Supplementary Information

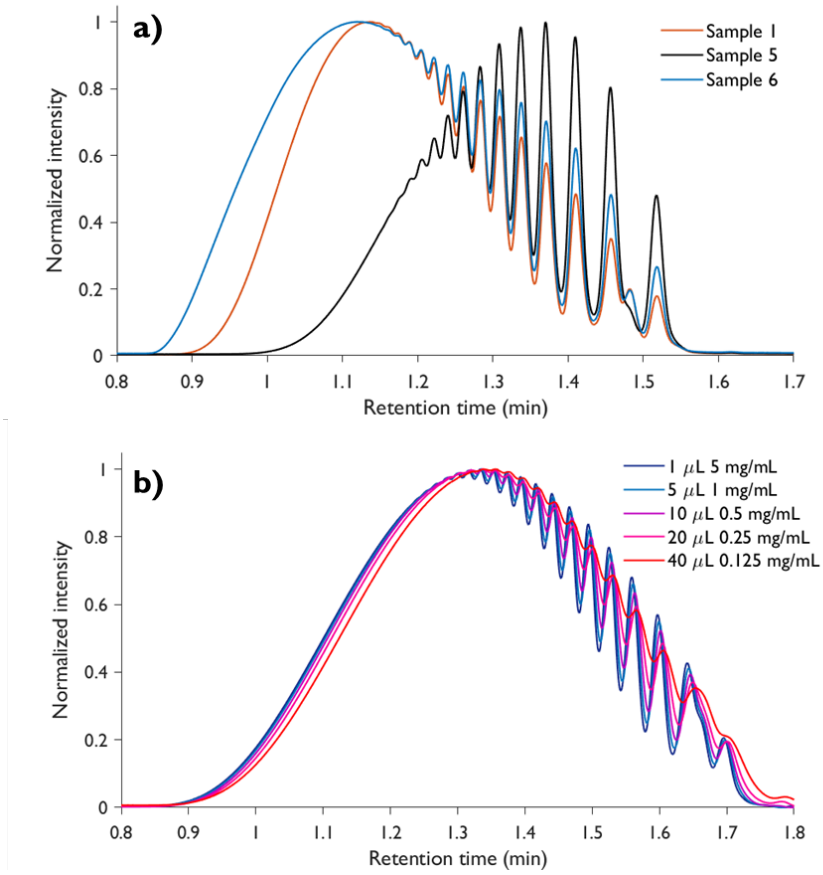

Figure S1: Typical SEC chromatograms were taken for a) a variety of polyester resins showing their differences over a broad range of molecular-weight and b) the effect of injection volume was studied for the potential use in the second dimension (sample 1). For SEC experiments, the column was thermostatted at 50 °C and operated at a *F* of 1.0 mL/min using THF containing 0.1% (v/v) formic acid at isocratic conditions. The default injection volume was 1.0 µL and varied from 1.0 – 40.0 µL to study the injection band broadening effects using a dilution series with concentrations of 5.0, 1.0, 0.5, 0.25 and 0.125 mg/mL in THF.

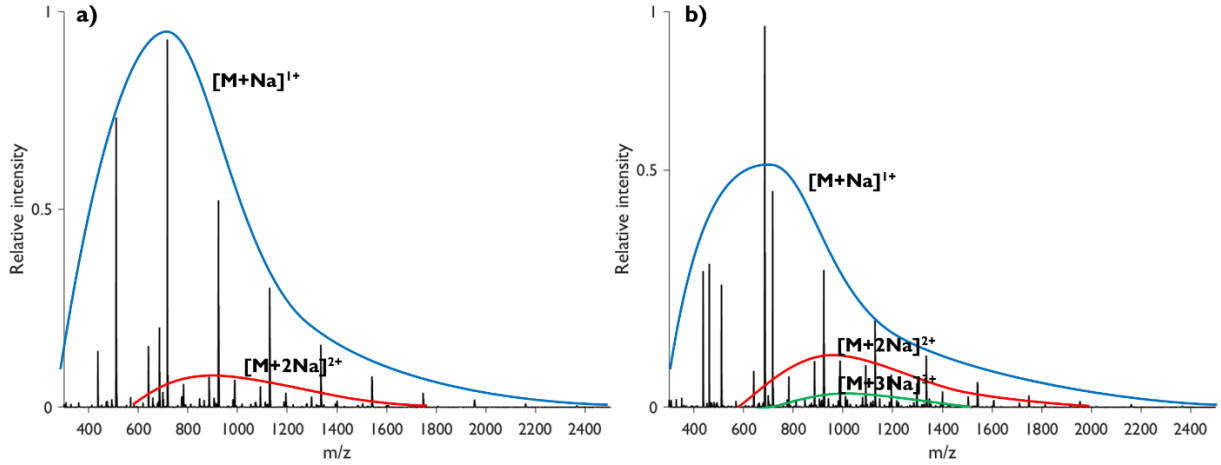

Figure S2: comparison of direct-infusion mass spectrometry using a) only 1 mM NaI as ionization agent and b) the addition of 0.5% (v/v) 3-nitrobenzyl alcohol as supercharging agent which shows relative increase of doubly charged ions and the detection of triply charged ions.

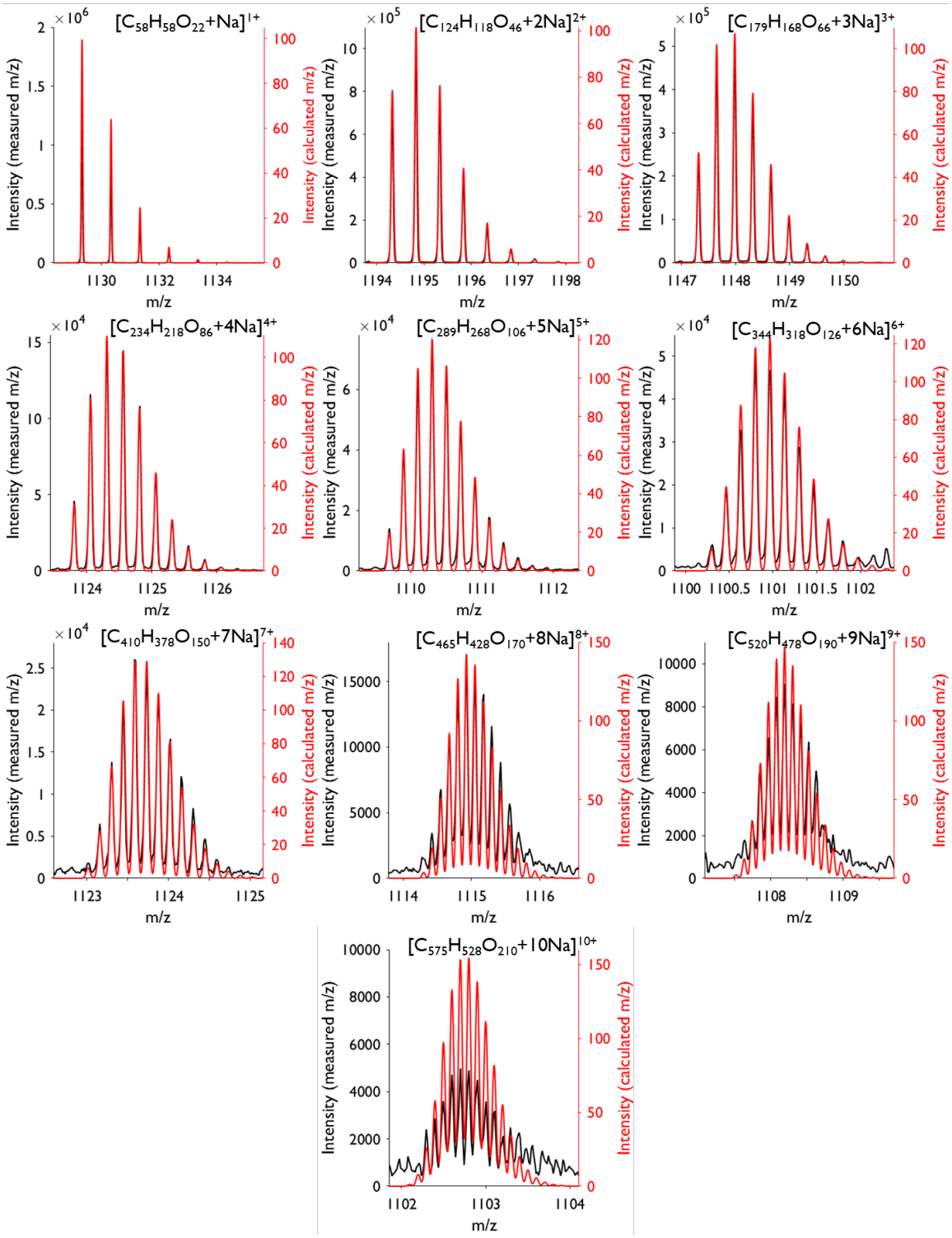

Figure S3: measured (black line) and calculated (red line) isotope distributions of specific ions detected at various charge states for TPA/PG diol species.

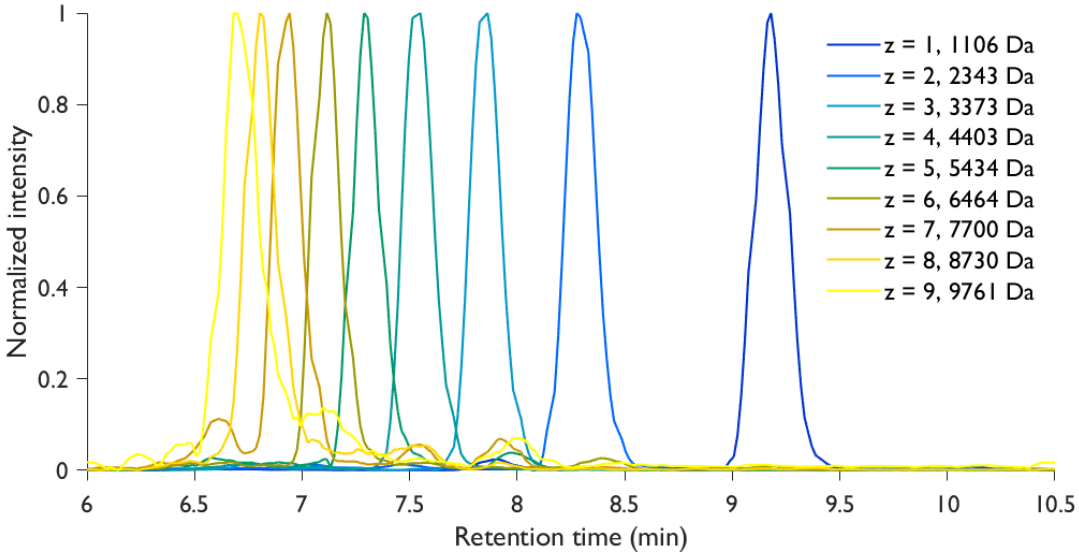

Figure S4: extracted ion chromatograms (EICs) of specific ions (corresponding to those in Figure S4) with increase in molecular weight for TPA/PG diol species. Such EICs were used to construct the calibration curves of different end-group species and were compared to those obtained for Polystyrene calibration (UV/Vis) as shown in Figure 2. The detected charge state (z) and deconvoluted mass (Da) is indicated in the legend of the Figure for each detected adduct.

SEC data treatment

The M_n and M_w values were calculated using the following equations where S is the signal and M the mass:

$$\overline{M_n} = \frac{\sum(S_t * M_t)}{\sum S_t}$$

$$\overline{M_w} = \frac{\sum(S_t * M_t) * M_t}{\sum(S_t * M_t)}$$

The relative signal intensity (Q) in percentages of the compounds were calculated with the following equation:

$$Q = \frac{S_i * 100}{S_{tot}}$$

Table S1: Average M_n, M_w, and relative peak area (%) values for identified distributions using NPLC×SEC-UV data

Sample	End-group distribution*							
	A_1	**B_1**	**C_1**	**D_1**	**F**	**G**	**H**	
1	900 // 1150 // 2.6	4700 // 6750 // 11.7	4450 // 7450 // 71.4	4849 // 6900 // 14.4	N/A	N/A	N/A	
2	950 // 1200 // 2.0	5400 // 7700 // 5.2	4900 // 7600 // 30.7	5500 // 7900 // 8.9	5100 // 7700 // 36.7	5650 // 7550 // 12.4	6200 // 8050 // 4.1	
3	900 // 1150 // 1.9	5300 // 7200 // 2.1	4850 // 7200 // 13.2	5850 // 7500 // 10.0	4800 // 7250 // 33.5	5450 // 7350 // 24.9	5850 // 7850 // 14.3	
	A_1	**B_1**	**C_1**	**D_1**	**I**	**J**	**K**	**M**
4	800 // 900 // 1.2	2400 // 3300 // 4.4	2400 // 3800 // 87.4	2629 // 3650 // 7.0	N/A	N/A	N/A	N/A
5	700 // 700 // 0.8	1700 // 2200 // 1.6	1700 // 2450 // 48.8	N/A	3150 // 4000 // 27.5	4400 // 5200 // 13.0	6350 // 7000 // 8.2	N/A
6	750 // 850 // 1.0	2250 // 3150 // 1.6	2350 // 3700 // 28.5	N/A	4500 // 5650 // 18.0	6500 // 7800 // 14.0	8150 // 9350 // 7.9	14850 // 16700 // 29.0
	A_2	**B_2**	**C_2**	**D_2**	**E_2**	**M_2**		
7	700 // 950 // 2.0	5900 // 8450 // 11.0	5600 // 8050 // 62.9	5700 // 8750 // 24.1	N // A	N // A		
8	750 // 950 // 3.6	N/A	N/A	9800 // 12300 // 7.7	10750 // 13600 // 82.9	10000 // 12600 // 5.7		
	A_3	**B_3**	**C_3**	**D_3**	**E_3**	**M_3**		
9	750 // 1300 // 4.4	7950 // 11100 // 16.3	7050 // 11100 // 62.9	7500 // 11300 // 16.3	N/A	N/A		
10	700 // 1650 // 3.6	N/A	N/A	7800 // 10600 // 8.9	8900 // 11850 // 73.7	8950 // 11950 // 13.9		

*Values according to M_n/M_w/Relative intensity (%)