Supporting Information

Global Trends for k_p? Expanding the Frontier of Ester Side Chain Topography in Acrylates and Methacrylates

*Alexander P. Haehnel, Maria Schneider-Baumann, Kai U. Hiltebrandt, Andrea M. Misske, Christopher Barner-Kowollik**

Exemplary SEC chromatograms are shown for each monomer at 4 temperatures as well as tables with the exact samples conditions. Furthermore, the temperature dependent density curves for each monomer and the differential scanning calorimetry (DSC) curves are provided and the results are summarized in Table 1 in the main article. Additionally, as a typical example, the success of the fractionation – required for the MHKS parameter determination – is demonstrated for pBeMA as polymer system; the data points incorporated into the individual MHKS plots of each monomer are stated in Table S9. Furthermore, exemplary triple detector SEC traces are shown for each polymer system.

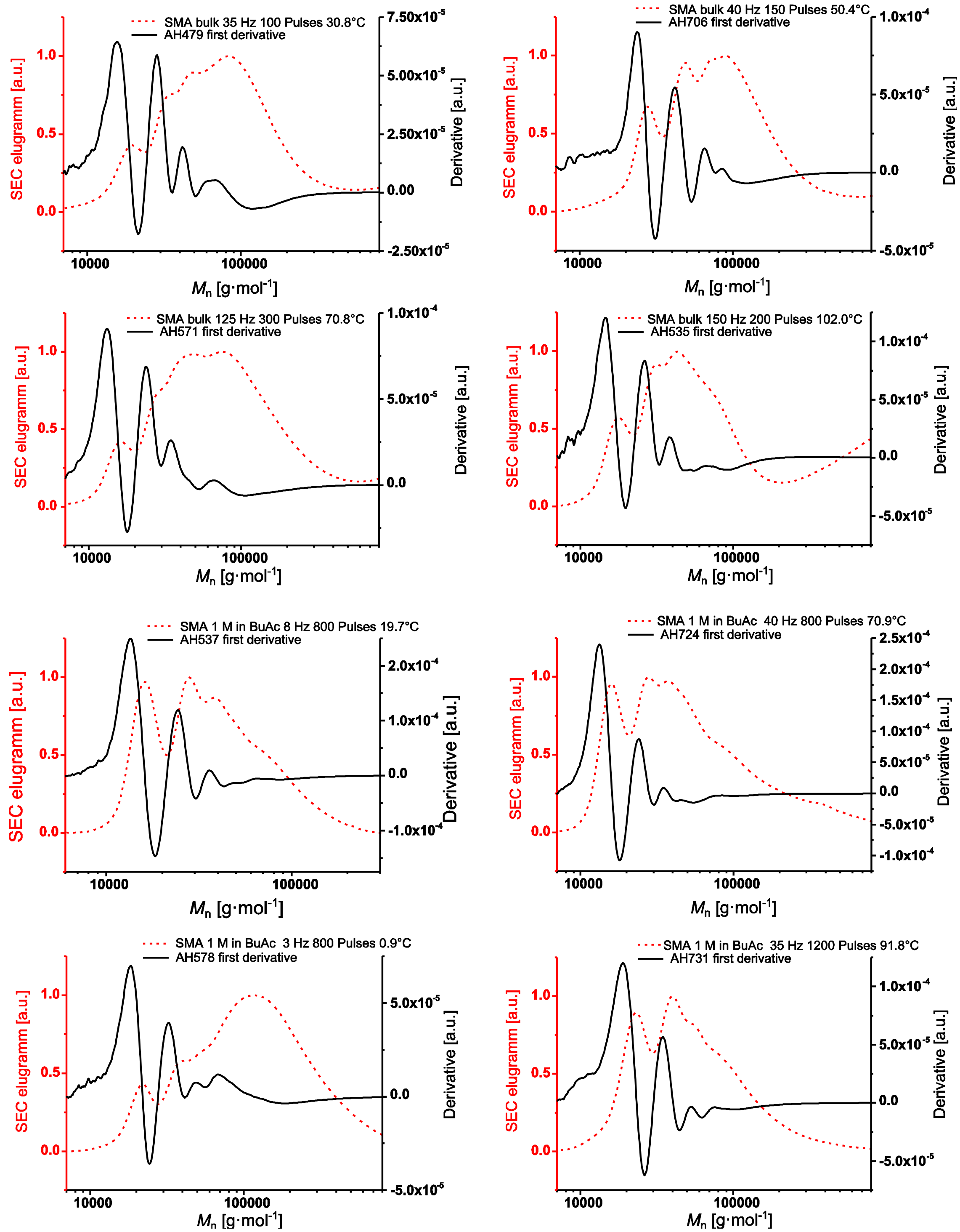


Figure S1. Exemplary molecular weight distributions (red dotted lines) and their first derivative (solid black lines) of SMA in bulk (upper four diagrams) and in 1 molar solution in butyl acetate (lower four diagrams). The sample specific conditions are displayed in the diagrams and also collated in Table S1 for bulk and in Table S2 for 1 molar solution in butyl acetate. The typical PLP structure is observed for all samples.

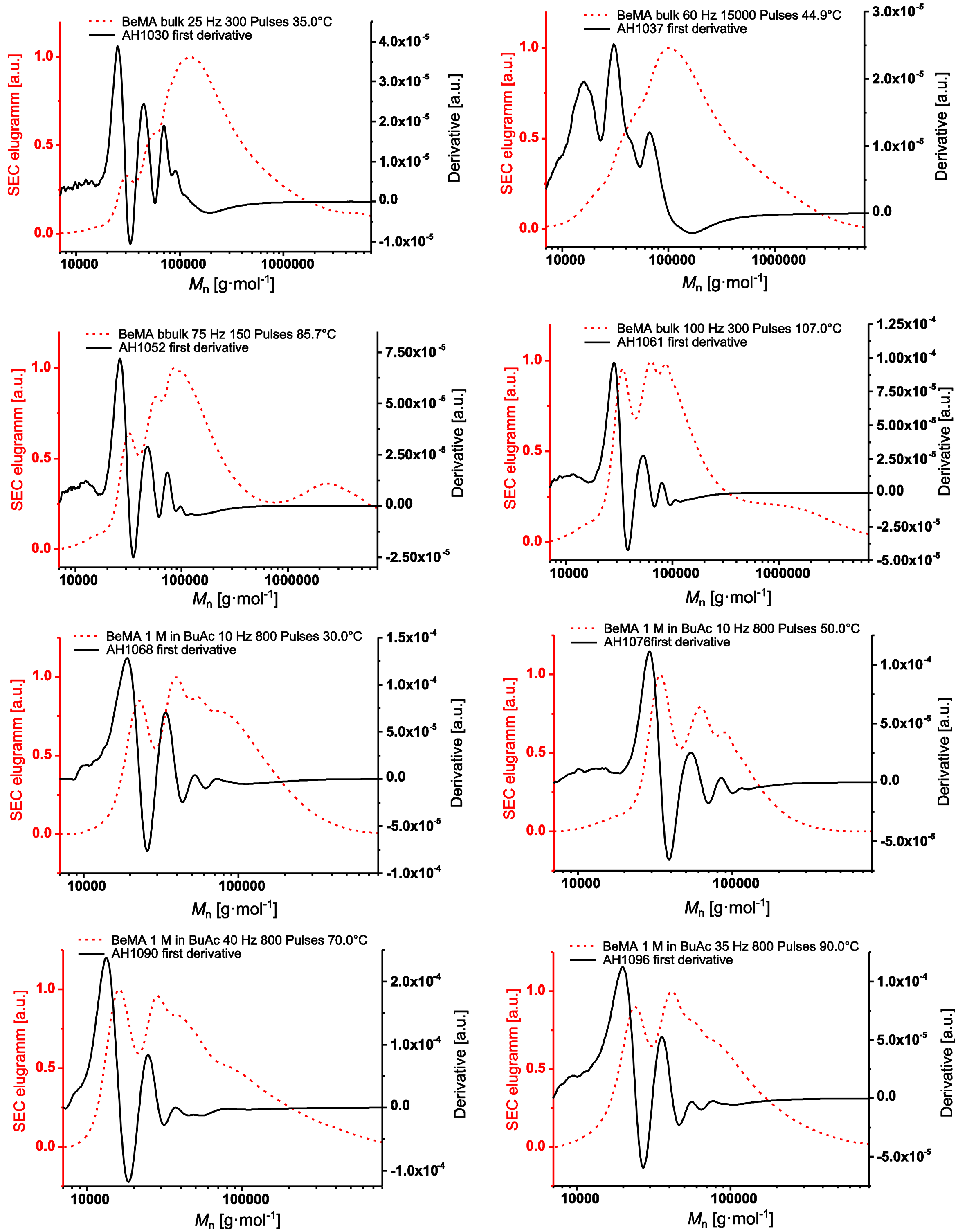


Figure S2. Exemplary molecular weight distributions (red dotted lines) and their first derivative (solid black lines) of BeMA in bulk (upper four diagrams) and in 1 molar solution in butyl acetate (lower four diagrams). The sample specific conditions are displayed in the diagrams and also collated in Table S3 for bulk and in Table S4 for 1 molar solution in butyl acetate. The typical PLP structure is observed for all samples.

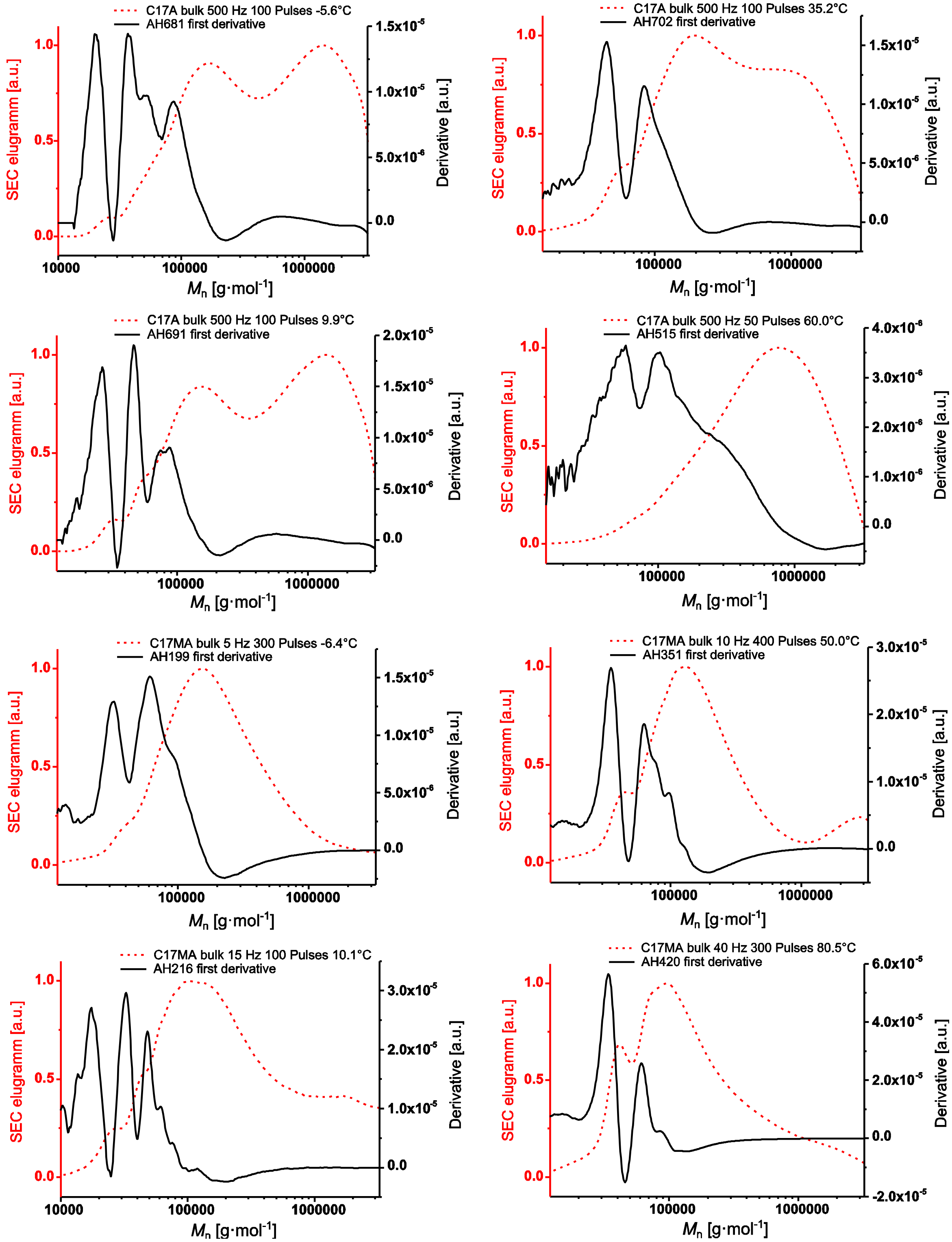


Figure S3. Exemplary molecular weight distributions (red dotted lines) and their first derivative (solid black lines) of C17A in bulk (upper four diagrams) and of C17MA (lower four diagrams). The sample specific conditions are displayed in the diagrams and also collated in Table S5 for C17A and in Table S6 for C17MA. The typical PLP structure is observed for all samples.

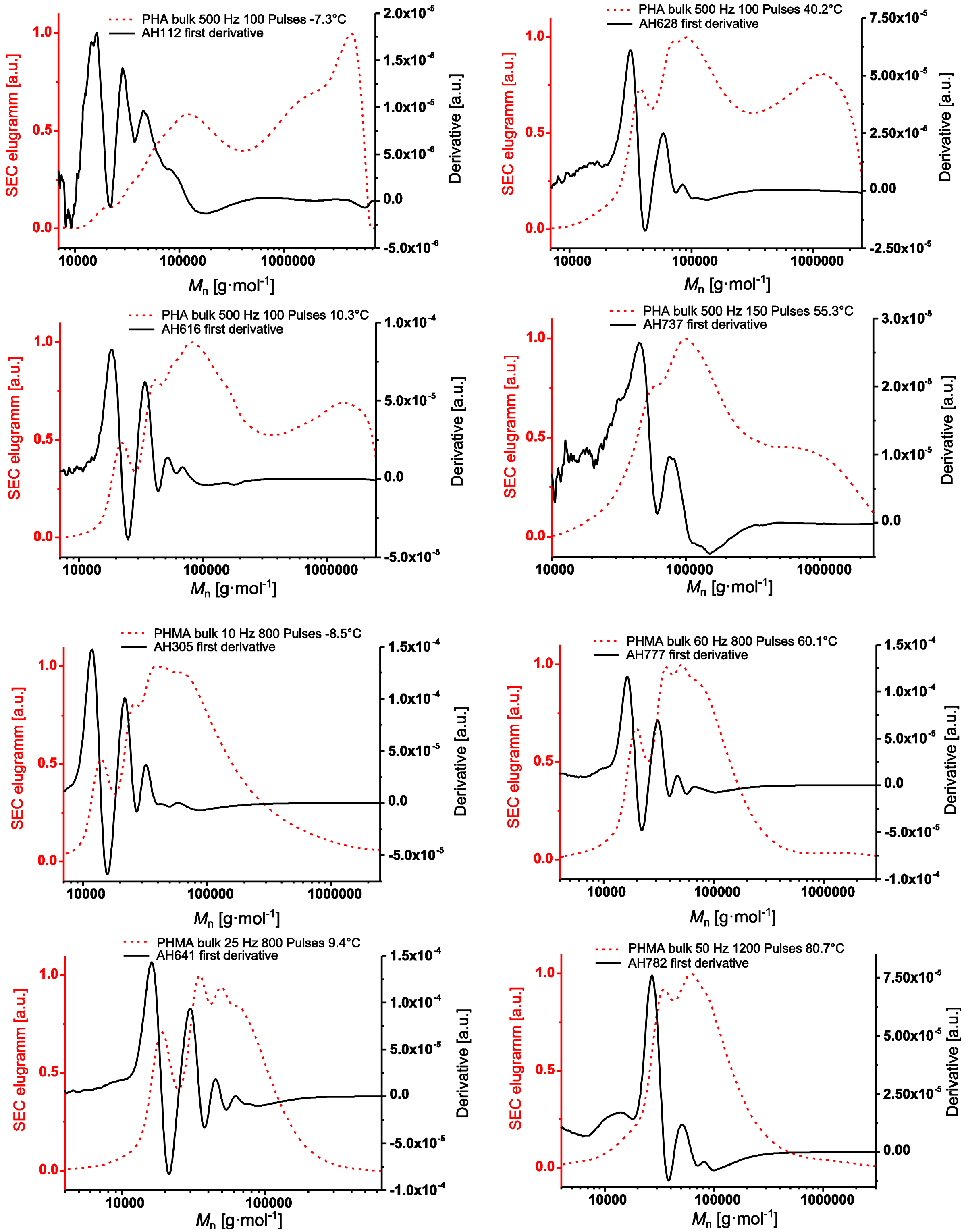


Figure S4. Exemplary molecular weight distributions (red dotted lines) and their first derivative (solid black lines) of PHA in bulk (upper four diagrams) and of PHMA (lower four diagrams). The sample specific conditions are displayed in the diagrams and also collated in Table S7 for PHA and in Table S8 for PHMA. The typical PLP structure is observed for all samples.

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} $mol \cdot L^{-1}$ s^{-1}	k_{p2} $mol \cdot L^{-1}$ s^{-1}
AH479	35	100	30.8	3.290	6.4627	1.101	15700	28600	2.602	641	582
AH558	25	150	31.7	3.280	6.4778	1.152	22300	38800	2.600	651	565
AH562	30	150	40.0	3.193	6.6809	1.153	22600	39300	2.582	797	691
AH565	50	300	40.2	3.191	6.7670	1.105	14800	26800	2.581	869	786
AH569	75	300	50.3	3.092	7.0944	1.103	13600	24600	2.559	1205	1093
AH706	40	150	50.4	3.091	7.0272	1.139	23800	41800	2.559	1127	990
AH708	50	150	60.3	2.999	7.2795	1.138	24300	42700	2.538	1450	1274
AH711	100	300	60.7	2.995	7.4072	1.104	13800	25000	2.537	1648	1493
AH438	75	300	70.2	2.912	7.4388	1.171	18800	32100	2.513	1701	1452
AH571	125	300	70.8	2.907	7.5921	1.107	13200	23800	2.515	1982	1790
AH443	150	300	80.2	2.830	7.7991	1.120	13400	23900	2.492	2439	2178
AH439	75	150	80.5	2.828	7.6465	1.153	23000	39800	2.491	2093	1815
AH485	100	150	90.8	2.748	7.9142	1.155	22300	38700	2.472	2736	2368
AH489	200	150	91.4	2.743	8.0562	1.116	12900	23100	2.471	3153	2826
AH531	100	150	102.0	2.666	8.0790	1.132	26100	46100	2.448	3226	2849
AH535	200	150	102.0	2.666	8.1922	1.111	14600	26300	2.448	3613	3252

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

sample	f Hz	n –	θ °C	T^{-1} 10^{-3} K^{-1}	$\ln(k_{p1})$ –	k_{p1}/k_{p2} –	M_1 g·mol^{-1}	M_2 g·mol^{-1}	c_M mol·L^{-1}	k_{p1} mol·L^{-1} s^{-1}	k_{p2} mol·L^{-1} s^{-1}
AH581	7	1200	0.8	3.650	5.3802	1.174	10000	17100	0.979	217	185
AH578	3	800	0.9	3.649	5.1523	1.136	18600	32800	0.978	173	152
AH713	10	1200	10.1	3.530	5.8302	1.164	11700	20100	1.041	340	292
AH582	5	800	11.1	3.518	5.4448	1.113	14800	26600	0.968	232	208
AH715	15	1200	18.7	3.426	6.1737	1.191	10900	18300	1.032	480	403
AH537	8	800	19.7	3.415	5.8093	1.103	13600	24600	0.987	333	302
AH327	10	800	29.9	3.300	6.1504	1.111	15500	28000	1.003	469	422
AH543	15	800	30.5	3.293	6.2135	1.122	10700	19100	0.976	499	445
AH545	10	800	39.9	3.194	6.3176	1.126	17700	31400	0.966	554	492
AH547	20	800	40.2	3.191	6.5301	1.143	10900	19100	0.966	685	600
AH333	10	800	50.0	3.095	6.5896	1.145	23600	41200	0.982	727	635
AH335	30	800	50.0	3.095	6.8911	1.195	10600	17800	0.982	983	823
AH550	15	1200	60.4	2.998	6.8605	1.149	19800	34600	0.945	954	830
AH551	30	800	60.4	2.998	7.0374	1.134	11800	20900	0.945	1138	1004
AH555	30	800	70.7	2.908	7.1776	1.109	13500	24300	0.935	1310	1181
AH724	40	800	70.9	2.907	7.4088	1.108	13300	24000	0.976	1650	1489
AH727	30	1200	80.9	2.824	7.4566	1.089	18400	33800	0.966	1731	1590
AH728	50	800	81.2	2.822	7.6204	1.097	13000	23700	0.965	2039	1859
AH731	35	1200	91.8	2.740	7.6550	1.108	19000	34300	0.954	2111	1906
AH732	70	800	91.6	2.742	7.8800	1.144	11900	20800	0.954	2644	2311

Table S2. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer SMA in 1molar solution in butyl acetate.

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} $mol\cdot L^{-1}$ s^{-1}	k_{p2} $mol\cdot L^{-1}$ s^{-1}
AH1030	25	300	35.0	3.245	6.6085	1.131	25300	44800	2.336	741	655
AH1031	50	150	35.0	3.245	6.7210	1.111	14200	25500	2.336	830	747
AH1033	30	150	44.8	3.145	6.8505	1.107	26700	48200	2.316	944	853
AH1035	50	150	44.9	3.144	6.9496	1.111	17000	31800	2.316	1043	939
AH1037	60	15000	44.9	3.144	7.0425	1.047	16200	30900	2.316	1144	1093
AH1041	40	300	55.2	3.046	7.1241	1.117	26100	46700	2.299	1242	1111
AH1043	80	300	55.2	3.046	7.2333	1.095	14600	26600	2.299	1385	1264
AH1044	50	150	65.9	2.949	7.3711	1.104	26500	48000	2.277	1589	1440
AH1047	100	300	66.3	2.946	7.5043	1.099	15100	27500	2.277	1816	1653
AH1048	75	150	75.4	2.869	7.6510	1.141	23200	40600	2.258	2103	1843
AH1051	150	300	75.4	2.869	7.7634	1.097	13000	23600	2.258	2353	2146
AH1052	75	150	85.7	2.787	7.7943	1.104	26500	48000	2.237	2427	2198
AH1054	150	150	86.0	2.784	7.9212	1.103	15000	27200	2.237	2755	2497
AH1056	100	150	96.2	2.707	8.0248	1.132	24800	43800	2.216	3056	2699
AH1059	200	300	96.2	2.707	8.1467	1.100	14000	25400	2.216	3452	3138
AH1061	100	300	107.0	2.631	8.1805	1.065	28600	53600	2.188	3571	3351
AH1062	200	150	107.0	2.631	8.2740	1.098	15700	28600	2.188	3921	3571

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

sample	f Hz	n –	θ °C	T^{-1} 10^{-3} K^{-1}	$\ln(k_{p1})$ –	k_{p1}/k_{p2} –	M_1 g·mol^{-1}	M_2 g·mol^{-1}	c_M mol·L^{-1}	k_{p1} mol·L^{-1} s^{-1}	k_{p2} mol·L^{-1} s^{-1}
AH1064	8	800	19.5	3.417	5.9243	1.109	17300	31200	1.012	374	337
AH1066	15	800	19.4	3.418	6.1702	1.146	11800	20600	1.012	478	417
AH1068	10	800	30.0	3.299	6.2623	1.129	19200	34000	1.001	524	464
AH1071	15	1200	30.3	3.295	6.3523	1.111	14000	25200	1.001	574	516
AH1072	10	800	40.0	3.193	6.5041	1.131	24200	42800	0.991	668	591
AH1074	20	800	40.0	3.193	6.6571	1.115	14100	25300	0.991	778	698
AH1076	10	800	50.0	3.095	6.7023	1.090	29200	53600	0.980	814	747
AH1078	30	800	50.0	3.095	6.9917	1.130	13000	23000	0.980	1088	962
AH1080	15	800	60.0	3.002	7.0022	1.118	26000	46500	0.970	1099	983
AH1082	30	800	60.0	3.002	7.1183	1.106	14600	26400	0.970	1234	1116
AH1084	20	800	70.0	2.914	7.2485	1.120	23800	42500	0.926	1406	1255
AH1090	40	800	70.0	2.914	7.3597	1.077	13300	24700	0.926	1571	1459
AH1093	30	1200	80.2	2.830	7.4707	1.110	19600	35300	0.915	1756	1581
AH1094	50	800	80.3	2.829	7.5711	1.088	13000	23900	0.915	1941	1784
AH1096	35	800	90.0	2.754	7.6507	1.115	19900	35700	0.906	2102	1886
AH1098	70	800	90.0	2.754	7.8380	1.086	12000	22100	0.906	2535	2335
AH1100	45	800	100.0	2.680	7.8182	1.074	18100	33700	0.896	2485	2314
AH1102	90	800	100.0	2.680	8.0313	1.103	11200	20300	0.896	3076	2788

Table S4. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer BeMA in 1molar solution in butyl acetate.

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} $mol \cdot L^{-1}$ s^{-1}	k_{p2} $mol \cdot L^{-1}$ s^{-1}
AH491	500	150	-8.4	3.777	9.1946	1.078	17700	32800	2.891	9844	9133
AH681	500	100	-5.6	3.738	9.3647	1.083	20500	37800	2.827	11669	10779
AH686	500	200	-0.1	3.662	9.4540	1.068	22300	41700	2.814	12759	11942
AH494	500	100	1.1	3.646	9.3004	1.026	19500	38000	2.869	10942	10667
AH690	500	200	5.0	3.595	9.6022	1.083	25800	47600	2.803	14797	13667
AH689	500	100	5.2	3.593	9.5567	1.102	24600	44700	2.802	14139	12832
AH498	500	100	9.5	3.538	9.8324	1.105	33000	59700	2.849	18627	16862
AH691	500	100	9.9	3.533	9.6376	1.129	26600	47100	2.791	15330	13582
AH694	500	200	14.4	3.478	9.8263	1.170	32000	54700	2.781	18515	15829
AH693	500	100	14.5	3.476	9.7740	1.158	30300	52400	2.781	17570	15177
AH501	500	100	19.8	3.414	10.0334	1.132	40000	70600	2.825	22776	20115
AH502	500	150	20.0	3.411	10.0497	1.096	40600	74100	2.825	23150	21122
AH697	500	100	25.6	3.347	9.9646	1.114	36400	65300	2.756	21260	19077
AH698	500	200	26.3	3.339	9.8564	0.931	32600	70100	2.754	19080	20494
AH699	500	100	30.1	3.298	9.9992	1.054	37500	71200	2.745	22008	20888
AH505	500	150	30.1	3.298	10.2662	1.041	50000	96100	2.801	28744	27622
AH597	500	100	35.1	3.244	10.1015	1.081	41100	76000	2.714	24380	22550
AH702	500	200	35.2	3.243	10.1740	1.060	44500	84000	2.734	26214	24741
AH507	500	50	40.1	3.192	10.4016	1.054	56800	107700	2.778	32912	31212
AH509	500	150	40.1	3.192	10.3032	0.938	51500	109700	2.778	29827	31808
AH599	500	50	44.6	3.147	10.2525	1.110	47400	85400	2.693	28354	25546
AH601	500	150	45.3	3.140	10.2932	1.110	49400	88900	2.691	29531	26609
AH511	500	50	50.0	3.095	10.4836	1.017	61100	120200	2.755	35726	35127
AH512	500	100	50.2	3.093	10.4463	1.095	58900	107500	2.754	34416	31432
AH602	500	50	54.5	3.052	10.3916	1.125	54000	96100	2.670	32585	28976
AH603	500	100	55.1	3.046	10.4128	1.126	55200	98000	2.669	33282	29566
AH515	500	50	60.0	3.002	10.6998	1.091	75200	137900	2.731	44347	40634
AH517	500	100	60.3	2.999	10.7376	1.171	78100	133400	2.731	46054	39344

Table S5. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer C17A.

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} $mol\cdot L^{-1}\ s^{-1}$	k_{p2} $mol\cdot L^{-1}\ s^{-1}$
AH201	15	300	-6.6	3.752	5.4519	1.028	13900	27000	2.756	233	227
AH199	5	300	-6.4	3.749	5.1861	1.020	32000	62700	2.755	179	175
AH206	15	600	0.8	3.650	5.6331	1.040	16600	31900	2.739	280	269
AH205	5	300	0.9	3.649	5.3744	1.040	38400	73700	2.739	216	207
AH211	5	200	9.9	3.533	5.6596	1.165	50700	86900	2.719	287	246
AH216	15	100	10.1	3.530	5.8589	1.087	20600	37900	2.718	350	322
AH218	10	700	20.0	3.411	5.9962	1.106	35200	63600	2.696	402	363
AH403	20	400	20.1	3.410	5.9307	1.117	16500	29500	2.693	376	337
AH407	40	400	30.0	3.299	6.3582	1.126	12500	22200	2.671	577	513
AH187	15	200	30.3	3.295	6.3254	1.129	32300	57200	2.674	559	495
AH347	20	200	40.0	3.193	6.5585	1.160	30400	52400	2.654	705	608
AH195	50	200	40.1	3.192	6.7743	1.119	15100	26900	2.652	875	782
AH408	40	250	49.9	3.095	6.8339	1.137	19800	34800	2.627	929	817
AH351	20	200	50.0	3.095	6.7232	1.125	35500	63100	2.632	831	739
AH411	30	500	60.1	3.001	6.9041	1.045	28100	53700	2.605	996	953
AH414	50	250	60.1	3.001	7.0480	1.132	19500	34400	2.605	1151	1016
AH417	40	500	70.3	2.912	7.2483	1.087	29500	54200	2.582	1406	1293
AH418	70	300	70.3	2.912	7.3570	1.114	18800	33700	2.582	1567	1407
AH420	40	300	80.5	2.828	7.4116	1.109	34400	62000	2.560	1655	1493
AH422	70	300	80.5	2.828	7.5605	1.157	22800	39400	2.560	1921	1660

Table S6. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer C17MA.

sample	f Hz	n –	θ °C	T^{-1} 10^{-3} K^{-1}	ln(k_{p1}) –	k_{p1}/k_{p2} –	M_1 g·mol^{-1}	M_2 g·mol^{-1}	c_M mol·L^{-1}	k_{p1} mol·L^{-1} s^{-1}	k_{p2} mol·L^{-1} s^{-1}
AH111	500	150	-7.3	3.762	8.7628	1.091	11400	20900	4.199	6392	5861
AH112	500	100	-7.3	3.762	8.7083	1.076	10800	20100	4.199	6053	5626
AH114	500	150	0.8	3.650	8.9330	1.014	13400	26500	4.179	7578	7472
AH115	500	100	0.1	3.660	8.9145	1.033	13200	25600	4.181	7439	7200
AH616	500	100	10.3	3.528	9.2835	1.079	18600	34500	4.076	10759	9970
AH617	500	150	10.3	3.528	9.2705	1.076	18400	34200	4.076	10620	9867
AH618	500	50	19.1	3.422	9.4489	1.110	21900	39400	4.055	12694	11436
AH619	500	100	19.6	3.416	9.5076	1.107	23200	41900	4.054	13462	12163
AH622	500	100	30.2	3.297	9.6487	1.101	26500	48200	4.029	15502	14074
AH623	500	150	30.3	3.295	9.6666	1.100	27000	49100	4.029	15782	14352
AH625	500	100	35.3	3.242	9.7583	1.079	29500	54700	4.017	17297	16024
AH626	500	150	35.3	3.242	9.7663	1.072	29700	55500	4.017	17437	16267
AH628	500	100	40.2	3.191	9.8388	1.076	31900	59300	4.006	18748	17425
AH629	500	150	40.2	3.191	9.8610	1.079	32600	60500	4.006	19168	17772
AH631	500	100	45.3	3.140	9.9446	1.102	35300	64100	3.994	20840	18904
AH632	500	150	45.3	3.140	9.9208	1.093	34500	63200	3.994	20348	18625
AH633	500	50	50.1	3.094	10.0030	1.095	37400	68200	3.982	22094	20177
AH734	500	150	50.2	3.093	10.1394	1.122	42800	76300	3.980	25322	22571
AH735	500	50	55.1	3.046	10.1835	1.115	44600	80000	3.969	26464	23734
AH737	500	150	55.3	3.045	10.1926	1.163	45000	77400	3.968	26704	22966
AH739	500	100	60.4	2.998	10.2725	1.193	48600	81500	3.956	28927	24255

Table S7. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer PHA.

sample	f Hz	n –	θ °C	T^{-1} 10^{-3} K^{-1}	$\ln(k_{p1})$ –	k_{p1}/k_{p2} –	M_1 g·mol^{-1}	M_2 g·mol^{-1}	c_M mol·L^{-1}	k_{p1} mol·L^{-1} s^{-1}	k_{p2} mol·L^{-1} s^{-1}
AH305	10	800	-8.5	3.779	4.8900	1.085	11900	22000	3.963	133	123
AH307	30	800	-8.8	3.783	5.1204	1.070	5000	9400	3.964	167	156
AH311	30	800	30.0	3.299	6.1508	1.081	13500	25000	3.828	469	434
AH313	50	800	30.1	3.298	6.4335	1.096	10800	19700	3.827	622	568
AH635	10	800	0.0	3.661	5.2054	1.072	16200	30300	3.933	182	170
AH637	20	800	-0.1	3.662	5.3481	1.133	9400	16500	3.933	210	185
AH639	12	800	9.9	3.533	5.5083	1.091	18100	33200	3.898	247	226
AH641	25	800	9.4	3.539	5.6389	1.112	9900	17800	3.900	281	253
AH643	15	800	19.8	3.414	5.8167	1.097	19600	35700	3.863	336	306
AH645	30	800	19.4	3.418	5.9217	1.079	10900	20100	3.865	373	346
AH647	30	800	39.6	3.197	6.3748	1.082	16800	31000	3.794	587	542
AH650	60	1200	40.3	3.190	6.5615	1.098	10100	18400	3.791	707	644
AH651	30	800	50.2	3.093	6.6880	1.123	22700	40500	3.757	803	715
AH653	60	800	50.3	3.092	6.8557	1.069	13400	25100	3.756	949	888
AH776	30	1200	60.2	3.000	6.9009	1.026	27900	54400	3.726	993	968
AH777	60	800	60.1	3.001	7.0748	1.071	16600	31000	3.726	1182	1103
AH779	40	800	69.9	2.915	7.2014	1.096	28000	51100	3.692	1341	1224
AH780	80	800	70.5	2.910	7.3292	1.067	15900	29800	3.690	1524	1428
AH782	50	1200	80.7	2.826	7.3985	1.061	27000	50900	3.654	1634	1540
AH783	100	800	80.3	2.829	7.5298	1.066	15400	28900	3.655	1863	1748

Table S8. Detailed PLP sample conditions, absolute molecular weights of the first two inflection points and the resulting propagation rate coefficients of the monomer PHMA.

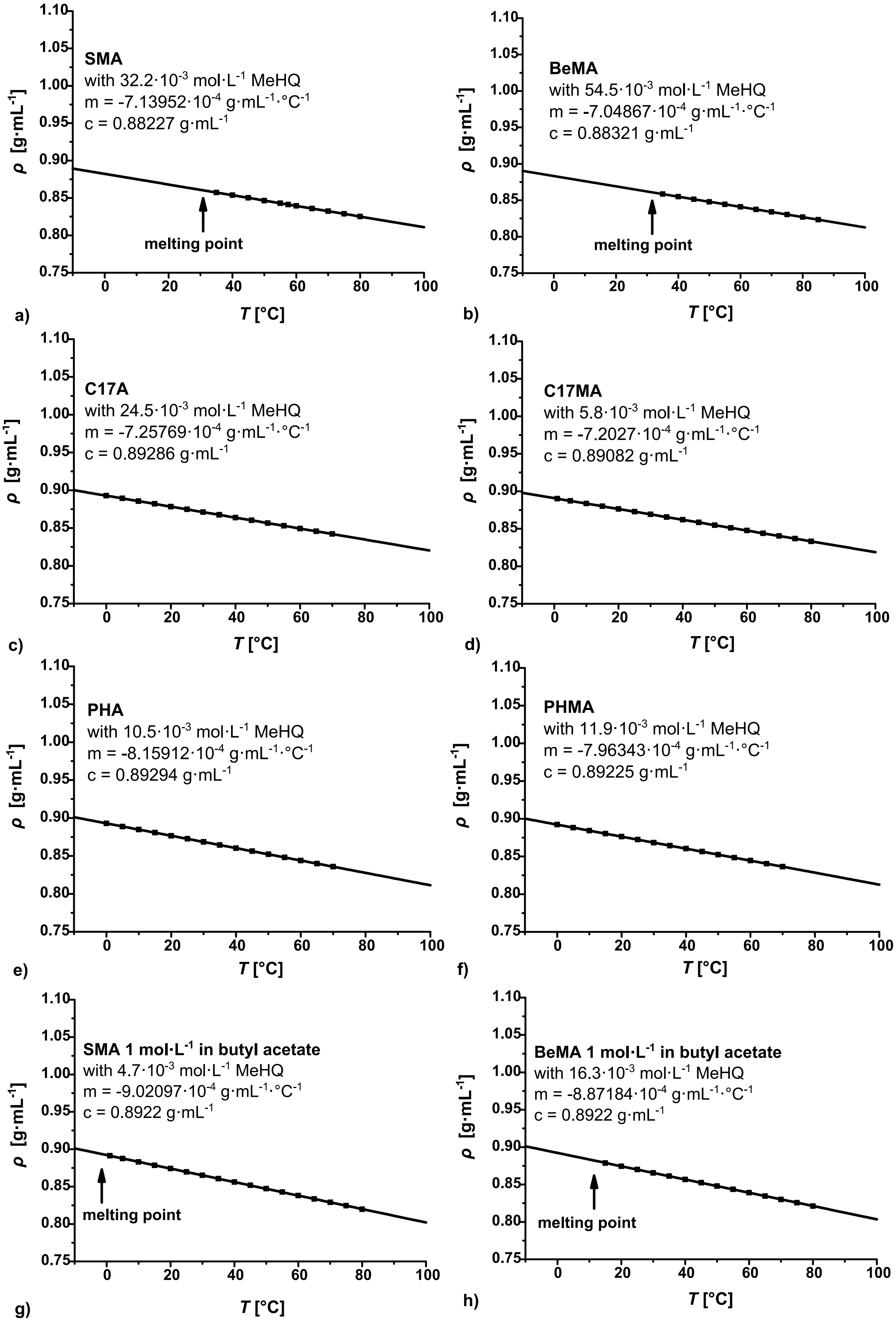

SMA
with 32.2·10-3 mol·L-1 MeHQ
m = -7.13952·10-4 g·mL-1·°C-1
c = 0.88227 g·mL-1
melting point
ρ [g·mL-1]
T [°C]
a)
BeMA
with 54.5·10-3 mol·L-1 MeHQ
m = -7.04867·10-4 g·mL-1·°C-1
c = 0.88321 g·mL-1
melting point
b)
C17A
with 24.5·10-3 mol·L-1 MeHQ
m = -7.25769·10-4 g·mL-1·°C-1
c = 0.89286 g·mL-1
c)
C17MA
with 5.8·10-3 mol·L-1 MeHQ
m = -7.2027·10-4 g·mL-1·°C-1
c = 0.89082 g·mL-1
d)
PHA
with 10.5·10-3 mol·L-1 MeHQ
m = -8.15912·10-4 g·mL-1·°C-1
c = 0.89294 g·mL-1
e)
PHMA
with 11.9·10-3 mol·L-1 MeHQ
m = -7.96343·10-4 g·mL-1·°C-1
c = 0.89225 g·mL-1
f)
SMA 1 mol·L-1 in butyl acetate
with 4.7·10-3 mol·L-1 MeHQ
m = -9.02097·10-4 g·mL-1·°C-1
c = 0.8922 g·mL-1
melting point
g)
BeMA 1 mol·L-1 in butyl acetate
with 16.3·10-3 mol·L-1 MeHQ
m = -8.87184·10-4 g·mL-1·°C-1
c = 0.8922 g·mL-1
melting point
h)

Figure S5. Temperature dependent densities for the studied monomers SMA, BeMA, C17A, C17MA, PHA and PHMA as well as the 1 molar solutions in butyl acetate of SMA and BeMA. Methyl hydroquinone (MeHQ) was added in replacement of 2,2-dimethoxy-2-phenylacetophenone (DMPA) to prevent the solutions from polymerization inside the density measurement device. The temperature dependent densities are summarized in Table 1.

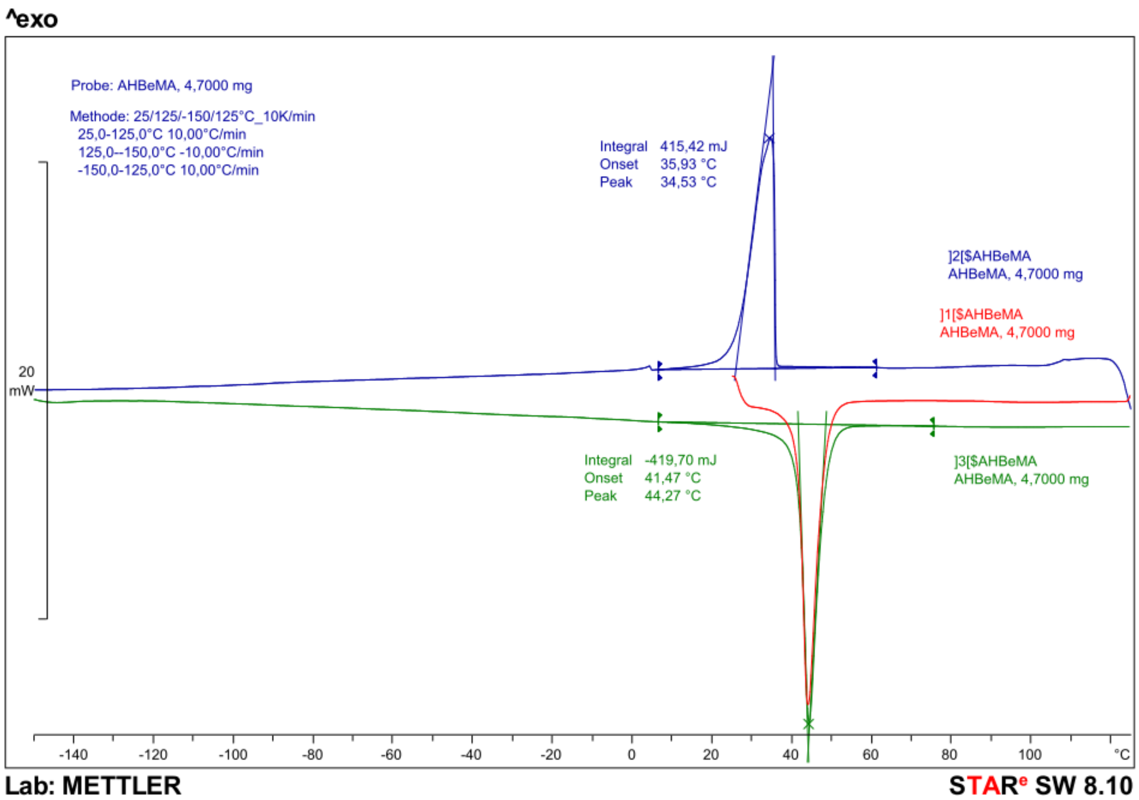


Figure S6. Differential scanning calorimetry of pBeMA. No glass transition temperature is detectable in the temperature range between -150°C and 125°C. The observed melting point is provided in Table 1.

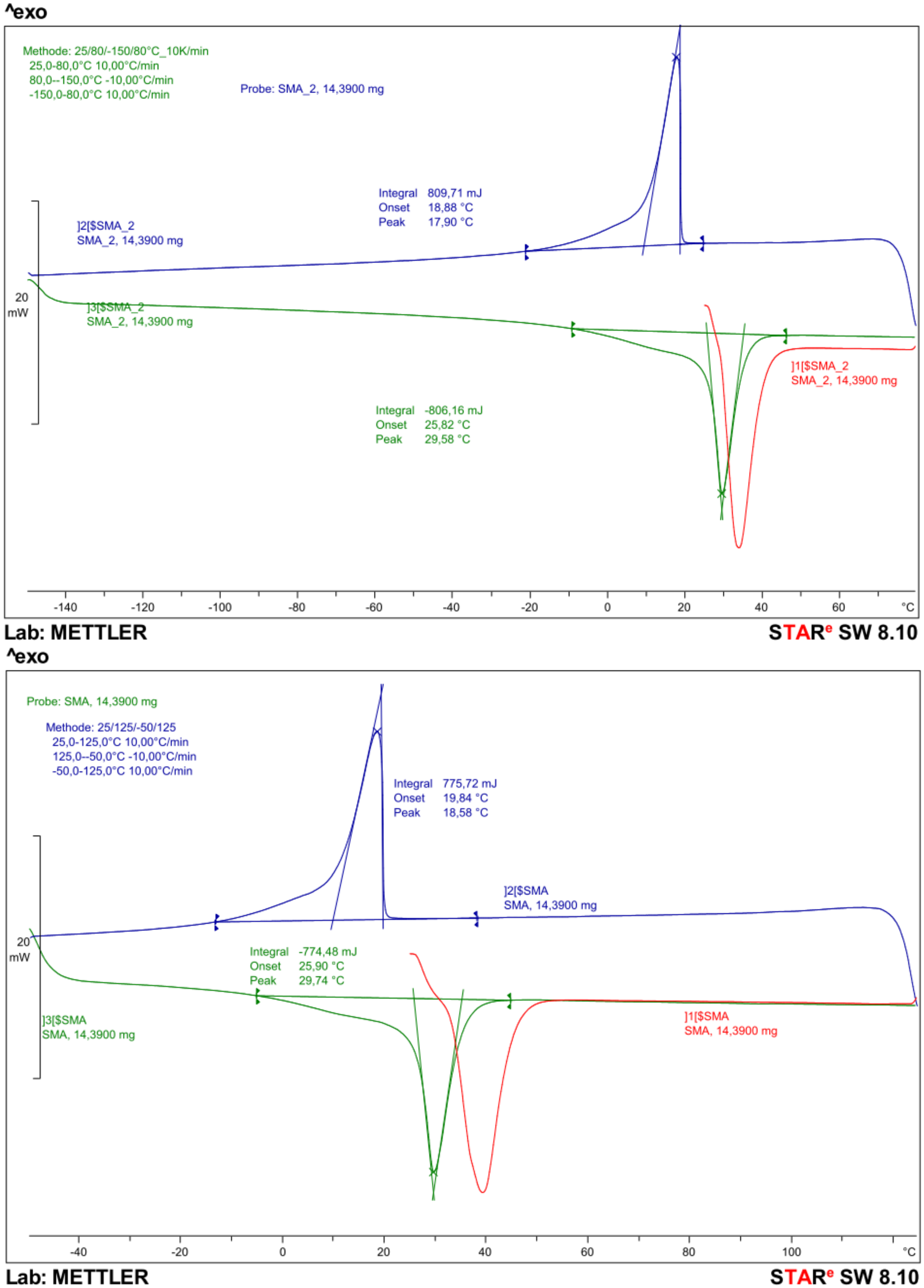


Figure S7. Differential scanning calorimetry of pSMA. No glass transition temperature is detectable in the temperature range between -150°C and 125°C. The observed melting point is provided in Table 1.

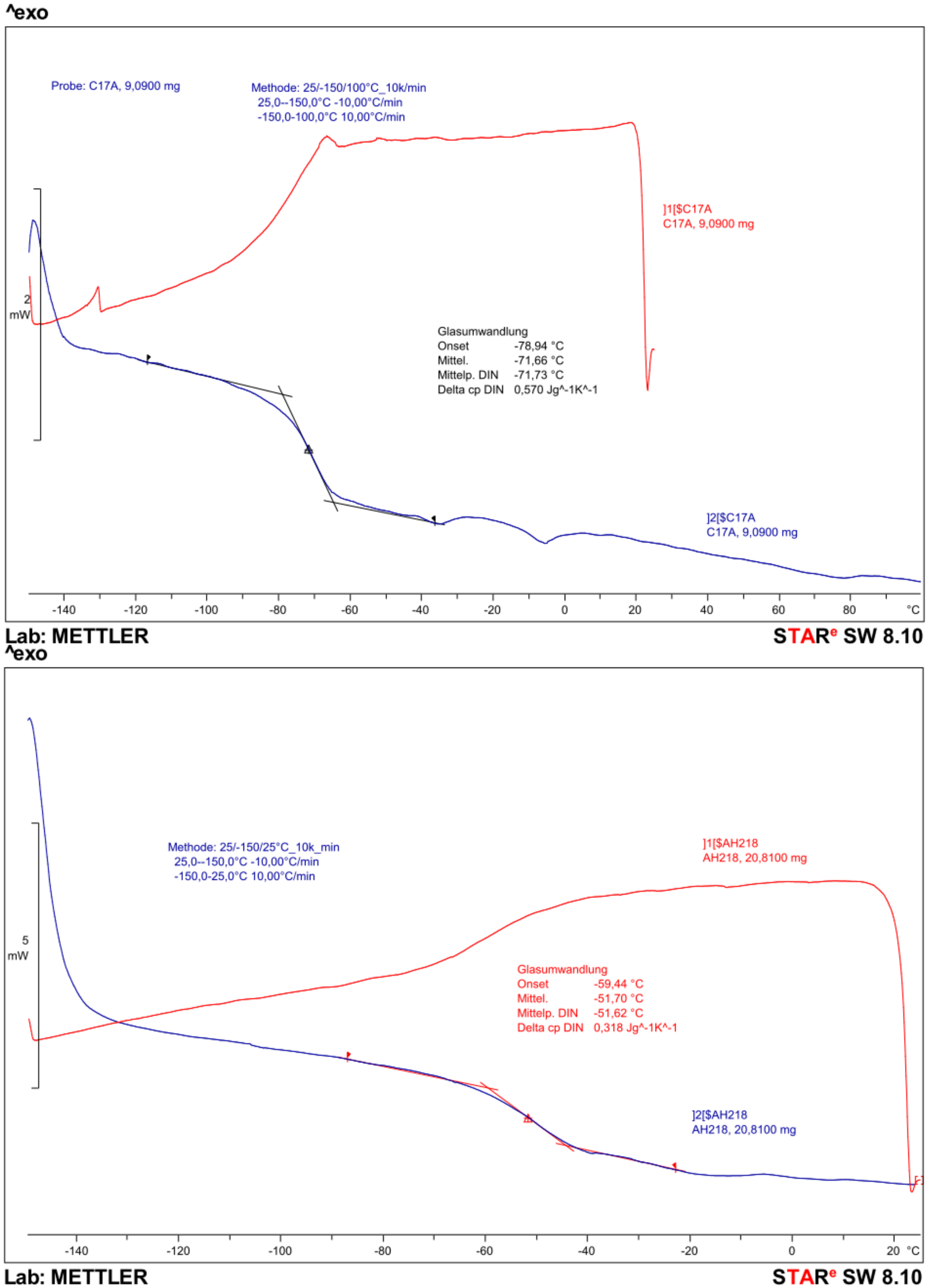
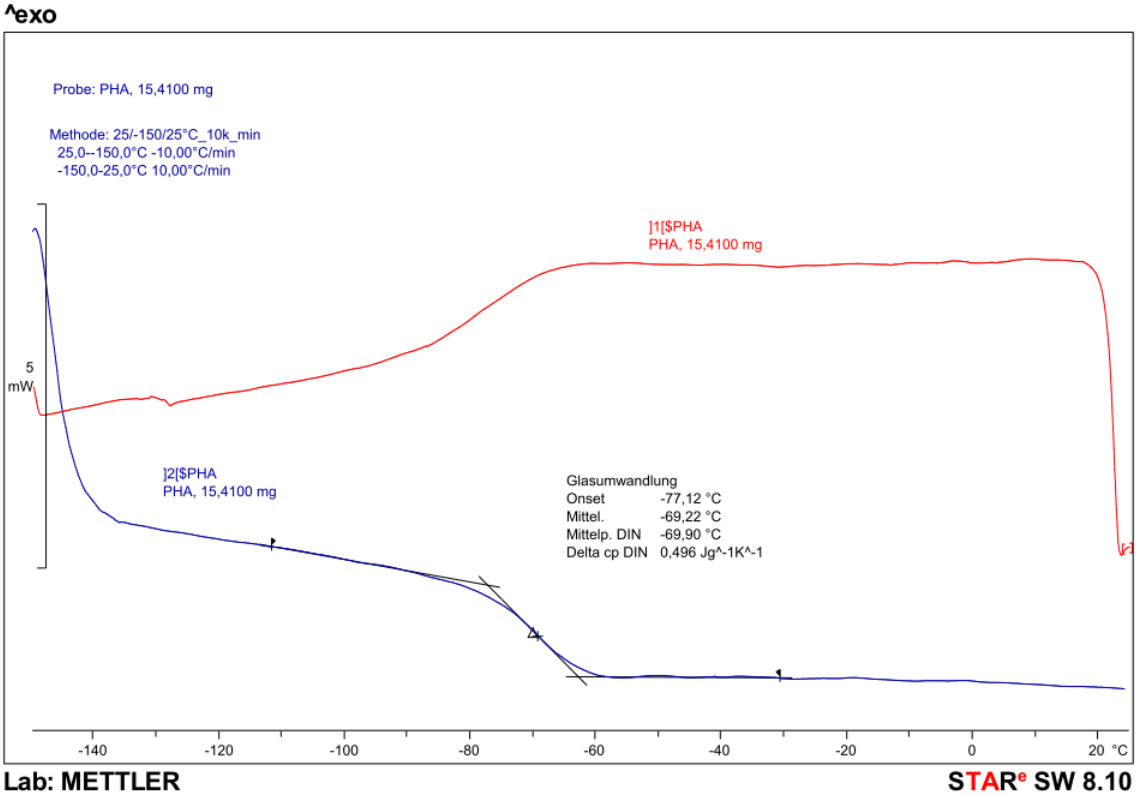


Figure S8. Differential scanning calorimetry of pC17A (upper part) and pC17MA (lower part). The glass transition temperatures are summarized in Table 1.



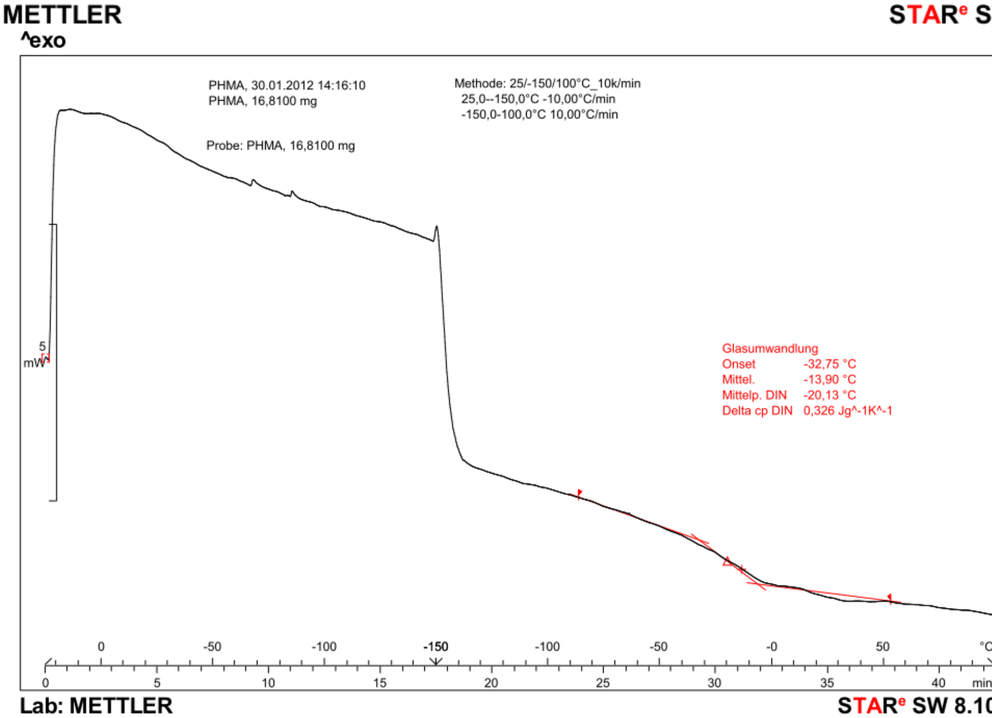


Figure S9. Differential scanning calorimetry of pPHA (upper part) and pPHMA (lower part). The glass transition temperatures are summarized in Table 1. The glass transition effect of PHMA is relatively less pronounced, however the handling experiences (brittle/hard below 20°C, chewy/sticky above 20°C) underpin the measured effect.

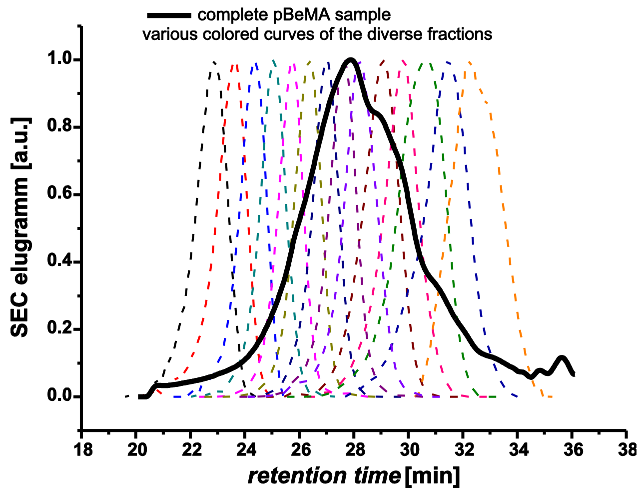


Figure S10. Typical fractions of a PLP polymer sample for the MHKS parameter determination procedure via triple detector SEC. The black, bold and solid line corresponds to the complete pBeMA (PDI = 13.35) polymer sample, produced under various PLP conditions (i.e. various PLP samples were combined and the polymer isolated), which was used for the fractionation. The various colored dashed lines correspond to the individual fractions obtained via a SEC fractionation as described in the Experimental Section. The PDI values of the obtained fractions range between 1.05 and 1.25.

SMA		BeMA		C17A		C17MA		PHA		PHMA	
M_1 g·mol^{-1}	[η] ml·g^{-1}	M_1 g·mol^{-1}	[η] ml·g^{-1}	M_1 g·mol^{-1}	[η] ml·g^{-1}	M_1 g·mol^{-1}	[η] ml·g^{-1}	M_1 g·mol^{-1}	[η] ml·g^{-1}	M_1 g·mol^{-1}	[η] ml·g^{-1}
420760	43.51	3196530	177.94	3141210	230.05	1860680	123.56	2241190	288.36	917986	110.89
415271	44.81	3285380	177.74	3162980	229.54	1046820	83.68	2332610	277.97	601755	86.19
298414	33.65	2146160	127.27	2384870	175.09	1124960	80.15	1415320	218.1	584072	84.23
265614	36.00	2038310	136.55	2272960	178.89	740137	70.82	1472620	211.05	417877	62.08
173082	29.40	1232840	86.28	1601770	142.68	748385	68.94	912463	156.35	419889	60.88
176468	28.05	1248200	95.88	1615360	145.11	522746	50.54	930324	152.79	282858	45.41
127826	20.04	481277	51.22	1153750	116.04	495502	54.04	587693	113.36	304783	42.46
129280	19.98	502077	45.15	1118750	115.39	344849	39.28	601895	113.13	192146	33.49
84883	16.19	311452	34.20	824059	92.38	330983	38.29	400524	82.6	189405	33.71
90591	16.75	320904	34.42	784855	91.30	257439	27.38	416109	78.21	129326	25.45
56633	12.81	206987	25.80	602561	64.81	254872	27.87	275266	62.2	132866	25.06
53393	12.85	216550	25.03	639773	65.85	172381	22.34	265763	60.45	88424	20.25
38965	11.18	126705	21.64	451774	49.59	156313	23.65	189829	41.89	95817	20.45
37796	9.95	125656	20.47	438230	52.10	112315	18.31	190774	40.29	47179	14.44
21207	6.98	82377	15.85	360878	42.32	116869	18.51	127922	34.2	68006	18.59
22259	7.05	80551	17.17	345812	41.04	74856	13.13	130556	35.39	47746	14.09
		49876	13.36	264632	32.11	85458	13.02	104454	26.75	42907	13.46
		54358	13.60	241880	30.13	50251	10.48	102663	27.99	32563	11.91
		34538	10.55	166412	25.77	51679	10.54	62919	21.95	31499	10.4
		32617	11.07	187979	26.75			62757	19.54		
		20008	8.94	123214	22.52			43143	16.68		
		24501	9.32					44191	16.64		
		14702	7.47								
		14946	6.36								

Table S9. Weight average molecular weight, M_W, and related intrinsic viscosity, [θ], data employed for the determination of the MHKS parameters. The M_W and [θ] were determined via the MALLS detector as well as the viscosimeter of the triple SEC set-up.

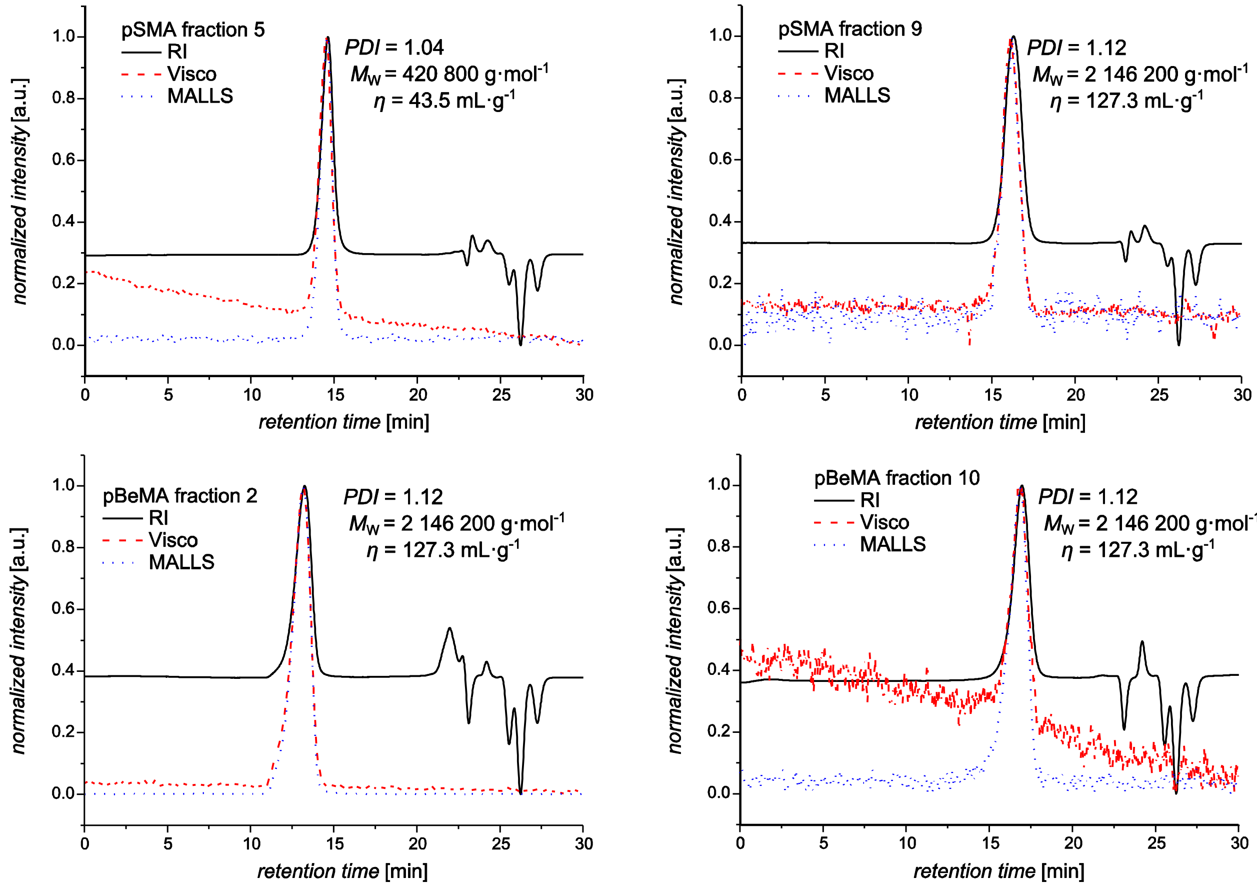


Figure S11. Exemplary triple detector SEC traces: refractive index (RI, black solid line), viscosimeter (Visco, red dashed line) and MALLS detector signal (MALLS at 90°, blue dotted line of pSMA (upper part) and pBeMA (lower part). The entire set of samples incorporated into the MHKS determination is collated in Table S9. All samples feature a sufficiently low signal to noise ratio in each detector signal.

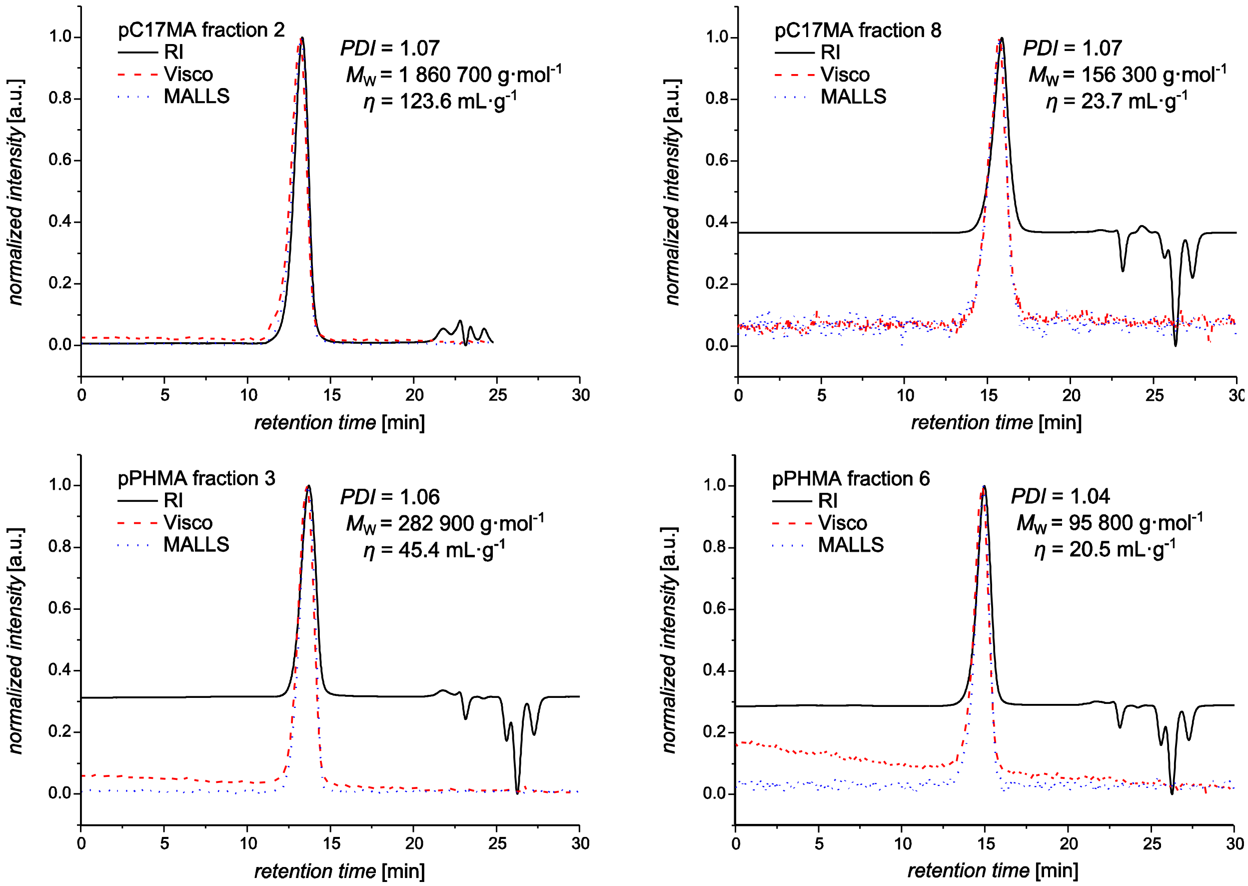


Figure S12. Exemplary triple detector SEC traces: refractive index (RI, black solid line), viscosimeter (Visco, red dashed line) and MALLS detector signal (MALLS at 90°, blue dotted line of pC17MA (upper part) and pPHMA (lower part). The entire set of samples incorporated into the MHKS determination is collated in Table S9. All samples feature a sufficiently low signal to noise ratio in each detector signal.

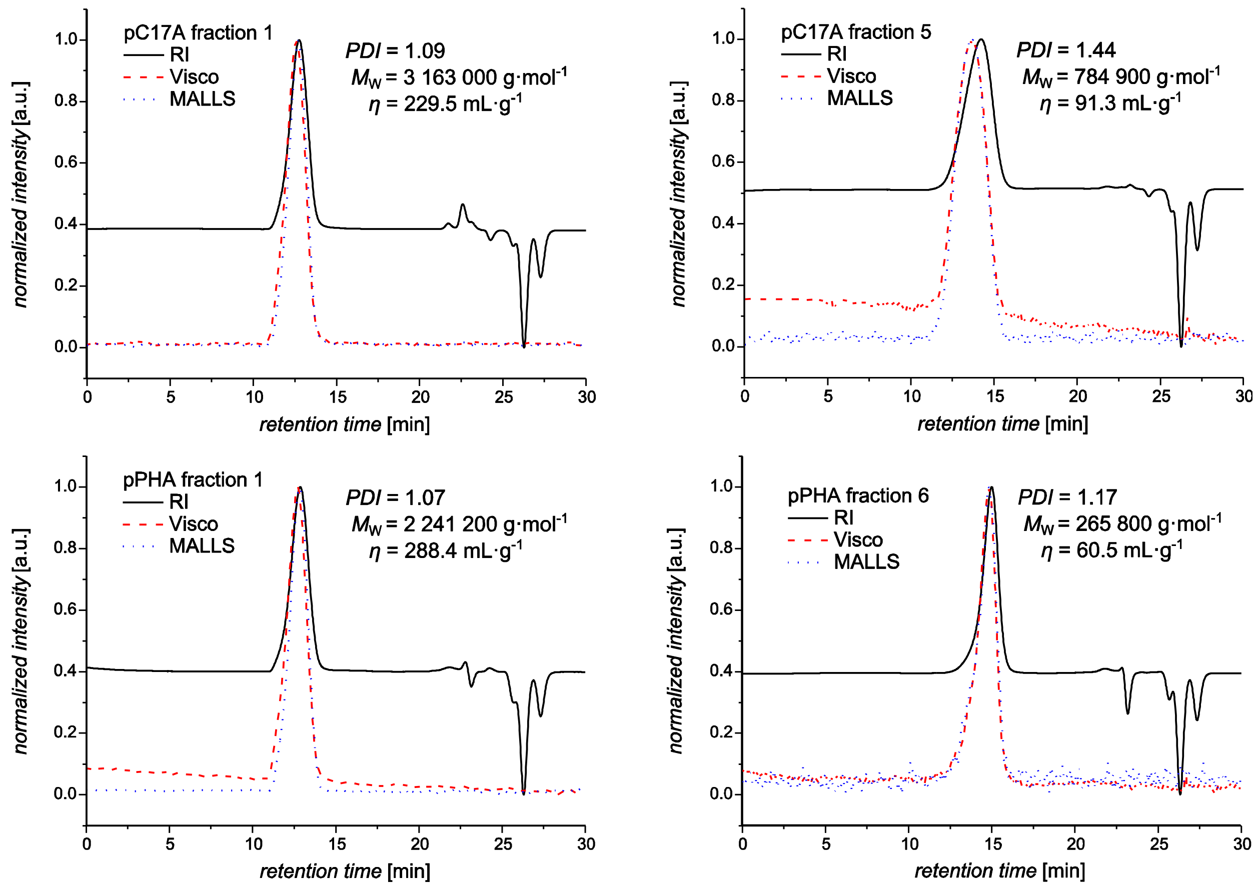
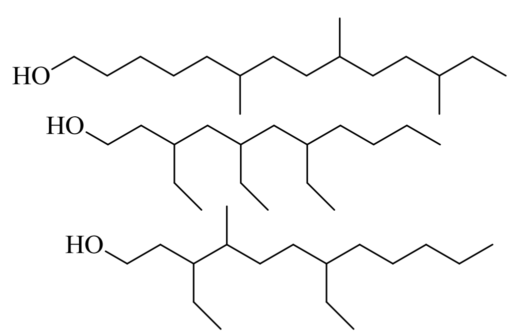


Figure S13. Exemplary triple detector SEC traces: refractive index (RI, black solid line), viscosimeter (Visco, red dashed line) and MALLS detector signal (MALLS at 90°, blue dotted line of pC17A (upper part) and pPHA (lower part). The entire set of samples incorporated into the MHKS determination is collated in Table S9. All samples feature a sufficiently low signal to noise ratio in each detector signal.



Scheme S1 Three possible structures of the highly branched heptadecanyl alcohol employed in the synthesis of the heptadecanyl methacrylate and acrylate.