SUPPLEMENTARY MATERIAL

Indirect Determination of Depolymerization Reactions in Dialdehyde Celluloses (DAC) by Gel Permeation Chromatography of Their Oxime Derivatives

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1) Additional data for Experiments 1

Table S1. Reaction times and GPC-MALLS statistical moments for the time dependent oximation of the samples **1a** which were soluble in the LiCl/DMAc medium. The values in **1a** did not change significantly from the beginning to the end of the monitoring, suggesting a quantitative transformation already after overnight reaction and the absence of severe side reactions.

	1a: DO = 7.1 ± 1.1 %					
Reaction time / h	Entry	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ	slope[a]
0	**CL**	94.6	145.6	200.2	1.5	0.67
19	**1a-1**	36.2	68.7	102.9	1.9	0.70
26	**1a-2**	38.6	70.8	105.7	1.8	0.58
42.5	**1a-3**	39.2	69.3	99.9	1.8	0.75
50	**1a-4**	38.1	69.5	102.3	1.8	0.72
74	**1a-5**	36.9	67.5	100.2	1.8	0.66
144.5	**1a-6**	35.4	66.8	100.7	1.9	0.64
170	**1a-7**	38.3	70.6	104.9	1.8	0.66

a) Slopes (scaling parameter) of the linear regression of the multiangle light-scattering data in the conformation plot.

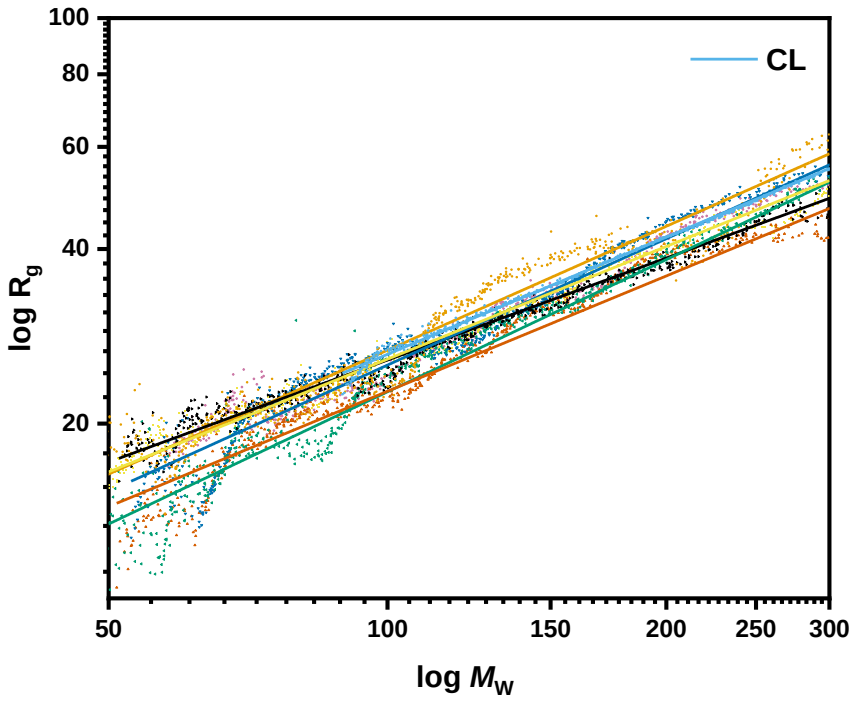

Figure S1. Conformation plots according to GPC for experiments **1a**.

Table S2. Reaction times and GPC-MALLS statistical moments for the time dependent oximation of the samples **1b** which were soluble in the LiCl/DMAc medium. In **1b** persistent crosslinks were observed and the values did not stabilize even after 170 h reaction time.

	1b: DO = 9.2 ± 0.3 %					
Reaction time / h	Entry	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ	slope[a]
0	**CL**	94.6	145.6	200.2	1.5	0.67
19	**1b-1**	40.5	125.3	290.7	3.1	0.56
26	**1b-2**	44.1	125.5	287.7	2.9	0.56
42.5	**1b-3**	41.1	123.3	297.1	3.0	0.46
50	**1b-4**	29.8	108.8	278.8	3.7	0.46
74	**1b-5**	43.7	119.4	276.4	2.7	0.45
144.5	**1b-6**	30.6	107.8	274.6	3.5	0.55
170	**1b-7**	32.3	110.2	271.2	3.4	0.46

a) Slopes of the linear regression of the multiangle light-scattering data in the conformation plot.

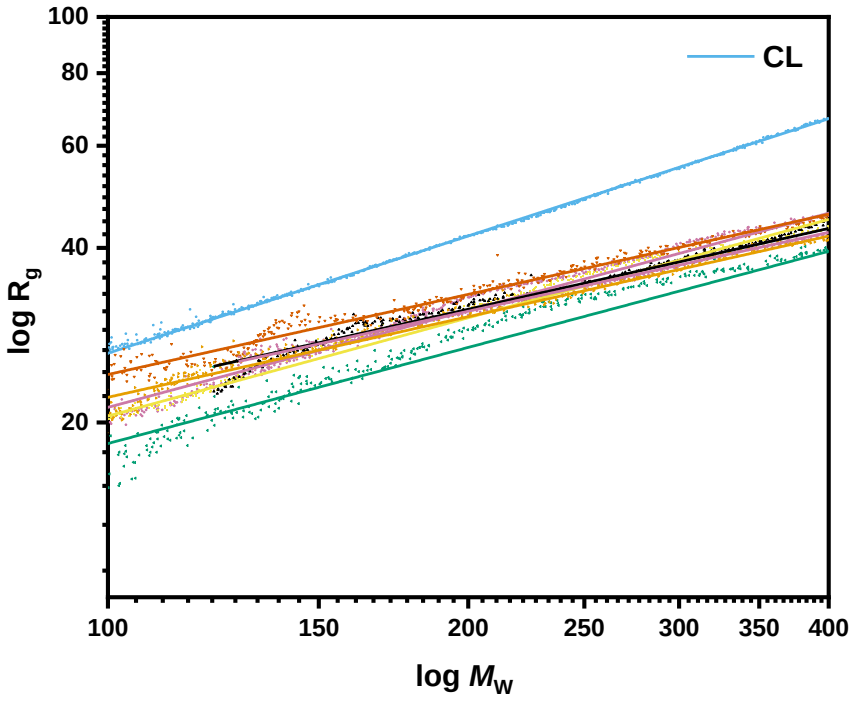

Figure S2. Conformation plots according to GPC for experiments **1b**.

2) Additional data for Experiments 2

Table S3. Reaction times, DO values and GPC-MALLS statistical moments for the time dependent periodate oxidation with 0.5 eq $NaIO_4$ (**Experiment 2a**).

Entry	Reaction time / h	DO / %	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ
CL	0.0	0	101.3	145.9	194.0	1.4
2a-1	0.33	1.7 ± 0.4	81.4	123.6	167.0	1.5
2a-2	0.67	1.8 ± 0.7	77.9	118.6	159.8	1.5
2a-3	1.0	2.3 ± 0.4	70.3	109.4	149.8	1.6
2a-4	1.33	2.0 ± 0.5	75.2	104.5	132.7	1.4
2a-5	1.67	4.1 ± 0.3	69.9	106.7	143.3	1.5
2a-6	2.0	3.9 ± 0.5	66.3	103.7	141.5	1.6
2a-7	2.75	3.6 ± 0.4	60.9	98.1	137.8	1.6
2a-8	20.0	7.4 ± 0.5	36.5	66.2	97.0	1.8
2a-9	22.0	8.0 ± 1.3	37.8	66.7	97.0	1.8
2a-10	24.0	8.7 ± 1.5	35.7	66.0	97.9	1.8

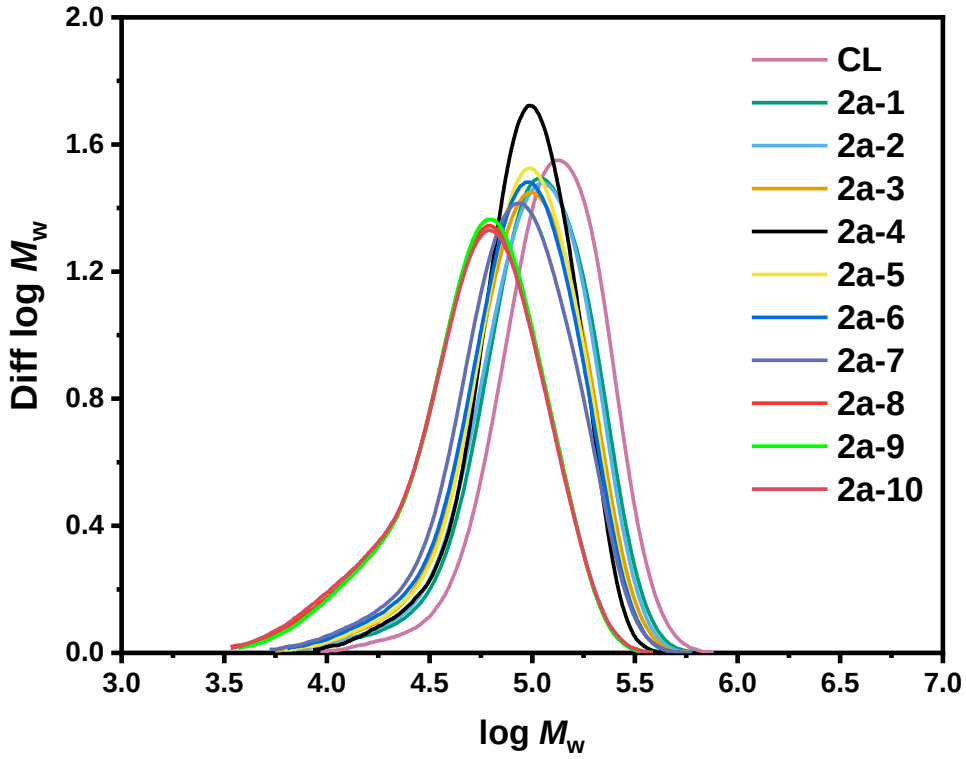

Figure S3. Molecular weight distributions according to GPC for experiments **2a**.

Table S4. Reaction times, DO values and GPC-MALLS statistical moments for the time dependent periodate oxidation with 1 eq $NaIO_4$ (**Experiment 2b**).

Entry	Reaction time / h	DO / %	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ
CL	0.0	0	94.6	145.6	200.2	1.5
2b-1	0.33	1.8 ± 0.5	65.0	111.6	159.8	1.7
2b-2	0.67	1.0 ± 0.7	64.6	108.6	154.7	1.7
2b-3	1.0	2.2 ± 0.8	58.5	96.4	134.5	1.6
2b-4	1.33	2.4 ± 1.0	59.3	95.4	132.5	1.6
2b-5	1.67	2.0 ± 1.3	62.6	97.6	131.7	1.6
2b-6	2.0	3.0 ± 1.7	55.1	86.2	117.9	1.6
2b-7	3.0	3.3 ± 0.4	54.8	84.0	111.7	1.5
2b-8	18.0	8.7 ± 0.3	Insoluble			
2b-9	21.0	9.6 ± 0.3				
2b-10	24.0	11.4 ± 0.3				

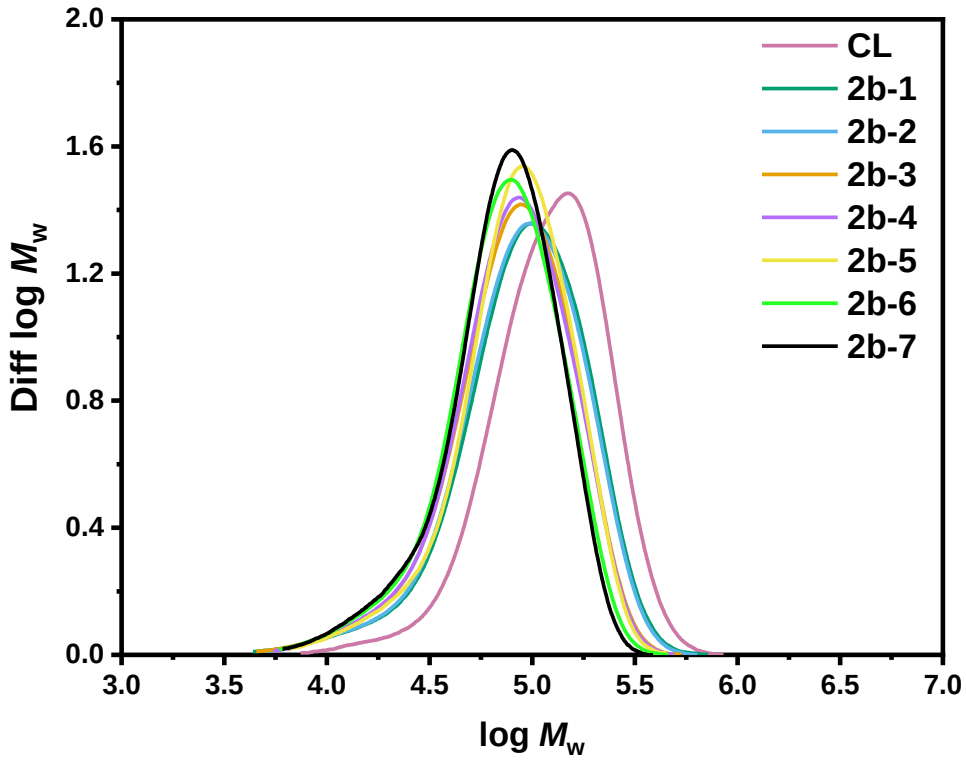

Figure S4. Molecular weight distributions according to GPC for experiments **2b**.

Table S5. Reaction times, DO values and GPC-MALLS statistical moments for the time dependent periodate oxidation with 2 eq $NaIO_4$ (**Experiment 2c**).

Entry	Reaction time / h	DO / %	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ
CL	0.0	0	87.3	146.2	212.9	1.7
2c-1	0.33	4.0 ± 0.7	58.8	98.4	138.9	1.7
2c-2	0.67	4.0 ± 0.5	56.4	91.5	124.9	1.6
2c-3	1.0	4.6 ± 0.3	49.4	84.0	118.1	1.7
2c-4	1.33	4.5 ± 0.4	48.3	83.6	118.6	1.7
2c-5	1.67	6.0 ± 0.4	46.4	81.3	117.2	1.8
2c-6	2.0	7.2 ± 1.9	45.4	78.2	112.8	1.7
2c-7	3.0	6.6 ± 0.6	40.8	73.2	108.0	1.8
2c-8	19.0	17.1 ± 0.3	Insoluble			
2c-9	21.5	18.6 ± 0.1				
2c-10	24.0	20.0 ± 0.5				

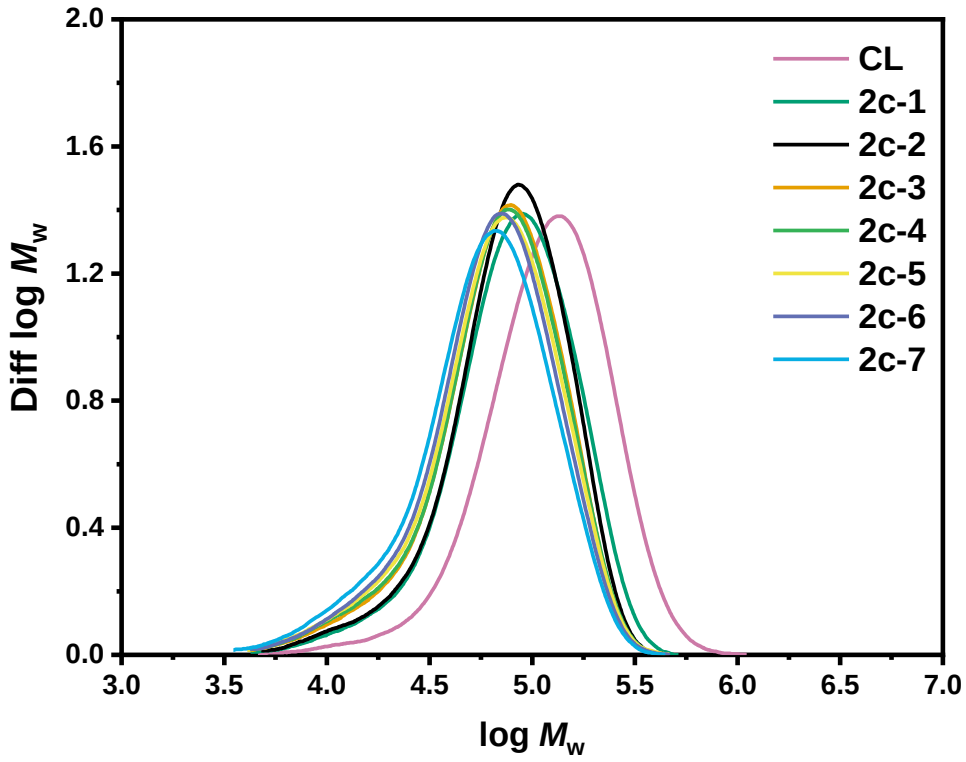

Figure S5. Molecular weight distributions according to GPC for experiments **2c**.

3) Additional data for Experiments 3

Table S6. Solvent systems, DO values after treatment and GPC-MALLS statistical moments for the pH dependent degradation study of unmodified DAC (**Experiment 3a**).

Entry	solvent	DO / %	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ
CL	-	-	90.2	142.9	197.0	1.6
3a-0[a]	-	5.9	55.2	83.5	113.9	1.5
3a-1	H_2O	5.6	52.7	80.8	112.0	1.5
3a-2	HCl	6.0	46.5	84.3	132.1	1.8
3a-3	HOAc	6.0	50.7	83.6	120.1	1.6
2a-4	pH3	6.0	53.8	85.4	120.6	1.6
3a-5	pH5	5.2	49.7	81.9	118.8	1.6
3a-6	pH7	5.4	55.4	80.0	107.0	1.4
3a-7	pH9	2.2	30.7	44.5	58.6	1.5
3a-8	pH11	-[b]	22.3	35.0	47.8	1.6
3a-9	NH_3	0.9	30.6	41.9	52.8	1.4
3a-10	NaOH	-[b]	22.3	32.3	42.6	1.4

a) DAC – Oxime before treatment. **b**) below detection limit of the FTIR analysis.

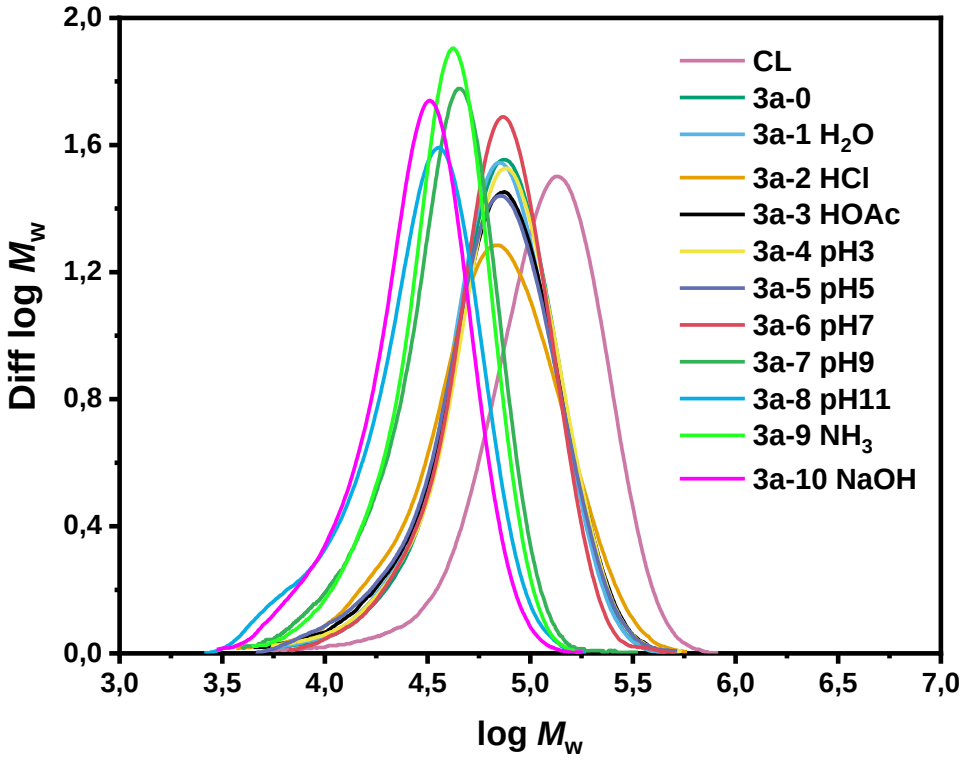

Figure S6. Molecular weight distributions according to GPC for experiments **3a**.

Table S7. Solvent systems and GPC-MALLS statistical moments for the pH dependent degradation study of DAC oximes (**Experiment 3b**). For the study the same DAC (DO = 5.9%) as in **Experiments 3a** were used.

Entry	solvent	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	Đ
CL	-	90.2	142.9	197.0	1.6
3b-0[a]	-	56.8	89.7	127.1	1.6
3b-1	H_2O	52.0	87.6	131.0	1.7
3b-2	HCl	33.7	69.3	118.2	2.1
3b-3	HOAc	42.6	88.6	148.2	2.1
2b-4	pH3	51.8	90.8	140.7	1.8
3b-5	pH5	48.7	82.6	123.1	1.7
3b-6	pH7	49.8	81.5	117.8	1.6
3b-7	pH9	58.4	70.2	81.5	1.2
3b-8	pH11	32.5	45.8	59.3	1.4
3b-9	NH_3	56.0	64.4	72.4	1.2
3b-10	NaOH	34.1	48.4	63.9	1.4

a) DAC – Oxime (sample **3a-0**) after storage at 4°C for 3 days

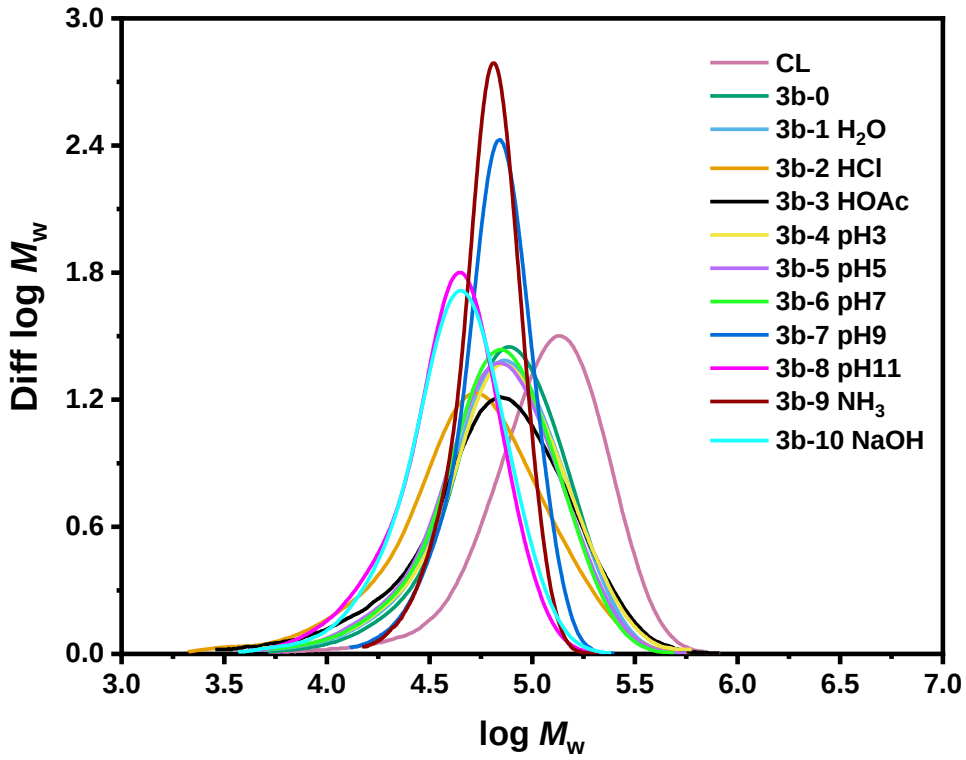

Figure S7. Molecular weight distributions according to GPC for experiments **3b**.

4) Preparation of solutions for Experiments 3

Solvent 1: **H_2O**

Solvent 2: **0.5 M HCl**

Diluted 20.8 mL 36% HCl to 500 mL

Solvent 3: **0.5 M HOAc**

Dissolved 15 g HOAc (100%) in 500 mL H_2O

Solvent 4: **pH3 buffer 0.5 M (Universal Buffer)**

Dissolved 0.125 mol citric acid monohydrate (26.27g) and 0.065 mol Na_2HPO_4 (9.18 g) in 250 mL H_2O

Solvent 5: **pH5 buffer 0.5 M (Universal Buffer)**

Dissolved 0.059 mol citric acid monohydrate (12.37 g) and 0.125 mol Na_2HPO_4 (17.75 g) in 250 mL H_2O

Solvent 6: **pH7 buffer 0.5 M (Universal Buffer)**

Dissolved 0.013 mol citric acid monohydrate (2.81 g) and 0.065 mol Na_2HPO_4 (17.75 g) in 250 mL H_2O

Solvent 7: **pH9 buffer 0.5 M (NH_3 / NH_4Cl)**

Dissolved 0.125 mol NH_4Cl (6.7 g) and 0.072 mol NH_3 (4.4 mL of 32% solution) in 250 mL H_2O

Solvent 8: **pH11 buffer 0.5 M (Na_2HPO_4 / NaOH)**

Dissolved 0.125 mol Na_2HPO_4 (17.75 g) and 0.021 mol NaOH (0.82 g) in 250 mL H_2O

Solvent 9: **0.5 M NH_3**

Diluted 15.2 mL 32% NH_3 to 500 mL

Solvent 10: **0.5 M NaOH**

Dissolved 10 g NaOH (100%) in 500 mL H_2O