Supporting Information

Superabsorbent Hydrogels made from Bio-sourced Butyrolactone Monomer in Aqueous Solution

Sharmaine B. Luk [a], Jozef Kollár [b], Anna Chovancová [b], Miroslav Mrlík [c], Igor Lacík [b], Jaroslav Mosnáček [*,b], and Robin A. Hutchinson [*,a]

[a] Queen's University, Department of Chemical Engineering, 19 Division St., Kingston, Ontario, Canada

[b] Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 845 41, Bratislava, Slovakia

[c] Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic

The structure of the MeMBL ring was confirmed using NMR as shown in Figure S1.

Table S1: Proton assignment of MeMBL NMR spectra in Figure S1.

Proton Label	Shift (ppm)	Multiplicity	Justification
1	6.1	Doublet	Geminal proton split by H_2 on double bond
2	5.7	Doublet	Geminal proton split by H_1 on double bond
3	3.1	Doublet of doublet of doublet	Geminal proton – large splitting by H_4, and small splitting by H_5
4	2.55	Doublet of doublet of doublet	Geminal proton – large splitting by H_3, and small splitting by H_5
5	4.75	Multiplet*	Split by H_6 methyl group and H_3 and H_4
6	1.3	Doublet	Methyl group split by H_5

After saponification of MeMBL, structure of the opened ring, SHMeMB, was confirmed by NMR in Figure S2.

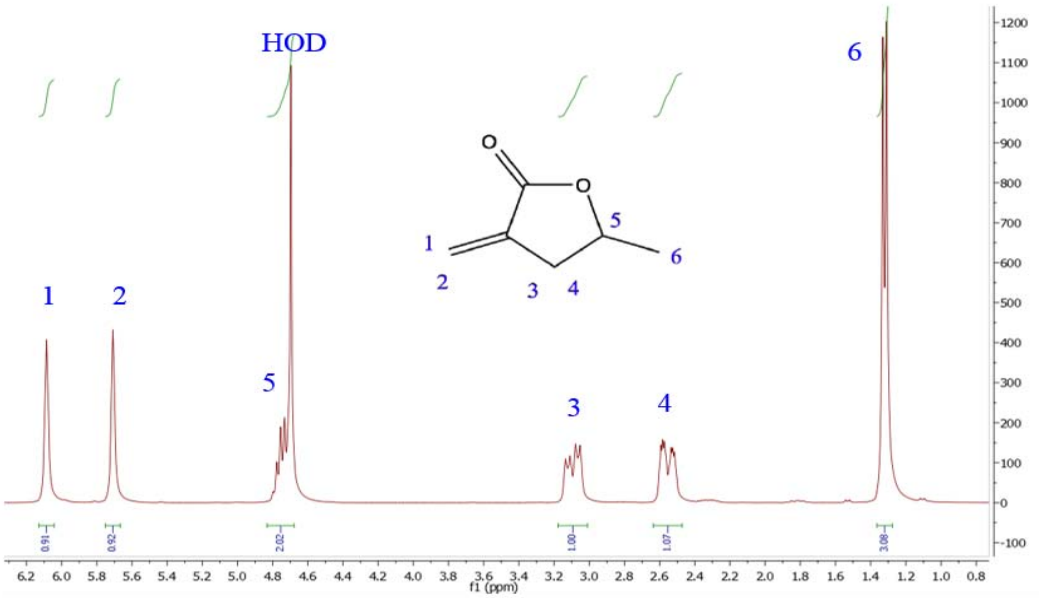

Figure S1: NMR spectra (500 MHz) of MeMBL in D_2O solvent (4.7 ppm) at room temperature and pH=7.

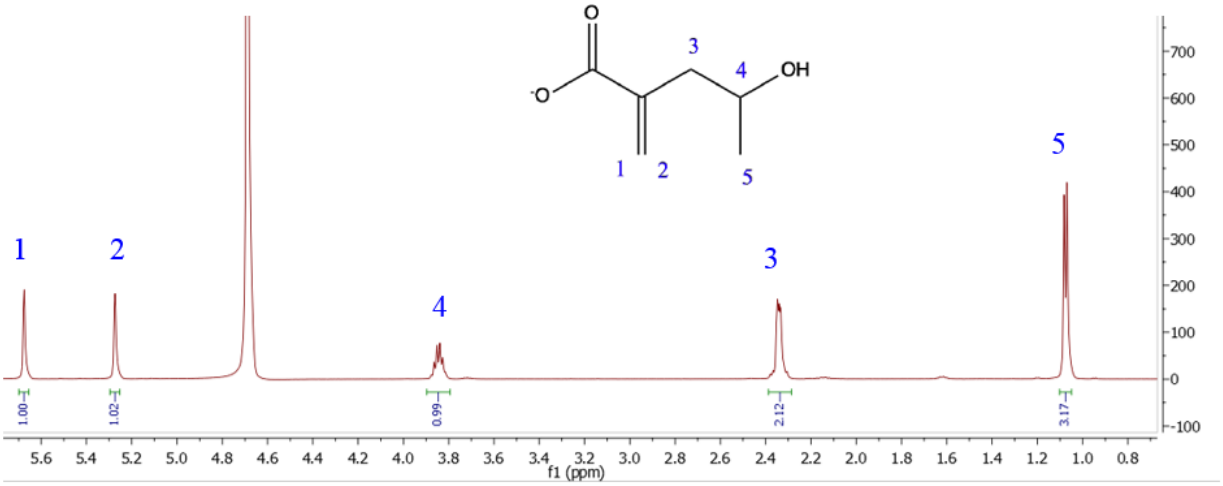

Figure S2: NMR spectra (500 MHz) of SHMeMB in D_2O (4.7 ppm) at room temperature and pH=7.

Table S2: Proton assignment of SHMeMB NMR spectra in Figure S2.

Proton Label	Shift (ppm)	Multiplicity	Justification
1	6.1	Doublet	Geminal proton split by H_2 on double bond
2	5.7	Doublet	Geminal proton split by H_1 on double bond
3	2.3	Multiplet	Two equivalent protons split by H_4, H_1 and H_2
4	3.85	Sextet	Split by H_5 methyl group and both H_3 protons
5	1.07	Doublet	Methyl group split by H_4

For experiments done at 50°C, SHMeMB monomer peak at 5.6 ppm was used for conversion calculation (Figure S3). Two AM monomer peaks overlap in the NMR spectra, so the two peaks at ~6.4 ppm are divided by two to determine conversion.

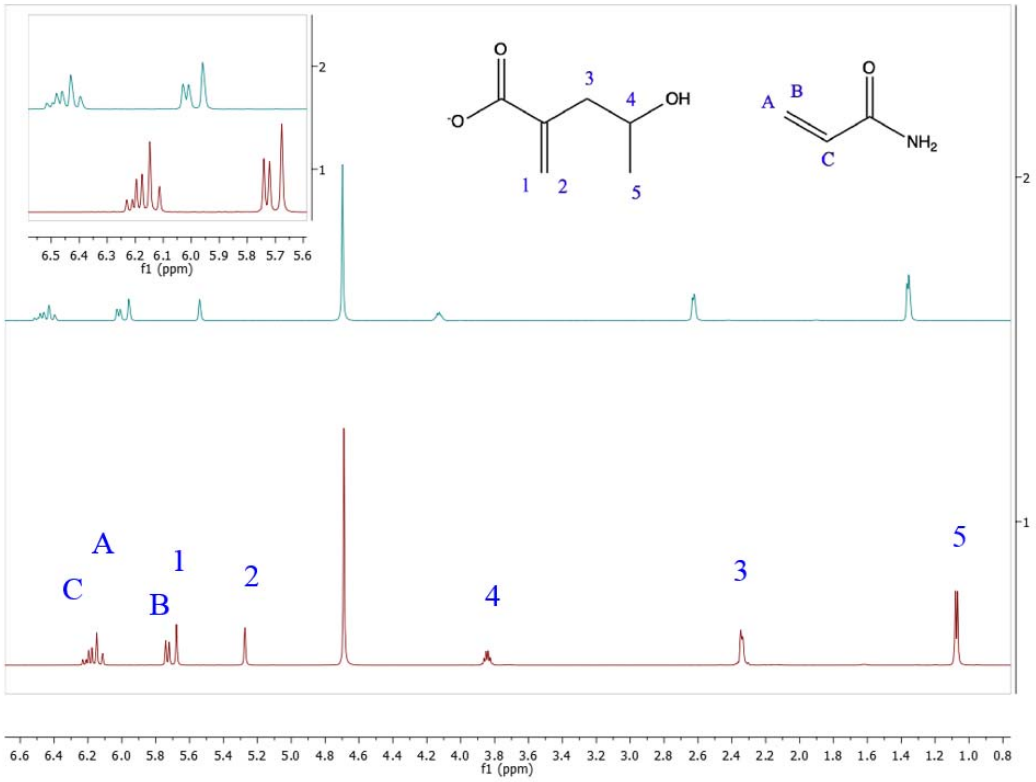

Figure S3: NMR spectra (500 MHz) of equimolar SHMeMB and AM at 25°C (bottom) and 50°C (top) in D_2O (4.7 ppm) and pH=7.

Table S3: Proton assignment of AM protons at 50°C in Figure S3.

Proton Label	Shift (ppm)	Multiplicity	Justification
A	6.4	Doublet	Geminal splitting by H_B on doublet bond and trans- to H_C
B	6.0	Doublet	Geminal splitting by H_A on doublet bond and cis- to H_C
C	6.48	Doublet of doublet	Split by H_A and H_B

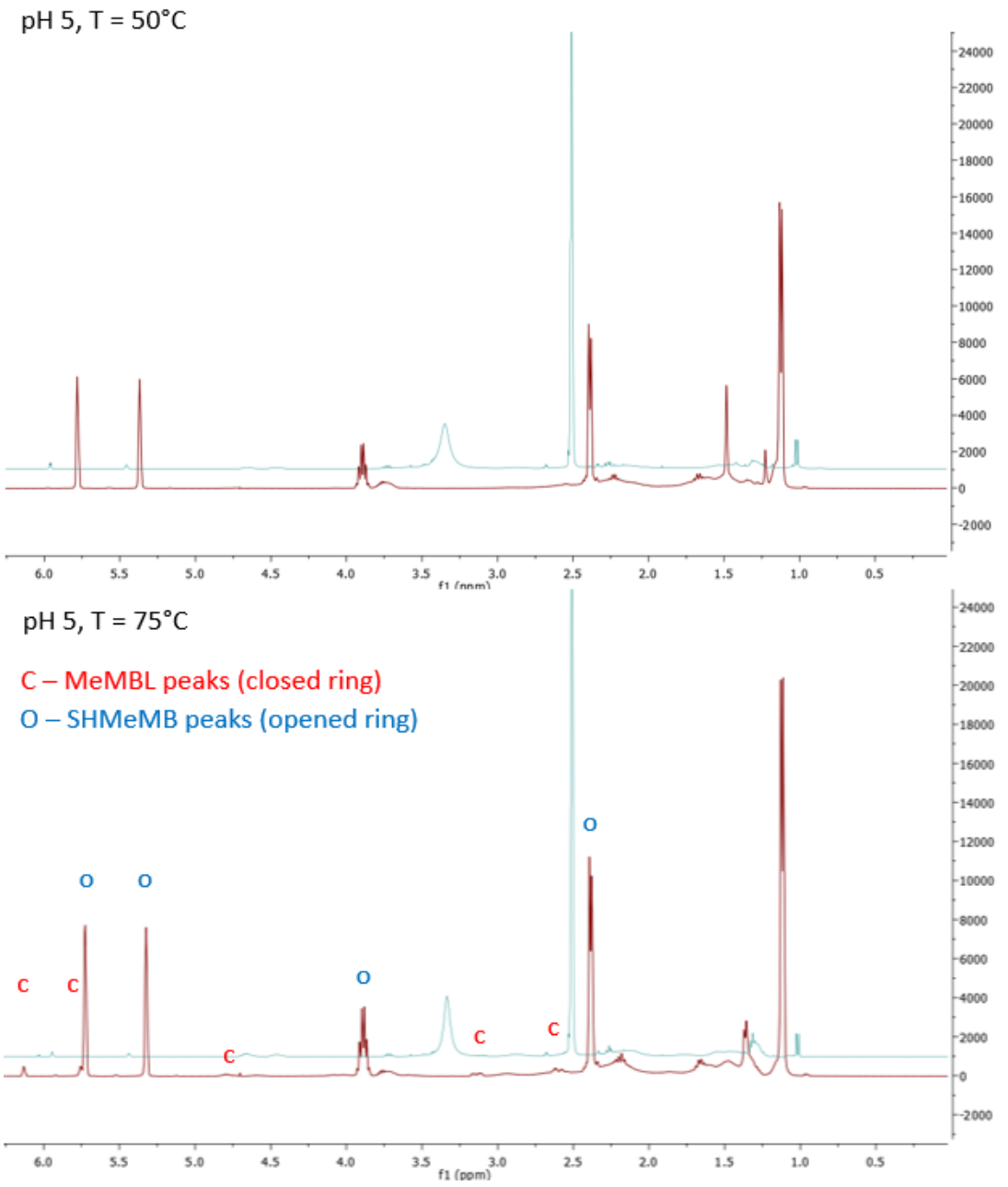

Figure S4: NMR analysis of SHMeMB homopolymer produced after 16 h at pH=5 and 15 wt% monomer at 50°C with 1 wt% V-50 (top) and 75°C with 1 wt% KPS (bottom). The red spectra are for the water-soluble phase in D_2O and the green spectra are of the organic phase in DMSO. The water phase at 75 ℃ shows proton peaks from MeMBL monomer as evidence of ring closure and the organic phase contains PMeMBL and PSHMeMB polymer.

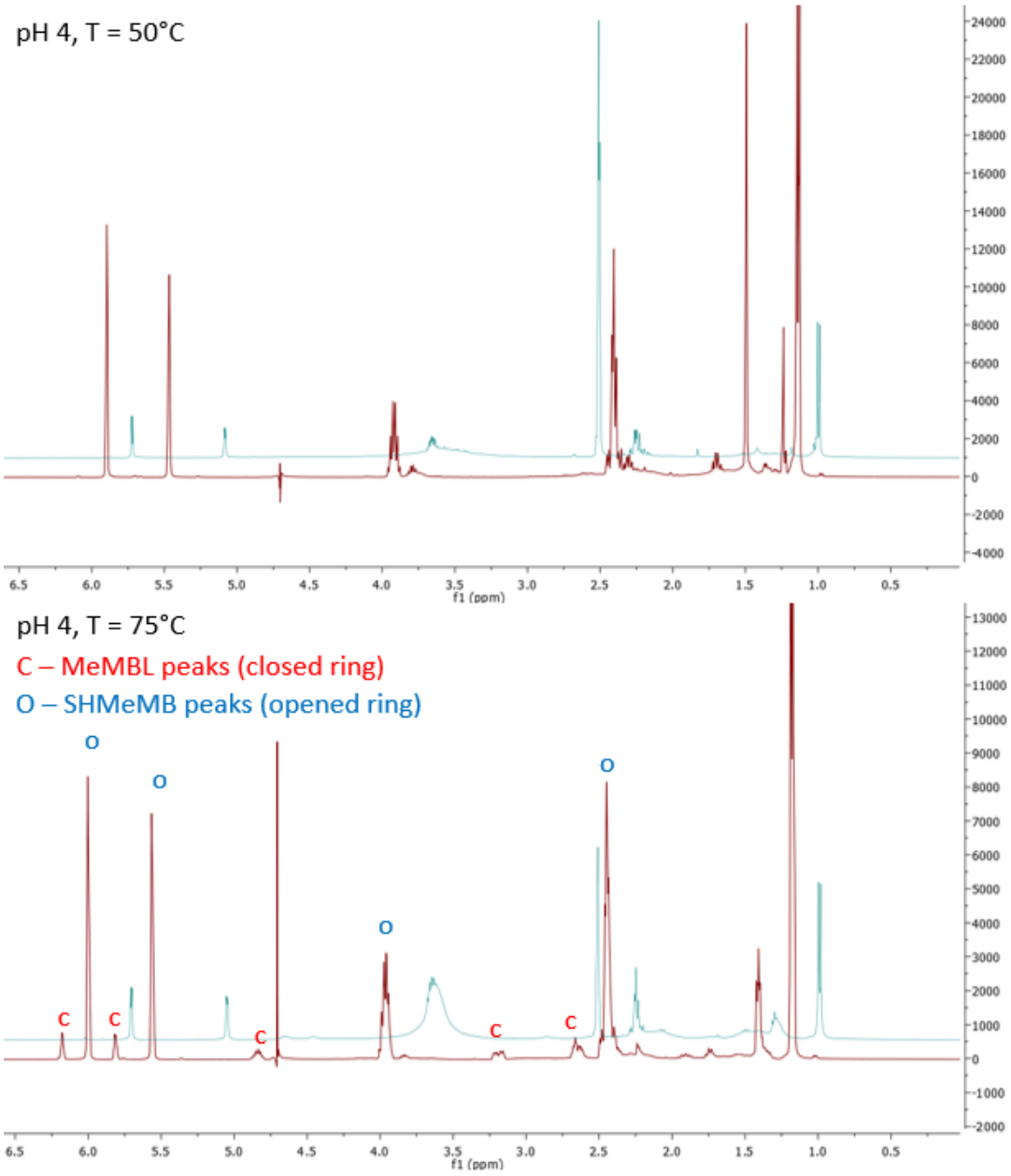

Figure S5.: NMR analysis of SHMeMB homopolymer produced after 16 h at pH=4 and 15 wt% monomer at 50°C with 1 wt% V-50 (top) and 75°C with 1 wt% KPS (bottom). The red spectra are of the water-soluble phase in D_2O and the green spectra are of the organic phase in DMSO. The water phase at 75 ℃ shows proton peaks from MeMBL monomer as evidence of ring closure and the organic phase contains PMeMBL and PSHMeMB polymer.

Table S4:Copolymer composition of SHMeMB:AM copolymers (F_{SHMeMB}) at low conversion (<10%) from batch studies at 50°C with varying initial comonomer compositions (f_{SHMeMB}).

f_{SHMeMB}	F_{SHMeMB}
0	0
0.11	0.088
0.197	0.164
0.267	0.216
0.383	0.285
0.487	0.318
0.534	0.372
0.8	0.539
1	1

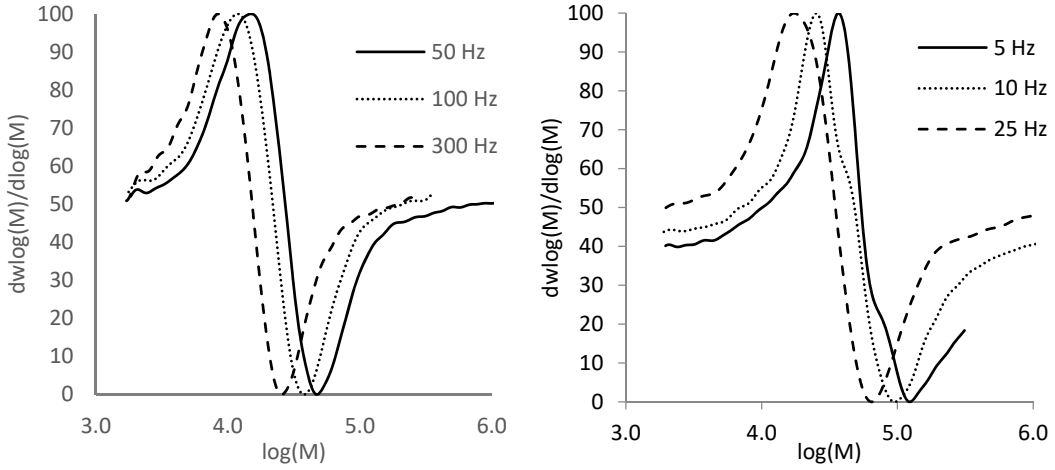

Figure S6: First derivatives of SHMeMB:AM copolymer MMDs produced by PLP-SEC with f_{SHMeMB}=0.1, number of pulses=1000, 10 wt% monomer, 3.4 mmol/L LiTPO, and 60°C.

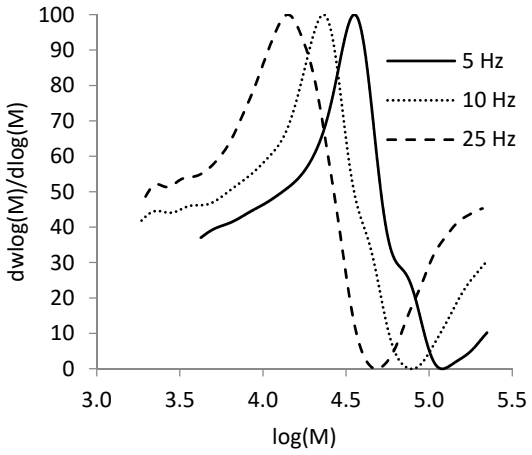

Figure S7: First derivatives of SHMeMB:AM copolymer MMDs produced by PLP-SEC with f_{SHMeMB}=0.1, number of pulses=1000, 10 wt% monomer, 6.8 mmol/L LiTPO, and 60°C.

Table S5: PLP-SEC conditions and results for SHMeMB:AM copolymers at 60°C, 6.8 mmol/L LiTPO and 10 wt% monomer.

mol% SHMeMB	Repetition rate	# of pulses	$logM_1$	$logM_2$	M_1/M_2	$k_p^{cop}{}_1$	$k_p^{cop}{}_2$	Conversion
5 mol%	1 Hz	100	5.56	6.05	0.32	3639	5613	19.0%
	2 Hz	100	5.30	5.69	0.41	4020	4941	15.0%
	4 Hz	100	4.98	5.37	0.41	3838	4709	12.4%
	5 Hz	100	4.89	5.28	0.41	3884	4760	7.9%
10 mol%	1 Hz	100	5.35	5.75	0.40	2040	2558	14.3%
	2 Hz	100	5.02	5.40	0.41	1890	2303	11.6%
	4 Hz	100	4.77	5.10	0.46	2133	2304	8.3%
	5 Hz	100	4.65	4.98	0.47	2045	2174	6.8%
15 mol%	2 Hz	50	4.84	5.22	0.41	1374	1662	4.7%
	4 Hz	50	4.57	4.87	0.50	1499	1496	3.1%
	5 Hz	50	4.52	4.78	0.54	1639	1520	3.3%

Table S6: PLP-SEC conditions and results of SHMB:AM copolymers at 60°C, 6.8 mmol/L LiTPO and 10 wt% monomer.

mol% SHMB	Repetition rate	# of pulses	$logM_1$	$logM_2$	M_1/M_2	$k_p^{cop}{}_1$	$k_p^{cop}{}_2$	Conversion
5 mol%	5 Hz	50	5.26	5.68	0.39	9177	11830	10.4%
10 mol%	4 Hz	50	5.13	5.55	0.38	5418	7165	5.2%
	5 Hz	50	4.94	5.42	0.33	4402	6590	4.3%
15 mol%	2 Hz	50	5.31	5.72	0.39	4132	5281	5.1%
	4 Hz	50	4.95	5.39	0.37	3573	4879	4.0%
	5 Hz	50	4.89	5.31	0.38	3872	5071	3.4%