Electronic Supplementary Information

Investigating the Propagation Kinetics of a Novel Class of Nitrogen-Containing Methacrylates via PLP-SEC

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Specific conditions of the PLP-SEC samples incorporated in the calculation of the Arrhenius parameters accompanied by exemplary molecular weight distributions are provided for each investigated monomer. Polymerization conditions of all samples polymerized via RAFT and thiol controlled polymerization are collated with the weight average molecular weights as well as intrinsic viscosities employed for the determination of Mark-Houwink-Kuhn-Sakurada parameters. Exemplary triple-SEC elugrams with RI, visco, and MALLS signals as well as temperature dependent densities are depicted for all investigated monomers.

NEAEMA

sample	f	n	ϑ	T^{-1}	$\ln(k_{p1})$	k_{p1}/k_{p2}	M_1	M_2	c_M	k_{p1}	k_{p2}
	Hz		°C	10^{-3} K^{-1}			$g \cdot mol^{-1}$	$g \cdot mol^{-1}$	$mol \cdot L^{-1}$	$mol \cdot L^{-1} \cdot s^{-1}$	$mol \cdot L^{-1} \cdot s^{-1}$
KK1038	7	1000	9.8	3.534	5.7619	1.02	47441	93430	4.477	318	313
KK1039	14	1000	10.0	3.532	5.8219	1.01	25182	50101	4.476	338	336
KK1040	12	1000	21.0	3.400	6.0809	0.98	37726	76605	4.436	437	444
KK1041	24	1000	20.3	3.408	6.1522	1.06	20269	38313	4.439	470	444
KK1042	20	1000	29.8	3.301	6.3641	0.98	29832	60782	4.405	581	591
KK1043	40	1000	29.8	3.301	6.4585	1.05	16392	31144	4.405	638	606
KK1044	25	1000	39.9	3.194	6.6479	0.98	31436	64057	4.368	771	786
KK1045	50	1000	40.0	3.193	6.7243	1.04	16965	32603	4.368	832	800
KK1046	35	1000	49.7	3.097	6.9104	0.99	28958	58255	4.333	1003	1009
KK1047	70	1000	49.7	3.097	6.8742	1.05	13965	26633	4.333	967	922
KK1048	40	1000	59.8	3.003	7.0524	0.98	28958	59146	4.296	1156	1180
KK1049	80	1000	59.8	3.003	7.1589	1.05	16106	30706	4.296	1285	1225
KK1050	45	1000	70.0	2.914	7.3412	0.98	34065	69576	4.260	1543	1575
KK1051	90	1000	70.0	2.914	7.3947	1.06	17969	33919	4.260	1627	1536
KK1052	50	1000	80.4	2.828	7.3657	0.97	31144	64057	4.222	1581	1626
KK1053	100	1000	80.5	2.828	7.5558	1.06	18830	35528	4.222	1912	1804
KK1054	60	1000	89.5	2.757	7.7280	0.99	36993	75108	4.189	2271	2305
KK1055	120	1000	89.5	2.757	7.7070	1.06	18112	34211	4.189	2224	2100

Table S1. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points, and resulting propagation rate coefficients of the monomer NEAEMA in bulk.

MOMA

sample	f Hz	n	ϑ °C	T^{-1} 10^{-3} K^{-1}	$\ln(k_{p1})$	k_{p1}/k_{p2}	M_1 $g \cdot mol^{-1}$	M_2 $g \cdot mol^{-1}$	c_M $mol \cdot L^{-1}$	k_{p1} $mol \cdot L^{-1} \cdot s^{-1}$	k_{p2} $mol \cdot L^{-1} \cdot s^{-1}$
KK511	24	300	20.0	3.411	6.1414	1.07	20256	37729	5.252	465	433
KK512	24	600	20.0	3.411	6.1344	1.09	20113	36869	5.252	461	423
KK513	20	300	30.8	3.290	6.3561	1.01	29848	59244	5.203	576	572
KK514	20	600	30.8	3.290	6.3845	1.03	30708	59388	5.203	593	573
KK515	40	300	30.9	3.289	6.4502	1.08	16395	30421	5.202	633	587
KK516	40	600	31.0	3.288	6.4590	1.07	16538	30994	5.202	638	598
KK517	25	300	40.1	3.192	6.5582	1.00	28989	58240	5.161	705	708
KK518	25	600	40.1	3.192	6.6064	1.04	30421	58383	5.161	740	710
KK519	50	300	40.1	3.192	6.6900	1.07	16538	30994	5.161	804	754
KK520	50	600	40.1	3.192	6.6814	1.07	16395	30564	5.161	797	743
KK521	30	300	49.8	3.096	6.9744	1.00	36296	72883	5.114	1069	1073
KK522	30	600	50.1	3.094	6.9506	0.99	35436	71878	5.113	1044	1059
KK523	60	300	50.1	3.094	6.9567	1.04	17825	34433	5.113	1050	1014
KK524	60	600	49.8	3.096	6.9957	1.03	18540	35866	5.114	1092	1056
KK525	35	300	60.2	3.000	7.2776	1.00	41743	83369	5.067	1447	1445
KK526	35	600	60.2	3.000	7.1417	0.99	36439	73889	5.067	1264	1281
KK527	70	300	60.2	3.000	7.1436	1.03	18254	35436	5.067	1266	1229
KK528	70	600	60.1	3.001	7.1819	1.04	18969	36439	5.067	1315	1263
KK529	45	300	70.2	2.912	7.3285	0.98	33859	69437	5.022	1523	1562
KK530	45	600	70.3	2.912	7.3244	0.96	33716	70586	5.021	1517	1588
KK531	90	300	70.3	2.912	7.3721	1.04	17682	33859	5.021	1591	1523
KK532	90	600	70.3	2.912	7.3640	1.04	17539	33859	5.021	1578	1523
KK533	50	300	80.7	2.826	7.4392	0.97	33716	69293	4.974	1701	1748
KK534	50	600	80.8	2.825	7.5090	0.98	36152	73745	4.974	1824	1861
KK535	100	300	80.7	2.826	7.4787	1.03	17539	34003	4.974	1770	1716
KK536	100	600	80.9	2.824	7.4625	1.03	17253	33430	4.973	1741	1687
KK537	60	300	90.8	2.748	7.8057	1.03	40166	77767	4.929	2455	2376
KK538	60	600	90.8	2.748	7.7162	0.96	36726	76187	4.929	2244	2328
KK539	120	300	90.7	2.748	7.7023	1.03	18111	35149	4.929	2213	2148
KK540	120	600	90.8	2.748	7.8693	1.04	21401	41313	4.929	2616	2525
KK541	8	300	-0.1	3.662	5.5429	0.97	33859	69724	5.324	255	263
KK542	8	600	-0.2	3.664	5.6004	0.98	35866	73027	5.324	271	275

KK543	16	300	-0.2	3.664	5.6259	1.03	18397	35579	5.324	278	268
KK544	16	600	-0.2	3.664	5.6715	1.07	19255	36152	5.324	290	273
KK545	10	300	10.3	3.528	5.8982	1.00	38302	76761	5.277	364	365
KK546	10	600	10.4	3.527	5.9278	1.00	39449	79059	5.277	375	376
KK547	20	300	10.5	3.525	5.9754	1.06	20686	39019	5.276	394	371
KK548	20	600	10.4	3.527	5.9959	1.02	21115	41599	5.277	402	396
KK549	12	300	20.5	3.405	6.2157	1.00	43463	86674	5.231	501	499
KK550	12	600	20.2	3.409	6.2350	1.02	44324	87105	5.232	510	501

Table S2. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points, and resulting propagation rate coefficients of the monomer MOMA in bulk.

PipEMA

sample	f	n	ϑ	T^{-1}	$\ln(k_{p1})$	k_{p1}/k_{p2}	M_1	M_2	c_M	k_{p1}	k_{p2}
	Hz		°C	10^{-3} K^{-1}			g·mol^{-1}	g·mol^{-1}	mol·L^{-1}	mol·L^{-1}·s^{-1}	mol·L^{-1}·s^{-1}
KK558	4	300	0.0	3.661	5.4354	1.10	67327	122367	5.032	229	208
KK559	4	600	0.0	3.661	5.4651	1.09	69358	126947	5.032	236	216
KK560	8	300	0.0	3.661	5.4539	0.96	34293	71393	5.032	234	243
KK561	8	600	0.0	3.661	5.4745	0.96	35004	73060	5.032	239	249
KK562	7	300	9.7	3.535	5.7717	1.02	53389	104332	4.989	321	314
KK563	7	600	9.9	3.533	5.8021	1.04	55030	105845	4.988	331	318
KK564	14	300	9.9	3.533	5.7914	0.98	27223	55395	4.988	327	333
KK565	14	600	9.9	3.533	5.8357	0.98	28453	58137	4.988	342	350
KK566	12	300	19.7	3.415	6.0963	0.98	42703	87029	4.945	444	453
KK567	12	600	20.2	3.409	6.1176	0.97	43603	89651	4.942	454	467
KK568	24	300	20.7	3.403	6.1264	1.00	21984	43964	4.940	458	458
KK569	24	600	20.7	3.403	6.1575	0.99	22679	45588	4.940	472	475
KK570	20	300	30.2	3.297	6.3550	0.96	32872	68619	4.898	575	601
KK571	20	600	30.3	3.295	6.4281	0.95	35361	74172	4.897	619	649
KK572	40	300	30.3	3.295	6.3980	1.00	17156	34293	4.897	601	600
KK573	40	600	30.3	3.295	6.4177	0.99	17499	35361	4.897	613	619
KK574	25	300	40.0	3.193	6.5762	0.96	32517	68065	4.854	718	751
KK575	25	600	40.1	3.192	6.7331	0.95	38038	80307	4.854	840	886
KK576	50	300	40.1	3.192	6.5997	0.98	16643	33937	4.854	735	749
KK577	50	600	40.1	3.192	6.6788	0.99	18014	36252	4.854	795	800

KK578	30	300	50.1	3.094	6.9733	0.94	39829	84411	4.797	1068	1131
KK579	30	600	50.2	3.093	6.9823	0.94	40187	85159	4.796	1077	1142
KK580	60	300	50.1	3.094	6.9901	0.99	20253	40726	4.797	1086	1092
KK581	60	600	50.2	3.093	6.9902	0.99	20253	40726	4.796	1086	1092
KK583	35	600	60.3	2.999	7.1723	0.95	41264	87029	4.752	1303	1374
KK584	70	300	60.4	2.998	7.2437	0.99	22158	44685	4.751	1399	1411
KK585	70	600	60.3	2.999	7.1873	0.99	20944	42343	4.752	1323	1337
KK586	45	300	70.3	2.912	7.4673	0.95	42703	90026	4.707	1750	1844
KK587	45	600	70.2	2.912	7.3885	0.94	39470	84038	4.708	1617	1722
KK588	90	300	70.2	2.912	7.3619	0.98	19217	39291	4.708	1575	1610
KK589	90	600	70.2	2.912	7.4885	0.97	21811	44865	4.708	1787	1838
KK591	50	600	80.3	2.829	7.5651	0.92	41983	90776	4.663	1930	2086
KK592	50	600	80.2	2.830	7.5434	0.93	41085	88527	4.663	1888	2034
KK593	100	600	80.3	2.829	7.6501	0.98	22853	46491	4.663	2101	2137
KK595	60	600	90.5	2.750	7.7268	0.94	40726	86281	4.617	2268	2403
KK596	120	300	90.4	2.751	7.7382	0.99	20598	41803	4.618	2294	2328
KK597	120	600	90.5	2.750	7.8268	0.99	22505	45588	4.617	2507	2539

Table S3. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points, and resulting propagation rate coefficients of the monomer PipEMA in bulk.

sample	reaction time	m(AIBN)	c(AIBN)	m(RAFT agent)	m(NEAEMA)	isolated yield
	h	mg	10^{-4} mol·L^{-1}	mg	g	%
1	3.5	0.10	2.08	1.20	3.0434	19
2	19.0	0.10	2.29	1.20	2.7670	58
3	18.5	0.20	6.36	3.50 (TRITT)	1.9920	65
4	25.0	0.20	6.35	3.50 (TRITT)	1.9944	84
5	25.0	0.20	6.04	3.50 (TRITT)	2.0960	87
17	19.0	0.04	1.29	0.62	1.9711	54
19	48.0	0.04	2.51	0.38	1.0104	4
21	40.5	0.02	1.30	0.19	0.9730	18
23	26.0	0.02	1.24	0.20	1.0198	31

Table S4. Detailed sample conditions and resulting isolated yield for the RAFT polymerization of NEAEMA in bulk at 66 °C.

sample	reaction time	m(AIBN)	c(AIBN)	m(RAFT agent)	m(MOMA)	isolated yield
	h	mg	10^{-4} mol·L^{-1}	mg	g	%
30	9.0	0.08	9.98	0.39	0.5000	65
31	15.0	0.08	9.68	0.39	0.5154	72
35	25.0	0.08	9.57	0.39	0.5211	85
36	30.0	0.08	9.78	0.39	0.5100	76

Table S5. Detailed sample conditions and resulting isolated yield for the RAFT polymerization of MOMA in bulk at 66 °C.

sample	reaction time	m(AIBN)	c(AIBN)	m(Thiole)	Thiole	m(NEAEMA)	isolated yield
	h	mg	10^{-3} mol·L^{-1}	mg	mol%	g	%
38	1.0	0.50	2.66	1.80	0.18	1.1890	50
39	1.0	0.20	1.16	5.30	0.53	1.0946	47
40	1.0	0.50	3.12	13.70	1.48	1.0140	54
41	1.0	0.40	2.32	21.80	2.19	1.0925	45
42	1.0	1.00	6.03	41.10	4.30	1.0509	50

Table S6. Detailed sample conditions and resulting isolated yield for the thiole controlled polymerization of NEAEMA in bulk at 66 °C.

sample	reaction time	m(AIBN)	c(AIBN)	m(Thiole)	Thiole	m(MOMA)	isolated yield
	h	mg	10^{-3} mol·L^{-1}	mg	mol%	g	%
49	1.0	0.40	2.49	3.20	0.29	1.0279	38
50	1.0	0.50	2.62	4.80	0.37	1.2198	28
51	1.0	0.40	2.59	4.80	0.46	0.9893	35
52	1.0	0.70	4.14	6.70	0.58	1.0800	39
53	1.0	0.80	5.06	7.10	0.66	1.0102	36
55	1.0	0.60	3.48	8.90	0.76	1.1016	30
57	0.75	0.80	4.92	1.50	0.14	1.0391	18
60	0.75	0.80	5.07	3.40	0.32	1.0090	32
61	0.75	0.80	5.07	2.90	0.27	1.0088	36
65	0.75	1.60	5.11	1.10	0.05	2.0026	42
66	0.75	1.60	5.11	1.30	0.06	2.0038	42
67	0.75	1.60	5.20	1.60	0.08	1.9667	35

Table S7. Detailed sample conditions and resulting isolated yield for the thiole controlled polymerization of MOMA in bulk at 66 °C.

sample	reaction time	m(AIBN)	c(AIBN)	m(Thiole)	Thiole	m(PipEMA)	m(solvent)	isolated yield
	h	mg	10^{-3} mol·L^{-1}	mg	mol%	g	g	%
20[a]	1.0	0.4	0.99	9.10	0.84	1.0093	1.0118	20
21[a]	1.0	0.5	1.41	7.30	0.67	1.0069	1.0096	24
33[a]	1.0	0.6	1.69	9.30	0.86	1.0003	1.0088	21
35[a]	1.0	0.7	1.92	0.60	0.05	1.0597	1.0121	18
40[a]	1.0	0.8	2.00	11.00	0.92	1.1158	1.1514	18
44	0.75	0.4	2.16	0.40	0.07	0.5045	0.4335	10
45	0.75	0.4	2.17	0.60	0.11	0.5073	0.4384	20
46	0.75	0.3	2.12	0.90	0.16	0.5126	0.4215	19
47	0.75	0.4	2.18	1.20	0.22	0.5010	0.4366	21
48	0.75	0.4	2.07	2.10	0.34	0.5764	0.4545	20
49	0.75	0.4	2.28	2.50	0.45	0.5106	0.4848	19
51	0.75	0.3	2.09	2.70	0.49	0.5134	0.4108	18
52	0.75	0.4	2.16	3.50	0.63	0.5120	0.4379	19
53	0.75	0.4	2.19	5.10	0.93	0.5111	0.4514	18

Table S8. Detailed sample conditions and resulting isolated yield for the thiole controlled polymerization of PipEMA in 50% solution in THF at 66 °C. [a]Polymerization carried out in BuAc.

NEAEMA				MOMA				PipEMA			
sample no.	M_w	[η]	Đ	sample no.	M_w	[η]	Đ	sample no.	M_w	[η]	Đ
	g·mol^{-1}	mL·g^{-1}			g·mol^{-1}	mL·g^{-1}			g·mol^{-1}	mL·g^{-1}	
1	172800	35.3	1.1	30	1193200	131.3	2.5	20	112600	18.2	1.8
2	562500	81.0	1.1	31	528600	76.7	1.8	21	126500	19.2	1.7
3	968800	89.5	2.5	35	372600	71.0	1.8	33	125800	18.0	1.6
4	1646000	130.2	2.2	36	874800	110.3	2.5	35	618400	49.6	1.7
5	1158800	112.6	2.2	49	113300	29.2	1.9	40	47000	10.5	1.5
17	993600	103.2	1.9	50	130300	32.0	1.5	44	357200	34.0	1.5
19	62600	20.5	2.1	51	128900	26.1	2.4	45	468900	45.6	1.3
21	1056500	115.3	2.2	52	86100	22.7	1.5	46	226300	25.7	1.7
23	1330000	152.2	1.6	53	96000	22.7	1.5	47	378000	38.0	1.4
38	590900	77.4	2.4	55	69100	17.4	1.7	48	107900	18.3	1.6
39	145400	24.9	1.7	57	301900	53.3	2.0	49	84700	16.4	1.5
40	49400	12.7	1.6	60	186300	36.7	1.6	51	75800	14.4	1.8
41	26600	10.5	1.4	61	219900	38.2	1.4	52	64000	13.2	1.5
42	23100	9.1	1.4	65	593100	89.6	1.5	53	46700	9.6	1.6
				66	724400	94.3	1.5				
				67	619100	76.9	1.7				

Table S9. Intrinsic viscosities and weight average molecular weights employed in the Mark-Houwink-Kuhn-Sakurada plots, alongside the polydispersity indices for each sample for NEAEMA, MOMA, and PipEMA.

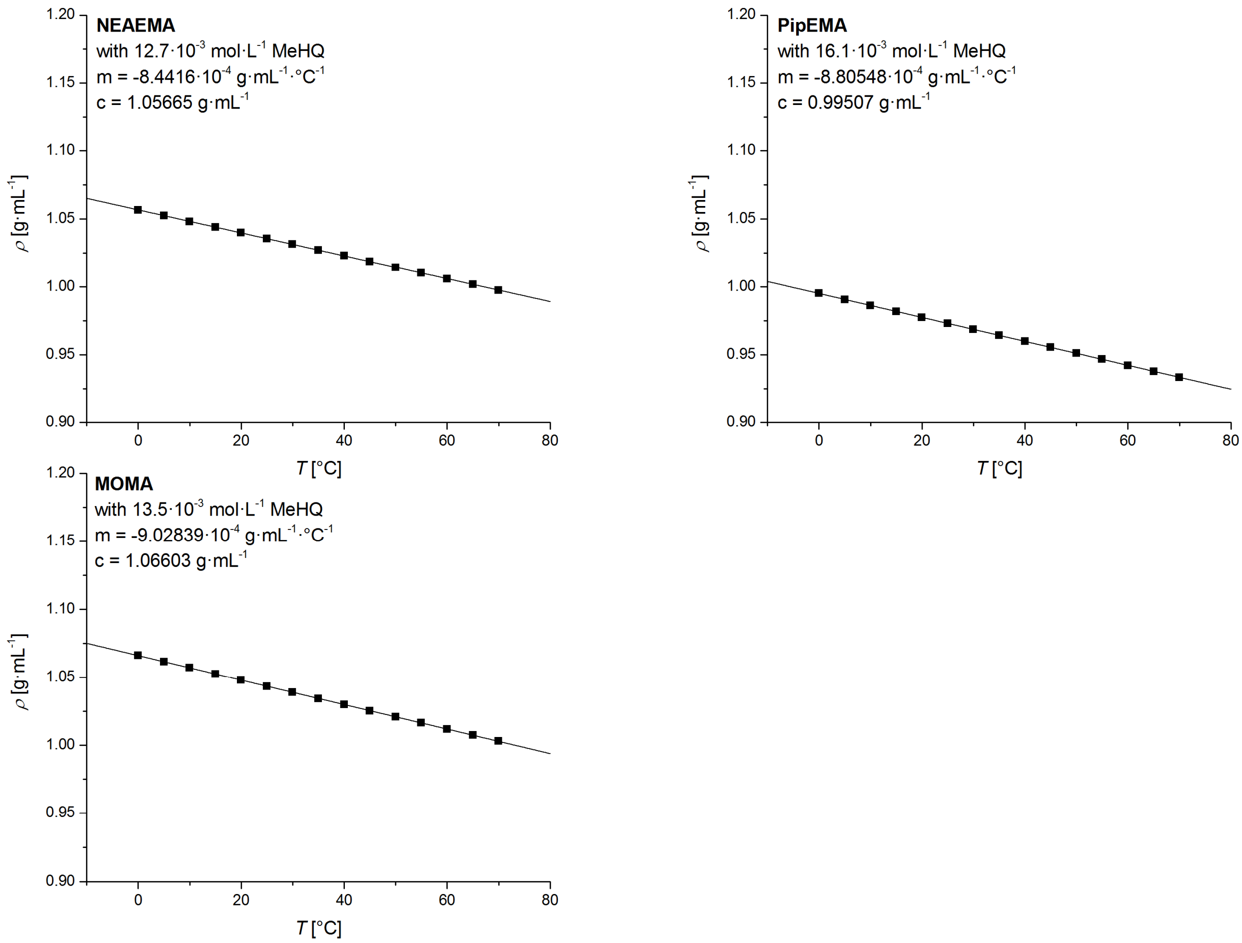

Figure S1. Temperature dependent densities for NEAEMA, MOMA, and PipEMA in bulk. Methyl hydroquinone (MeHQ) was added to prevent the solutions from polymerizing. The temperature dependent densities are summarized in Table 1.

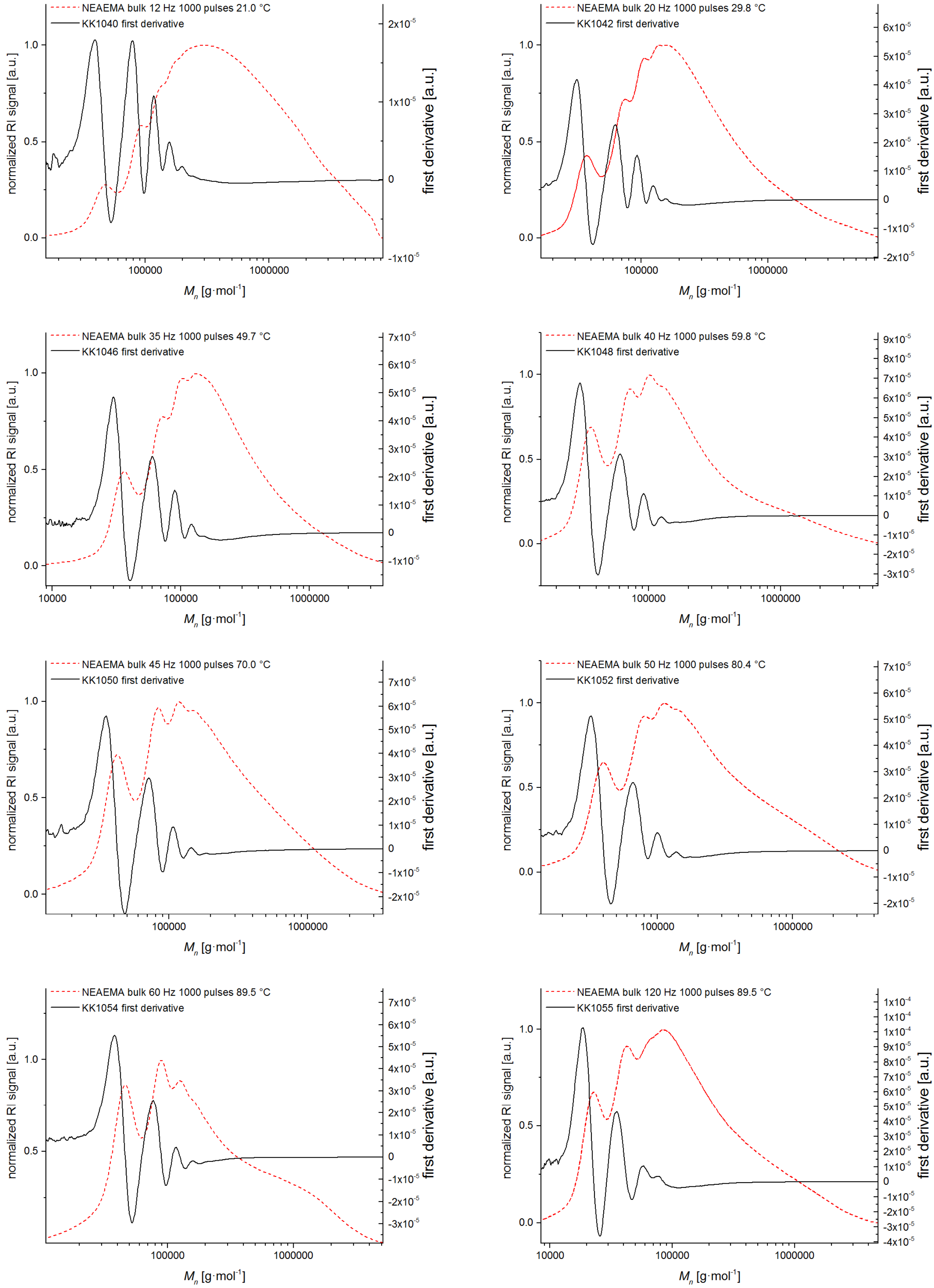

Figure S2. Exemplary molecular weight distributions (red dotted lines) and their first derivatives (black solid lines) of NEAEMA in bulk. Sample specific conditions are collated in Table S1.

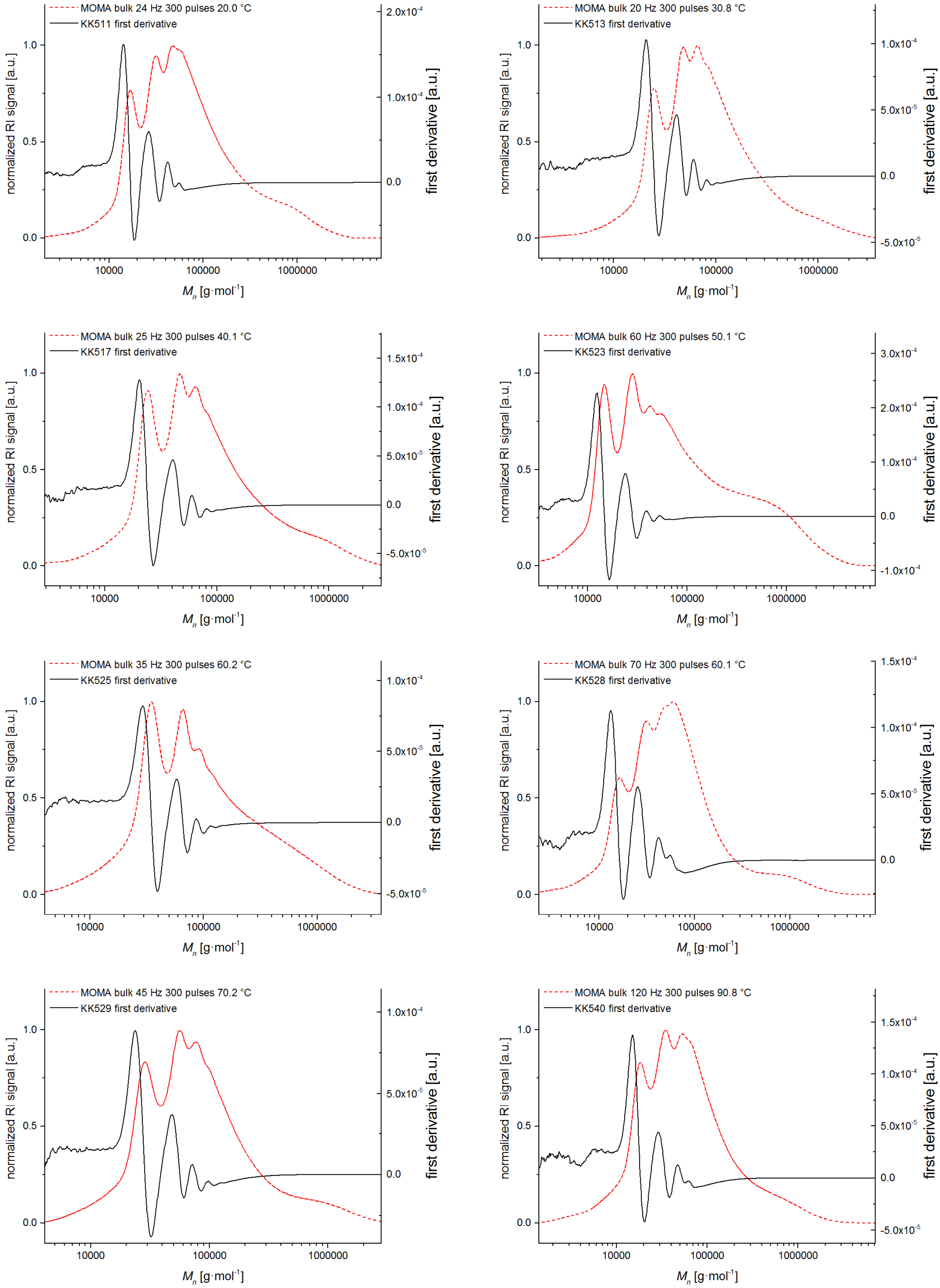

Figure S3. Exemplary molecular weight distributions (red dotted lines) and their first derivatives (black solid lines) of MOMA in bulk. Sample specific conditions are collated in Table S2.

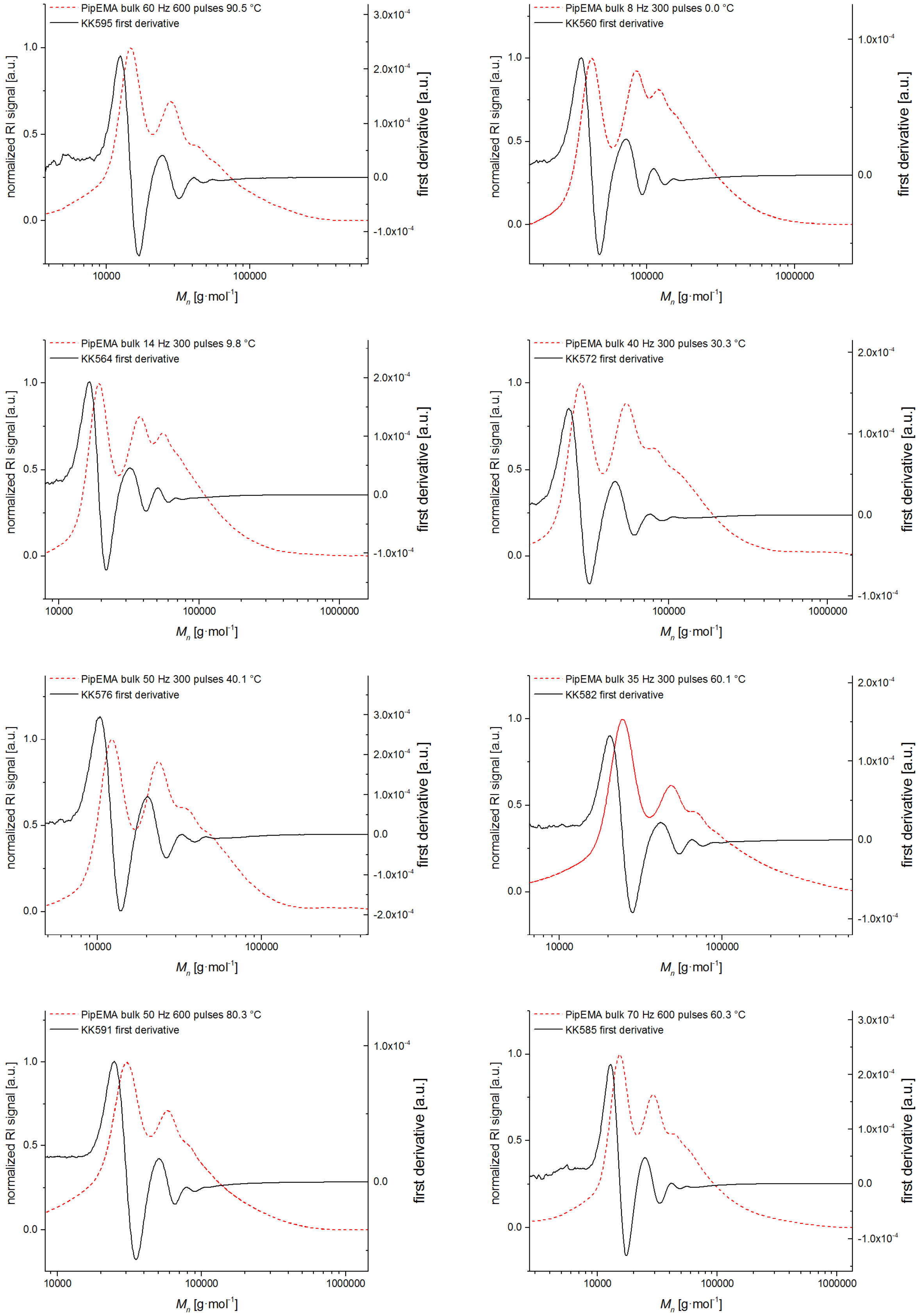

Figure S4. Exemplary molecular weight distributions (red dotted lines) and their first derivatives (black solid lines) of PipEMA in bulk. Sample specific conditions are collated in Table S3.

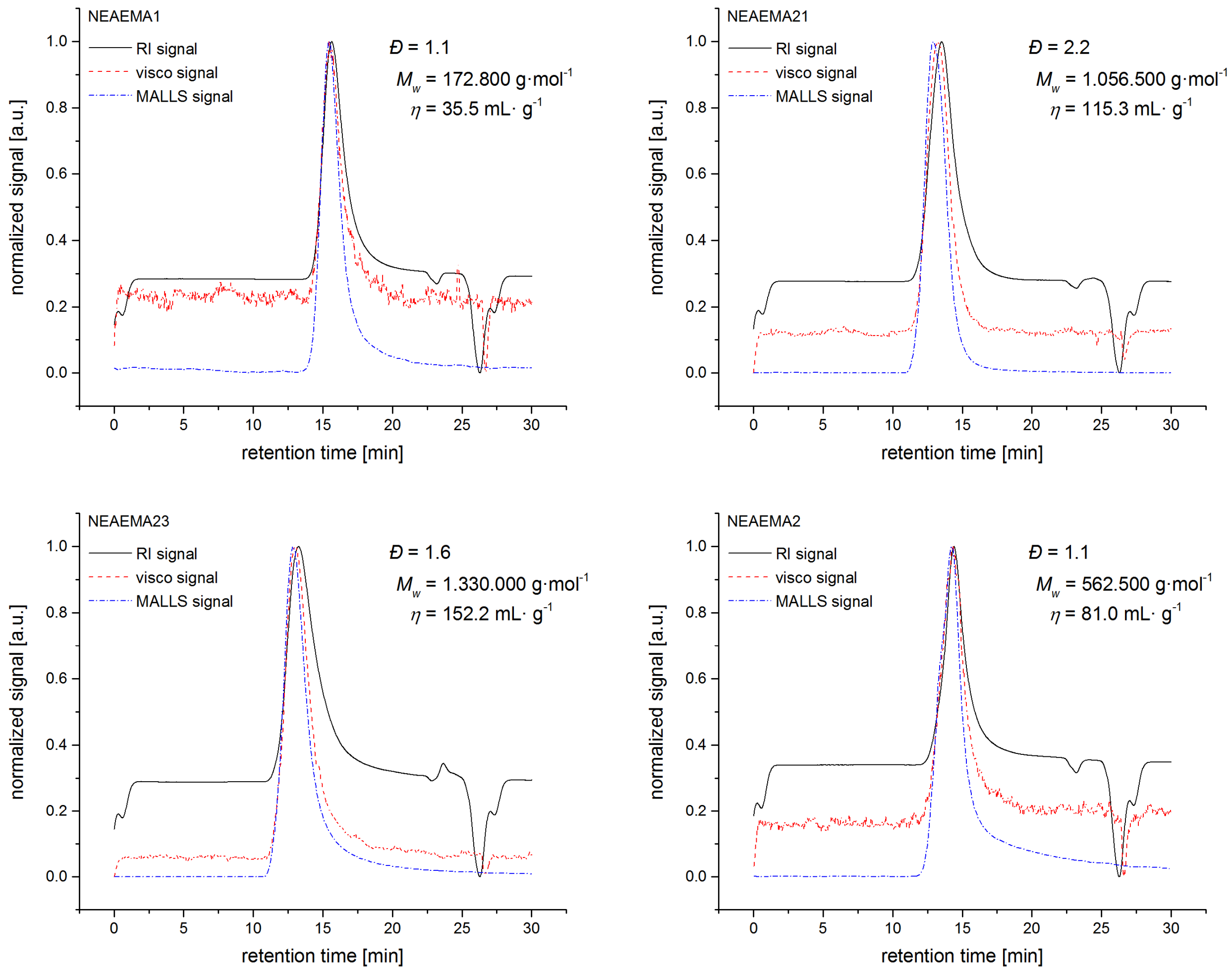

Figure S5. Exemplary triple-SEC elugrams with RI signals (black solid lines), visco signals (red dashed lines), and MALLS signals (blue dot-dashed lines) for NEAEMA in bulk. The sample specific conditions are collated in Table S4 and S6 and the resulting absolute molecular weights and intrinsic viscosities are collated in Table S9.

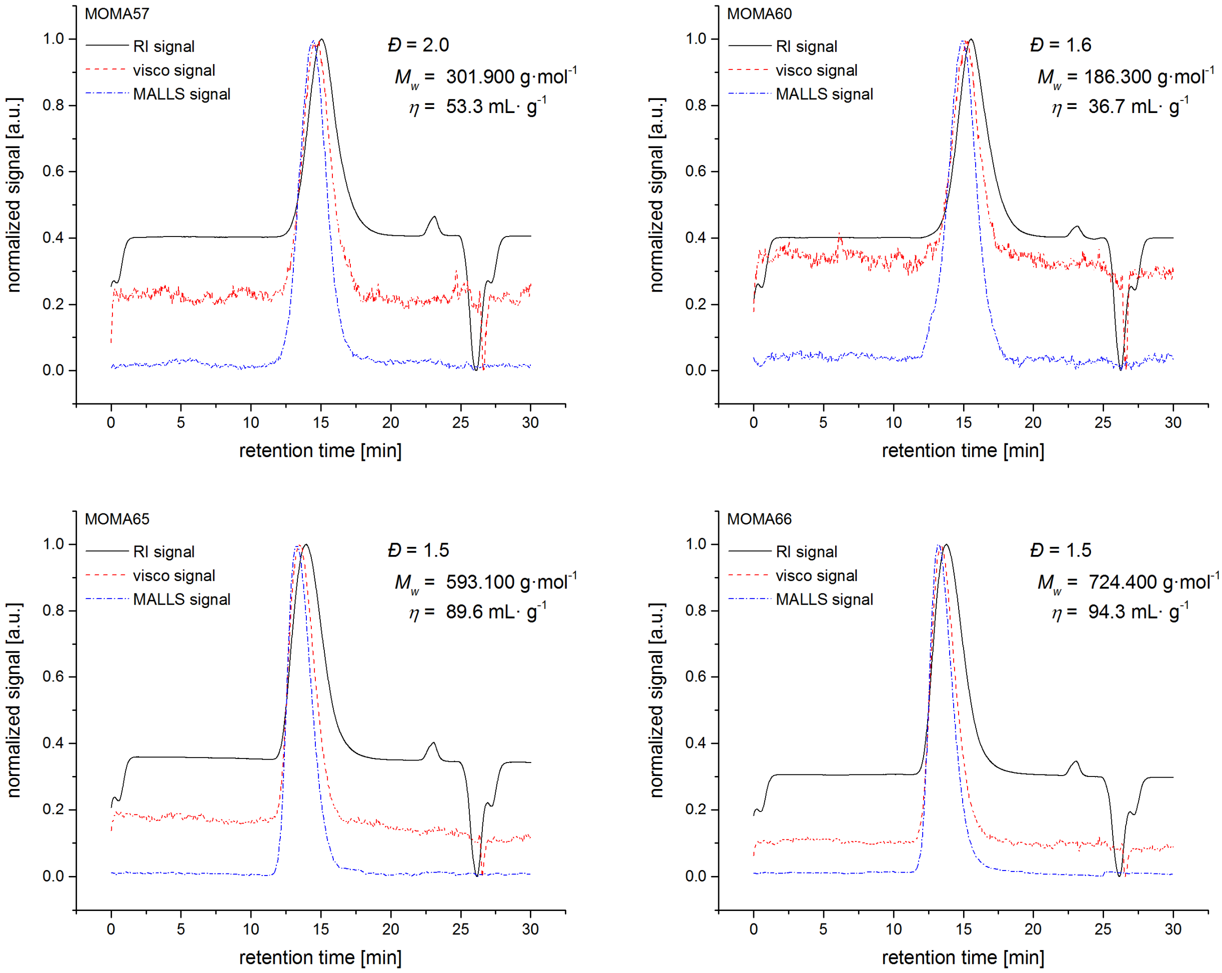

Figure S6. Exemplary triple-SEC elugrams with RI signals (black solid lines), visco signals (red dashed lines), and MALLS signals (blue dot-dashed lines) for MOMA in bulk. The sample specific conditions are collated in Table S5 and S7 and the resulting absolute molecular weights and intrinsic viscosities are collated in Table S9.

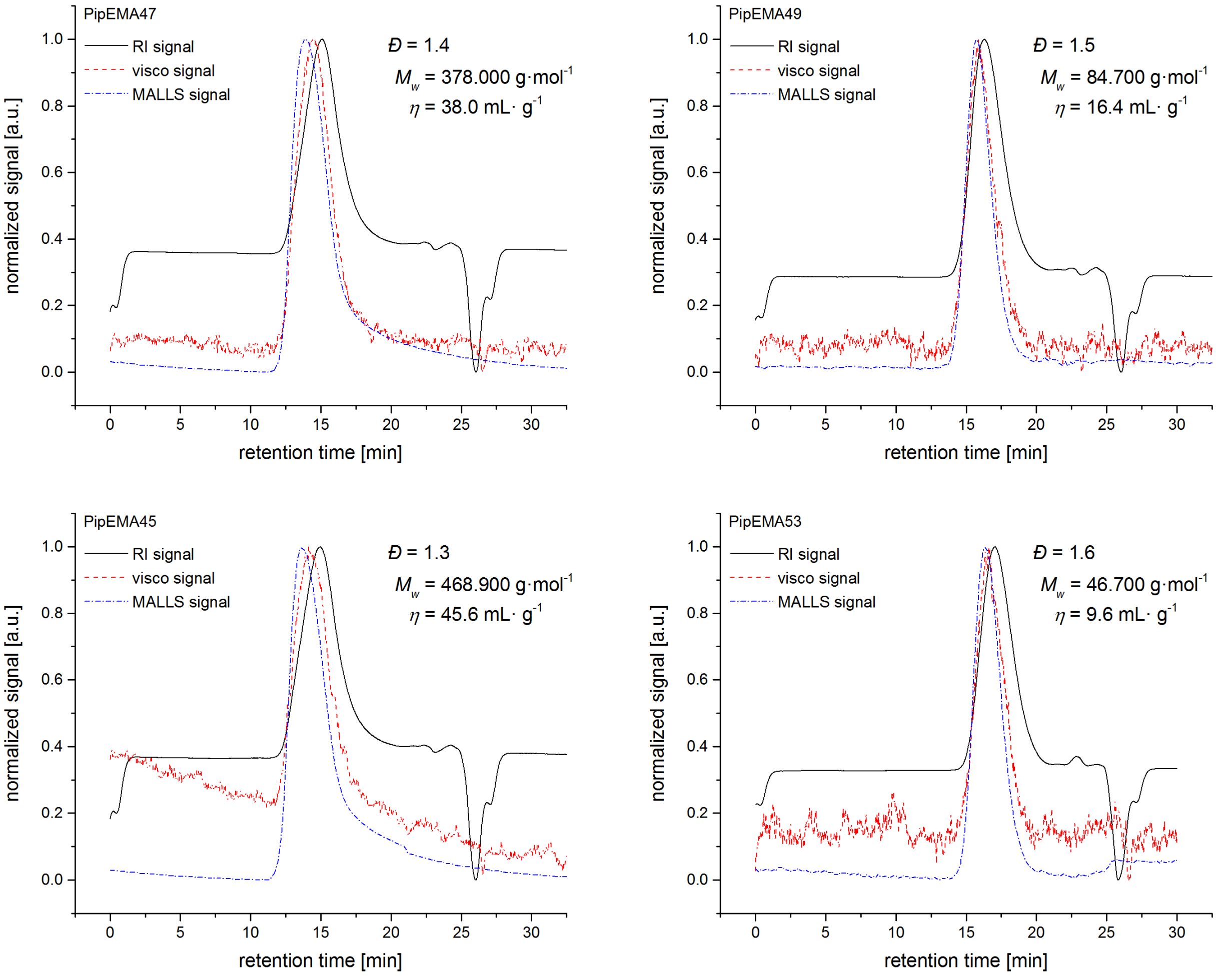

Figure S7. Exemplary triple-SEC elugrams with RI signals (black solid lines), visco signals (red dashed lines), and MALLS signals (blue dot-dashed lines) for PipEMA in 50 % solution in THF. The sample specific conditions are collated in Table S8 and the resulting absolute molecular weights and intrinsic viscosities are collated in Table S9.