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Polymer Chemistry

Controlled poly(olefin)s via decarboxylation of poly(acrylic acid)

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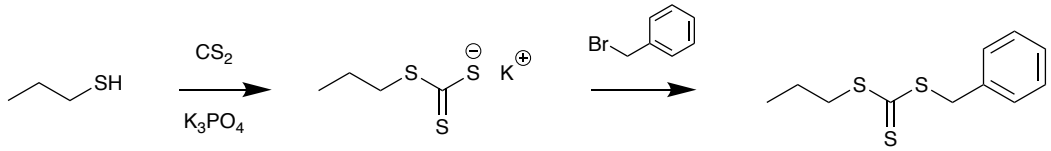
SUPPORTING INFORMATION

Experimental Procedures

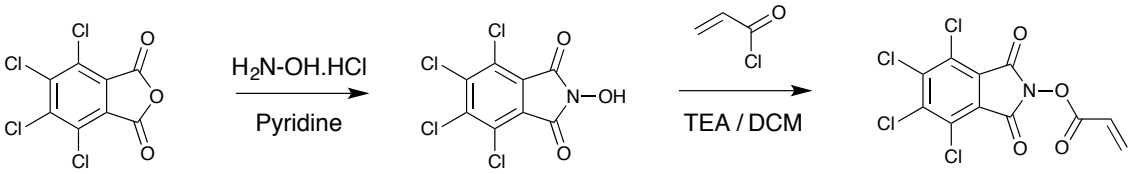
Additional synthetic protocols

Synthesis of S-benzyl S'-propyltrithiocarbonate (BPTT) RAFT agent:



Propanethiol (1.5 g, 19.7 mmol) was dissolved in acetone (30 mL) with K_3PO_4 (4.18 g, 19.7 mmol) and carbon disulphide (1.8 mL, 29.5 mmol) was added dropwise with stirring. After 30 min, benzyl bromide (4.2 g, 24.6 mmol) was added dropwise in acetone (10 mL), and the reaction was left to stir for a further 2h. The mixture was then diluted with dichloromethane (100 mL) and washed with water (1 x 50 mL), HCl (1M, 1 x 50 mL), water (1 x 50 mL) and brine (1 x 50 mL). The organic phase was dried with $MgSO_4$, concentrated, and the crude purified by column chromatography (silica, 5% EtOAc / cyclohexane), to yield the product as a yellow oil (4.45 g, 93%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.47 – 7.26 (m, 5H), 4.64 (s, 2H), 3.39 (t, J = 7.30 Hz, 2H), 1.77 (h, J = 7.34 Hz, 2H), 1.05 (t, J = 7.36 Hz, 3H).

Synthesis of Activated Monomer:



Tetrachlorophthalic anhydride (11.5 g, 40 mmol) was added portionwise to an ice cold stirred mixture of hydroxylamine hydrochloride (5.6 g, 80 mmol) in pyridine (30 mL). The orange suspension was heated to 50 °C for 2 h, and then diluted with 1M HCl (200 mL). The precipitate was filtered and washed extensively with HCl and then water to yield tetrachloro N-hydroxyphthalimide (TCNHPI) as an off-white powder (11.6 g, 96%). TCNHPI (8.0 g, 26.5 mmol) was then suspended in anhydrous dichloromethane (50 mL) under an atmosphere of nitrogen. Upon addition of triethylamine (3.8 mL, 29.2 mmol) the solid dissolved resulting in a dark red solution. Acryloyl chloride (3.2 mL, 39.9 mmol) was added dropwise over ice and the solution was stirred at RT overnight. The solution was washed with

water (2 x 100 mL), $NaHCO_3$ (sat) (2 x 100 mL) and brine (2 x 50 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The product was purified by column chromatography over silica gel with $CHCl_3$, and isolated as a white solid (5.7 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.74 (d, 1H), 6.41 (dd, J = 17.3, 10.6 Hz, 1H), 6.31 – 6.21 (d, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.56, 157.45, 141.07, 136.87, 130.54, 124.71, 122.62.

Synthesis of $NiCl_2$.glyme: Nickel (II) chloride hexahydrate (10 g, 42 mmol) was dried under vacuum (< 0.1 mbar) at 130°C for 1 h. After cooling, triethylorthoformate (2.2 eq, 14 g, 94 mmol) and dimethoxyethane (20 mL) were added and the solution was stirred under reflux for 2.5h. The resulting suspension was filtered and washed with dimethoxyethane (1 x 20 mL) and anhydrous pentane (3 x 20 mL), and then dried *in vacuo* to yield the product as a light yellow powder in quantitative yield (8.4 g).

References

[1] M. H. Stenzel, T. P. Davis, A. G. Fane, *J. Mater. Chem.* **2003**, *13*, 2090–2097.

Supplementary Figures and Tables

Table S1. Summary of copolymers prepared and GPC results

#	Polymer	[M] / [CTA]	X (%)	DP_{theo}	$M_{n\ theo}$ (g/mol)	M_n GPC (g/mol)	Đ
8	PEGMEA macroRAFT	44	90	40	19440	19720	1.21
9	PEGMEA-AA	34	76	26	21300	24770 [b]	1.39
9a	**9** + Me_2Zn				20530	24490	1.45
9c	**9** + Pr_2Zn				21250	25640	1.49
10	PEGMEA-AA	50	70	35	21960	24700 [b]	1.33
10a	**10** + Me_2Zn				20910	24320	1.44
10c	**10** + Pr_2Zn				21900	-	-

Note: [a] Polymers **8**-**10c** were run on DMF GPC, and Polymers **11**-**13c** were run on the THF GPC. [b] Samples methylated prior to analysis with trimethylsilyldiazomethane [c] Samples methylated prior to analysis with methylamine.

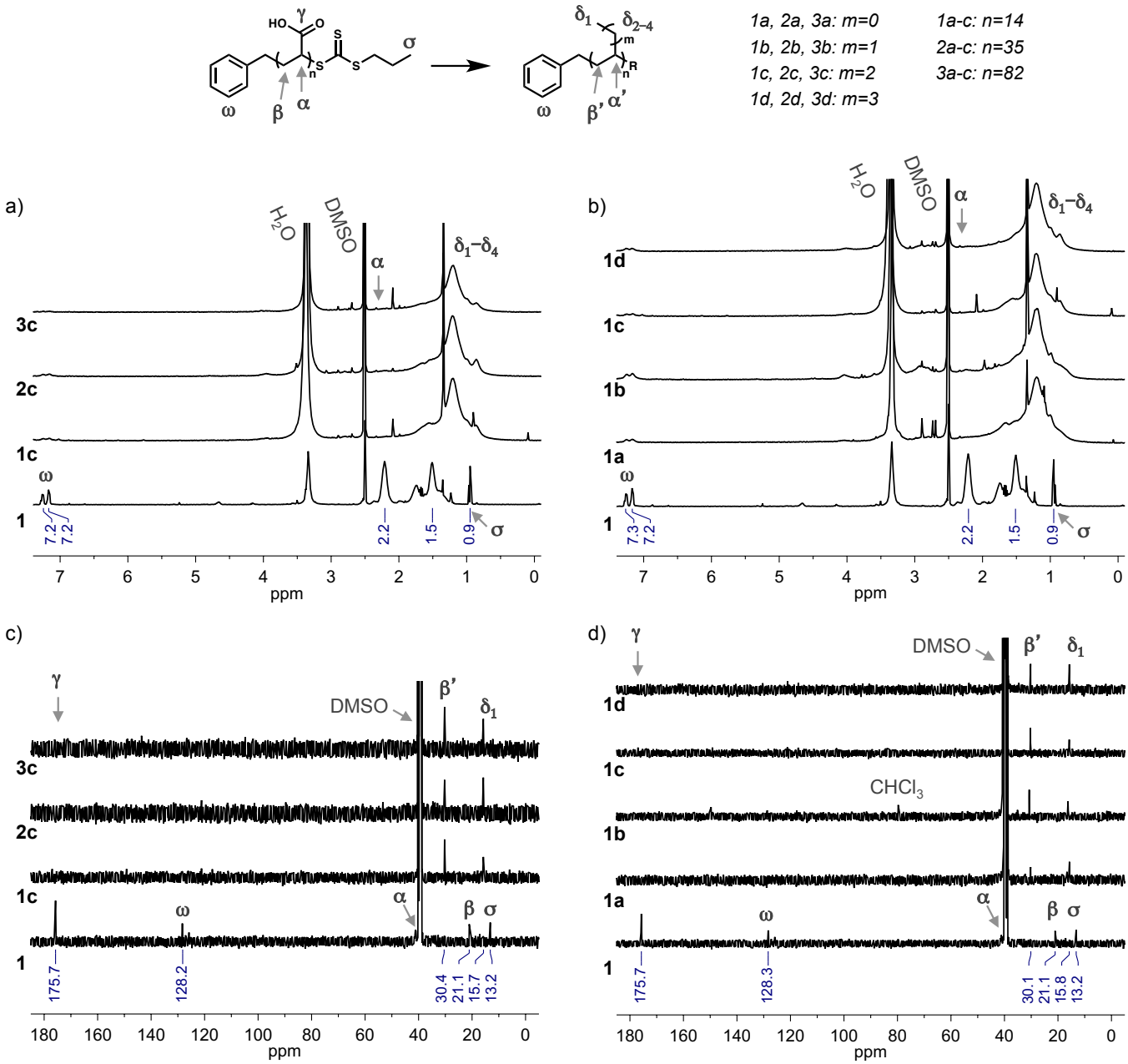


Figure S1. a-b) ^{1}H-NMR and c-d) ^{13}C-NMR in *d6*-DMSO at 298K for poly(acrylic acid) **1-3** and subsequent polyolefins from alkylation with dimethyl- (**1a**), diethyl- (**1b**), dipropyl- (**1c**), and dibutyl-zinc (**1d**) showing the disappearance of the acid moieties and appearance of the new side chains.

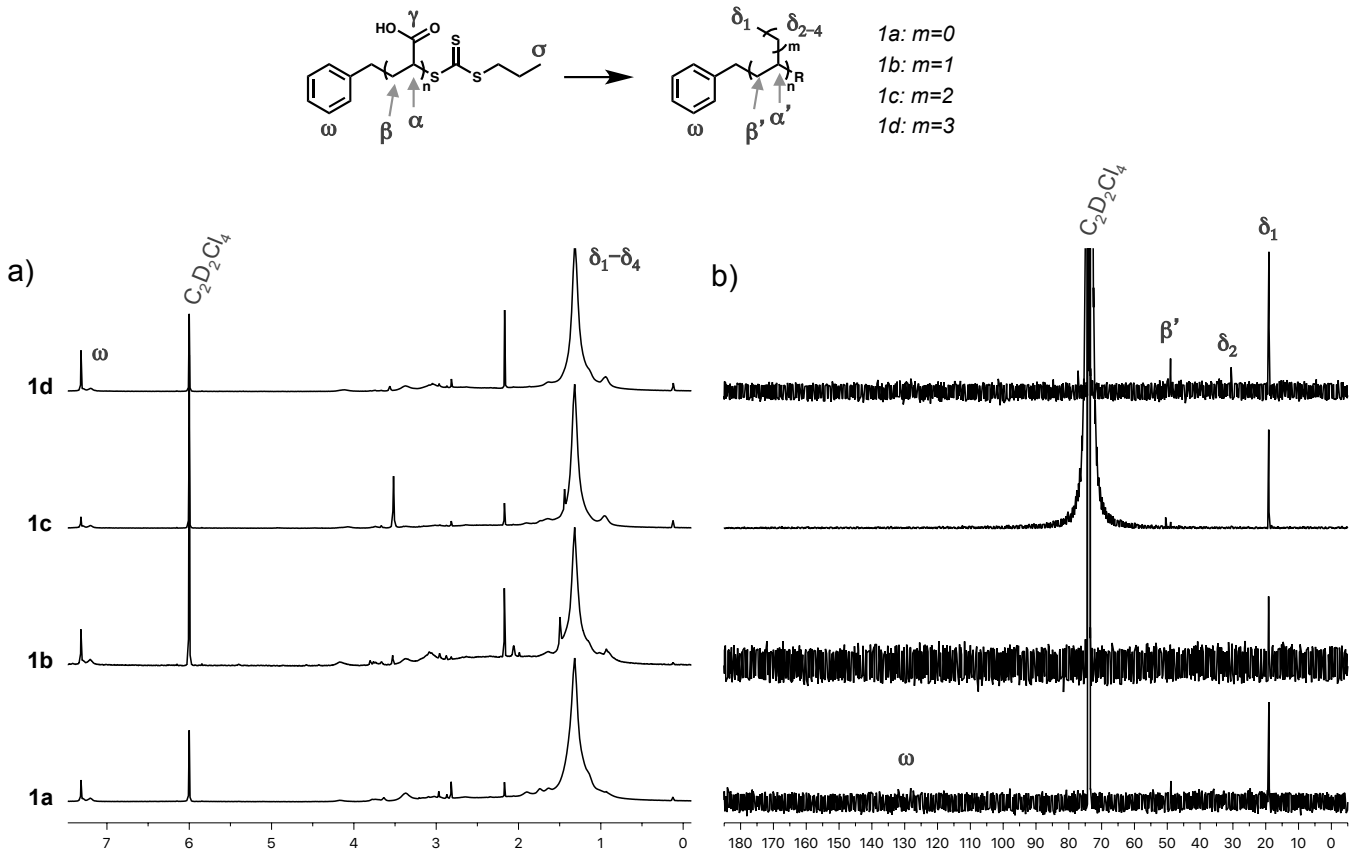


Figure S2. a) ^{1}H-NMR and b) ^{13}C-NMR in $C_2D_2Cl_4$ at 343K for polyolefins formed from reaction of poly(acrylic acid) **1** with dimethyl- (**1a**), diethyl- (**1b**), dipropyl- (**1c**), and dibutyl-zinc (**1d**).

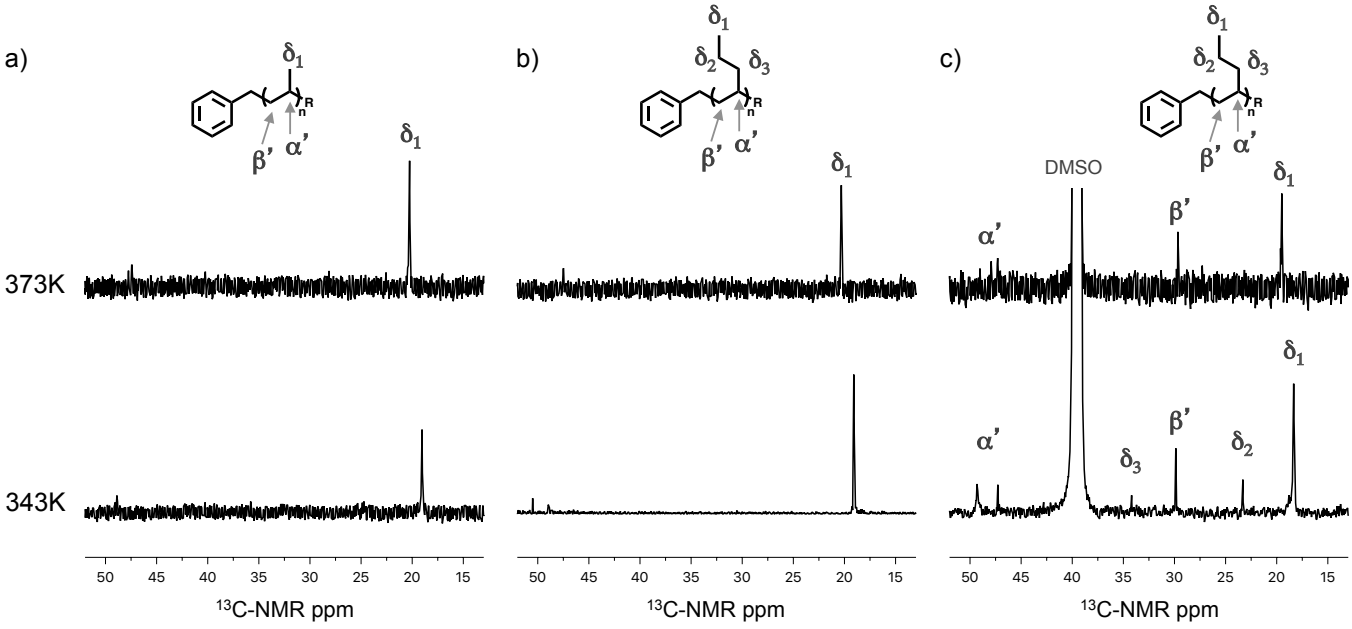


Figure S3. ^{13}C-NMR of a) polymer **1a** in $C_2D_2Cl_4$; b) polymer **1c** in $C_2D_2Cl_4$, at 343K; and c) polymer **1c** in *d6*-DMSO, at 343K and 373K.

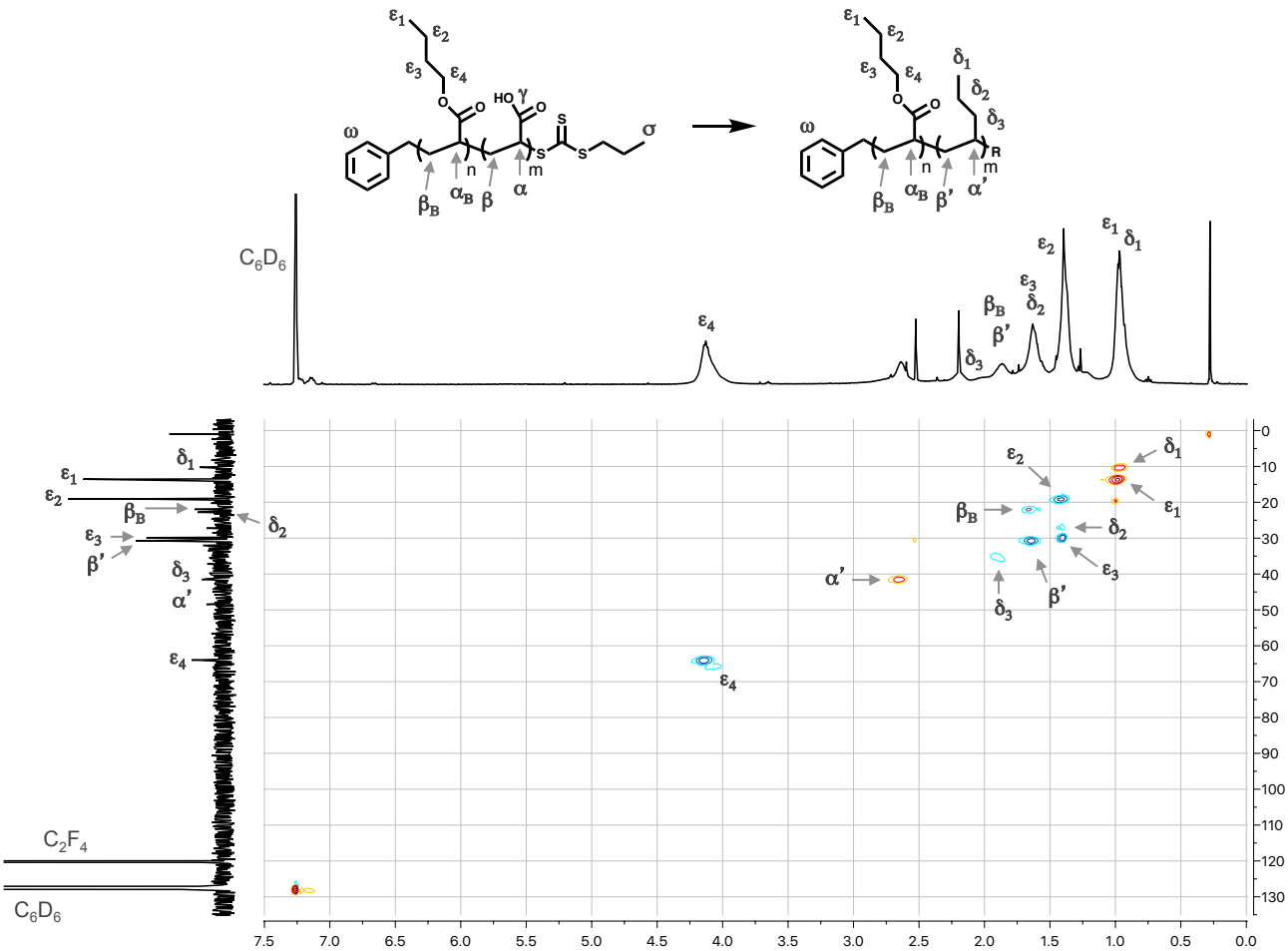


Figure S4. ^{1}H-^{13}C HSQC NMR of polymer **7c** (24h) in C_6D_6/TFE (3:1) showing the peak assignments.

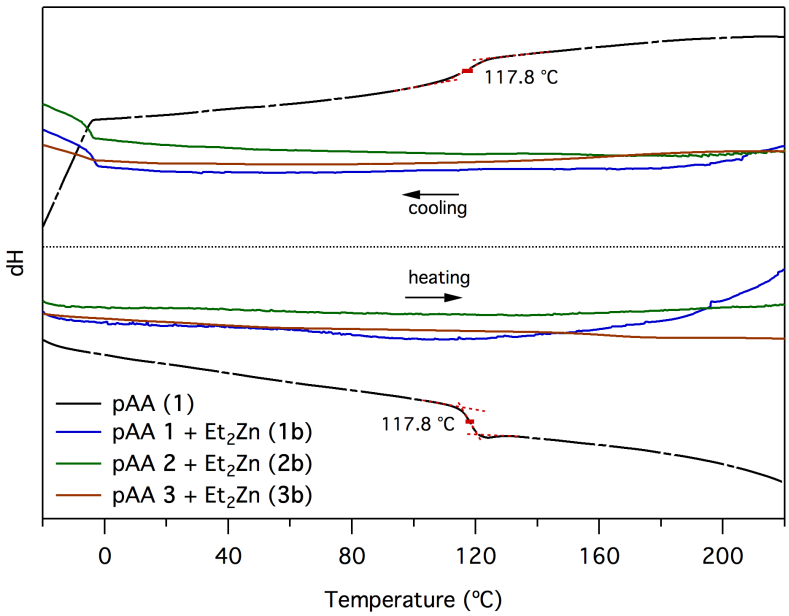


Figure S5. Differential scanning calorimetry (DSC) traces of poly(acrylic acid) (DP 14) and subsequent poly(butylene)s (DP 14, 35 and 82) showing loss of the glass transition temperature and lack of crystallinity in the product.

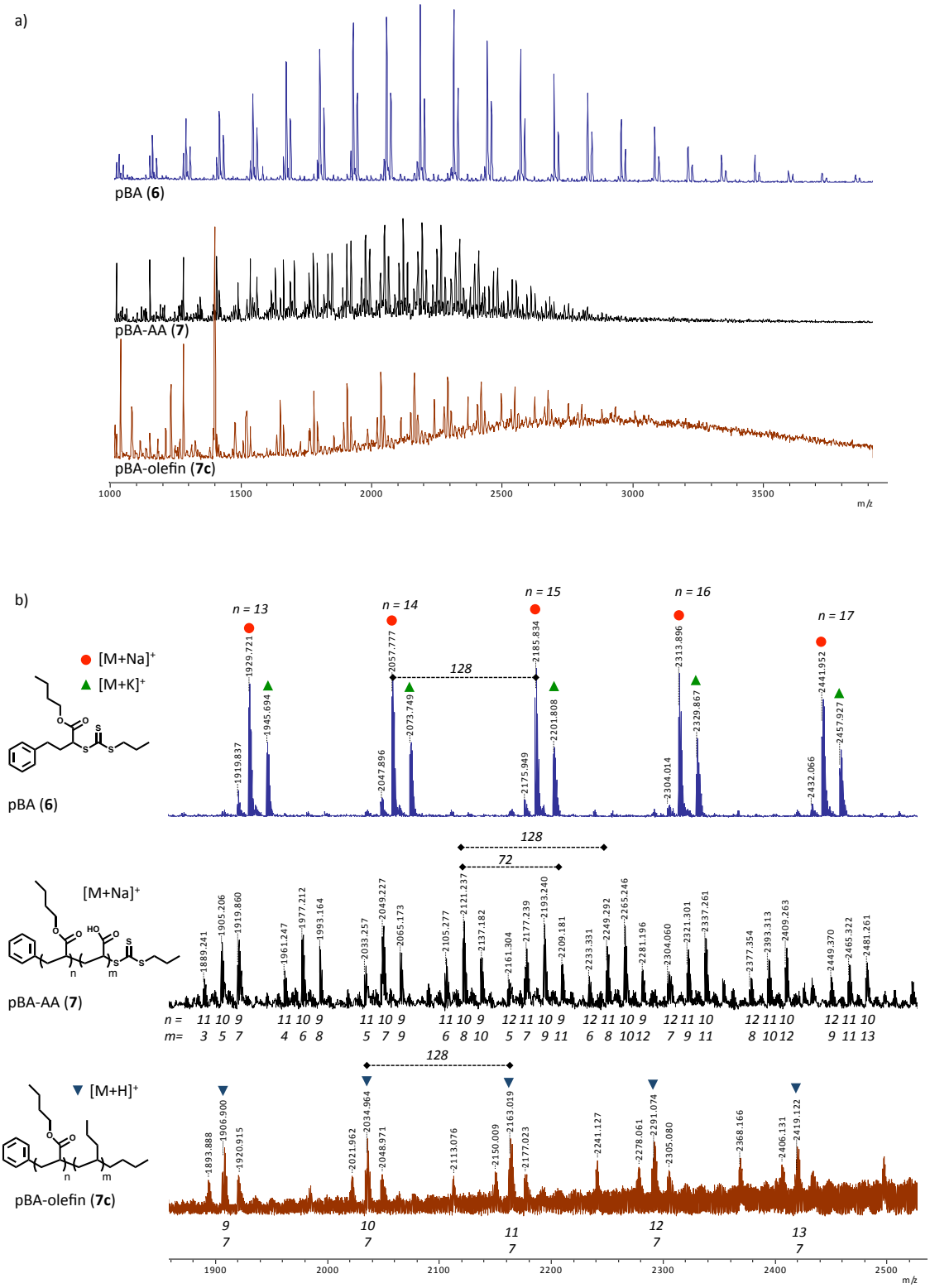


Figure S6. MALDI-TOF septra of pBA (polymer **6**) in a matrix of super-DHB, after chain extension with AA (polymer **7**) and after decarboxylation with dipropylzinc (polymer **7c**, 24h), both in a matrix of trans-3-indoleacrylic acid. The entire spectrum (a) is shown along with peak assignments for a narrow range (b).

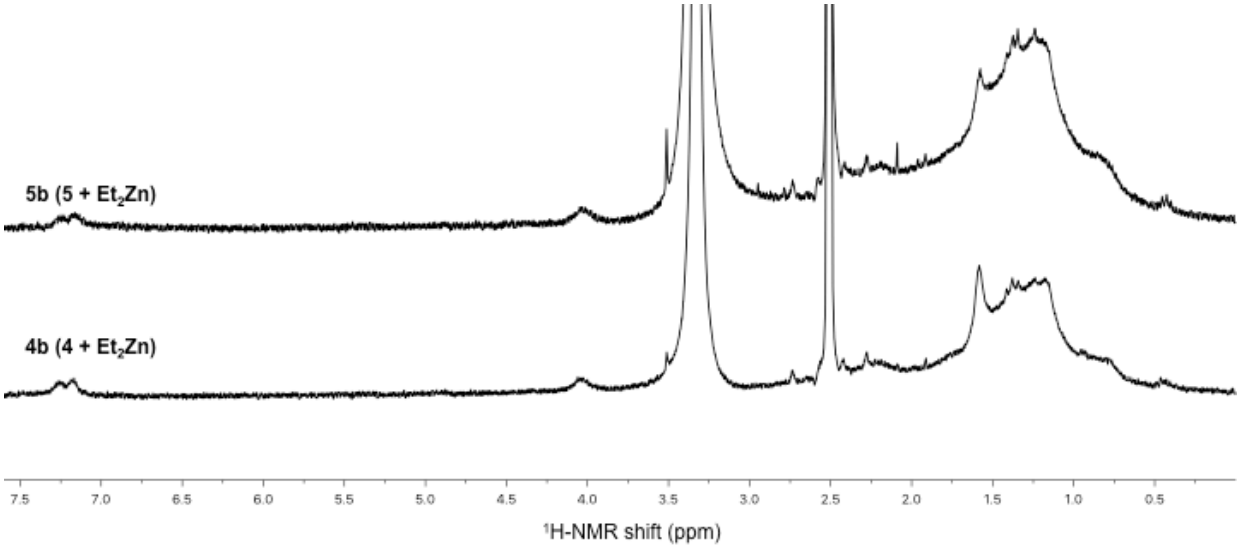


Figure S7. ^{1}H-NMR spectra of pActAA polymers **4** and **5** in d6-DMSO after reaction with diethylzinc.

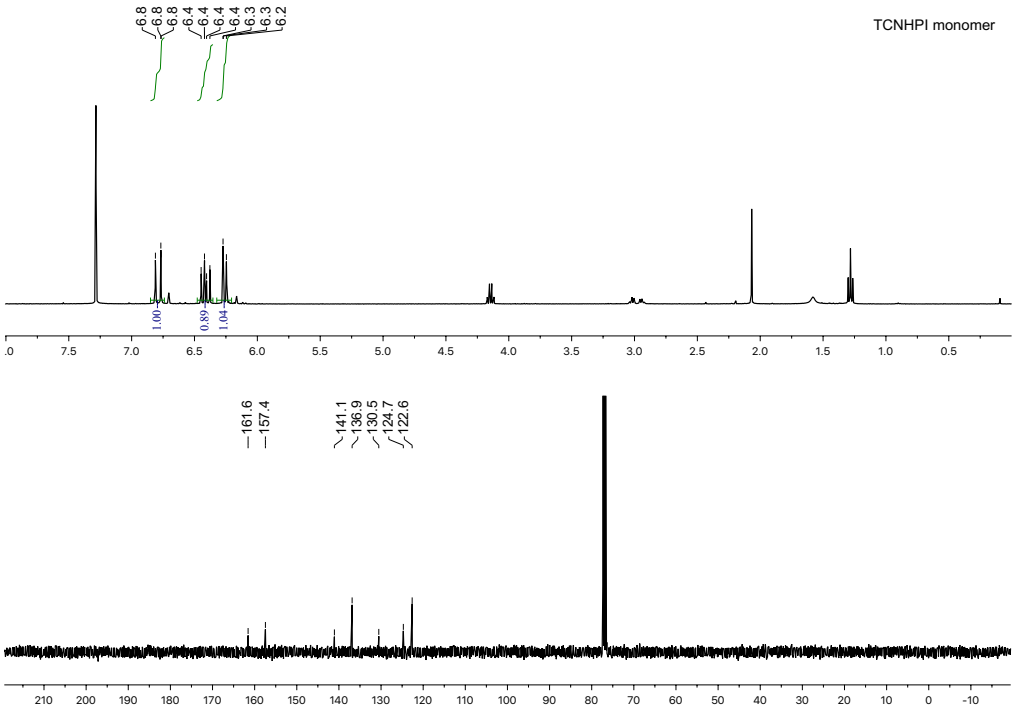


Figure S8. ^{1}H-NMR and ^{13}C-NMR spectra of the TCNHPI activated AA monomer in $CDCl_3$