

SUPPLEMENTARY INFORMATION

**Effect of Ionization by Proton Transfer on Propagation Rate Coefficients: A PLP-SEC Study of
Methacrylic Acid-Amine Monomers**

Samuel Wierzbicki,^{*a} Szczepan Bednarz,^{*a} Igor Lacík^{*b}

^a*Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24,
31-155 Krakow, Poland*

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

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TABLES

Table S1. Pulsed-laser polymerizations in aqueous solution for MAA-IBA (experiments 1-120) and MAA-TEA (experiments 121-240): initial monomer concentration, c_M in wt% and mol·L⁻¹, temperature, T , number of pulses, N_p , frequency, f , conversions, x , primary and secondary points of inflection, M_1 , ratio M_1/M_2 , and resulting k_p value. All of the experiments were conducted at $c_{D1173} = 20$ mmol·dm⁻³.

No.	c_M		T (°C)	N_p	f (Hz)	x (%)	M_1 (g·mol ⁻¹)	M_1/M_2	k_p (L·mol ⁻¹ ·s ⁻¹)
	(wt%)	(mol·L ⁻¹)							
1	28.5	1.82	20	100	4	4.3	18621	0.49	379
2	28.5	1.82	20	200	4	4.3	18664	0.50	380
3	28.5	1.82	20	100	2	4.6	36475	0.57	371
4	28.5	1.82	20	200	2	4.6	35810	0.56	365
5	28.5	1.82	20	100	1	4.8	63241	0.61	322
6	28.5	1.82	20	200	1	4.8	62661	0.61	319
7	28.5	1.82	30	100	4	4.4	23281	0.52	477
8	28.5	1.82	30	200	4	4.4	23014	0.52	471
9	28.5	1.82	30	100	2	4.6	44463	0.59	455
10	28.5	1.82	30	200	2	4.6	43752	0.59	448
11	28.5	1.82	30	100	1	4.9	73961	0.60	379
12	28.5	1.82	30	200	1	4.9	72778	0.60	372
13	28.5	1.82	40	100	8	4.2	14256	0.48	587
14	28.5	1.82	40	200	8	4.2	14322	0.48	590
15	28.5	1.82	40	100	4	4.5	29174	0.54	600
16	28.5	1.82	40	200	4	4.5	28445	0.54	585
17	28.5	1.82	40	100	2	4.7	52966	0.60	545
18	28.5	1.82	40	200	2	4.7	51523	0.60	530
19	28.5	1.82	50	100	16	3.9	8730	0.45	723
20	28.5	1.82	50	200	16	4.0	8933	0.47	740
21	28.5	1.82	50	100	8	4.3	18072	0.49	748
22	28.5	1.82	50	200	8	4.3	17947	0.50	743
23	28.5	1.82	50	100	4	4.6	35727	0.56	740
24	28.5	1.82	50	200	4	4.5	34594	0.56	716
25	28.5	1.82	60	100	16	4.0	10889	0.48	908
26	28.5	1.82	60	200	16	4.0	10495	0.46	875
27	28.5	1.82	60	100	8	4.3	22233	0.51	927
28	28.5	1.82	60	200	8	4.3	22029	0.51	918
29	28.5	1.82	60	100	4	4.6	42756	0.58	891
30	28.5	1.82	60	200	4	4.6	41020	0.58	855
31	21.46	1.36	20	100	4	4.1	13552	0.47	368
32	21.46	1.36	20	200	4	4.1	13740	0.48	373
33	21.46	1.36	20	100	2	4.4	27290	0.53	370
34	21.46	1.36	20	200	2	4.4	26485	0.53	359
35	21.46	1.36	20	100	1	4.5	34041	0.56	231
36	21.46	1.36	20	200	1	4.7	49204	0.60	334
37	21.46	1.36	30	100	4	4.2	17258	0.49	470
38	21.46	1.36	30	200	4	4.2	16904	0.49	461
39	21.46	1.36	30	100	2	4.7	50119	0.60	683

40	21.46	1.36	30	200	2	4.5	33266	0.56	453
41	21.46	1.36	30	100	1	4.8	59566	0.61	406
42	21.46	1.36	30	200	1	4.8	57810	0.60	394
43	21.46	1.36	40	100	8	4.0	10839	0.47	594
44	21.46	1.36	40	200	8	4.0	10666	0.46	584
45	21.46	1.36	40	100	4	4.3	22029	0.51	603
46	21.46	1.36	40	200	4	4.3	22284	0.52	610
47	21.46	1.36	40	100	2	4.6	43351	0.59	594
48	21.46	1.36	40	200	2	4.6	42364	0.59	580
49	21.46	1.36	50	100	16	3.9	7482	0.46	824
50	21.46	1.36	50	200	16	3.8	6699	0.44	738
51	21.46	1.36	50	100	8	4.1	13709	0.48	755
52	21.46	1.36	50	200	8	4.1	13243	0.47	729
53	21.46	1.36	50	100	4	4.4	26792	0.52	738
54	21.46	1.36	50	200	4	4.4	26242	0.53	723
55	21.46	1.36	60	100	16	3.9	7603	0.43	842
56	21.46	1.36	60	200	16	3.9	7870	0.45	872
57	21.46	1.36	60	100	8	4.2	16749	0.48	928
58	21.46	1.36	60	200	8	4.2	16293	0.49	903
59	21.46	1.36	60	100	4	4.5	32961	0.55	913
60	21.46	1.36	60	200	4	4.5	31915	0.55	884
61	14.36	0.91	20	100	4	3.9	7674	0.43	312
62	14.36	0.91	20	200	4	3.9	7962	0.46	324
63	14.36	0.91	20	100	2	4.3	18750	0.49	382
64	14.36	0.91	20	200	2	4.2	15417	0.48	314
65	14.36	0.91	20	100	1	4.5	31405	0.55	320
66	14.36	0.91	20	200	1	4.5	30200	0.54	307
67	14.36	0.91	30	100	4	4.0	10069	0.46	412
68	14.36	0.91	30	200	4	4.0	10691	0.46	437
69	14.36	0.91	30	100	2	4.3	20654	0.51	422
70	14.36	0.91	30	200	2	4.3	19815	0.50	405
71	14.36	0.91	30	100	1	4.6	39719	0.58	406
72	14.36	0.91	30	200	1	4.6	41305	0.58	422
73	14.36	0.91	40	100	8	3.8	6668	0.45	547
74	14.36	0.91	40	200	8	3.8	6412	0.44	526
75	14.36	0.91	40	100	4	4.1	12706	0.46	522
76	14.36	0.91	40	200	4	4.4	26607	0.52	1092
77	14.36	0.91	40	100	2	4.4	26485	0.52	544
78	14.36	0.91	40	200	2	4.4	25003	0.52	513
79	14.36	0.91	50	100	16	3.6	4395	0.49	725
80	14.36	0.91	50	200	16	3.6	4355	0.49	719
81	14.36	0.91	50	100	8	3.9	7998	0.45	660
82	14.36	0.91	50	200	8	3.9	7798	0.45	643
83	14.36	0.91	50	100	4	4.2	16368	0.48	675
84	14.36	0.91	50	200	4	4.2	15524	0.05	640
85	14.36	0.91	60	100	16	3.7	5000	0.46	830
86	14.36	0.91	60	200	16	3.7	4831	0.45	802
87	14.36	0.91	60	100	8	4.0	9817	0.45	814
88	14.36	0.91	60	200	8	4.0	9506	0.45	789
89	14.36	0.91	60	100	4	4.3	20091	0.50	833

90	14.36	0.91	60	200	4	4.3	19588	0.50	813
91	7.22	0.45	20	100	4	n.d.	n.d.	n.d.	n.d.
92	7.22	0.45	20	200	4	n.d.	n.d.	n.d.	n.d.
93	7.22	0.45	20	100	2	3.8	6053	0.41	246
94	7.22	0.45	20	200	2	3.8	5715	0.42	233
95	7.22	0.45	20	100	1	4.1	11722	0.46	238
96	7.22	0.45	20	200	1	4.1	11324	0.46	230
97	7.22	0.45	30	100	4	n.d.	n.d.	n.d.	n.d.
98	7.22	0.45	30	200	4	n.d.	n.d.	n.d.	n.d.
99	7.22	0.45	30	100	2	3.9	7762	0.44	317
100	7.22	0.45	30	200	2	3.9	7362	0.44	301
101	7.22	0.45	30	100	1	4.2	15488	0.47	316
102	7.22	0.45	30	200	1	4.2	14555	0.47	297
103	7.22	0.45	40	100	8	n.d.	n.d.	n.d.	n.d.
104	7.22	0.45	40	200	8	n.d.	n.d.	n.d.	n.d.
105	7.22	0.45	40	100	4	3.7	5297	0.47	434
106	7.22	0.45	40	200	4	3.7	5058	0.45	414
107	7.22	0.45	40	100	2	4.0	10069	0.45	413
108	7.22	0.45	40	200	2	4.0	9397	0.45	385
109	7.22	0.45	50	100	16	n.d.	n.d.	n.d.	n.d.
110	7.22	0.45	50	200	16	n.d.	n.d.	n.d.	n.d.
111	7.22	0.45	50	100	8	3.6	3556	0.49	585
112	7.22	0.45	50	200	8	3.5	3499	0.48	576
113	7.22	0.45	50	100	4	3.8	6607	0.44	544
114	7.22	0.45	50	200	4	3.8	6180	0.44	509
115	7.22	0.45	60	100	16	n.d.	n.d.	n.d.	n.d.
116	7.22	0.45	60	200	16	n.d.	n.d.	n.d.	n.d.
117	7.22	0.45	60	100	8	3.6	4074	0.45	674
118	7.22	0.45	60	200	8	3.6	3936	0.45	651
119	7.22	0.45	60	100	4	3.9	7980	0.44	661
120	7.22	0.45	60	200	4	3.9	7482	0.43	619
121	33.64	1.82	20	100	4	2.2	22387	0.51	455
122	33.64	1.82	20	200	4	2.9	21528	0.50	438
123	33.64	1.82	20	100	2	2.2	42267	0.58	430
124	33.64	1.82	20	200	2	3.9	40458	0.57	411
125	33.64	1.82	20	100	1	2.9	70632	0.59	359
126	33.64	1.82	20	200	1	4.5	67453	0.58	343
127	33.64	1.82	30	100	4	2.7	27353	0.53	559
128	33.64	1.82	30	200	4	3.0	26669	0.53	545
129	33.64	1.82	30	100	2	2.5	50582	0.59	517
130	33.64	1.82	30	200	2	3.9	47973	0.58	491
131	33.64	1.82	30	100	1	3.1	81283	0.56	416
132	33.64	1.82	30	200	1	4.5	77625	0.57	397
133	33.64	1.82	40	100	8	1.6	16520	0.48	680
134	33.64	1.82	40	200	8	2.7	16255	0.48	669
135	33.64	1.82	40	100	4	2.3	33343	0.55	686
136	33.64	1.82	40	200	4	2.9	32359	0.55	666
137	33.64	1.82	40	100	2	2.2	58210	0.58	599
138	33.64	1.82	40	200	2	3.9	55335	0.58	569
139	33.64	1.82	50	100	16	1.5	9616	0.45	797

140	33.64	1.82	50	200	16	1.9	9506	0.44	788
141	33.64	1.82	50	100	8	1.3	19724	0.49	817
142	33.64	1.82	50	200	8	2.5	19634	0.49	813
143	33.64	1.82	50	100	4	1.9	39174	0.57	812
144	33.64	1.82	50	200	4	2.9	37757	0.56	782
145	33.64	1.82	60	100	16	1.5	11588	0.45	967
146	33.64	1.82	60	200	16	2.3	11350	0.45	947
147	33.64	1.82	60	100	8	2.1	24044	0.52	1003
148	33.64	1.82	60	200	8	1.6	23659	0.51	987
149	33.64	1.82	60	100	4	1.9	45499	0.58	949
150	33.64	1.36	60	200	4	3.1	43551	0.57	908
151	25.34	1.36	20	100	4	2.3	20277	0.50	550
152	25.34	1.36	20	200	4	3.4	20324	0.50	551
153	25.34	1.36	20	100	2	2.7	39174	0.56	531
154	25.34	1.36	20	200	2	4.2	37239	0.56	505
155	25.34	1.36	20	100	1	3.3	66222	0.58	449
156	25.34	1.36	20	200	1	5.4	62230	0.57	422
157	25.34	1.36	30	100	4	n.d.	n.d.	n.d.	n.d.
158	25.34	1.36	30	200	4	3.5	24099	0.51	656
159	25.34	1.36	30	100	2	n.d.	46559	0.57	634
160	25.34	1.36	30	200	2	4.3	44771	0.57	610
161	25.34	1.36	30	100	1	3.7	78163	0.57	532
162	25.34	1.36	30	200	1	5.2	72444	0.56	493
163	25.34	1.36	40	100	8	2.1	15205	0.47	833
164	25.34	1.36	40	200	8	3.1	14555	0.47	797
165	25.34	1.36	40	100	4	2.4	30549	0.53	836
166	25.34	1.36	40	200	4	3.6	29512	0.53	808
167	25.34	1.36	40	100	2	2.8	54954	0.59	752
168	25.34	1.36	40	200	2	4.0	53088	0.58	727
169	25.34	1.36	50	100	16	1.9	8851	0.44	975
170	25.34	1.36	50	200	16	2.3	8770	0.44	966
171	25.34	1.36	50	100	8	2.1	18535	0.49	1021
172	25.34	1.36	50	200	8	3.2	18155	0.48	1000
173	25.34	1.36	50	100	4	2.6	36224	0.55	997
174	25.34	1.36	50	200	4	3.9	34834	0.55	959
175	25.34	1.36	60	100	16	2.5	10740	0.45	1190
176	25.34	1.36	60	200	16	2.9	10280	0.44	1139
177	25.34	1.36	60	100	8	3.2	22182	0.50	1229
178	25.34	1.36	60	200	8	2.3	21627	0.50	1198
179	25.34	1.36	60	100	4	2.6	42073	0.56	1165
180	25.34	0.91	60	200	4	4.0	40644	0.56	1126
181	15.98	0.91	20	100	4	n.d.	13932	0.47	567
182	15.98	0.91	20	200	4	n.d.	13964	0.46	568
183	15.98	0.91	20	100	2	n.d.	28119	0.52	572
184	15.98	0.91	20	200	2	n.d.	26730	0.51	544
185	15.98	0.91	20	100	1	n.d.	51404	0.58	523
186	15.98	0.91	20	200	1	n.d.	48978	0.57	498
187	15.98	0.91	30	100	4	n.d.	18113	0.49	744
188	15.98	0.91	30	200	4	n.d.	17338	0.48	712
189	15.98	0.91	30	100	2	n.d.	35481	0.55	729

190	15.98	0.91	30	200	2	n.d.	33884	0.54	696
191	15.98	0.91	30	100	1	n.d.	61376	0.58	630
192	15.98	0.91	30	200	1	n.d.	58345	0.56	599
193	15.98	0.91	40	100	8	n.d.	10740	0.44	891
194	15.98	0.91	40	200	8	n.d.	10447	0.44	867
195	15.98	0.91	40	100	4	n.d.	22542	0.50	935
196	15.98	0.91	40	200	4	n.d.	21677	0.50	899
197	15.98	0.91	40	100	2	n.d.	42855	0.56	889
198	15.98	0.91	40	200	2	n.d.	40365	0.56	837
199	15.98	0.91	50	100	16	n.d.	6486	0.42	1088
200	15.98	0.91	50	200	16	n.d.	6368	0.43	1068
201	15.98	0.91	50	100	8	n.d.	13583	0.46	1139
202	15.98	0.91	50	200	8	n.d.	12972	0.45	1088
203	15.98	0.91	50	100	4	n.d.	27669	0.52	1160
204	15.98	0.91	50	200	4	n.d.	26669	0.52	1118
205	15.98	0.91	60	100	16	n.d.	7603	0.41	1289
206	15.98	0.91	60	200	16	n.d.	n.d.	n.d.	n.d.
207	15.98	0.91	60	100	8	n.d.	n.d.	n.d.	n.d.
208	15.98	0.91	60	200	8	n.d.	15704	0.47	1331
209	15.98	0.91	60	100	4	n.d.	32509	0.53	1377
210	15.98	0.45	60	200	4	n.d.	31189	0.53	1321
211	8.52	0.45	20	100	4	3.4	5636	0.41	458
212	8.52	0.45	20	200	4	4.5	5236	0.43	426
213	8.52	0.45	20	100	2	4.5	10715	0.45	436
214	8.52	0.45	20	200	2	4.1	10116	0.44	411
215	8.52	0.45	20	100	1	4.1	21928	0.50	446
216	8.52	0.45	20	200	1	6.3	20464	0.49	416
217	8.52	0.45	30	100	4	4.9	6516	0.41	531
218	8.52	0.45	30	200	4	6.0	6546	0.42	534
219	8.52	0.45	30	100	2	4.0	13900	0.45	567
220	8.52	0.45	30	200	2	6.1	13274	0.46	541
221	8.52	0.45	30	100	1	3.4	28054	0.52	572
222	8.52	0.45	30	200	1	6.8	26122	0.51	533
223	8.52	0.45	40	100	8	4.0	n.d.	n.d.	n.d.
224	8.52	0.45	40	200	8	4.0	4276	0.44	700
225	8.52	0.45	40	100	4	5.5	8670	0.42	710
226	8.52	0.45	40	200	4	5.8	8433	0.42	690
227	8.52	0.45	40	100	2	5.6	17989	0.48	736
228	8.52	0.45	40	200	2	6.2	17258	0.48	706
229	8.52	0.45	50	100	16	5.5	n.d.	n.d.	n.d.
230	8.52	0.45	50	200	16	4.2	2716	n.d.	893
231	8.52	0.45	50	100	8	5.1	5483	0.43	902
232	8.52	0.45	50	200	8	4.4	5321	0.43	875
233	8.52	0.45	50	100	4	4.4	11482	0.44	944
234	8.52	0.45	50	200	4	5.0	10304	0.43	847
235	8.52	0.45	60	100	16	3.3	3365	0.44	1113
236	8.52	0.45	60	200	16	4.4	3206	0.44	1060
237	8.52	0.45	60	100	8	4.7	6368	0.41	1053
238	8.52	0.45	60	200	8	5.5	6339	0.42	1048
239	8.52	0.45	60	100	4	3.9	13646	0.46	1128

240	8.52	0.45	60	200	4	4.0	12677	0.44	1048
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Table S2. Pulsed-laser polymerizations in DMSO solution for MAA-IBA (experiments 241-360) and MAA-TEA (experiments no. 361-480): initial monomer concentration, c_M in wt% and mol·L⁻¹, temperature, T , number of pulses, N_p , frequency, f , conversions, x , primary and secondary points of inflection, M_1 , ratio M_1/M_2 , and resulting k_p value. All of the experiments were conducted at $c_{D1173} = 20$ mmol·dm⁻³.

No.	c_M		T (°C)	N_p	f (Hz)	x (%)	M_1 (g·mol ⁻¹)	M_1/M_2	k_p (L·mol ⁻¹ ·s ⁻¹)
	(wt%)	(mol·L ⁻¹)							
241	27.3	1.82	20	100	4	0.5	3311	0.45	67
242	27.3	1.82	20	200	4	0.4	2951	0.43	60
243	27.3	1.82	20	100	2	0.5	5754	0.43	59
244	27.3	1.82	20	200	2	0.8	5754	0.43	59
245	27.3	1.82	20	100	1	0.5	12882	0.45	66
246	27.3	1.82	20	200	1	1.1	12882	0.46	66
247	27.3	1.8	30	100	4	0.6	n.d.	n.d.	n.d.
248	27.3	1.8	30	200	4	0.7	4074	0.43	84
249	27.3	1.8	30	100	2	0.8	9120	0.44	94
250	27.3	1.8	30	200	2	0.9	8318	0.45	85
251	27.3	1.8	30	100	1	0.8	17378	0.47	89
252	27.3	1.8	30	200	1	1.2	17378	0.46	89
253	27.3	1.79	40	100	4	0.6	5623	0.42	117
254	27.3	1.79	40	200	4	1.0	6457	0.45	134
255	27.3	1.79	40	100	2	0.9	13183	0.46	137
256	27.3	1.79	40	200	2	0.8	12023	0.45	125
257	27.3	1.79	40	100	1	1.2	25704	0.51	133
258	27.3	1.79	40	200	1	1.5	26915	0.50	139
259	27.3	1.77	50	100	4	0.7	8710	0.45	182
260	27.3	1.77	50	200	4	1.0	9120	0.45	191
261	27.3	1.77	50	100	2	0.8	19055	0.50	199
262	27.3	1.77	50	200	2	1.2	17378	0.47	182
263	27.3	1.77	50	100	1	0.6	38019	0.58	199
264	27.3	1.77	50	200	1	1.4	34674	0.52	181
265	27.3	1.75	60	100	4	0.9	12589	0.46	266
266	27.3	1.75	60	200	4	1.1	12303	0.47	260
267	27.3	1.75	60	100	2	0.9	24547	0.48	259
268	27.3	1.75	60	200	2	1.2	24547	0.50	259
269	27.3	1.75	60	100	1	1.1	45709	0.54	241
270	27.3	1.75	60	200	1	1.3	48978	0.58	258
271	20.27	1.36	20	100	4	0.6	2754	0.50	75
272	20.27	1.36	20	200	4	0.8	2512	0.47	68
273	20.27	1.36	20	100	2	1.2	4677	0.41	63
274	20.27	1.36	20	200	2	0.9	4571	0.40	62
275	20.27	1.36	20	100	1	0.5	8913	0.36	60
276	20.27	1.36	20	200	1	1.0	8511	0.36	58
277	20.27	1.35	30	100	4	0.7	3162	0.41	87
278	20.27	1.35	30	200	4	1.0	3311	0.47	91
279	20.27	1.35	30	100	2	1.0	6761	0.44	93
280	20.27	1.35	30	200	2	1.3	6310	0.42	86
281	20.27	1.35	30	100	1	1.1	14125	0.46	97

282	20.27	1.35	30	200	1	1.7	14125	0.47	97
283	20.27	1.34	40	100	4	0.8	4467	0.40	123
284	20.27	1.34	40	200	4	0.9	4677	0.42	129
285	20.27	1.34	40	100	2	1.1	9550	0.45	132
286	20.27	1.34	40	200	2	1.1	9772	0.44	135
287	20.27	1.34	40	100	1	1.3	20417	0.49	141
288	20.27	1.34	40	200	1	1.8	19055	0.44	132
289	20.27	1.33	50	100	4	0.9	6761	0.43	189
290	20.27	1.33	50	200	4	0.9	6310	0.42	176
291	20.27	1.33	50	100	2	1.2	14454	0.47	202
292	20.27	1.33	50	200	2	1.2	12303	0.41	172
293	20.27	1.33	50	100	1	1.1	28840	0.52	201
294	20.27	1.33	50	200	1	1.9	25704	0.49	179
295	20.27	1.32	60	100	4	1.1	8710	0.42	245
296	20.27	1.32	60	200	4	1.1	8710	0.41	245
297	20.27	1.32	60	100	2	0.9	19055	0.48	268
298	20.27	1.32	60	200	2	1.2	18197	0.49	256
299	20.27	1.32	60	100	1	0.9	38019	0.55	267
300	20.27	1.32	60	200	1	1.4	35481	0.54	250
301	13.4	0.91	20	100	4	1.5	n.d.	n.d.	n.d.
302	13.4	0.91	20	200	4	1.0	n.d.	n.d.	n.d.
303	13.4	0.91	20	100	2	0.6	3388	0.43	69
304	13.4	0.91	20	200	2	1.9	3236	0.42	66
305	13.4	0.91	20	100	1	1.4	6310	0.40	64
306	13.4	0.91	20	200	1	1.3	6457	0.41	66
307	13.4	0.9	30	100	4	0.7	n.d.	n.d.	n.d.
308	13.4	0.9	30	200	4	0.9	n.d.	n.d.	n.d.
309	13.4	0.9	30	100	2	0.9	4467	0.41	92
310	13.4	0.9	30	200	2	1.0	4571	0.41	94
311	13.4	0.9	30	100	1	1.0	9333	0.41	96
312	13.4	0.9	30	200	1	1.7	9550	0.43	98
313	13.4	0.89	40	100	4	0.5	3467	0.42	144
314	13.4	0.89	40	200	4	1.0	3162	0.42	131
315	13.4	0.89	40	100	2	1.1	6026	0.36	125
316	13.4	0.89	40	200	2	1.5	6166	0.41	128
317	13.4	0.89	40	100	1	1.3	13490	0.45	140
318	13.4	0.89	40	200	1	1.1	13183	0.45	137
319	13.4	0.88	50	100	4	1.3	4365	0.41	183
320	13.4	0.88	50	200	4	1.0	4365	0.41	183
321	13.4	0.88	50	100	2	1.2	9550	0.43	200
322	13.4	0.88	50	200	2	1.3	9333	0.43	195
323	13.4	0.88	50	100	1	0.9	19498	0.47	204
324	13.4	0.88	50	200	1	1.2	18621	0.47	195
325	13.4	0.88	60	100	4	1.4	6310	0.41	267
326	13.4	0.88	60	200	4	0.7	6166	0.42	260
327	13.4	0.88	60	100	2	0.9	13804	0.46	292
328	13.4	0.88	60	200	2	1.3	12882	0.45	272
329	13.4	0.88	60	100	1	1.0	27542	0.51	291
330	13.4	0.88	60	200	1	1.0	25119	0.49	265
331	6.64	0.45	20	100	4	0.8	n.d.	n.d.	n.d.

332	6.64	0.45	20	200	4	n.d.	977	0.30	80
333	6.64	0.45	20	100	2	1.2	1995	0.38	81
334	6.64	0.45	20	200	2	1.4	n.d.	n.d.	n.d.
335	6.64	0.45	20	100	1	1.3	3981	0.38	81
336	6.64	0.45	20	200	1	2.2	4074	0.35	83
337	6.64	0.45	30	100	4	1.0	n.d.	n.d.	n.d.
338	6.64	0.45	30	200	4	1.4	n.d.	n.d.	n.d.
339	6.64	0.45	30	100	2	1.1	2455	0.34	101
340	6.64	0.45	30	200	2	1.3	2630	0.39	108
341	6.64	0.45	30	100	1	2.0	5129	0.38	105
342	6.64	0.45	30	200	1	1.8	5370	0.39	110
343	6.64	0.45	40	100	4	3.3	n.d.	n.d.	n.d.
344	6.64	0.45	40	200	4	2.5	n.d.	n.d.	n.d.
345	6.64	0.45	40	100	2	2.2	3548	0.36	147
346	6.64	0.45	40	200	2	2.6	3467	0.37	144
347	6.64	0.45	40	100	1	2.2	7943	0.41	165
348	6.64	0.45	40	200	1	2.1	7244	0.41	150
349	6.64	0.45	50	100	4	1.7	2630	0.41	220
350	6.64	0.45	50	200	4	3.3	2754	0.42	231
351	6.64	0.45	50	100	2	1.1	5495	0.40	230
352	6.64	0.45	50	200	2	1.7	5012	0.38	210
353	6.64	0.45	50	100	1	1.0	10965	0.44	229
354	6.64	0.45	50	200	1	1.7	10965	0.43	229
355	6.64	0.45	60	100	4	2.1	3631	0.40	307
356	6.64	0.45	60	200	4	2.7	3715	0.40	314
357	6.64	0.45	60	100	2	1.3	7244	0.40	306
358	6.64	0.45	60	200	2	2.1	6918	0.41	292
359	6.64	0.45	60	100	1	2.1	15849	0.46	335
360	6.64	0.45	60	200	1	0.9	15136	0.45	320
361	32.99	1.82	20	100	4	1.3	11482	0.45	234
362	32.99	1.82	20	200	4	1.9	10471	0.46	213
363	32.99	1.82	20	100	2	1.3	20893	0.49	212
364	32.99	1.82	20	200	2	2.0	22387	0.50	228
365	32.99	1.82	20	100	1	2.0	45709	0.58	232
366	32.99	1.82	20	200	1	2.8	45709	0.59	232
367	32.99	1.8	30	100	4	1.8	16596	0.48	341
368	32.99	1.8	30	200	4	2.5	19055	0.49	392
369	32.99	1.8	30	100	2	1.9	36308	0.55	373
370	32.99	1.8	30	200	2	2.7	33113	0.54	340
371	32.99	1.8	30	200	2	1.7	31623	0.54	325
372	32.99	1.8	30	200	1	2.9	57544	0.59	296
373	32.99	1.78	40	100	8	1.4	10233	0.43	425
374	32.99	1.78	40	200	8	1.9	11220	0.46	466
375	32.99	1.78	40	100	4	2.0	25119	0.51	522
376	32.99	1.78	40	200	4	2.0	20893	0.50	434
377	32.99	1.78	40	100	2	2.3	42658	0.56	443
378	32.99	1.78	40	200	2	2.4	38019	0.56	395
379	32.99	1.76	50	100	16	1.4	7943	0.44	667
380	32.99	1.76	50	200	16	1.8	8318	0.44	699
381	32.99	1.76	50	100	8	1.5	18197	0.49	765

382	32.99	1.76	50	200	8	1.8	15136	0.48	636
383	32.99	1.76	50	100	4	1.2	27542	0.51	579
384	32.99	1.76	50	200	4	3.2	36308	0.55	763
385	32.99	1.74	60	100	16	1.5	10233	0.45	869
386	32.99	1.74	60	200	16	1.5	9772	0.45	830
387	32.99	1.74	60	100	8	2.2	21878	0.50	929
388	32.99	1.74	60	200	8	2.2	23442	0.51	996
389	32.99	1.74	60	100	4	1.9	42658	0.56	906
390	32.99	1.74	60	200	4	3.0	40738	0.56	865
391	24.33	1.36	20	100	4	1.7	10965	0.45	297
392	24.33	1.36	20	200	4	2.0	10000	0.45	271
393	24.33	1.36	20	100	2	2.0	18197	0.48	247
394	24.33	1.36	20	200	2	2.3	16218	0.46	220
395	24.33	1.36	20	100	1	1.9	34674	0.54	235
396	24.33	1.36	20	200	1	2.7	33884	0.52	230
397	24.33	1.35	30	100	4	2.0	12589	0.44	345
398	24.33	1.35	30	200	4	2.1	12023	0.44	329
399	24.33	1.35	30	100	2	1.7	27542	0.52	377
400	24.33	1.35	30	200	2	2.6	29512	0.51	404
401	24.33	1.35	30	100	1	2.0	57544	0.56	394
402	24.33	1.35	30	200	1	2.9	44668	0.55	306
403	24.33	1.34	40	100	8	1.5	8710	0.44	482
404	24.33	1.34	40	200	8	2.2	8511	0.44	471
405	24.33	1.34	40	100	4	1.9	19498	0.48	540
406	24.33	1.34	40	200	4	2.2	19953	0.48	552
407	24.33	1.34	40	100	2	1.7	38905	0.54	539
408	24.33	1.34	40	200	2	2.6	36308	0.52	503
409	24.33	1.32	50	100	16	n.d.	5623	0.44	629
410	24.33	1.32	50	200	16	1.8	5623	0.41	629
411	24.33	1.32	50	100	8	1.9	12589	0.45	705
412	24.33	1.32	50	200	8	2.2	12023	0.45	673
413	24.33	1.32	50	100	4	2.2	25119	0.49	703
414	24.33	1.32	50	200	4	2.9	23988	0.50	671
415	24.33	1.31	60	100	16	2.3	8318	0.44	941
416	24.33	1.31	60	200	16	2.0	7943	0.44	899
417	24.33	1.31	60	100	8	2.1	15849	0.47	897
418	24.33	1.31	60	200	8	3.2	16596	0.46	939
419	24.33	1.31	60	100	4	2.1	33884	0.52	959
420	24.33	1.31	60	200	4	2.8	32359	0.52	915
421	15.98	0.91	20	100	4	2.0	7762	0.43	316
422	15.98	0.91	20	200	4	2.2	6310	0.42	257
423	15.98	0.91	20	100	2	2.1	13183	0.46	268
424	15.98	0.91	20	200	2	2.7	12882	0.45	262
425	15.98	0.91	20	100	1	1.8	26915	0.51	274
426	15.98	0.91	20	200	1	2.6	30200	0.50	307
427	15.98	0.9	30	100	4	1.7	10471	0.44	430
428	15.98	0.9	30	200	4	2.5	9772	0.44	401
429	15.98	0.9	30	100	2	1.7	22387	0.49	460
430	15.98	0.9	30	200	2	2.8	22387	0.48	460
431	15.98	0.9	30	100	1	2.2	38905	0.54	400

432	15.98	0.9	30	200	1	3.5	43652	0.55	448
433	15.98	0.89	40	100	8	2.6	8318	0.44	690
434	15.98	0.89	40	200	8	2.5	6026	0.43	500
435	15.98	0.89	40	100	4	n.d.	17378	0.47	721
436	15.98	0.89	40	200	4	1.9	12303	0.44	511
437	15.98	0.89	40	100	2	2.2	21380	0.48	444
438	15.98	0.89	40	200	2	3.1	25704	0.49	533
439	15.98	0.88	50	100	16	1.6	5012	0.44	840
440	15.98	0.88	50	200	16	2.6	4898	0.43	821
441	15.98	0.88	50	100	8	2.4	10715	0.43	898
442	15.98	0.88	50	200	8	2.7	10233	0.45	858
443	15.98	0.88	50	100	4	n.d.	20417	0.48	856
444	15.98	0.88	50	200	4	3.4	19953	0.48	837
445	15.98	0.87	60	100	16	2.1	6166	0.43	1045
446	15.98	0.87	60	200	16	3.0	6166	0.43	1045
447	15.98	0.87	60	100	8	2.5	13804	0.45	1170
448	15.98	0.87	60	200	8	n.d.	13183	0.46	1117
449	15.98	0.87	60	100	4	3.2	28184	0.50	1194
450	15.98	0.87	60	200	4	5.2	27542	0.50	1167
451	7.88	0.45	20	100	4	4.3	3548	0.43	288
452	7.88	0.45	20	200	4	3.5	3162	0.42	257
453	7.88	0.45	20	100	2	3.2	6310	0.44	256
454	7.88	0.45	20	200	2	3.2	7586	0.42	308
455	7.88	0.45	20	100	1	4.2	16596	0.47	337
456	7.88	0.45	20	200	1	3.5	16596	0.46	337
457	7.88	0.45	30	100	4	4.4	4898	0.41	402
458	7.88	0.45	30	200	4	3.9	4571	0.38	375
459	7.88	0.45	30	100	2	4.2	10233	0.43	420
460	7.88	0.45	30	200	2	3.8	10233	0.43	420
461	7.88	0.45	30	100	1	5.3	21380	0.47	438
462	7.88	0.45	30	200	1	4.4	21380	0.48	438
463	7.88	0.45	40	100	8	4.3	3311	0.40	548
464	7.88	0.45	40	200	8	3.7	3467	0.44	574
465	7.88	0.45	40	100	4	4.8	6761	0.40	560
466	7.88	0.45	40	200	4	3.6	6166	0.41	511
467	7.88	0.45	40	100	2	3.5	15136	0.43	627
468	7.88	0.45	40	200	2	5.0	14125	0.45	585
469	7.88	0.45	50	100	16	3.0	n.d.	n.d.	n.d.
470	7.88	0.45	50	200	16	4.5	n.d.	n.d.	n.d.
471	7.88	0.45	50	100	8	3.7	4571	0.41	765
472	7.88	0.45	50	200	8	3.7	4467	0.42	747
473	7.88	0.45	50	100	4	5.2	10471	0.44	876
474	7.88	0.45	50	200	4	5.5	9333	0.42	780
475	7.88	0.45	60	100	16	4.9	3090	0.45	1044
476	7.88	0.45	60	200	16	4.5	2692	0.40	909
477	7.88	0.45	60	100	8	4.4	4898	0.39	827
478	7.88	0.45	60	200	8	4.8	6310	0.42	1066
479	7.88	0.45	60	100	4	3.7	12589	0.43	1063
480	7.88	0.45	60	200	4	3.7	12303	0.43	1039

FIGURES

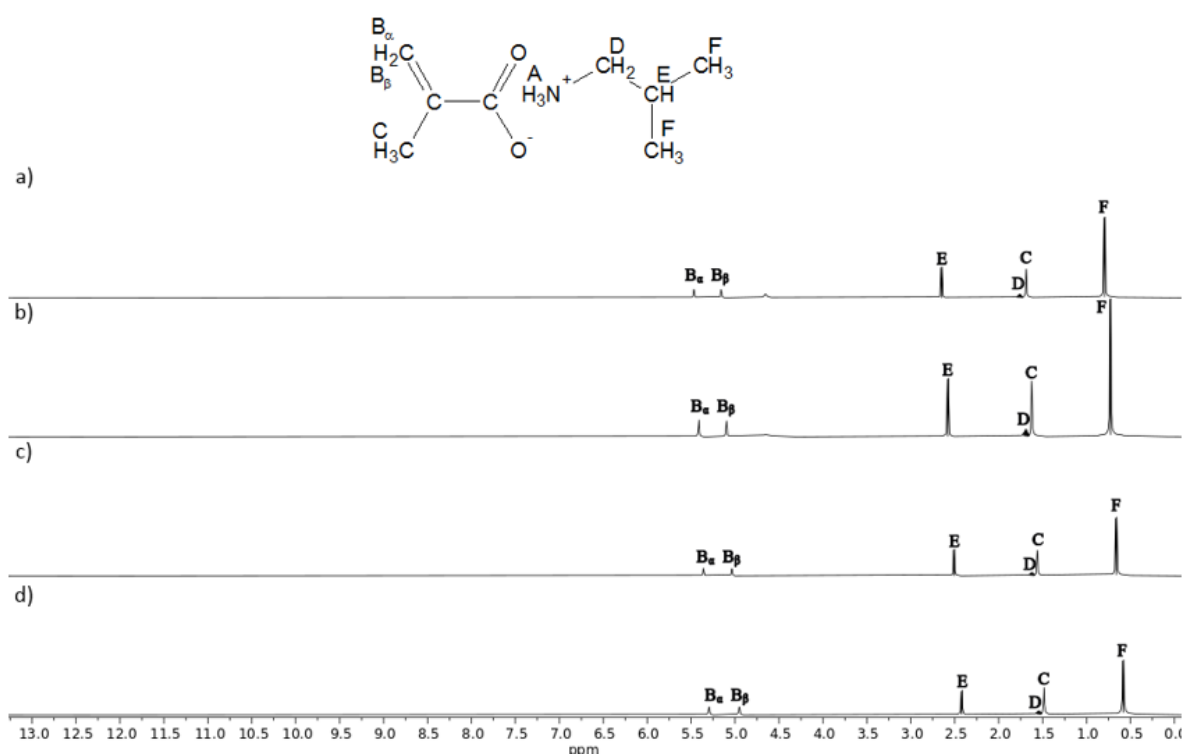


Figure S1. ^1H NMR spectra of MAA-IBA in D_2O solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$.

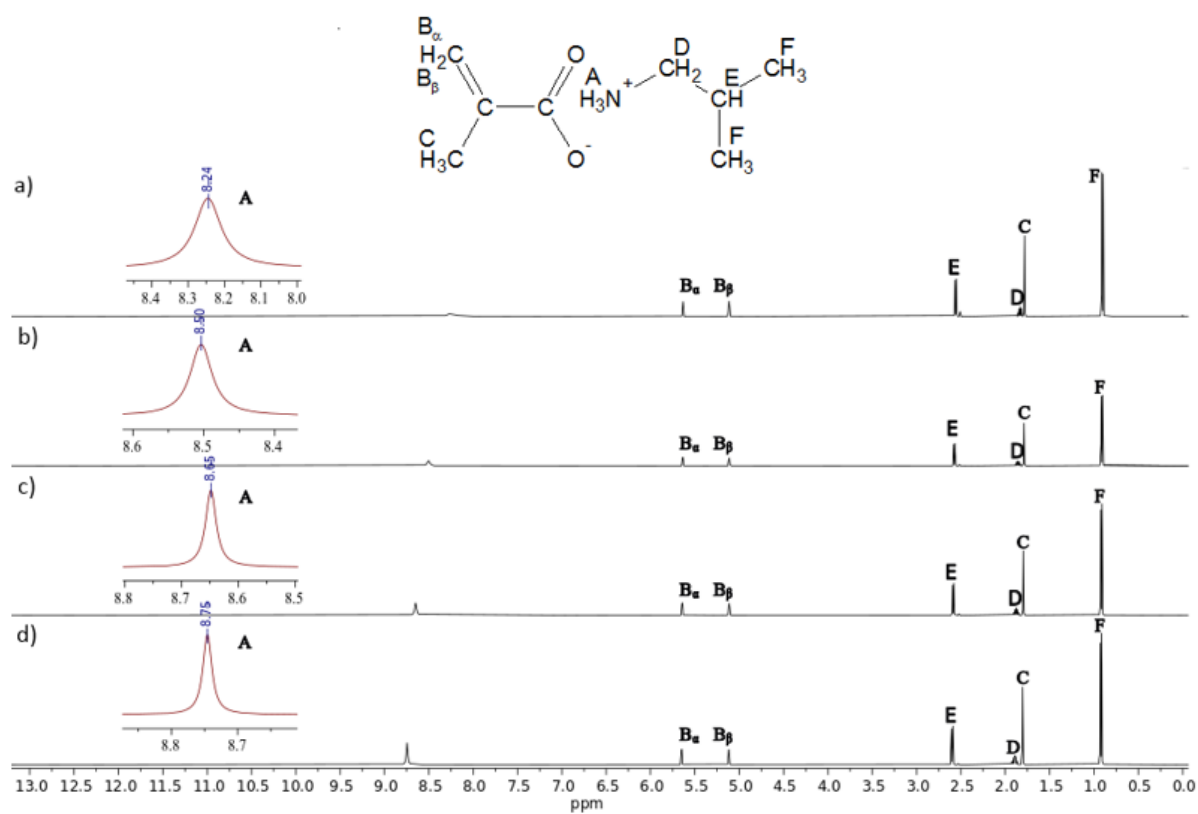


Figure S2. ^1H NMR spectra of MAA-IBA in DMSO-d_6 solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$.

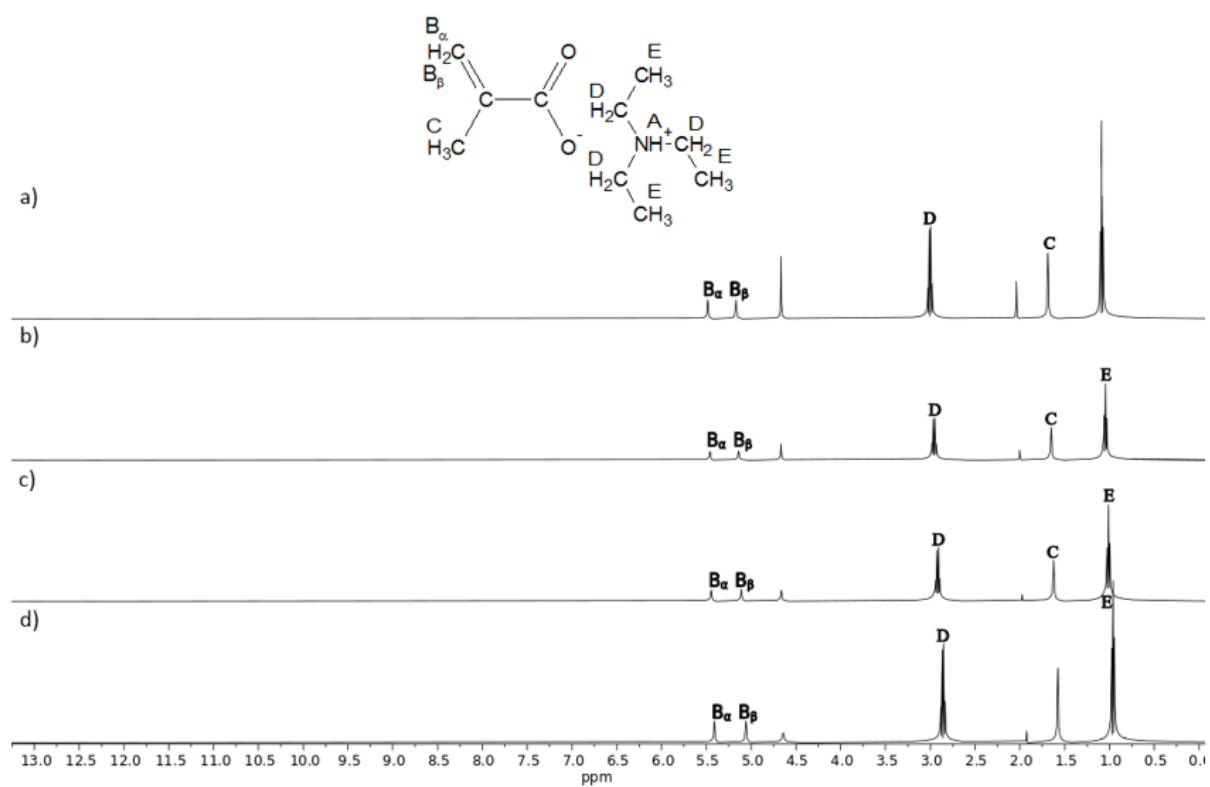


Figure S3. ¹H NMR spectra of MAA-TEA in D₂O solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 mol·L⁻¹.

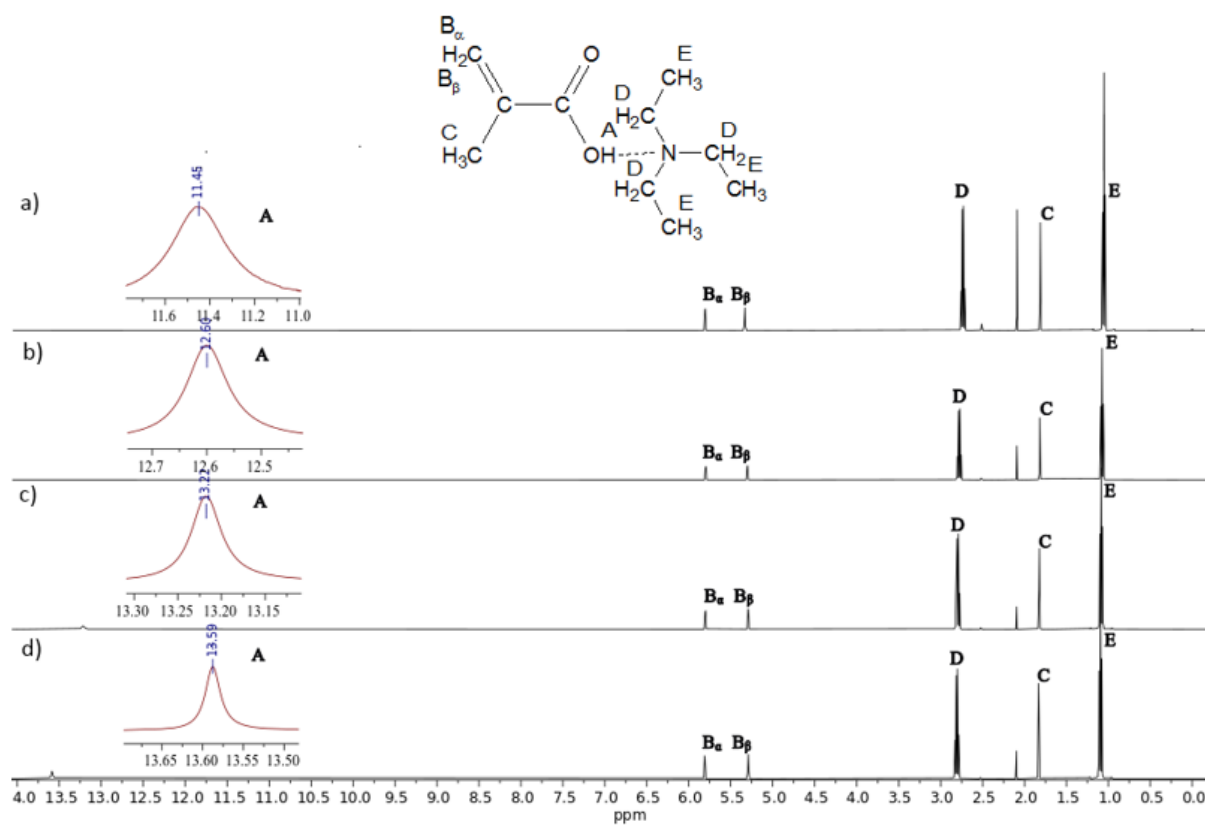


Figure S4. ^1H NMR spectra of MAA-TEA in DMSO-d_6 solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 mol·L⁻¹.

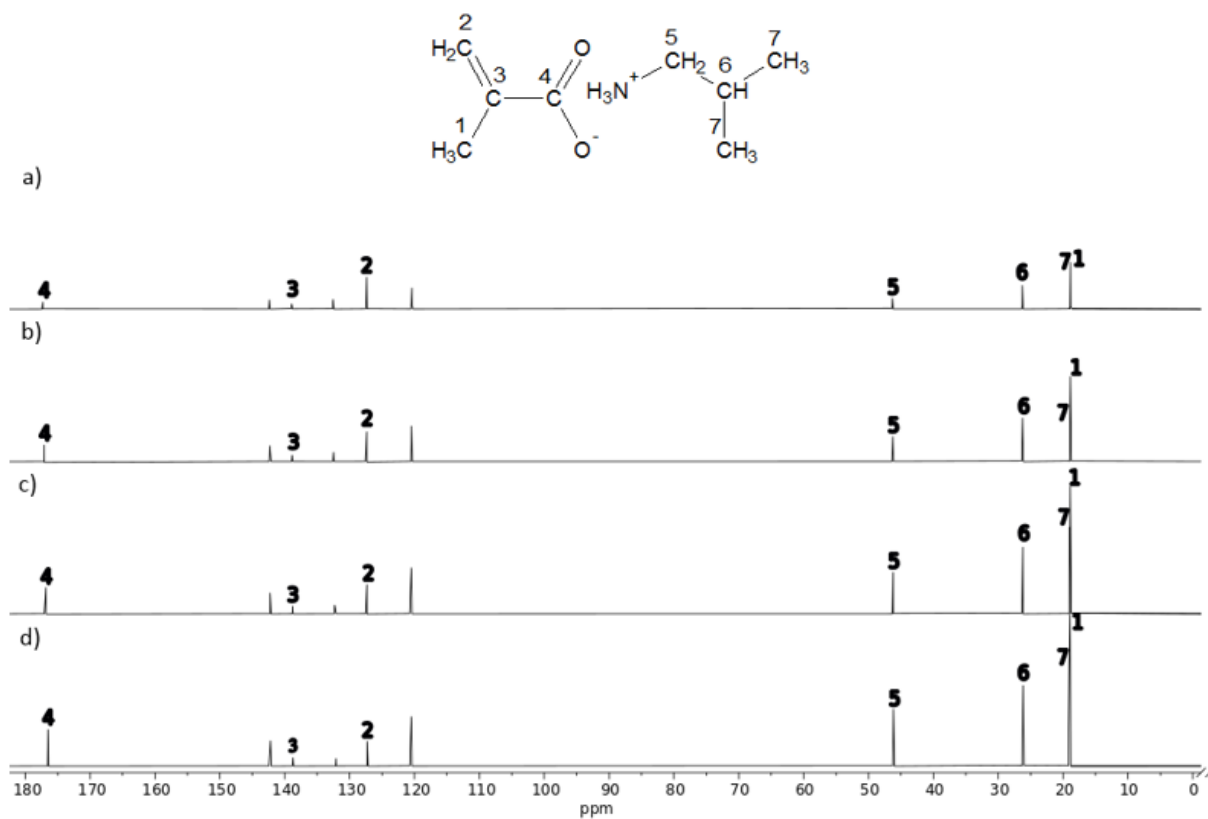


Figure S5. ^{13}C NMR spectra of MAA-IBA in D_2O solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$. Unsigned signals corresponding to PNO, which were used to calculate α parameter.

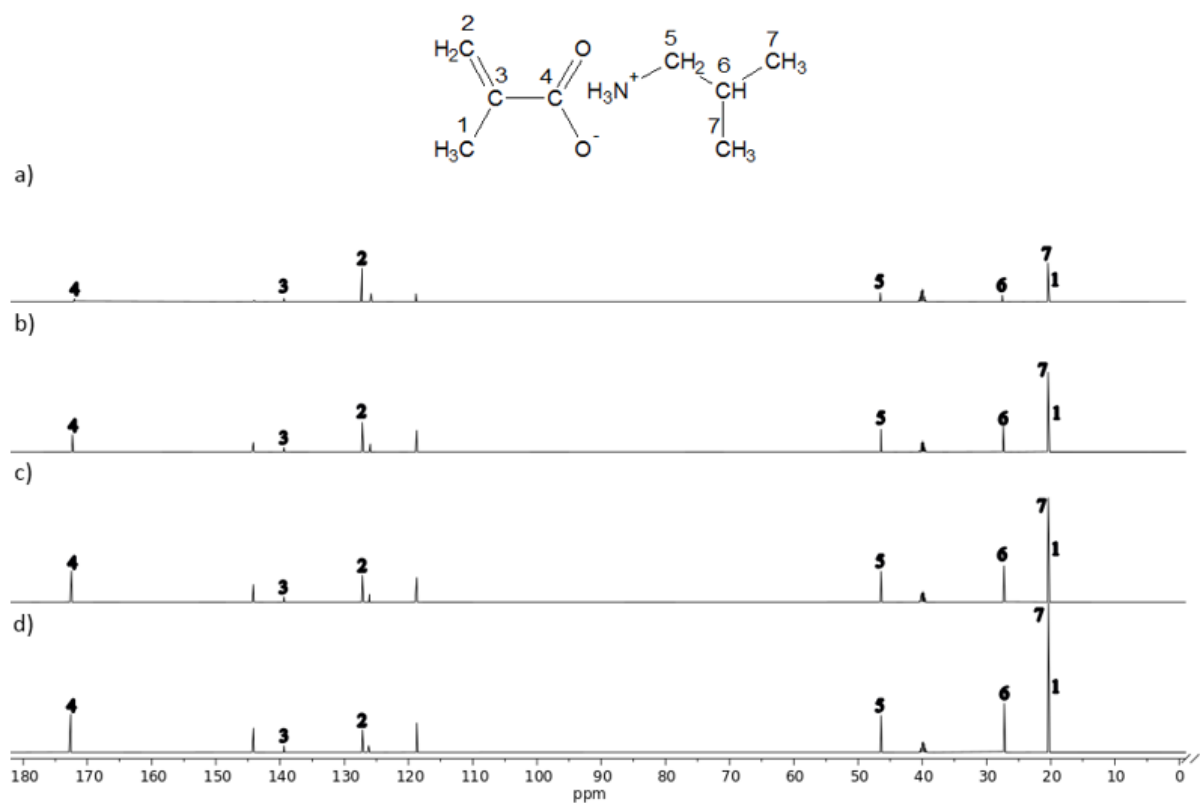


Figure S6. ^{13}C NMR spectra of MAA-IBA in DMSO-d_6 solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$. Unsigned signals corresponding to PNO, which were used to calculate α parameter.

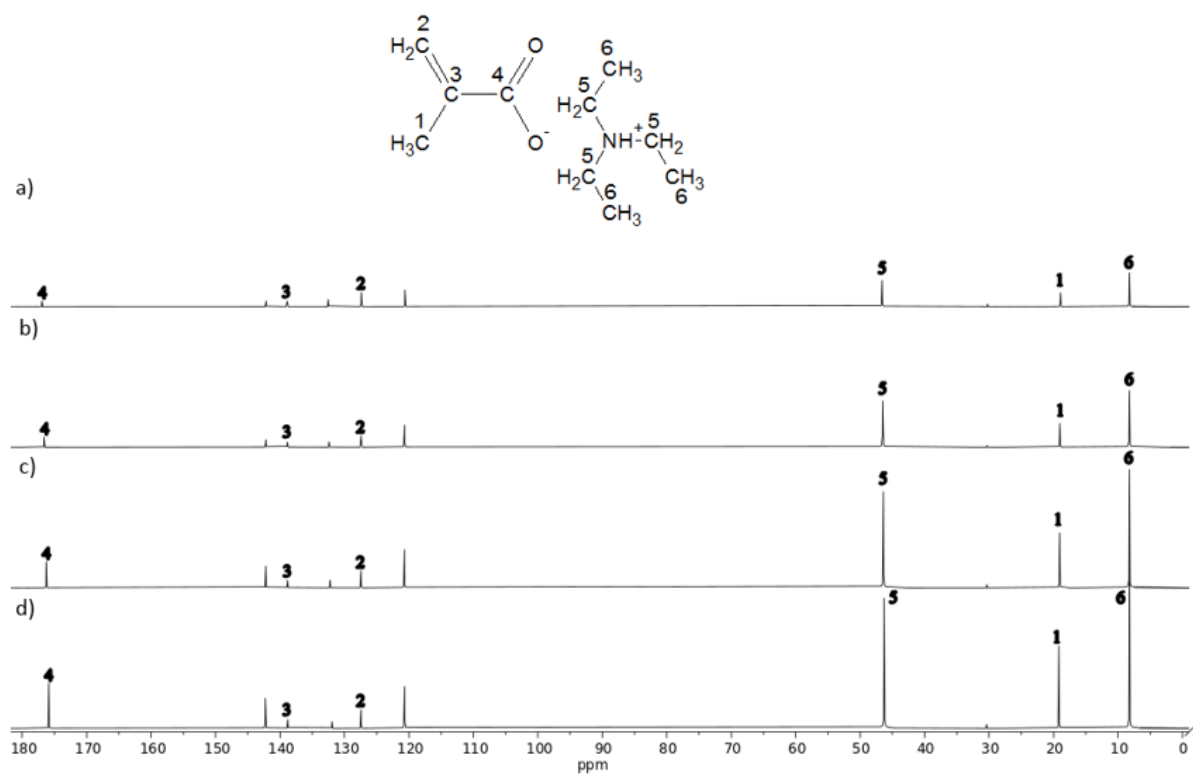


Figure S7. ^{13}C NMR spectra of MAA-TEA in D_2O solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$. Unsigned signals corresponding to PNO, which were used to calculate α parameter.

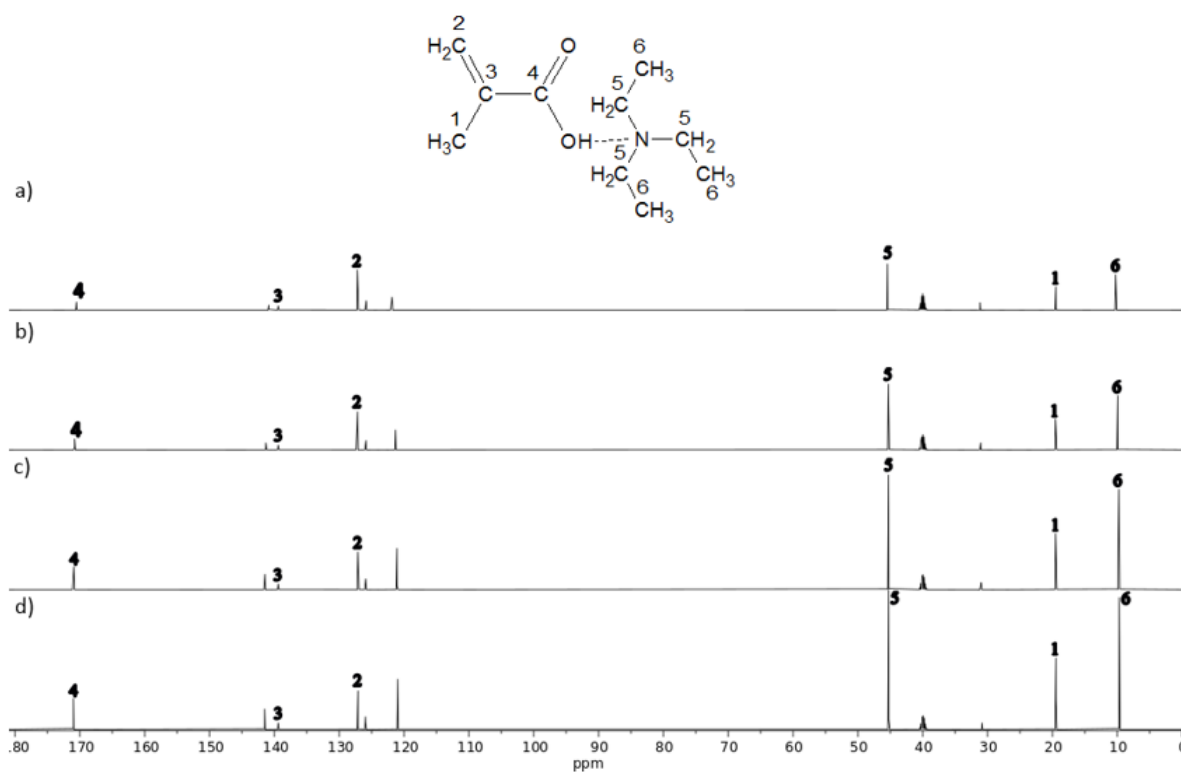


Figure S8. ^{13}C NMR spectra of MAA-TEA in DMSO-d_6 solution at different concentration: a) 0.45, b) 0.91, c) 1.36, d) 1.82 $\text{mol}\cdot\text{L}^{-1}$. Unsigned signals corresponding to PNO, which were used to calculate α parameter.

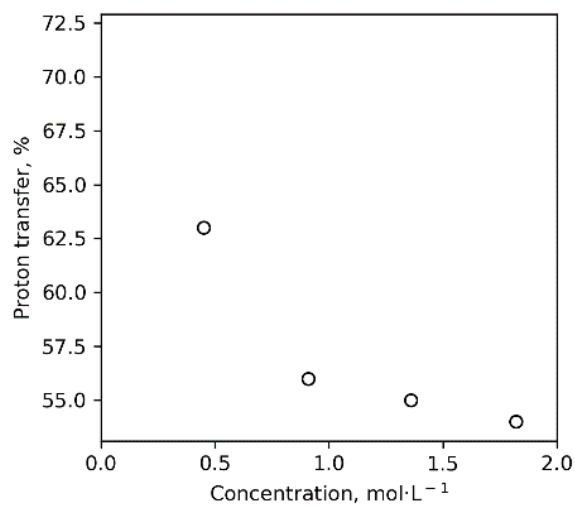


Figure S9. The degree of ionization by proton transfer estimated for MAA-TEA from FTIR as a function of MAA-TEA molar concentration in DMSO solution. The proton transfer (in %) is determined as a ratio between the areas of the $\text{C}=\text{O}$ band in MAA-TEA monomer and in the non-ionized analogue, i.e., MAA in DMSO, at identical molar concentration.

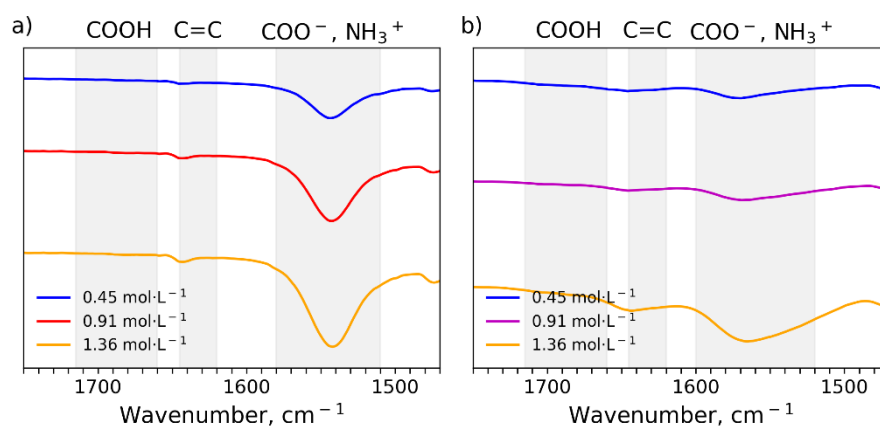


Figure S10. FTIR-ATR spectra in the 1750-1450 cm^{-1} region for MAA-IBA at various concentration in (a) aqueous and (b) DMSO solutions.

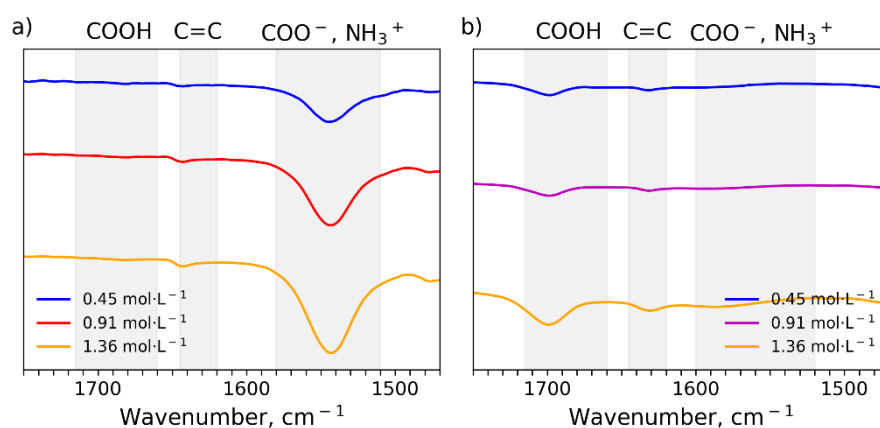


Figure S11. FTIR-ATR spectra in the 1750-1450 cm^{-1} region for MAA-TEA at various concentration in (a) aqueous and (b) DMSO solutions.

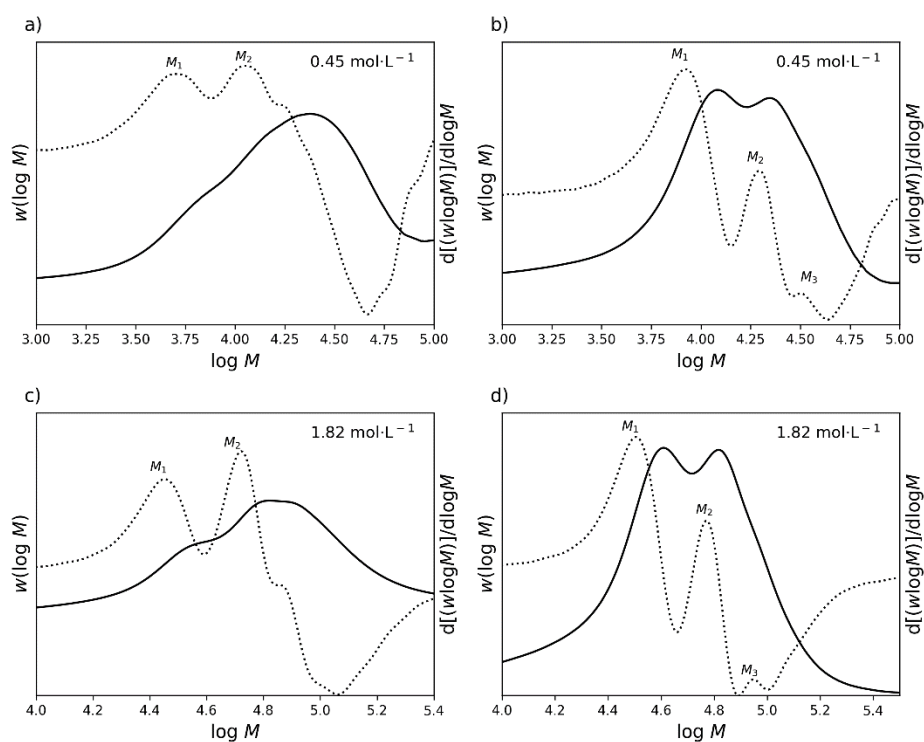


Figure S12. Molar mass distributions (full lines) and associated first derivate curves (dotted lines) obtained from PLP-SEC experiments of 0.45 and 1.82 mol·L⁻¹ (a,c) MAA-IBA and (b,d) MAA-TEA at 40 °C in aqueous solution. The pulse frequency of 4 Hz and photoinitiator concentration c_{D1173} of 20×10^{-3} mol·L⁻¹ were applied.

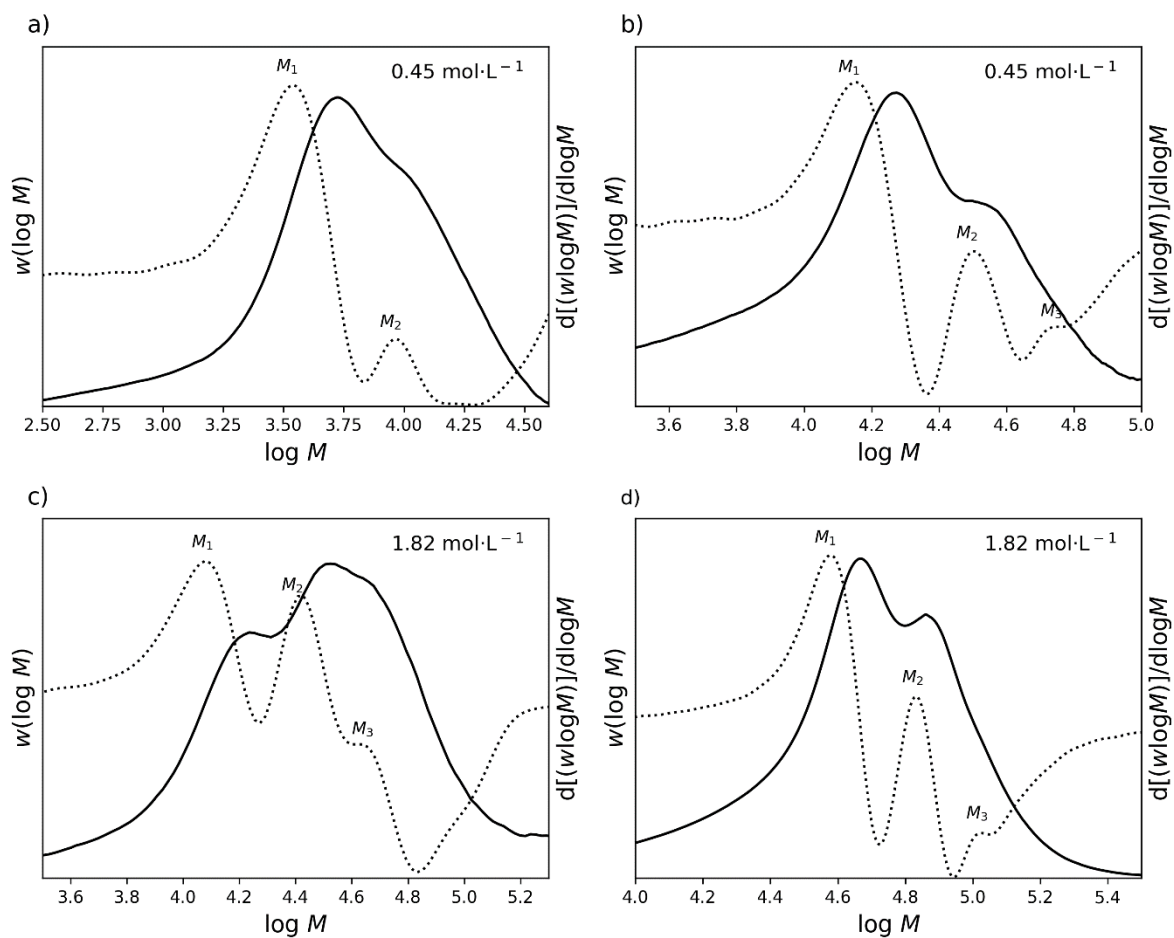


Figure S13. Molar mass distributions (full lines) and associated first-derivative curves (dotted lines) obtained from PLP-SEC experiments of 0.45 and $1.82 \text{ mol}\cdot\text{L}^{-1}$ MAA-IBA and MAA-TEA at 40°C in DMSO solution. The laser repetition rate was 2 Hz and photoinitiator concentration c_{D1173} was $20 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$