically (15 kV, 20 s) at 10 g·L⁻¹ and the capillary is 90 cm long, the buffer is ammonium acetate, 150 mM. More details on the 3 peaks corresponding to DP of two are given in Figure 3.

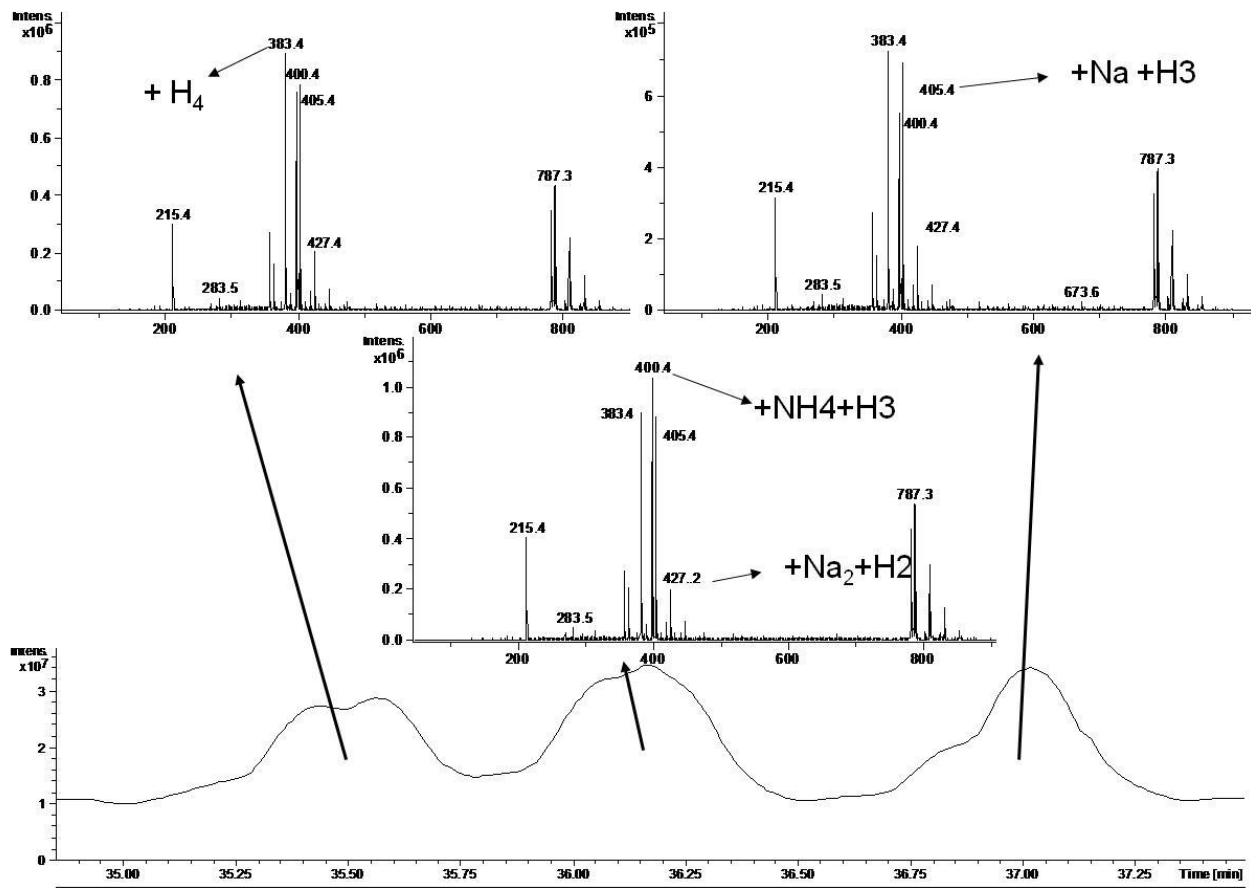


Figure 3: Zoom section from 34.85 to 37.5 min of the CE-MS electropherogram shown in Figure 2 (DP of two) and corresponding ESI-MS spectra.

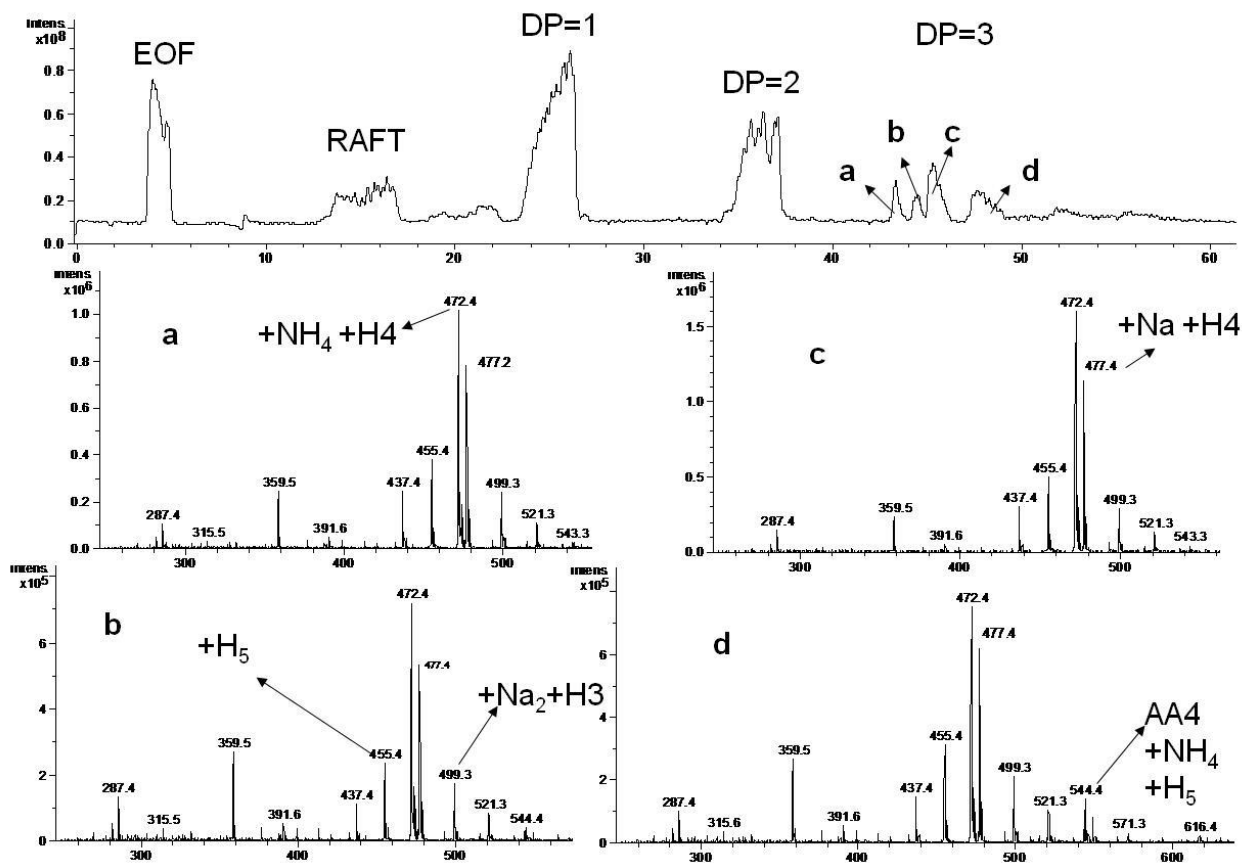


Figure 4 : CE-MS electropherogram (top) for the sample AA2 injected in the same conditions as in Figure 2, but at double concentration ($20 \text{ g}\cdot\text{L}^{-1}$) and the four ESI-MS spectra corresponding to DP of 3 (bottom).

Discussion

We will first discuss the nature of the isobaric molecules. There are two possible explanations for isobaric polymers (or oligomers): branching or tacticity. Branching has been observed in poly(acrylic acid) obtained by RAFT polymerisation.^[35-36] Branching is, however, not consistent with our separations. The isobaric peaks have similar UV intensities and the degree of branching will thus correspond to at least 50% of the chains being branched. This is not consistent with the few % of branched monomer units detected by NMR. Furthermore, branching is obtained by a transfer to polymer mechanism, predominantly through backbiting.^[37] The backbiting proceeds through a 6-member ring

formation, thus it cannot happen for degree of polymerisation below three. The isobaric peaks correspond to degree of polymerisation two and three and can definitely not be attributed to branching.

Tacticity

The number of possible isomers due to tacticity can be calculated. They are three for degree of polymerisation of one (Figure 5) and four for degree of polymerisation of two (Figure 6). Note that each type of tacticity corresponds to two different diastereoisomers. The numbers of separated peaks by CE is three for the DP of one and four for the DP of two (Figure 1 to 4) and thus is completely consistent with separation according to tacticity. There is no separation of the diastereoisomers, although the presence of shoulders on each peak of Figure 3 may be attributed to the two diastereoisomers corresponding to each peak.

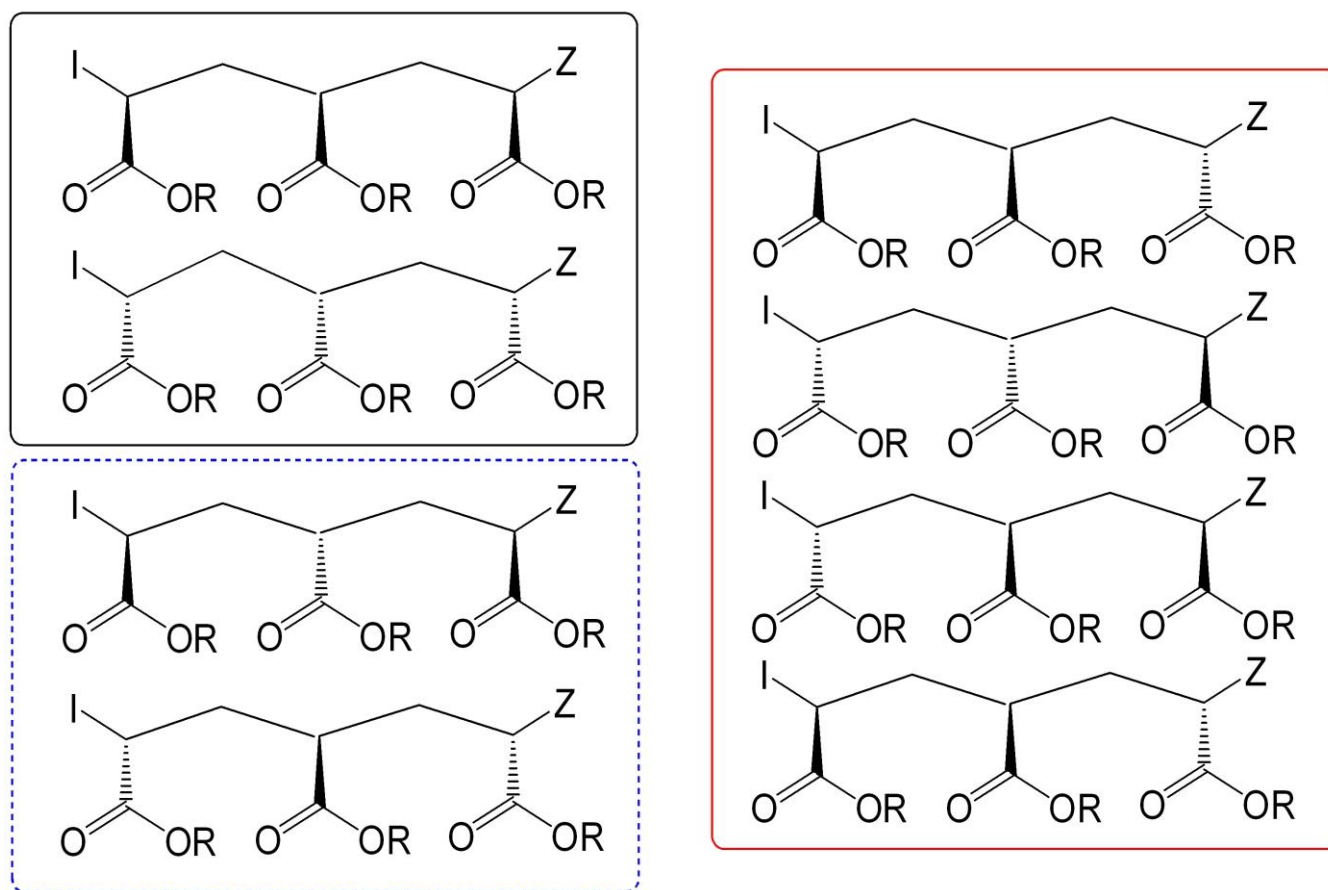


Figure 5: The three possible tacticities corresponding to a DP of two: isotactic (top left black full), syndiotactic (bottom left blue dashed), atactic (right red full). *R* is ammonium or another counter-ion, *I*

the initiating species and Z the Z -group of the RAFT agent. Note that the DP of two have three carboxylate group: two from monomer units and one arising from the RAFT agent.

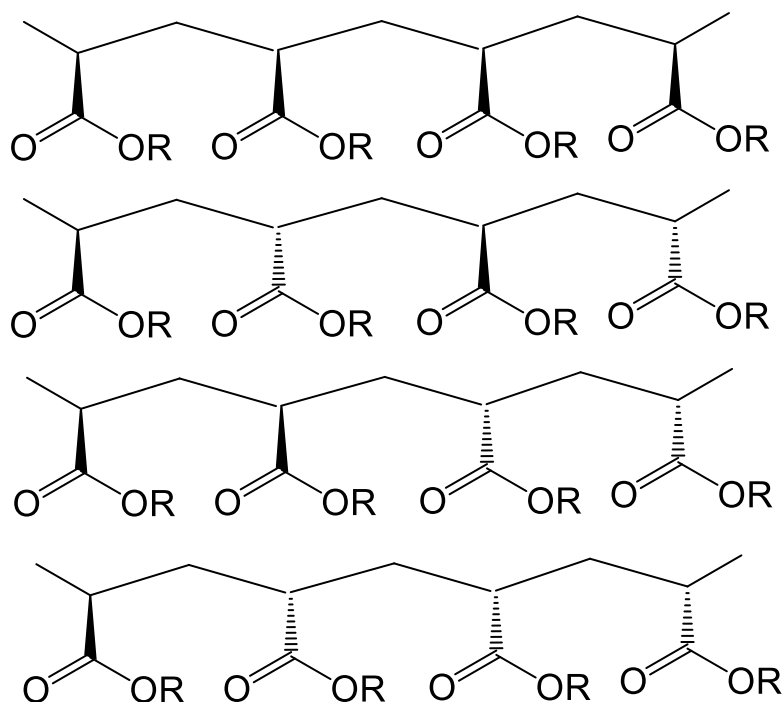


Figure 6: The four possible tacticities corresponding to a DP of three, from top to bottom: isotactic, syndiotactic, atactic1, atactic2 (for sake of simplicity, only one of the two possibilities is drawn each time contrary to Figure 5).

The number of isomers of different tacticities increase dramatically with the DP.^[38] This explains the very large number of peaks obtained for the largest oligomers. Further identification of the isobaric peaks would consist of identifying the isotactic, syndiotactic and various atactic species. This is not possible from the UV or ESI-MS detection or from the knowledge of the separation mechanism at this stage, but it is also not possible using other techniques such as liquid chromatography (LC)^[39]. In order to identify which peak corresponds to isotactic, which one to syndiotactic etc., one will need either to synthesize model compounds or to simulate differences in hydrodynamic behaviour of the tacticity

isomers, which is out of the scope of this work. At the simplest level, the quantification of the three peaks corresponding to a DP of two have different intensities of around 25, 50 and 25% (quantified using UV detection) as shown in Table 1. Note that an overall atactic oligomer mixture would contain 25% of each of the isotactic and syndiotactic and 50% of the atactic (see Figure 5). Poly(acrylic acid) synthesized by radical polymerisation was determined by NMR to be atactic.^[40-41] For our short oligomers, the presence of significant chain end signals complicates the spectrum and the tacticity quantification (see supporting information, Figure S3 to S6). The spectrum of AA2 is in qualitative agreement with atactic oligomers of DP 2. Both ¹H and ¹³C NMR spectra of all other oligomers are too complex to draw further conclusions on tacticity.

| Sample | First peak DP 2 (mol%) | Second peak DP 2 (mol%) | Third peak DP 2 (mol%) | Buffer |
|---------------|-------------------------------|--------------------------------|-------------------------------|---------------|
| AA5 | 25.6 | 50.7 | 23.7 | NB400 |
| AA5 | 24.6 | 51.2 | 24.3 | LB200 |
| AA7 | 26.6 | 49.1 | 24.2 | KB200 |

Table 1: Relative areas of the three peaks observed in CE with UV detection at 290 nm corresponding to degree of polymerisation (DP) of two in different samples and different buffer (NB is sodium borate, LB is lithium borate and KB is potassium borate; the numbers correspond to the buffer concentration in mM).

Tacticity of polymers is extensively studied, however nearly exclusively through an average value determined using NMR.^[40] Polyolefins are the most studied, and separation according to their tacticity has been recently obtained using liquid adsorption chromatography^[42] and is more commonly achieved by TREF^[43] or CRYSTAF^[44]. Separation of methacrylics has been obtained using LC at the critical conditions.^[45] Oligomers of styrenics have also received some attention. Using LC it is possible to study variation of their tacticity with molecular weight.^[38-39, 46] In the case of poly(acrylic acid), continuous fractionation has been hypothesized to be influenced by the tacticity and not to be only by molecular weight.^[47] However, since then, branching has been detected in poly(acrylic acid) using

NMR^[35-36] and long-chain branching has been detected in poly(alkyl acrylates)^[13], with branching likely to explain the continuous fraction better than tacticity. Separation according to tacticity has not been performed for hydrophilic polymers before this work. However, tacticity can drastically change the solubility of a small molecule (e.g. a drug) in a polymer (e.g. for drug delivery)^[48] and has a considerable effect on the glass transition of poly(acrylic acid).^[49] The role of tacticity in stabilization of emulsion by oligoacrylates is not known. Note that oligoacrylates also act as transfer agent during emulsion polymerisation.^[50] Thus, oligomethacrylates have also been synthesized to act as stabilizers in RAFT in emulsion process.^[51] The conditions used for separation of oligoacrylates lead also to very high resolution using CE. These preliminary results are presented in supporting information (Figure S7 to S12), but were not investigated further. They show that the oligomethacrylates exhibit an even higher complexity than the oligoacrylates. This may be ascribed to a stronger influence of isomeric structure in methacrylics and acrylics, i.e. separation of all diastereoisomers. However, this may also be attributed to the known instability of the RAFT-moiety end-groups chosen in that case.^[51] Clearly from this work CE has a strong potential to study oligomethacrylates, e.g. produced by RAFT, but the latter synthesis require a more stable RAFT agent or end-group removal prior to analyses.

Potential application to RAFT polymerisation

The oligomers are obtained by the RAFT process.^[52-53] This controlled radical polymerisation technique is based on a two-step addition-fragmentation mechanism using thiocarbonylthio compounds as transfer agents, although the precise mechanism is still under debate.^[54-55] For instance, Klumperman *et al.*^[56-59] have investigated the early polymerisation behaviour of several RAFT-mediated polymerisations. The period during which the initial RAFT agent was consumed was termed initialization, and different reaction behaviour was observed before and after this period. While NMR is used by the Stellenbosh group^[57] for real-time monitoring of the quantities, CE allows a fast off-line determination of these quantities in the case of the RAFT polymerisation of acrylic acid. The molar fraction of RAFT agent and DP one and two have been determined in the different oligoacrylates using CE with UV detection. Average values and their standard deviations are given in Table 2. The complete

list of results is given in supporting information (Table S1). This quantification yields similar results in twelve different buffer compositions, varying the nature of the buffer (ammonium acetate, but also lithium borate, sodium borate and potassium borate, with or without additional 10 wt% methanol) and buffer concentration (40 to 1000 mM). Different capillaries have also been successfully used, on four different piece of equipment by three different operators confirming the good reproducibility of the results. These results are also consistent with SEC using tetrahydrofuran with 0.1 wt% trifluoroacetic acid as eluents and refractive index detection. Note that SEC can only quantify the RAFT agent (DP of one is not resolved in the case of SEC). SEC yields a weight fraction and the quantity contains a systematic error due to likely difference of specific refractive index increment (dn/dc) between the RAFT agent and poly(acrylic acid) and within oligo(acrylic acid)s depending on their degree of polymerisation.^[60] Direct infusion by ESI-MS yielded well resolved and easy-to-interpret spectra. However, quantification is completely inaccurate using direct infusion ESI-MS (see AA2 in table 2). This is expected^[61] and likely due to a significantly weaker ionization of the RAFT Z-group compared to the propanoic acid monomer unit. Analysis of formation pathways and end-group patterns in polymerisation of acrylic acid proved valuable using direct infusion ESI-MS ^[62] and it can now be done in a quantitative way using our CE methods with UV detection. Quantification is performed using UV detection and not ESI-MS because of discrimination as already detailed by the group of Barner-Kowollik in the case of coupling of SEC to ESI-MS.^[61, 63]

| Sample | RAFT | | DP of 1 | | DP of 2 | | Method |
|--------|-------|-------------|--------------|-------------|---------|-------------|--------|
| | mol% | std dev (%) | mol% | std dev (%) | mol% | std dev (%) | |
| AA2 | 53.5 | 5.6 | 28.1 | 2.4 | 9.4 | 4.2 | CE |
| | 2 | - | 8 | - | 9 | - | ESI-MS |
| AA3 | 15.1 | 2.5 | 20.3 | 3.4 | 18.2 | 2.0 | CE |
| AA5 | 9.0 | 0.4 | 14.2 | 0.4 | 15.4 | 0.4 | CE |
| | 13 wt | - | not resolved | | | | SEC |
| AA7 | 0.5 | 0.1 | 1.5 | 0.2 | 2.3 | - | CE |

| | | | | | | | |
|------|-----|---|-----|---|--------------|---|--------|
| AA15 | 0.0 | - | 0.2 | - | not resolved | | CE |
| | 0.0 | - | 0.0 | - | 0.0 | - | ESI-MS |

Table 2: Quantification of the fraction of RAFT agent, DP of A and DP of 2 using CE with UV

detection at 290 nm or THF/TFA SEC using differential refractive index detection or direct infusion in ESI-MS.

The results presented in Table 2 show that in this system there is no selective initialization since non-negligible amounts of RAFT agent remained whereas the polymer conversion is important (> 50%). Nevertheless, the comparison of these data and especially the result for AA2 and the one obtained by Klumperman *et al.* on methyl acrylate^[56] is difficult since two phenomena could explain this result. First, the alkyl leaving group of the RAFT agent is the 1-carboxyethyl radical which mimics the polymer chain and therefore has a close radical reactivity and is less prone to initialization process. Second, since very short chains are targeted in our study, that is with a very different $[\text{monomer}]_0/[\text{RAFT agent ratio}]_0$, the synthesis of such short oligomers could unveil unusual behaviours as we already observed during the RAFT polymerisation of methacrylic acid.^[51]

Conclusions

We have presented a simple method to separate oligoacrylates (salt of oligo(acrylic acid)) with a far higher resolution than SEC using free solution capillary electrophoresis.^[32] Using online ESI-MS detection, we can explain why such a high resolution is obtained. Free solution CE separates not only according to the degree of polymerisation, but also according to the tacticity. The advantage is that separation by both parameters can be achieved at the same time. However, this is currently limited to oligomers with degree of polymerisation of 3 in the case of complex oligoelectrolytes such as oligoacrylates. Note that these oligoacrylates are especially complex samples because of a still relatively broad molecular weight distribution associated with no control of the tacticity during the polymerisation. For these oligoacrylates, it is thus possible to quantify the amount of unreacted RAFT

agent and DP of one and two. CE is thus a relevant and fast method to study kinetics of polymerisation of RAFT, especially its initialization. It would be particularly interesting to perform the CE analysis of oligomers in the case of a polymerisation targeting higher molecular weights. The quantification is robust and yields the same results in a number of different buffers, buffer concentrations, capillaries, capillary materials and operators. The resolution can, however, be optimised using these parameters, and the influence of counter-ion nature and ionic strength on electrophoretic mobility can be studied; this is the topic of a future publication. Recent publications of the group of Barner-Kowollik have demonstrated the importance of SEC coupled to ESI-MS^[61] for the characterization of organosoluble oligomers related to process engineering (kinetics of polymerisation)^[64] or materials science.^[63] Our free solution CE method is complementary and allows the same type of study with polyelectrolytes.

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Experimental

RAFT-controlled polymerisation and ESI MS spectra

The synthesis of the oligoacrylates by RAFT controlled/living polymerisation^[2] and direct Electrospray ionization-Mass spectrometry (ESI-MS) infusion^[32] have already been described and is summarized in the Supporting Information.

Capillary Electrophoresis – Mass Spectrometry (CE-MS)

The capillary electrophoresis and conditions were the same as in our communication^[32] unless stated otherwise. Ammonium acetate buffer was prepared by dissolution of ammonium acetate in Milli-

Q water (1 M), titration with ammonia (pH 9.26) and further dilution with Milli-Q water. Quantification using CE-UV was performed using the plots of the UV signal at 290 nm divided by migration against migration time.

All CE-MS experiments were conducted on an Agilent ^{3D}CE system interfaced with an Agilent 6320 ion trap MS system using an Agilent G1607A ESI interface and controlled with Agilent Chemstation software. A single 90 cm (22.5 cm to UV detector), 50 µm ID fused silica capillary was used for all experiments. The capillary was rinsed with 1 M NaOH for 5 minutes before each run followed by 5 min with separation buffer. Analyte solutions were injected electrokinetically for 20 seconds at 15 kV. Separations were run in ammonium acetate buffers prepared as described above with an applied potential of 27 kV. Sheath liquid flow was supplied by an Agilent 1200 pump fitted with a 1:100 flow splitter. The sheath liquid composition consisted of 1:1 methanol:water with 5 mM ammonium acetate adjusted to pH 9.24 with ammonia. Sheath liquid flow rate was 4 µL/min. Nebulizer pressure was set to a minimum to provide stable electrospray operation (21 kPa). Additional spray chamber parameters were set as follows: dry gas flow rate 8.0 L/min., drying gas temperature 150 °C, electrospray voltage +3.0 kV (end plate voltage -3.0 kV).

Some MS electropherograms were smoothed using the Bruker software DataAnalysis for 6300 Series Ion Trap LC/MS Version 3.4 using a Gauss smoothing algorithm with 1.111 smoothing width and a number of cycles multiple of 10.

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Supporting Information for

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

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Synthesis of the oligoacrylates¹

The 2-[[Butylsulfanyl]carbonothioyl]sulfanyl}propanoic acid (RAFT agent, 1equiv, 3.31 g, 1.39×10^{-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, 1.39×10^{-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 ¹ |
| | 59.8 | 25.5 | 9.9 | Amm150 | bare fused silica ¹ |
| | 59.1 | 25.9 | 10.1 | Amm150 | bare fused silica ¹ |
| | 48.4 | 29.2 | 14.1 | LB50 | C18 coated ² |
| | 48.7 | 28.6 | 3.8 | LB500M10 | bare fused silica ² |
| AA3 | 17.1 | 20.2 | 17.2 | Amm150 | bare fused silica ³ |
| | 15.8 | 23.8 | 20.5 | Amm150 | bare fused silica ³ |
| | 12.4 | 16.9 | 16.9 | Amm150 | bare fused silica ³ |
| AA5 | 8.9 | 14.5 | 15.7 | LB1000 | bare fused silica ⁴ |
| | 9.7 | 15.1 | 16.0 | LB1000 | bare fused silica ⁴ |
| | 8.8 | 14.3 | 15.3 | LB200 | bare fused silica ⁴ |
| | 8.6 | 13.7 | NR | LB200 | bare fused silica ⁴ |
| | 8.7 | 13.7 | NR | LB200 | bare fused silica ⁴ |

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

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.

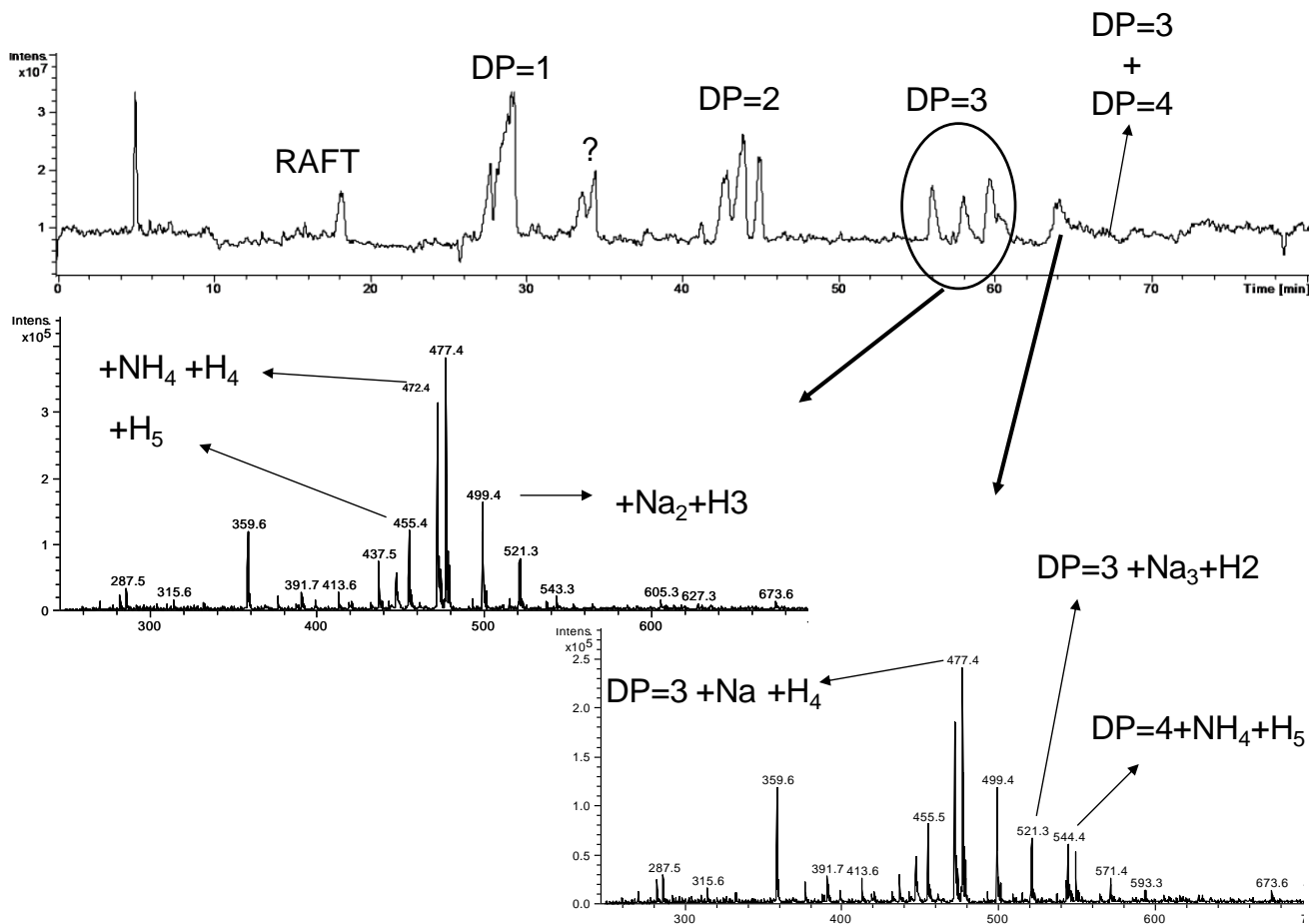
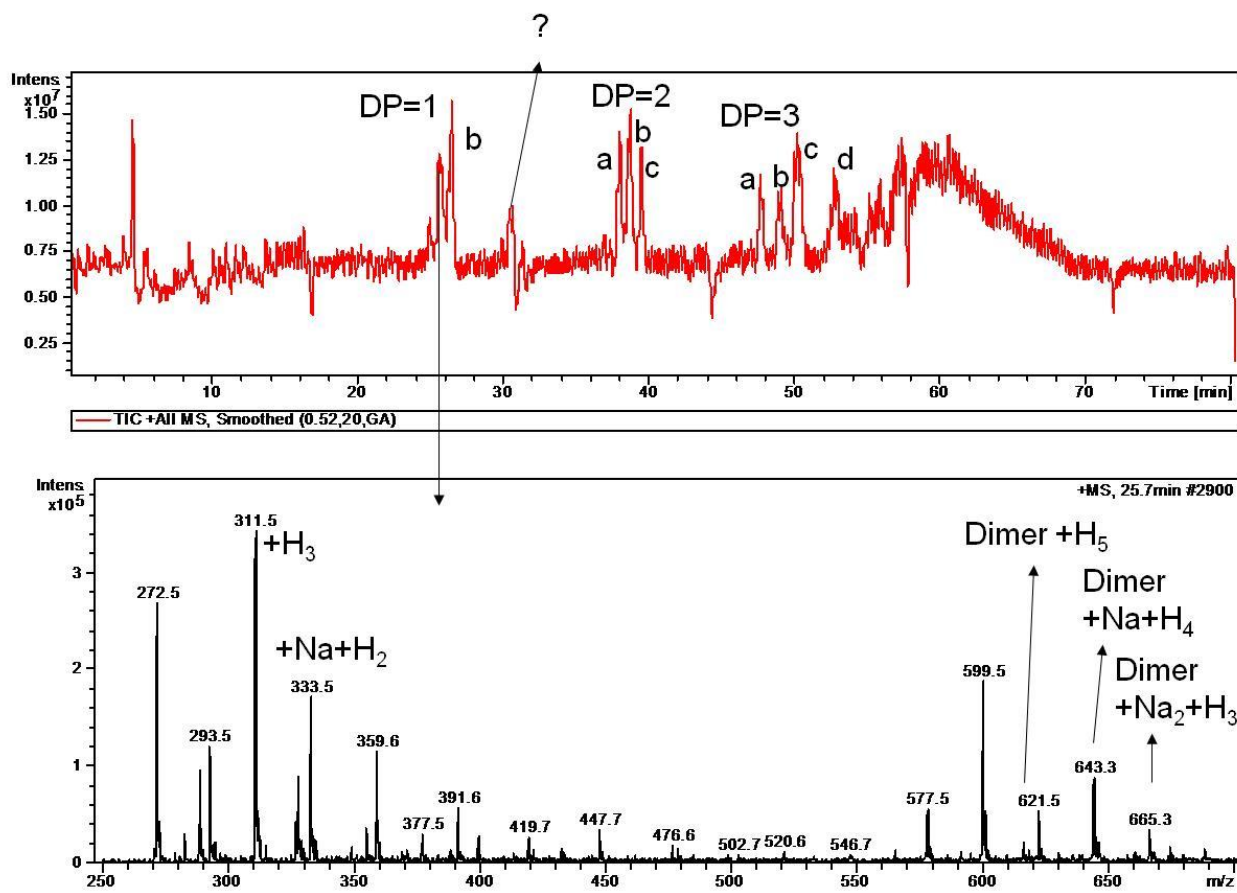
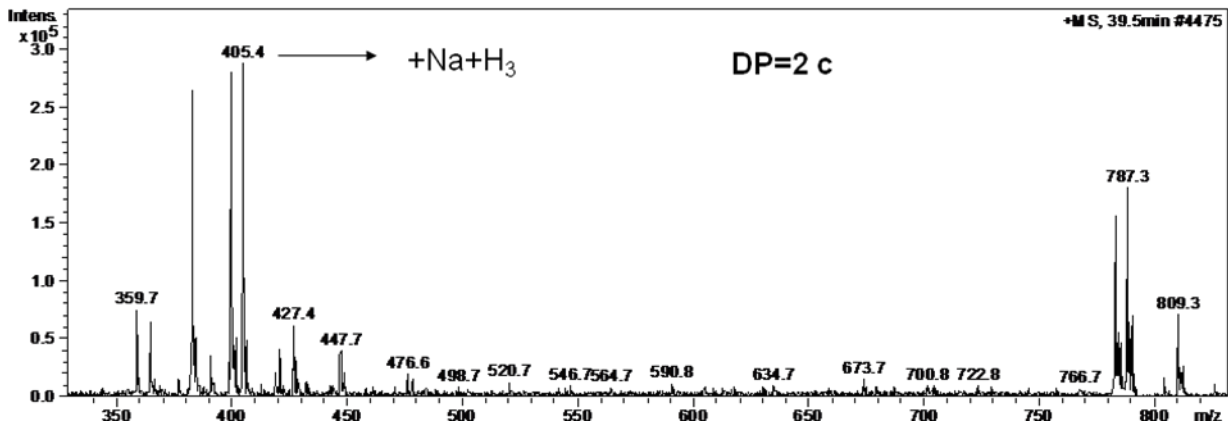
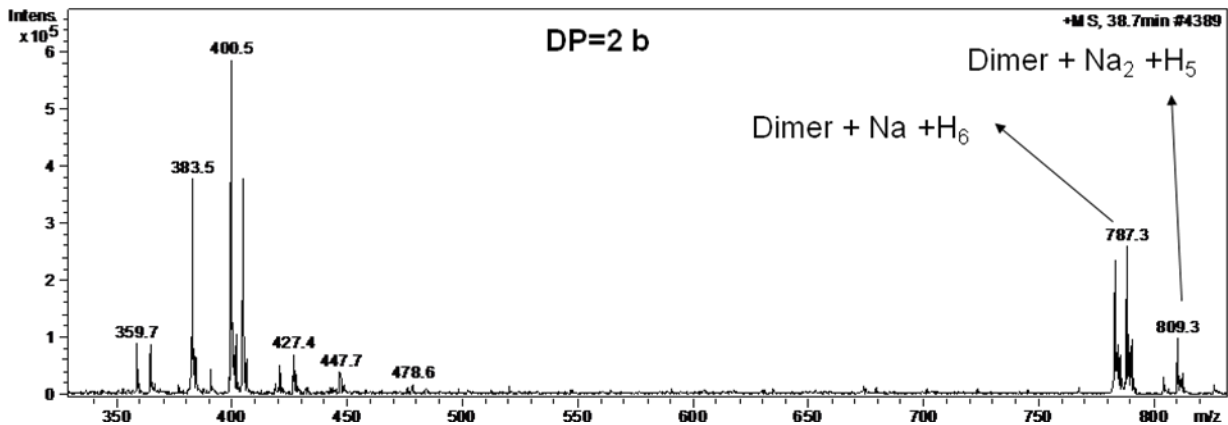
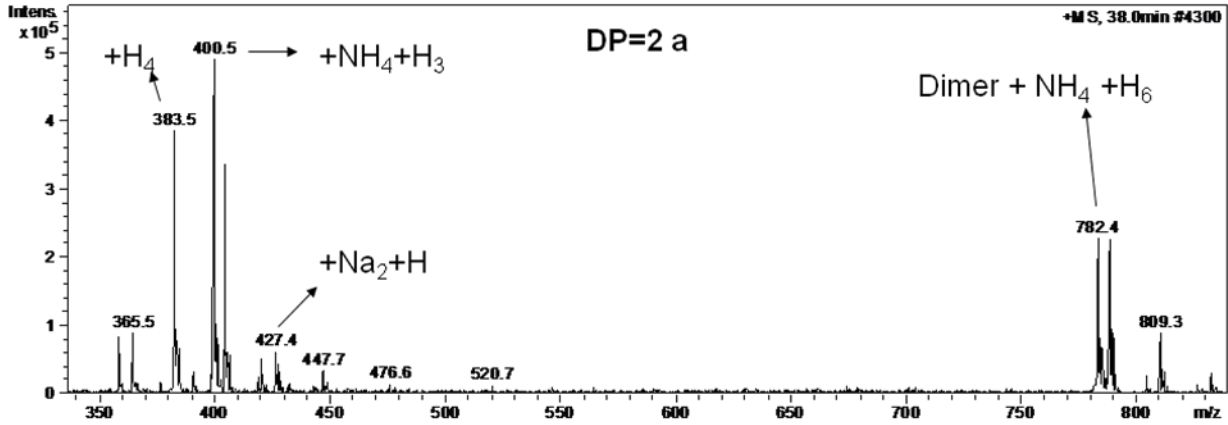
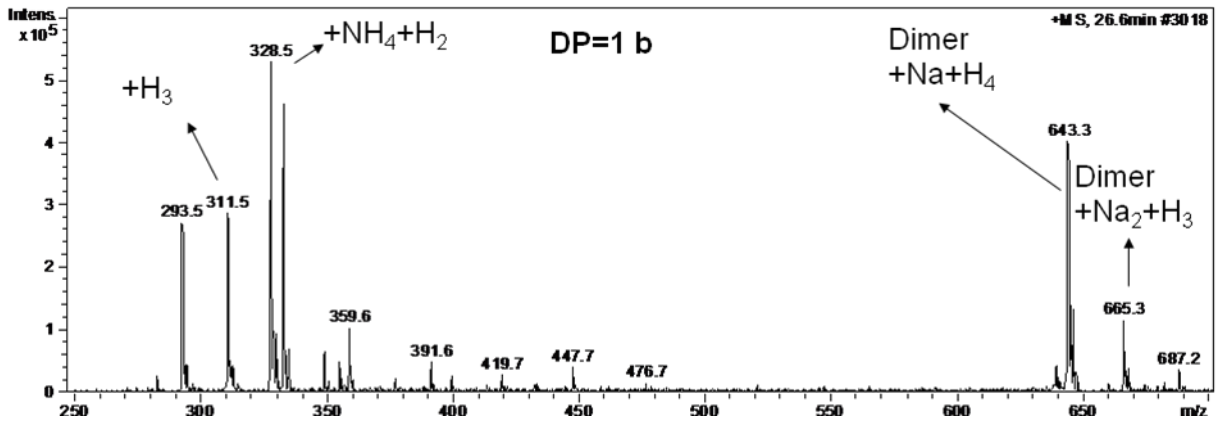


Figure S1: MS electropherogram (top) and some average mass spectra (bottom) for the peaks corresponding to the DP of three (and four) for the sample AA3.





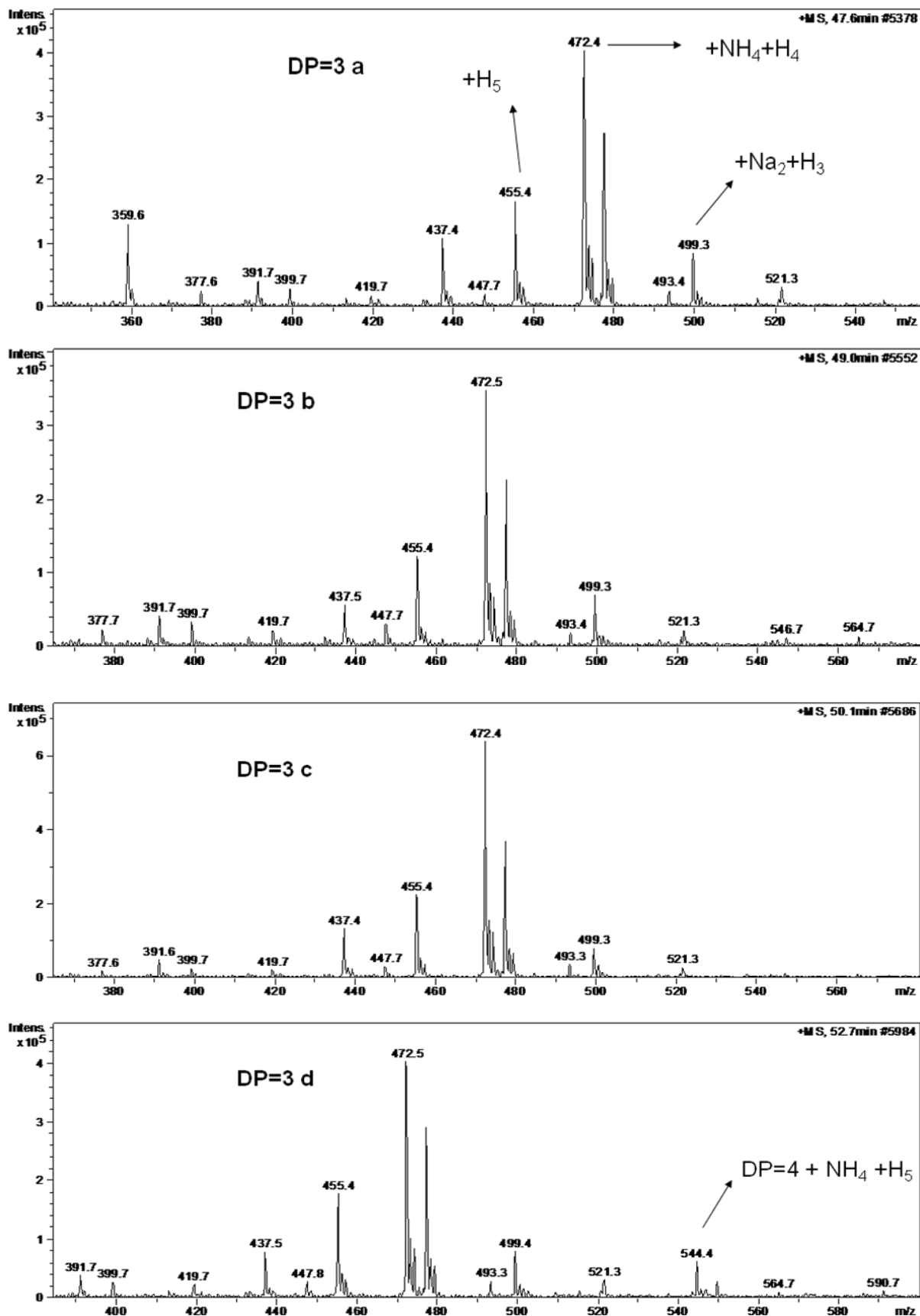


Figure S2: MS electropherogram (top, red line) and some average mass spectra (bottom, black lines) for the peaks corresponding to the DP of 1; 2 and 3 for the sample AA4.

^1H and ^{13}C solution-state NMR of oligo(acrylic acid)

Samples AA2, AA4, AA7 and AA15 were dissolved in D_2O at ca 130, 130, 165 and 160 $\text{mg}\cdot\text{mL}^{-1}$ respectively. NMR spectra were recorded at 25°C on a Bruker Avance spectrometer operating at 500 MHz Larmor frequency for ^1H , using a BBO probe (unless otherwise specified). Quantitative ^1H NMR spectra of samples AA2 and AA4 were recorded using a TXI5z probe, with 20 s relaxation delay and 128 transients. ^1H NMR spectra of samples AA7 and AA15 were recorded with 2 s relaxation delay and 32 transients. ^{13}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 ^1H NMR spectra using the CH_2 signal around 1.6-2.1 ppm.² For DP higher than two, the signal at ca 1.75 ppm are the CH_2 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_2 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 ^{13}C NMR spectra using the CH and CH_2 signals at ca 44 and 37 ppm respectively.² 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).

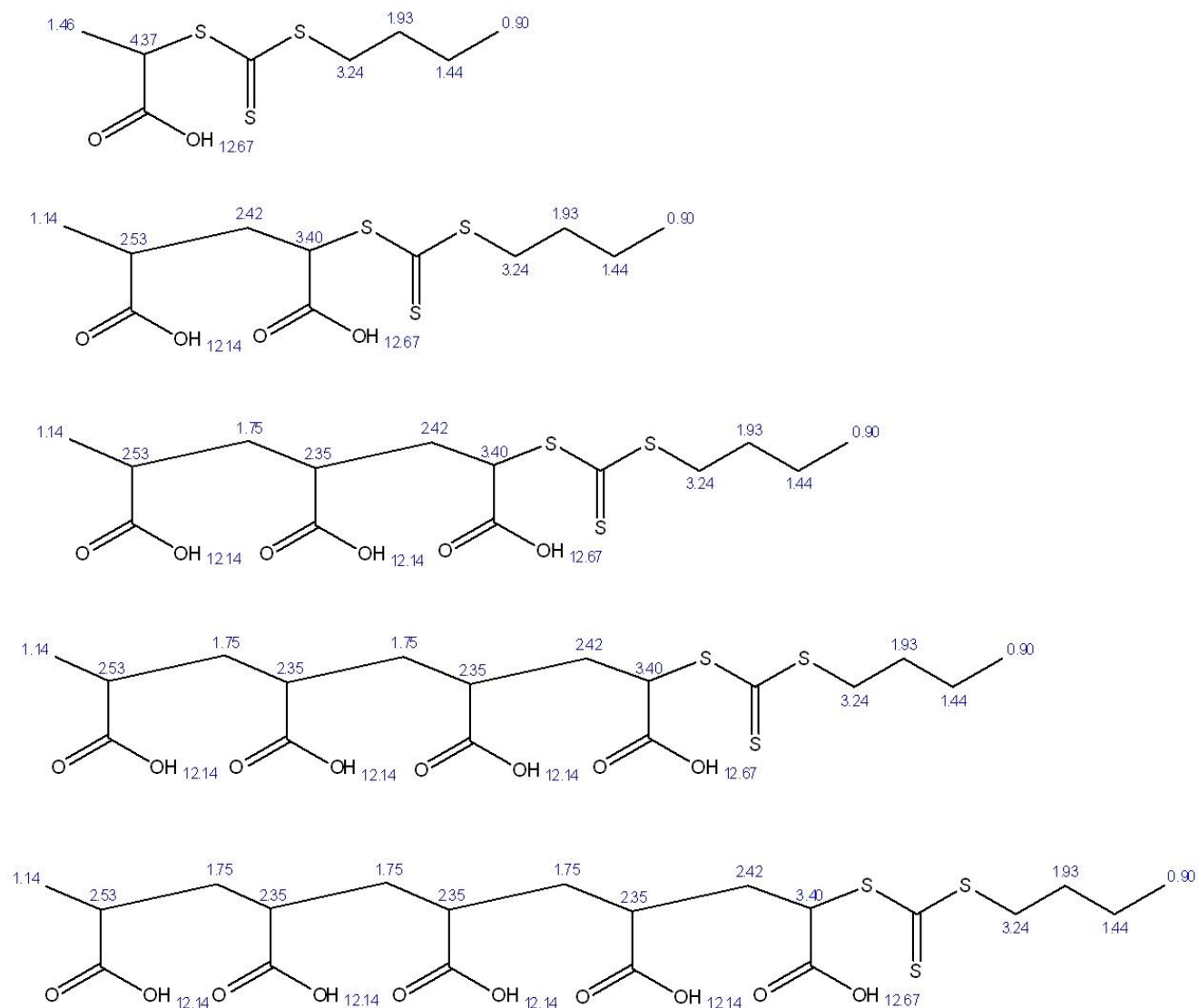


Figure S3: expected ^1H NMR chemical shifts for short oligo(acrylic acid). Calculations done with the ChemBioDraw Ultra 11.0.1 software (CambridgeSoft Inc.).

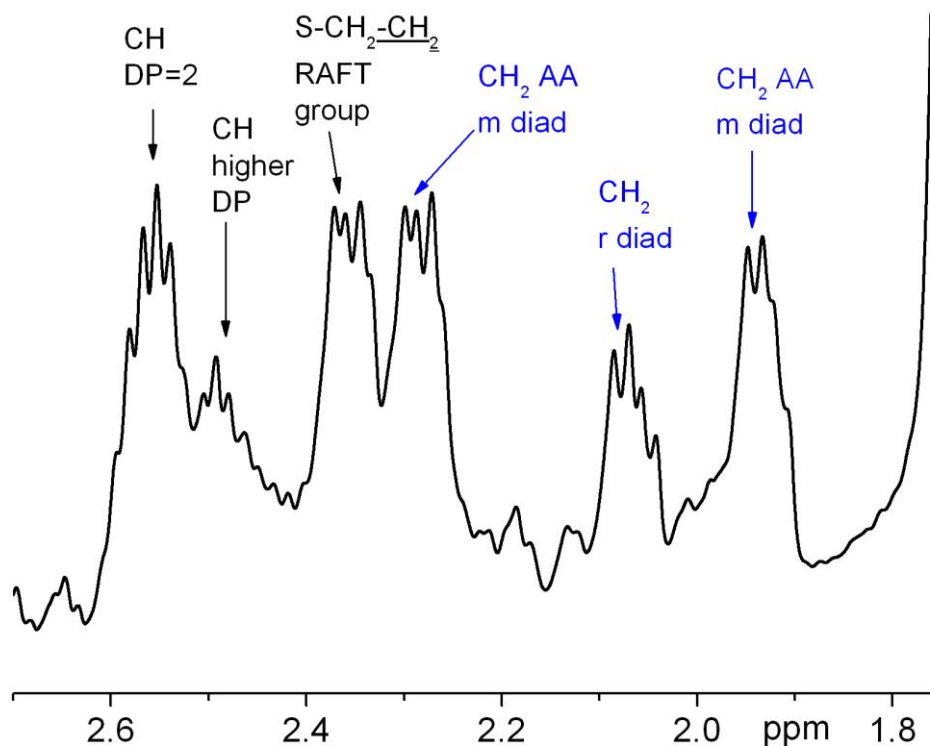


Figure S4: ¹H NMR spectrum of sample AA2, zoom on region of interest for determination of tacticity.

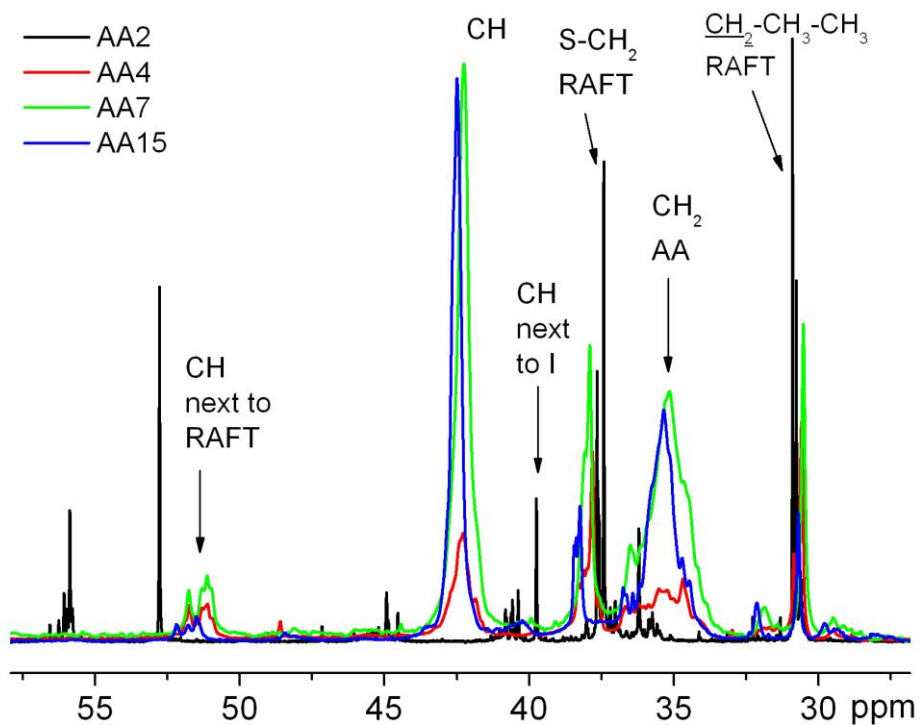


Figure S5: ¹³C NMR spectra of samples AA2, AA4, AA7 and AA15, zoom on region of interest for determination of tacticity.

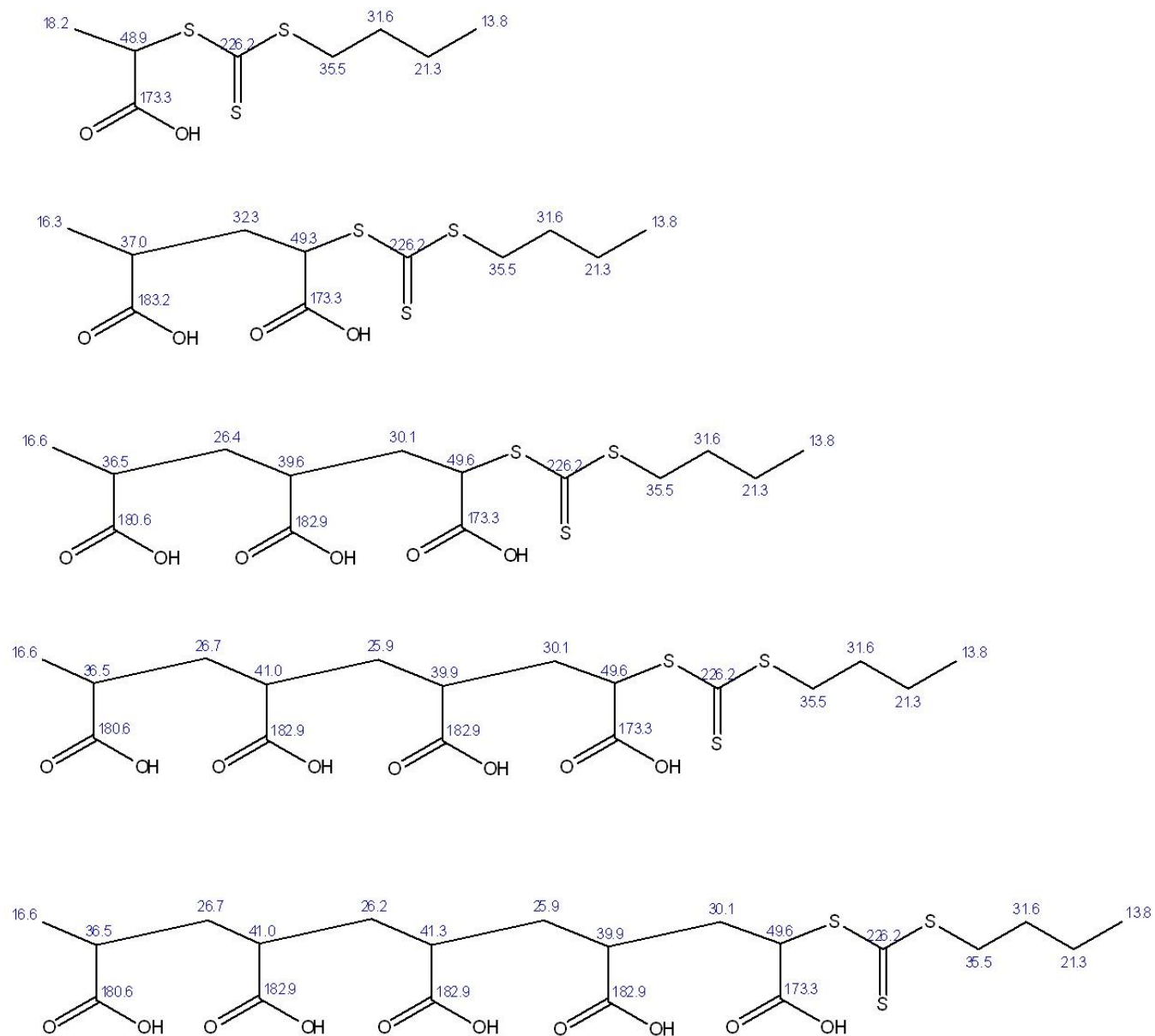


Figure S6: expected ^{13}C NMR chemical shifts for short oligo(acrylic acid). Calculations done with the ChemBioDraw Ultra 11.0.1 software (CambridgeSoft Inc.).

CE separation of one oligomethacrylate

Oligo(methacrylic acid) has been synthesized using RAFT and characterized by THF double-detection SEC.³ 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).

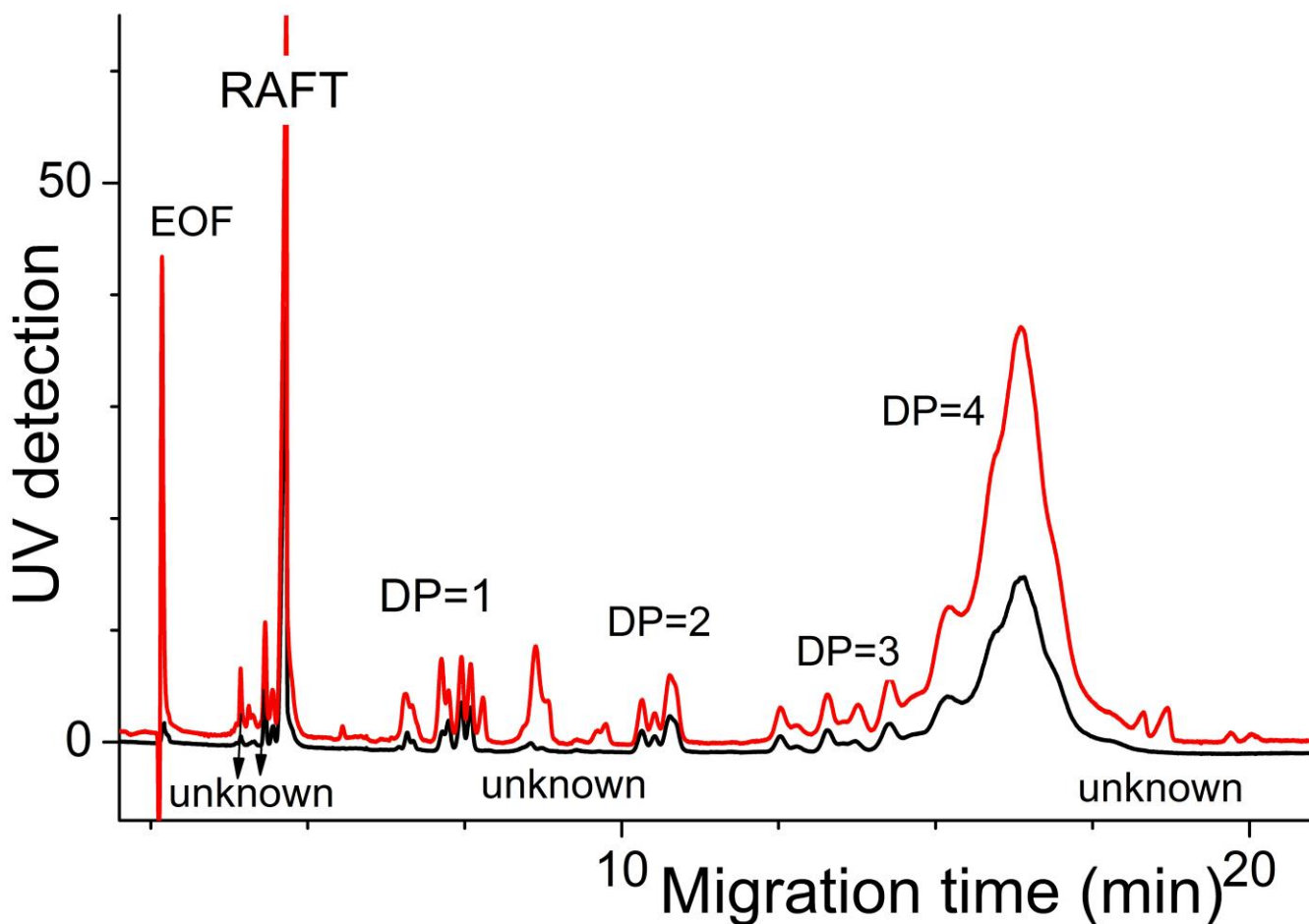


Figure S7: Separation of oligomethacrylate using CE with UV detection at 200 nm (red) and 290 nm (blue).

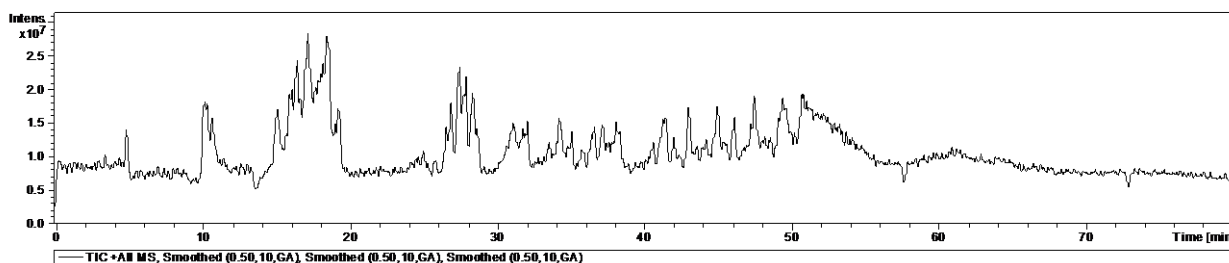


Figure S8: Separation of oligomethacrylate using CE with ESI-MS detection.

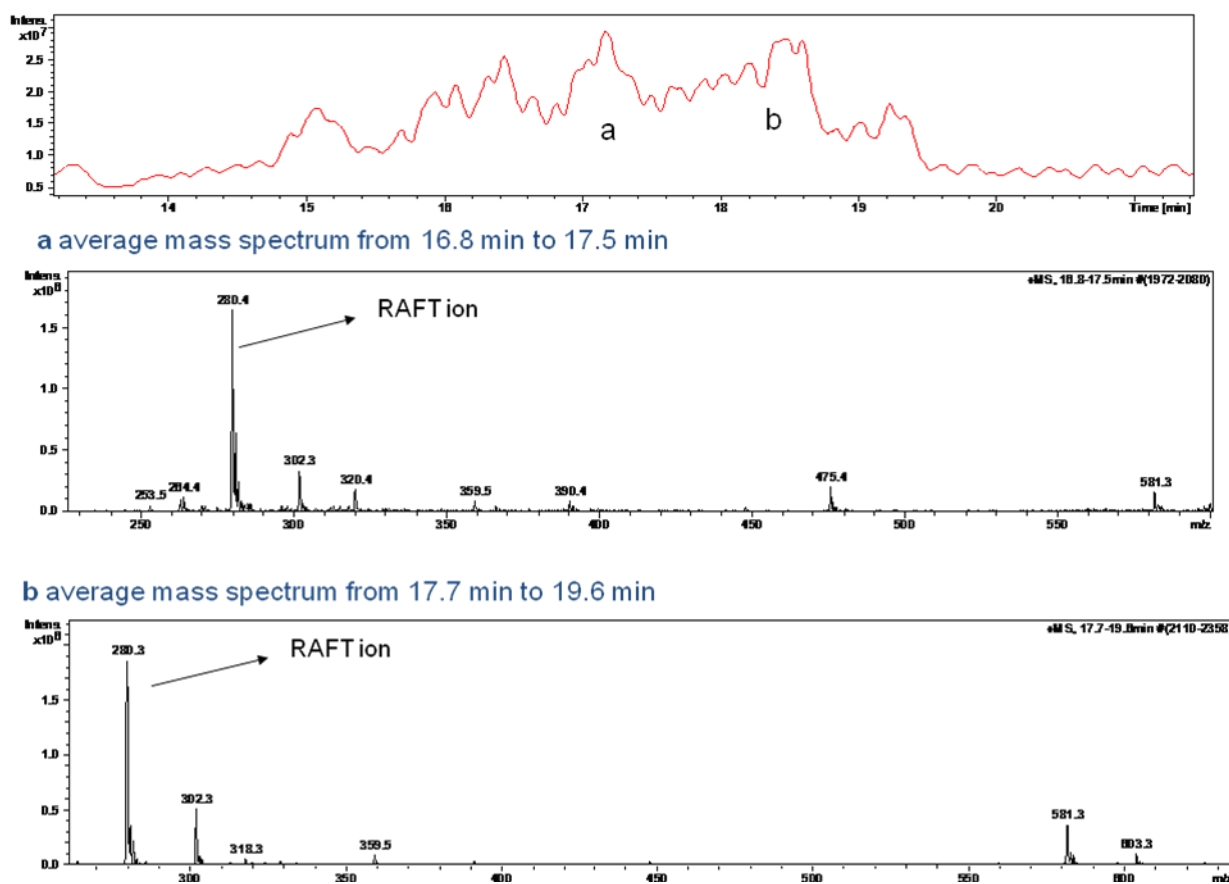
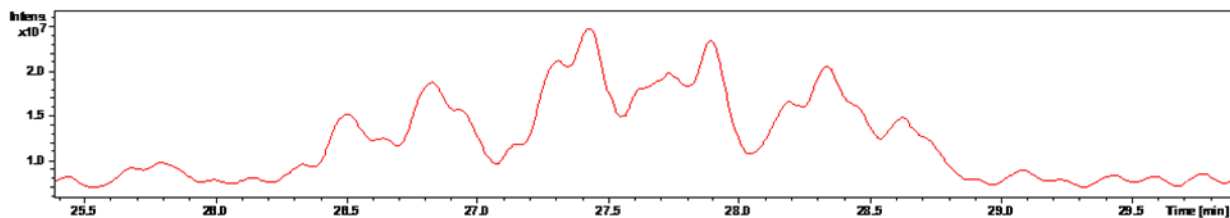


Figure S9: Zoom on the MS electropherogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectra (middle and bottom, a and b)



average mass spectrum from 26.3 min to 28.8 min

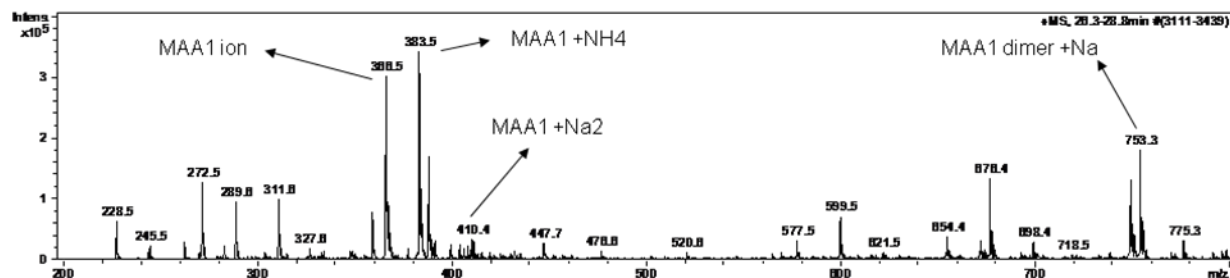
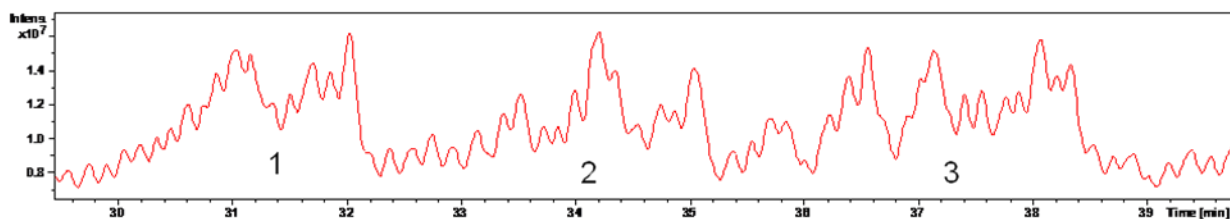


Figure S10: Zoom on the MS chromatogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectrum (bottom)



3 average mass spectrum from 35.7 min to 38.4 min

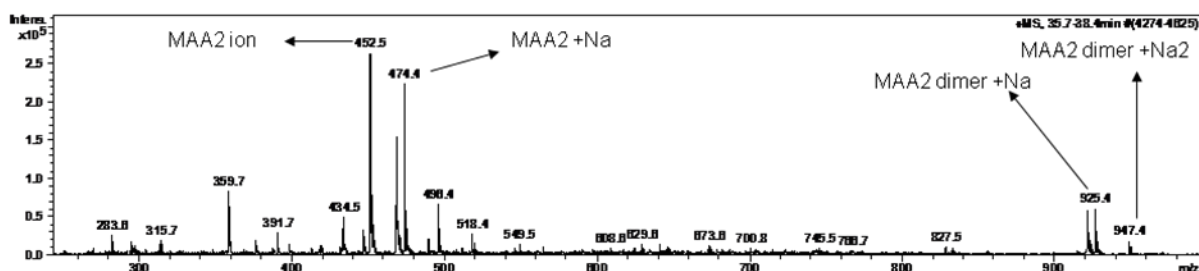
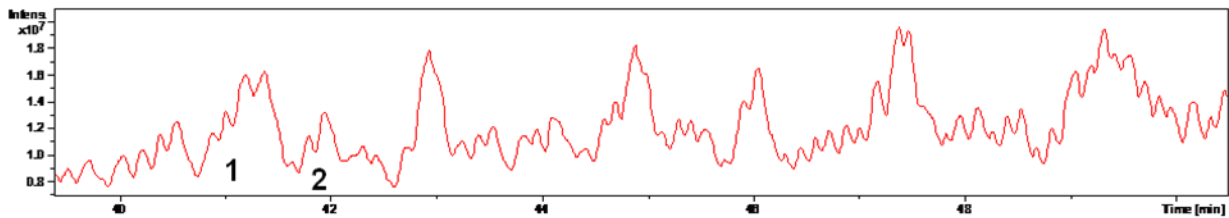
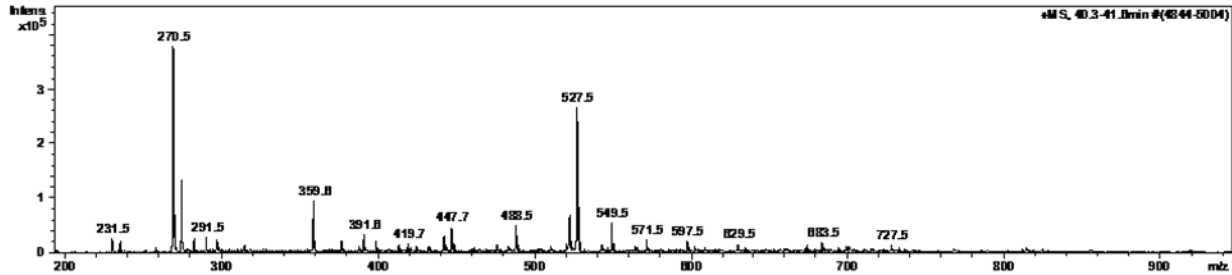


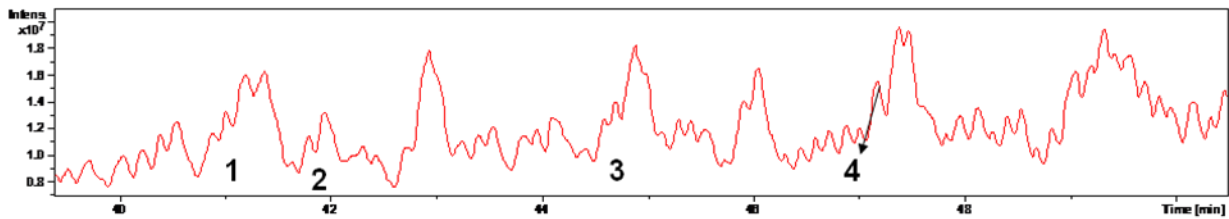
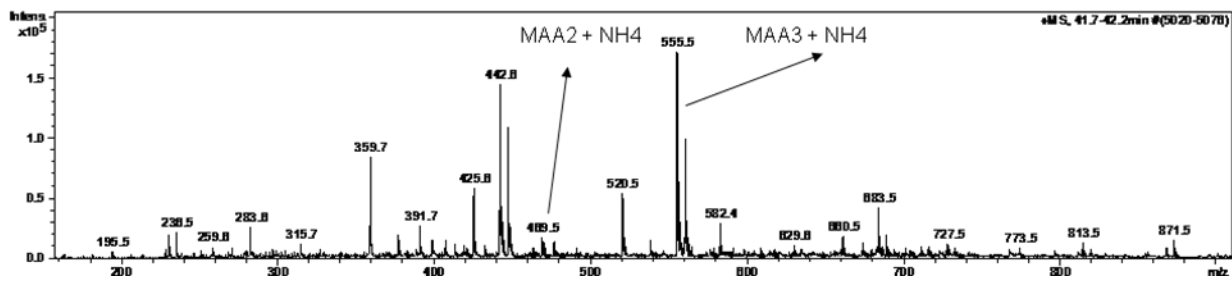
Figure S11: Zoom on the MS chromatogram corresponding to figure S7 (top, red line) and corresponding ESI-MS spectrum (bottom)



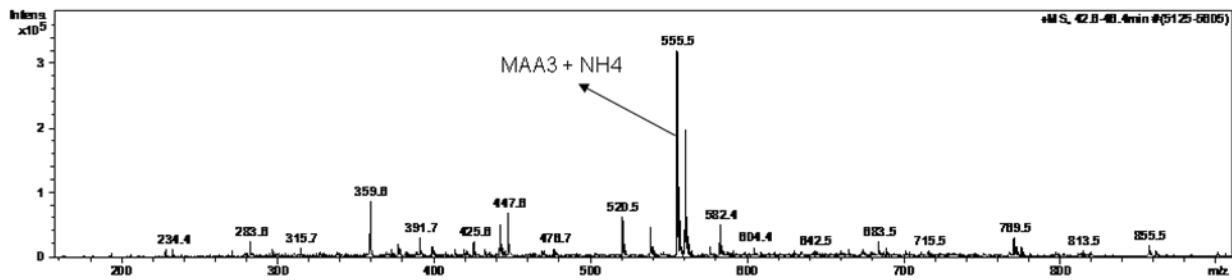
1 average mass spectrum from 40.3 min to 41.6 min



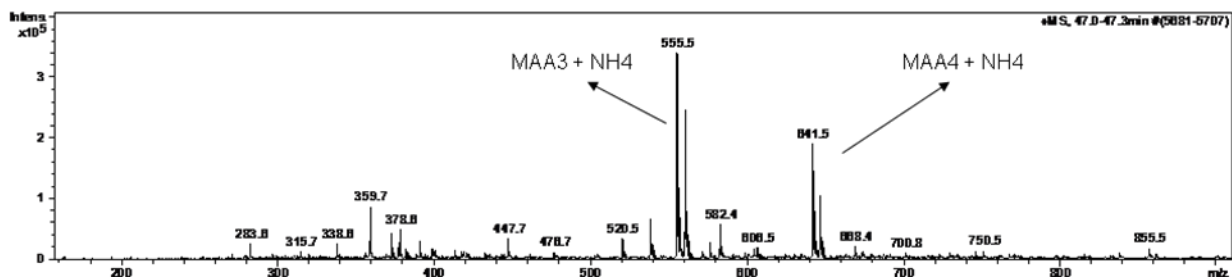
2 average mass spectrum from 41.7 min to 42.2 min

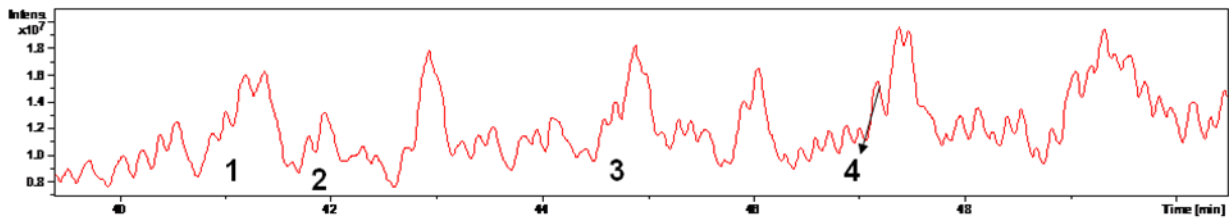


3 average mass spectrum from 42.6 min to 46.4 min

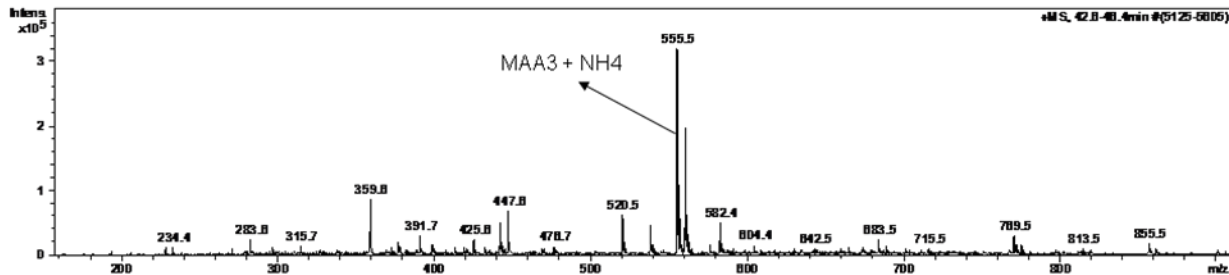


4 average mass spectrum from 47.0 min to 47.3 min

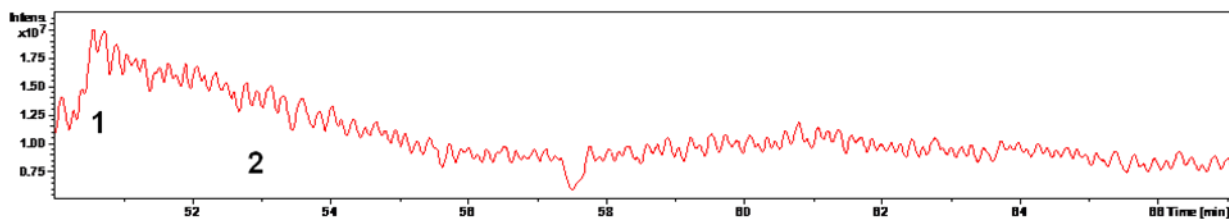
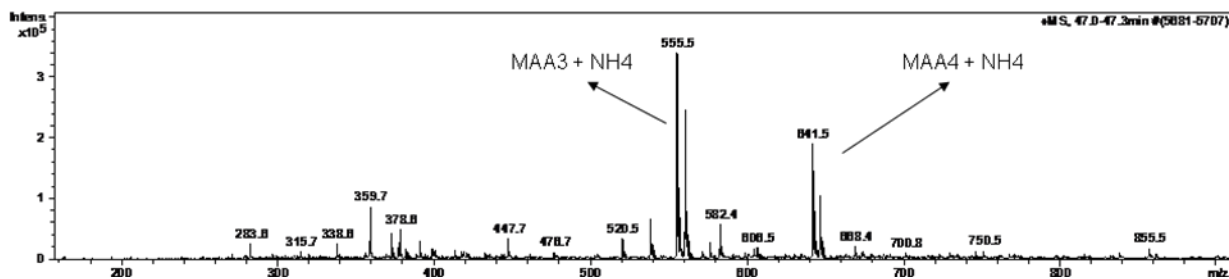




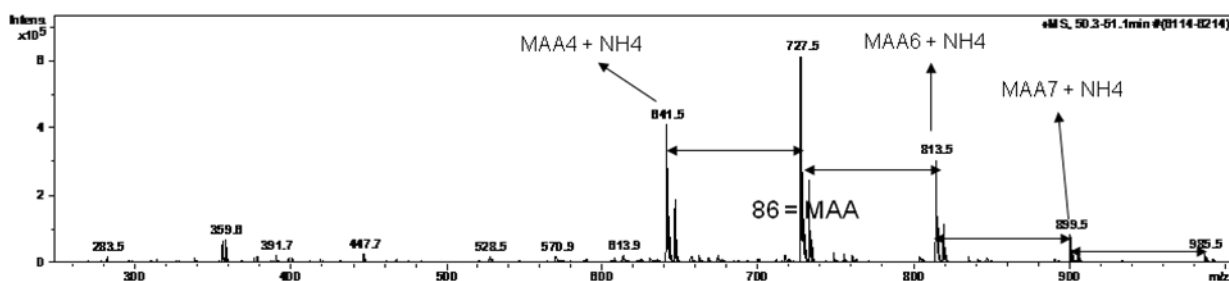
3 average mass spectrum from 42.6 min to 46.4 min



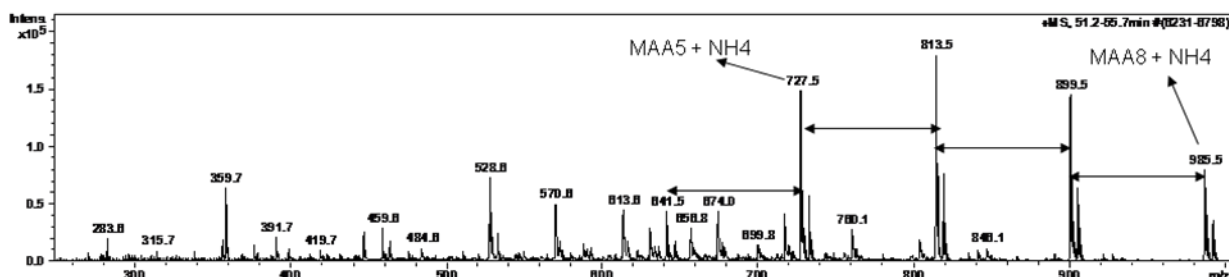
4 average mass spectrum from 47.0 min to 47.3 min

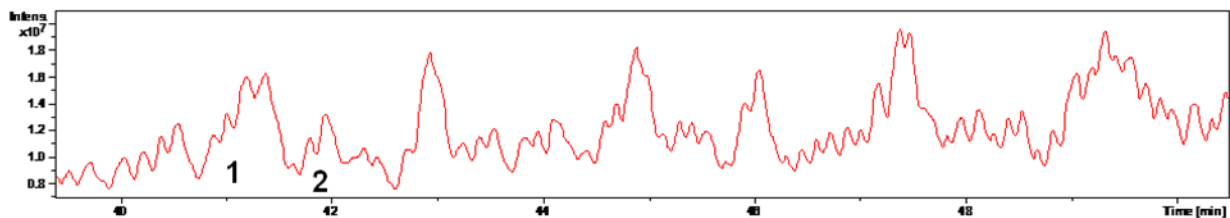


1 average mass spectrum from 50.3 min to 51.1 min

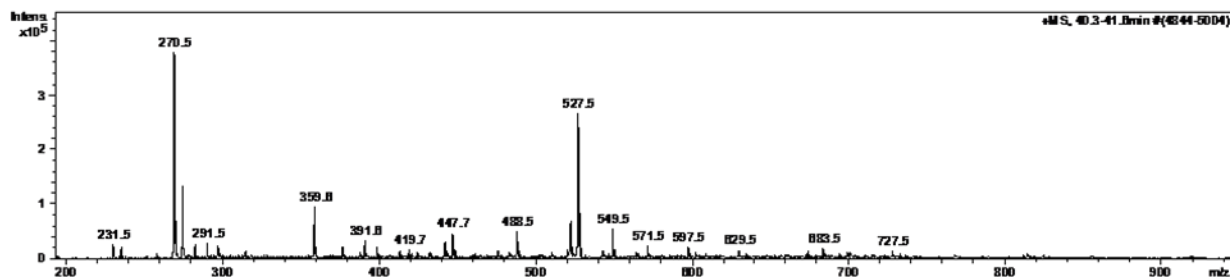


2 average mass spectrum from 51.2 min to 55.7 min





1 average mass spectrum from 40.3 min to 41.6 min



2 average mass spectrum from 41.7 min to 42.2 min

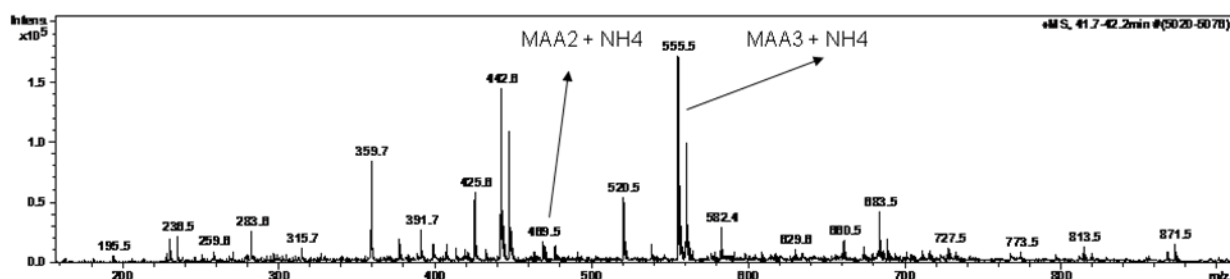


Figure S12: Zooms on the MS chromatogram corresponding to figure S7 (red lines) and corresponding ESI-MS spectra (corresponding black line below each zoom)

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