Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Tacticity, Molecular Weight, and Temporal Control by Lanthanide Triflate-Catalyzed Stereoselective Radical Polymerization of Acrylamides with an Organotellurium Chain Transfer Agent

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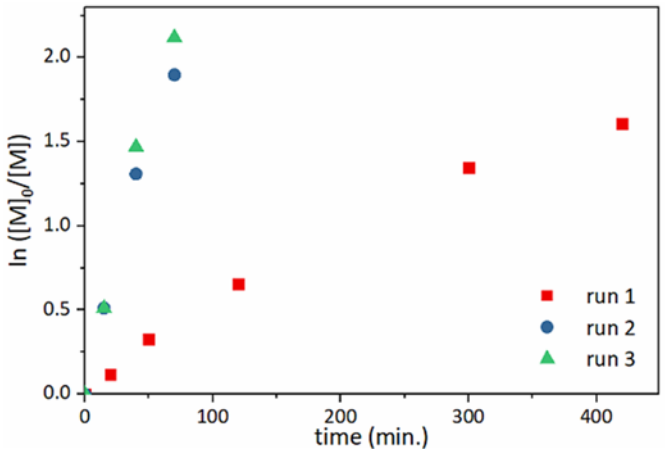

Figure S1. Kinetics of TERP of DMAA in the presence or absent of $Y(OTf)_3$ (runs 1-3).

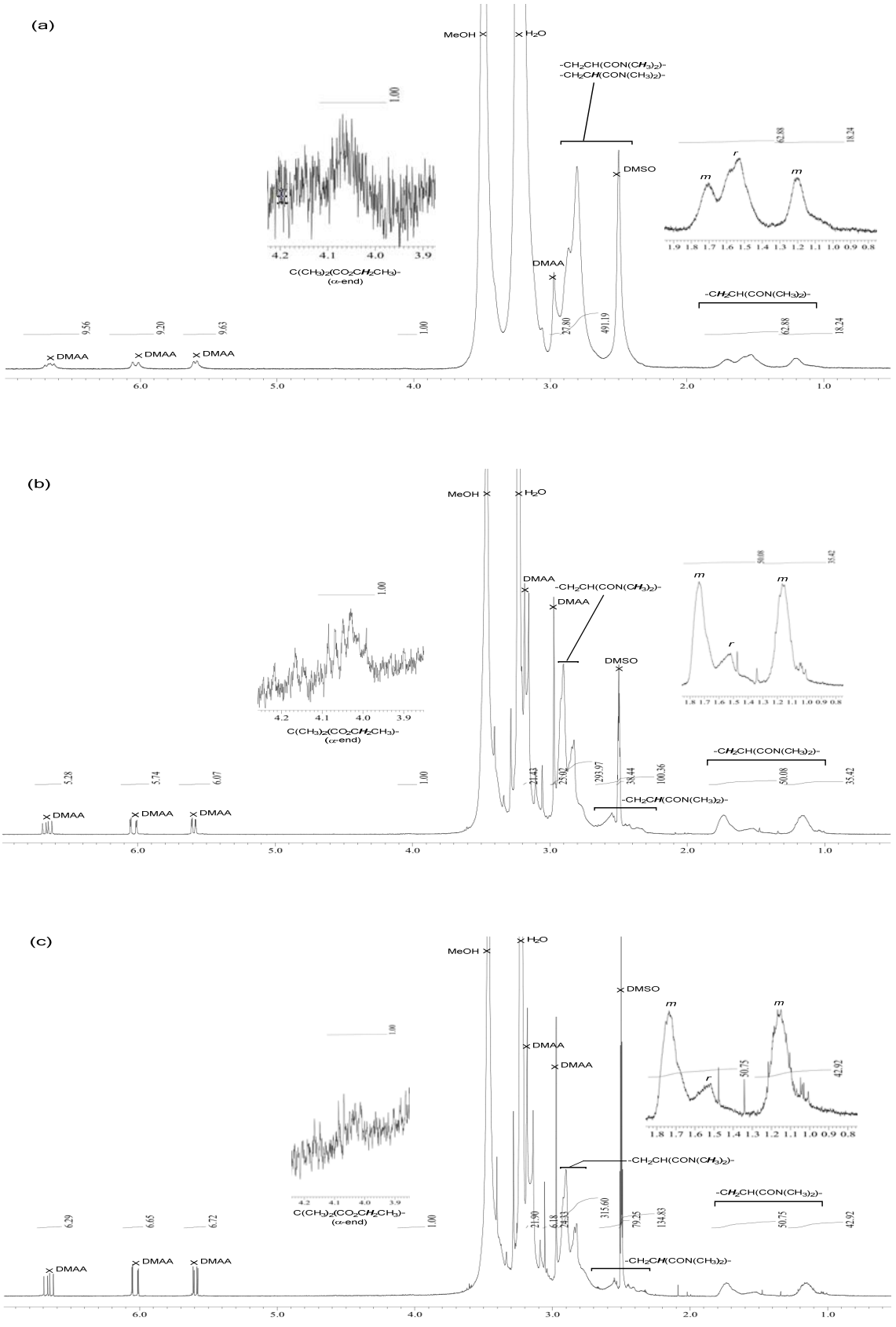

Figure S2. ^{1}H NMR of spectra of PDMAA samples synthesized (a) without $Y(OTf)_3$ (run 1), (b) with 10 mol% of $Y(OTf)_3$ (run 2), and (c) with 20 mol% of $Y(OTf)_3$ (run 3) measured in DMSO-d_6 at 130 °C.

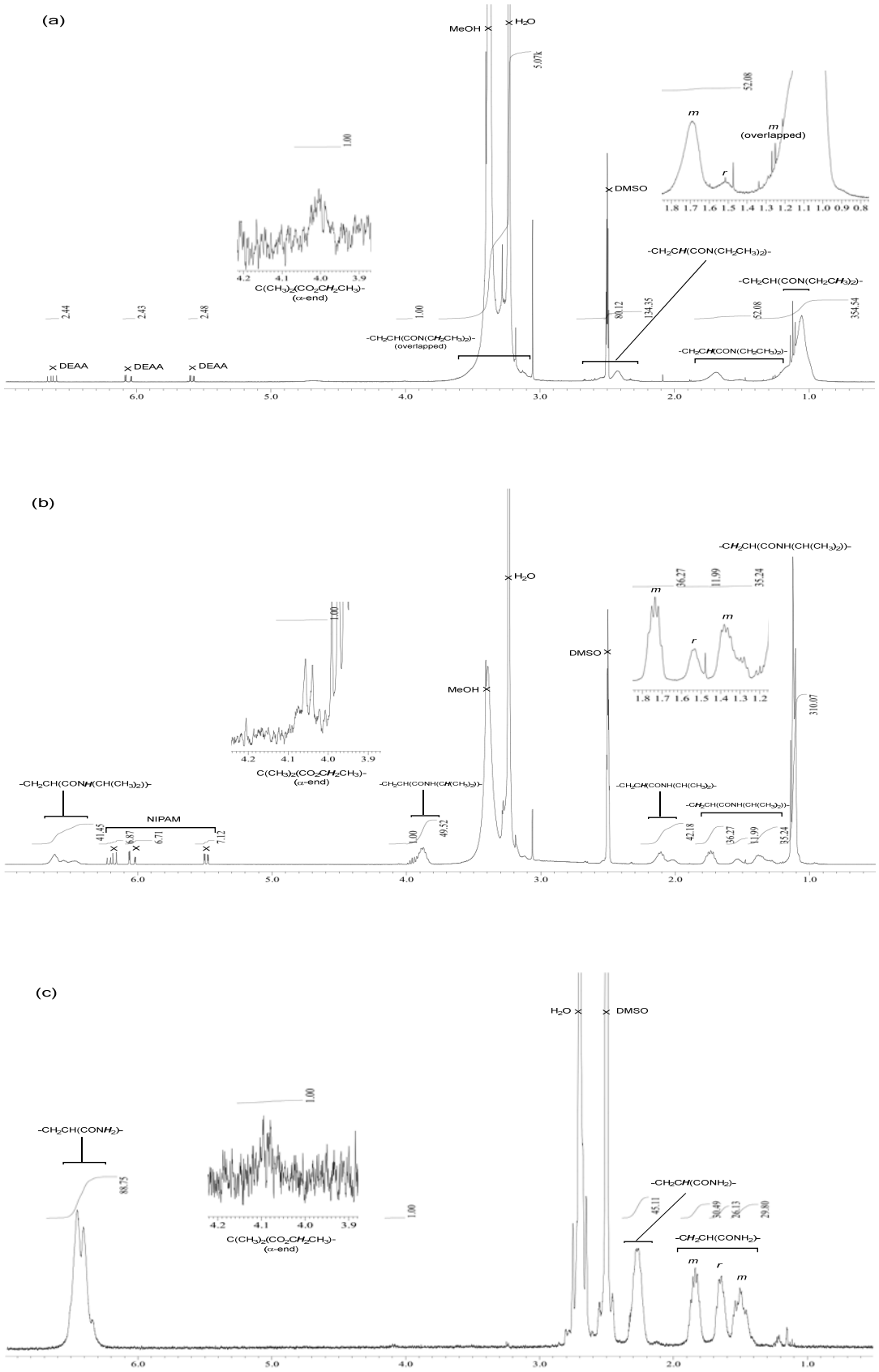

Figure S3. ^{1}H NMR spectra of (a) PDEAA, (b) PNIPAM and (c) PAM samples synthesized with 20 mol% of $Y(OTf)_3$ (runs 10, 15 and 21) measured in DMSO-d_6 at 130 °C for (a) and 145 °C for (b) and (c).

Table S1. Conditions and results of the chain extension reactions (Table 1, runs 1-12, 14 and 15).

run	Monomer (equiv.)	time (h)	conv. (%)[a]	$M_{n(SEC)}$[b] ×10^{-3}	$Đ$[b]	f (%)[c]
1	500	4	90	71.6	1.50	>98
2	500	4.5	88	80.1	1.36	>96
3	500	4.5	87	54.4	1.52	>96
4	500	4	95	72.5	1.49	>95
5	3000	19	97	297.5	1.84	>95
6	3000	11	90	195.5	1.90	>95
7	5000	19	88	326.6	2.13	>95
8	5000	18	79	298.9	1.78	>93
9	500	4	80	45.5	1.28	98
10	500	2.5	94	93.0	1.09	>98
11	2000	5	86	121.2	1.51	>97
12	3000	11	94	401.6	1.45	>96
14	1000	5.5	98	61.5	1.86	>96
15	1000	5	82	56.8	1.88	>94

[a]Determined by ^{1}H NMR in DMSO-d_6 at 25 °C. [b]Determined by SEC with DMF containing LiBr (0.010 mol L^{-1}) at 40 °C against PMMA standards. [c]End group fidelity.

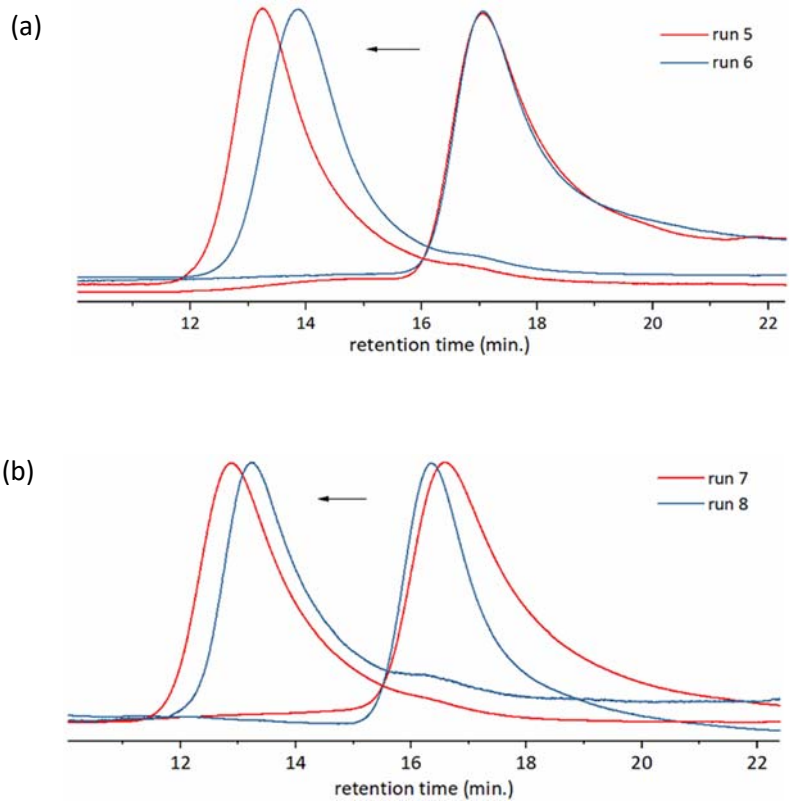

Figure S4. SEC traces before and after the chain extension by the addition of (a) 300 equivalents and (b) 500 equivalents of DMAA (red line: runs 5 or 7, blue line: runs 6 or 8).

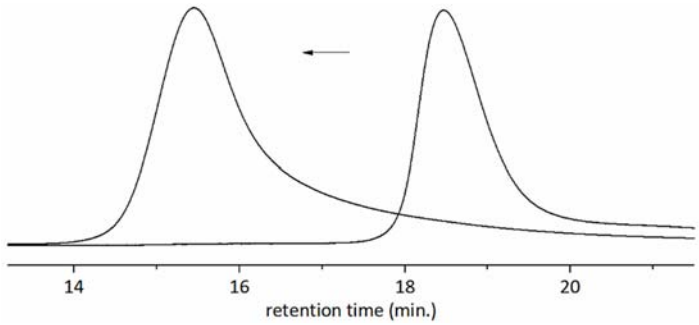

Figure S5. SEC traces before and after the chain extension by the addition of 100 equivalents of NIPAM (run 15).

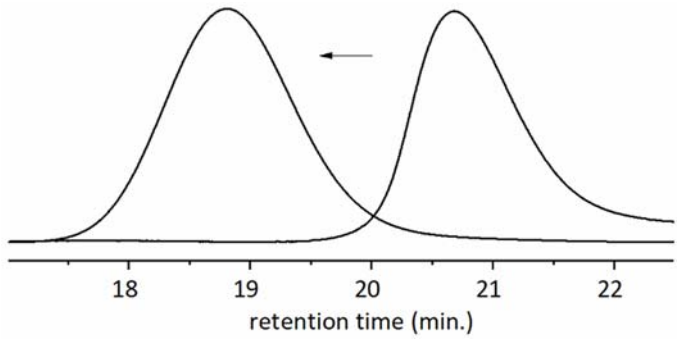

Figure S6. SEC traces before and after addition of $Y(OTf)_3$ in the synthesis of stereoblock PDEAA (Table 2, run 1).

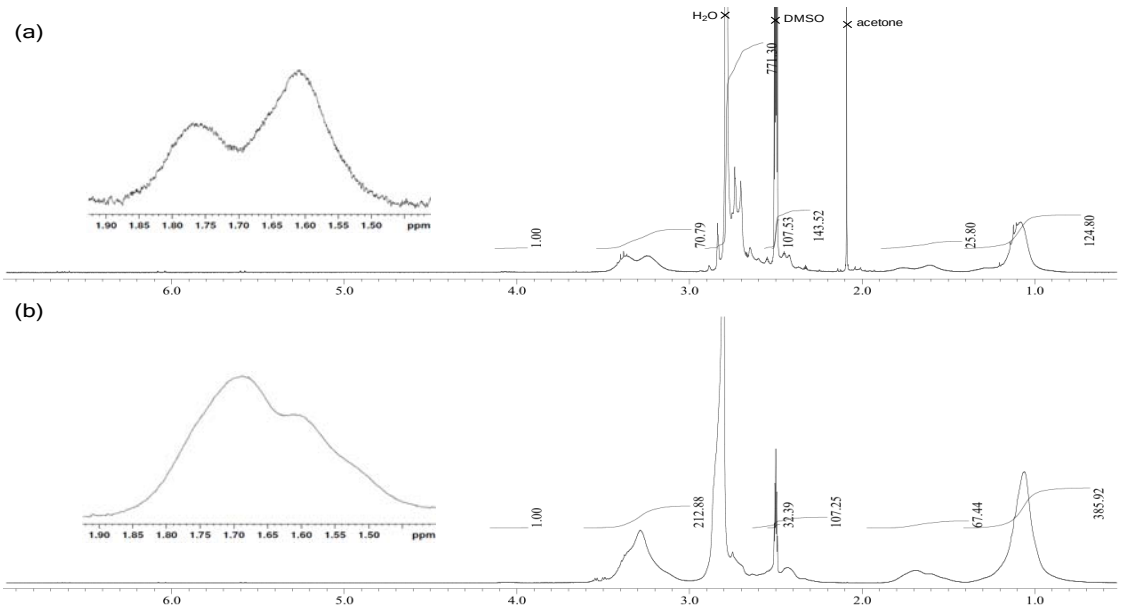

Figure S7. ^1H NMR spectra of (a) atactic and (b) stereoblock PDEAAs.

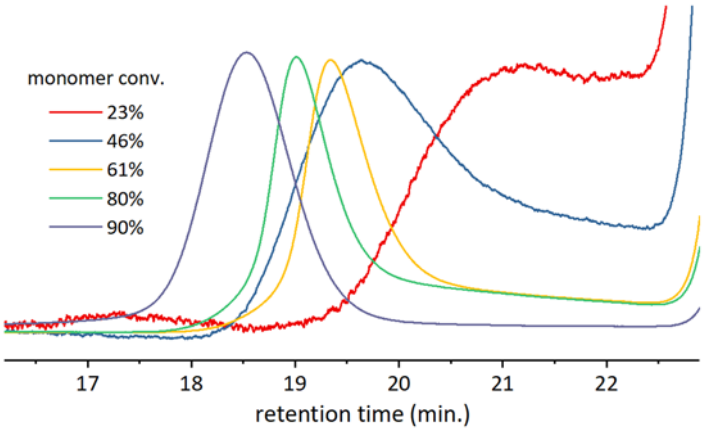

Figure S8. SEC traces of PDEAAs during the temporal control (Figure 2)

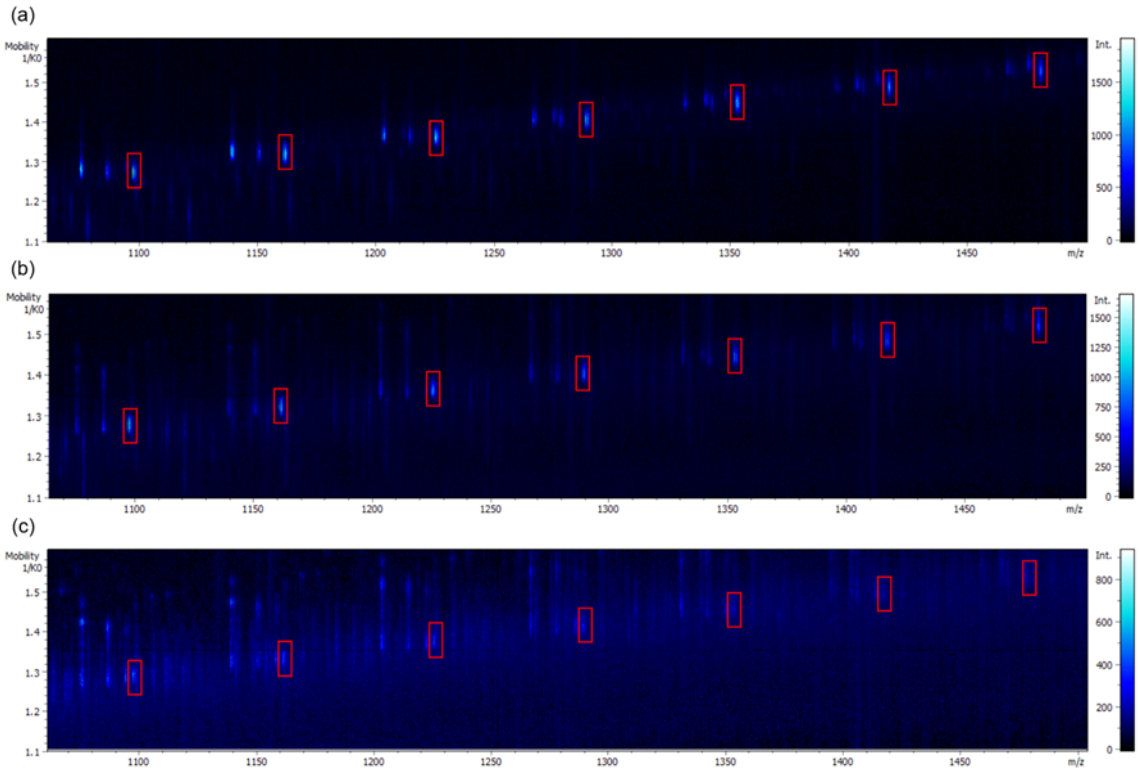

Figure S9. Heat maps of ion mobility spectrometry of PDEAAs with different *meso* diad selectivity. (a) 56%, (b) 85%, (c) 93% (*m*/*z* vs. inversion of the ion mobility [$1/K_0$ (V s cm^{-2})]). Peaks corresponding to *m*/*z* = 1097, 1161, 1224, 1288, 1352, 1415 and 1479 are marked with red rectangles.