Electronic Supporting Information

for

A Complete Kinetic Study of a Versatile Functional Monomer: Acetoacetoxyethyl Methacrylate (AAEMA)

Alexander Zoller,[a] Katrin B. Kockler,[b,c] Marion Rollet,[a] Catherine Lefay,[a] Didier Gigmes,[a]

Christopher Barner-Kowollik,[b,c] and Yohann Guillaneuf[a,]**

[a]Aix-Marseille-Université, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille, France

[b]Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr 18, 76128 Karlsruhe, Germany.

[c]Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

**Fax: +33 (0)4 91 28 87 58; Tel: +33 (0)4 91 28 28 10*

**Fax: +49 (0)721 608 45647; Tel: +49 (0)721 608 45641*

E-mail: yohann.guillaneuf@univ-amu.fr, christopher.barner-kowollik@kit.edu

1. MHKS-parameters

a. Polymer Synthesis

1 mol% AIBN (0.0193 g, 0.00012 mol) was dissolved in 6 mL ethyl acetate and AAEMA (2.57 g, 0.012 mol) was added. The solution was degassed with argon and heated to 65 °C. The reaction was quenched after 3 h by oxygen and precipitated in cold MeOH (-20 °C). The conversion was calculated by ^{1}H NMR. The polymerization was carried out with 0.1 – 10 mol% azobisisobutyronitrile (AIBN).

A second series was synthesized by using dodecanethiol. 1 mol% AIBN (9.65 mg, 5×10^{-6} mol) was dissolved in 3 mL ethyl acetate and AAEMA (1.28 g, 0.006 mol) was well as different amounts of dodecanethiol was added. The degassed solution was heated to 65 °C and quenched after 3 h by oxygen. The polymer was quenched in cold methanol (-20 °C). It was used dodecanethiol between 0.1 – 10 mol% with respect to the monomer.

Table S1: Experimental conditions of PAAEMA synthesis for determination of MHKS parameters.

AIBN		AAEMA		EtOAc	AIBN/AAEMA	Dodecanethiol
m_{AIBN}	c_{AIBN}	m_{AAEMA}	c_{AAEMA}	V_{EtOAc}	AIBN/AAEMA	V_{Thiol}
g	mol/l	g	mol/l	ml	-	µl
0.1935	0.2	2.568	2	6	0.1000	
0.0967	0.1	2.568	2	6	0.0500	
0.0484	0.05	2.568	2	6	0.0250	
0.0193	0.02	2.568	2	6	0.0100	
0.0097	0.01	2.568	2	6	0.0050	
0.0048	0.005	2.568	2	6	0.0025	
0.00965	0.2	1.284	2	3	0.01	1.56
0.00965	0.2	1.284	2	3	0.01	10.95
0.00965	0.2	1.284	2	3	0.01	31.29
0.00965	0.2	1.284	2	3	0.01	78.22
0.00965	0.2	1.284	2	3	0.01	156.43

b. Triple Detection Size Exclusion Chromatography (SEC^3)

Molar masses for the determination of the Mark–Houwink–Kuhn–Sakurada (MHKS) parameters of AAEMA were determined by triple detection size exclusion chromatography (SEC^3). The apparatus was equipped with a 1260 infinity pump (Agilent Technologies), a 1260 infinity autosampler (Agilent Technologies), a 1260 infinity UV photodiode array detector (Agilent Technologies), a 1260 infinity RI detector (Agilent Technologies), a MALLS detector (BIC) and a viscometer detector (PSS). The stationary phase was composed of 2 PSS-SDV Linear M column and a precolumn at 40°C. Mobile phase was THF at 1 mL·min^{-1}. Samples were solubilized in a mixture of THF and toluene (0.25 wt%) and filtered through 0.45 µm PTFE syringe filter (Interchim). The sample concentration was close to 5 mg·mL^{-1}.

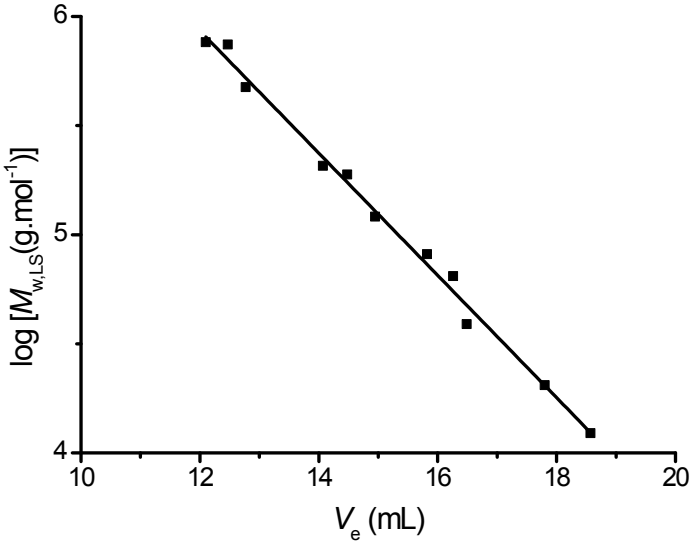


Figure S1: log M_w *vs*. elution volume V_e of the prepared PAAEMA samples.

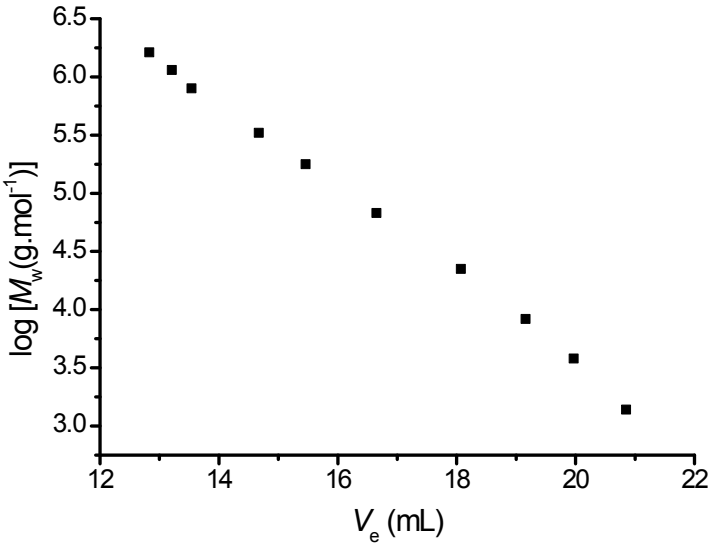


Figure S2: log M_w *vs*. elution volume V_e of PS standards.

2. Pulse Laser Polymerization-Size Exclusion Chromatography

a. Pulse-Laser-Polymerization (PLP)

0.5 mL of the monomer stock solution with AAEMA (20.1960 g, 0.131 mol) and the photoinitiator DMPA (0.0461 g, 0.00025 mol) was transferred into sample vials and degassed with nitrogen for 5 – 10 min. The temperature of the sample was equilibrated by placing it into a thermostat (VWR 1196D) sample holder for approx. 2-3 min. Polymerization is initiated by a pulsed laser between 5 and 180 Hz using a Coherent Xantos XS-500 operated at the XeF line at 351 nm wavelength. The laser beam was directed by a mirror-system to hit the sample from the bottom; the energy of the laser beam was close to 1.5 mJ/pulse. The polymerization temperature ranged from 0 °C to 100 °C, with a variation of the sample temperature always below 0.1 °C for each measurement, with the temperature measured directly at the sample. After pulsed laser polymerization, the sample was dissolved in THF containing MeHQ for inhibiting further polymerization. The samples are filtered and analyzed immediately by SEC. All samples which

were used for the calculation of the propagation rate coefficient k_p showed at least three inflection points and were assessed for consistency by using different pulse repetitions (250 and 500) and two different frequencies. All samples showed a $k_{p,1}/k_{p,2}$ ratio between 0.95 and 1.1 and were incorporated in the Arrhenius plot.

b. Size Exclusion Chromatography

Samples prepared by pulsed laser- polymerization were analyzed on a PL-SEC 50 Plus IntegratedSystem, comprising an autosampler and a PLgel 5 μm bead-size guard column (50 × 7.5 mm) followed by one PLgel 5 μm mixed E column (300 × 7.5 mm), three PLgel 5 μm mixed C columns (300 × 7.5 mm), and a differential refractive index (RI) detector using THF as eluent at 35 °C with a flow rate of 1 mL·min^{-1}. The SEC system is calibrated using linear poly(styrene) standards ranging from 160 to 6 × 10^6 g·mol and linear poly(methyl methacrylate) standards ranging from 700 to 2 × 10^6 g·mol. The obtained molecular weight distributions were smoothed to remove noise from the signal and the first derivatives were used to determine the molecular weights at the inflection points. The SEC calculations were carried out applying a universal calibration by using the specific Mark–Houwink–Kuhn–Sakurada (MHKS) parameters for PAAEMA.

c. PLP-results

Table S2: Values for 95 % confidence interval of pre-exponential factor A and activation energy E_a of $k_{p,AAEMA}$.

A	E_a
L.mol^{-1}.s^{-1}	kJ.mol^{-1}
2130106	19.69
1401951	18.49
1487616	18.64
1487616	18.72
1573281	18.80
1573281	18.88
1658947	18.95
1658947	19.03
1744612	19.11
1744612	19.18
1830277	19.26
1830277	19.34
1915942	19.34
1915942	19.42
2001608	19.49
2001608	19.57
2087273	19.57
2087273	19.65
2087273	19.72
2172938	19.72
2172938	19.80
2258603	19.80
2258603	19.88
2258603	19.96
2344269	19.96
2344269	20.03
2429934	20.03
2429934	20.11
2515599	20.11
2515599	20.19
2601265	20.27
2601265	20.34
2686930	20.34
2686930	20.42
2772595	20.42
2772595	20.50

2858260	20.50
2858260	20.57
2943926	20.65
3029591	20.73
3115256	20.81
3200921	20.88
1401951	18.49

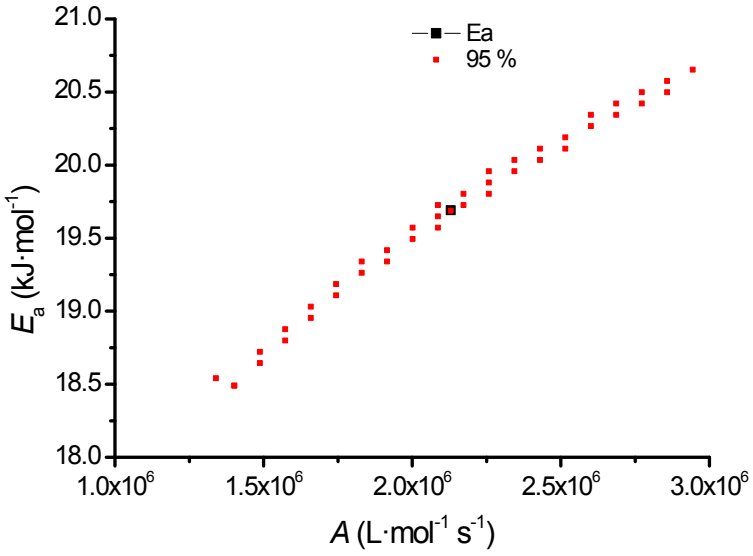
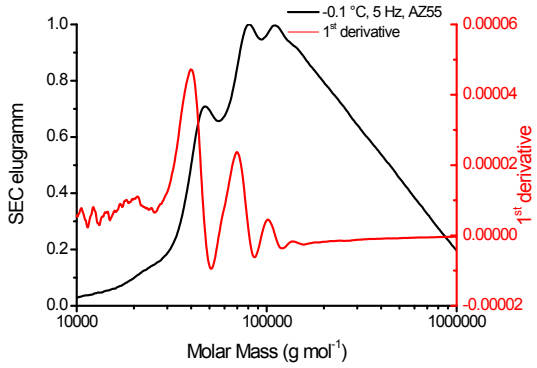
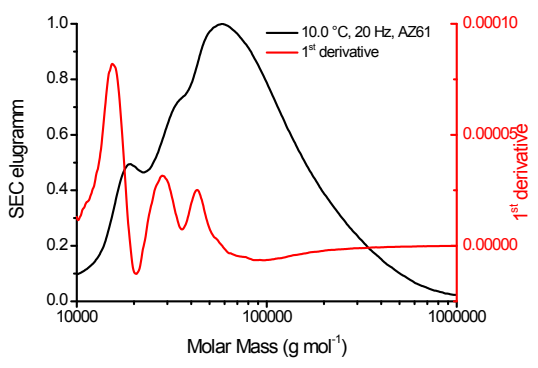
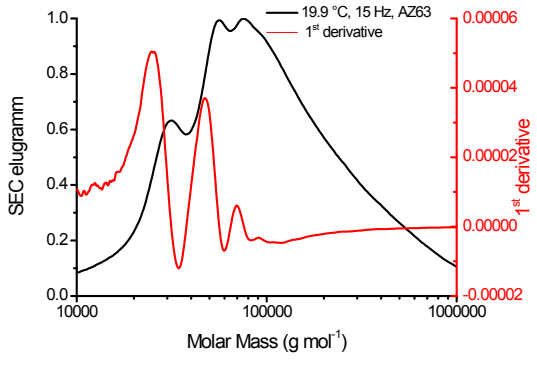


Figure S3: E_a vs. A of $k_{p,AAEMA}$ with 95% confidence interval.


-0.1 °C, 5 Hz, AZ55
1st derivative
SEC elugramm
1st derivative
Molar Mass (g mol-1)


10.0 °C, 20 Hz, AZ61
1st derivative
SEC elugramm
1st derivative
Molar Mass (g mol-1)


19.9 °C, 15 Hz, AZ63
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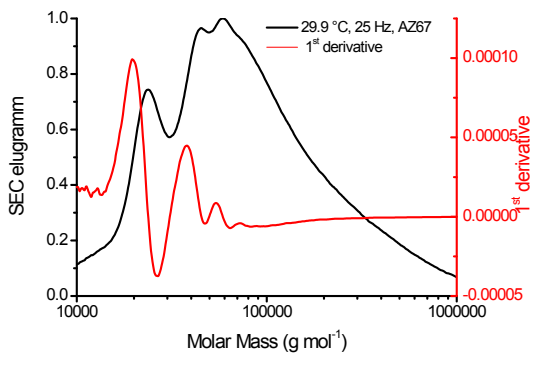
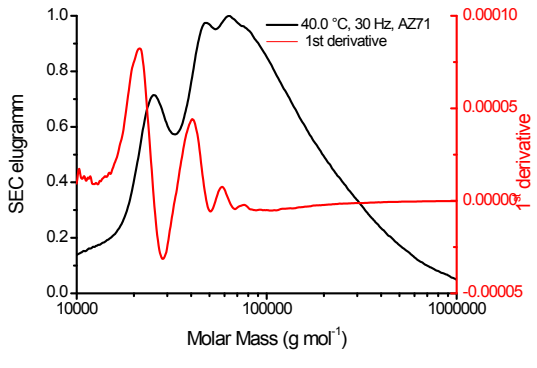
SEC elugramm
1st derivative
Molar Mass (g mol-1)


29.9 °C, 25 Hz, AZ67
1st derivative
SEC elugramm
1st derivative
Molar Mass (g mol-1)


40.0 °C, 30 Hz, AZ71
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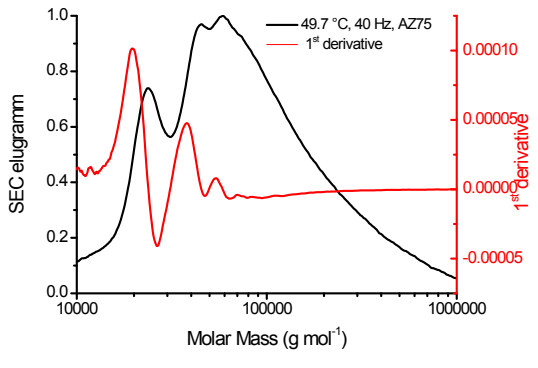
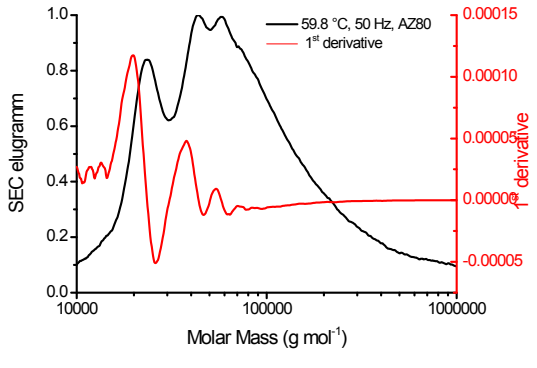
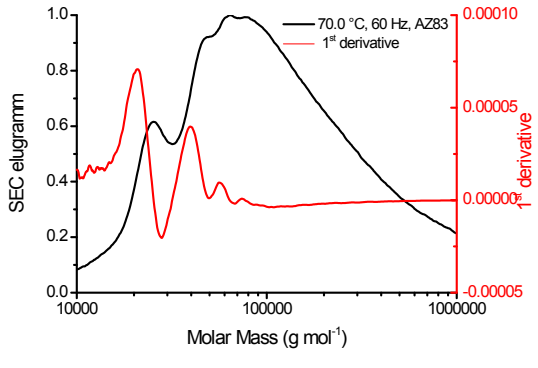
SEC elugramm
1st derivative
Molar Mass (g mol-1)


49.7 °C, 40 Hz, AZ75
1st derivative
SEC elugramm
1st derivative
Molar Mass (g mol-1)


59.8 °C, 50 Hz, AZ80
1st derivative
SEC elugramm
1st derivative
Molar Mass (g mol-1)


70.0 °C, 60 Hz, AZ83
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SEC elugramm
1st derivative
Molar Mass (g mol-1)

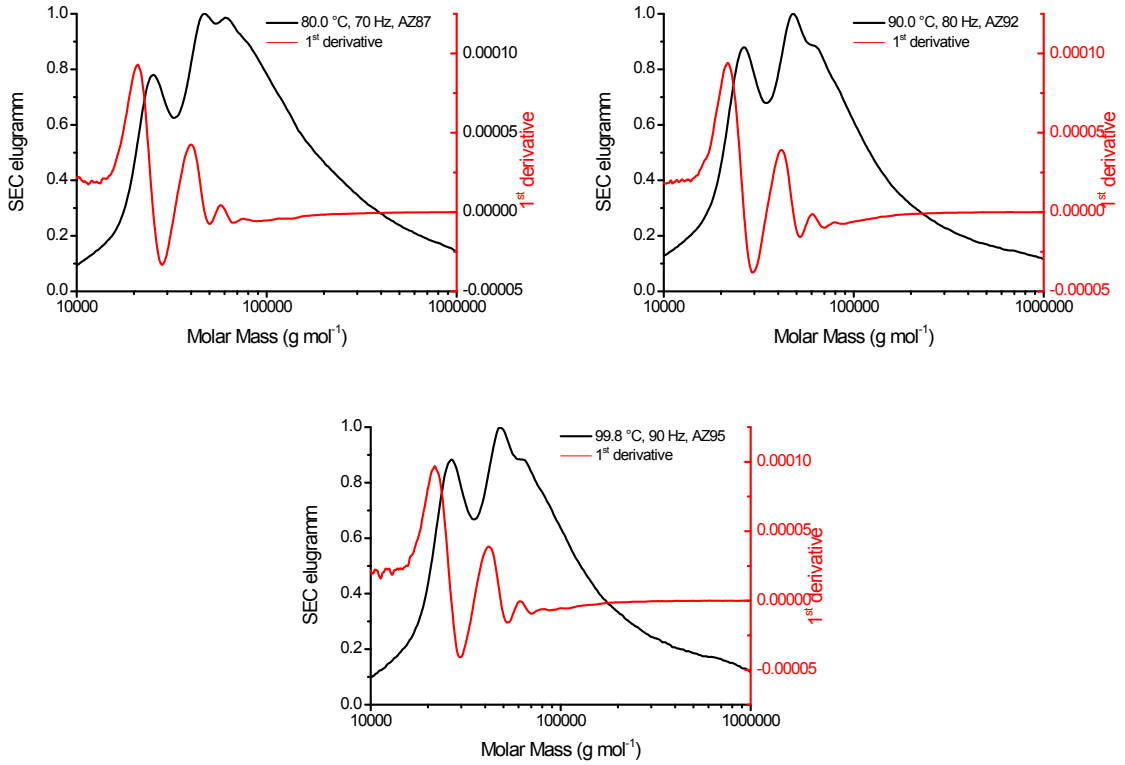

Figure S4: Chromatograms and first derivatives of PAAEMA in bulk for one representative sample at each temperature (0 – 100 °C). Detailed information is collated in Table S2.

Table S3: Detailed collation of experimental PLP-SEC conditions and results.

sample	f	n	θ	T^{-1}	ρ	c_M	M1	M2	M3	kp.1	kp.2	kp.3	ln(kp1)	kp.1/kp.2
	Hz	-	°C	K^{-1}	$g \cdot mL^{-1}$	$mol \cdot L^{-1}$	$g \cdot mol^{-1}$	$g \cdot mol^{-1}$	g·mol	$L \cdot mol^{-1} \cdot s^{-1}$	$L \cdot mol^{-1} \cdot s^{-1}$	$L \cdot mol^{-1} \cdot s^{-1}$	$\ln(L \cdot mol^{-1} \cdot s^{-1})$	-
AZ-PLP-55	5	500	-0.1	0.003662333	1.141517956	5.316726043	77918	145259	219434	342.06	318.84	321.11	5.8350	1.073
AZ-PLP-56	5	250	0.0	0.003660992	1.14142	5.316269804	77918	144573	217062	342.09	317.37	317.66	5.8351	1.078
AZ-PLP-57	10	500	0.0	0.003660992	1.14142	5.316269804	39824	82687	121884	349.69	363.03	356.74	5.8570	0.963
AZ-PLP-58	10	250	0.0	0.003660992	1.14142	5.316269804	38807	77918	116492	340.76	342.09	340.96	5.8312	0.996
AZ-PLP-59	10	500	10.1	0.00353045	1.131526444	5.270189646	53028	103335	156963	469.70	457.65	463.44	6.1521	1.026
AZ-PLP-60	10	250	10.3	0.003527959	1.131330532	5.269277168	51568	102005	154892	456.84	451.83	457.40	6.1243	1.011
AZ-PLP-61	20	500	10.0	0.003531697	1.1316244	5.270645886	27599	52819	83557	488.88	467.81	493.37	6.1921	1.045
AZ-PLP-62	20	250	10.1	0.00353045	1.131526444	5.270189646	27993	54282	85736	495.90	480.81	506.27	6.2064	1.031
AZ-PLP-63	15	500	19.9	0.003412387	1.121926756	5.225478207	47003	95379	145487	629.84	639.04	649.84	6.4455	0.986
AZ-PLP-64	15	250	19.8	0.003413552	1.122024712	5.225934446	44735	90546	135910	599.40	606.60	607.01	6.3959	0.988
AZ-PLP-65	30	500	20.0	0.003411223	1.1218288	5.225021968	25050	46383	77053	671.40	621.59	688.40	6.5094	1.080
AZ-PLP-66	30	250	19.8	0.003413552	1.122024712	5.225934446	24270	44941	73389	650.38	602.16	655.55	6.4776	1.080
AZ-PLP-67	25	500	29.9	0.003299786	1.112131156	5.179854289	36176	74465	110453	815.04	838.85	829.51	6.7032	0.972
AZ-PLP-68	25	250	29.9	0.003299786	1.112131156	5.179854289	35571	72744	109338	801.41	819.47	821.13	6.6864	0.978
AZ-PLP-69	50	500	29.9	0.003299786	1.112131156	5.179854289	19641	36984	61016	885.01	833.25	916.46	6.7856	1.062
AZ-PLP-70	50	250	29.9	0.003299786	1.112131156	5.179854289	18688	35369	57430	842.07	796.87	862.60	6.7359	1.057
AZ-PLP-71	30	500	40.0	0.003193358	1.1022376	5.133774132	39417	80516	119185	1075.25	1098.19	1083.74	6.9803	0.979
AZ-PLP-72	30	250	40.1	0.003192338	1.102139644	5.133317892	37793	76405	114028	1031.05	1042.22	1036.94	6.9383	0.989
AZ-PLP-73	60	500	40.0	0.003193358	1.1022376	5.133774132	20790	38807	64408	1134.23	1058.62	1171.32	7.0337	1.071
AZ-PLP-74	60	250	40.1	0.003192338	1.102139644	5.133317892	20598	38199	61862	1123.86	1042.10	1125.12	7.0245	1.078
AZ-PLP-75	40	500	49.7	0.003097414	1.092735868	5.089518931	36176	74465	109784	1327.21	1365.99	1342.58	7.1908	0.972
AZ-PLP-76	40	250	49.7	0.003097414	1.092735868	5.089518931	35974	73389	108892	1319.81	1346.25	1331.68	7.1852	0.980
AZ-PLP-77	80	500	49.6	0.003098373	1.092833824	5.08997517	19832	36378	60593	1455.04	1334.50	1481.89	7.2828	1.090
AZ-PLP-78	80	250	49.7	0.003097414	1.092735868	5.089518931	18878	35369	57219	1385.19	1297.63	1399.51	7.2336	1.067
AZ-PLP-80	50	250	59.8	0.003003454	1.082842312	5.043438774	36378	73819	110007	1683.52	1708.14	1697.00	7.4286	0.986
AZ-PLP-81	100	500	59.9	0.003002552	1.082744356	5.042982535	20023	36378	61016	1853.45	1683.67	1882.67	7.5248	1.101

AZ-PLP-82	100	250	59.9	0.003002552	1.082744356	5.042982535	19641	36984	62710	1818.06	1711.72	1934.94	7.5055	1.062
AZ-PLP-83	60	500	70	0.002914177	1.0728508	4.996902378	38402	77918	115372	2152.48	2183.72	2155.60	7.6744	0.986
AZ-PLP-84	60	250	70	0.002914177	1.0728508	4.996902378	36984	76405	112463	2073.01	2141.34	2101.25	7.6368	0.968
AZ-PLP-85	120	500	70	0.002914177	1.0728508	4.996902378	20406	38199	63346	2287.59	2141.11	2367.13	7.7353	1.068
AZ-PLP-86	120	250	70	0.002914177	1.0728508	4.996902378	19832	36378	59959	2223.21	2039.03	2240.55	7.7067	1.090
AZ-PLP-87	70	500	80	0.002831658	1.0630552	4.95127846	39011	78783	117838	2574.56	2599.70	2592.30	7.8534	0.990
AZ-PLP-88	70	250	79.9	0.00283246	1.063153156	4.951734699	38402	77918	116941	2534.13	2570.91	2572.32	7.8376	0.986
AZ-PLP-89	140	500	80	0.002831658	1.0630552	4.95127846	20982	38807	64196	2769.43	2561.16	2824.47	7.9264	1.081
AZ-PLP-90	140	250	79.9	0.00283246	1.063153156	4.951734699	21174	39011	63559	2794.55	2574.32	2796.18	7.9354	1.086
AZ-PLP-91	80	500	90	0.002753683	1.0532596	4.905654542	40843	83122	124137	3109.21	3163.88	3150.01	8.0421	0.983
AZ-PLP-92	80	250	90	0.002753683	1.0532596	4.905654542	40435	82253	124137	3078.16	3130.79	3150.01	8.0321	0.983
AZ-PLP-93	160	500	90.1	0.002752925	1.053161644	4.905198302	21752	40028	65685	3312.02	3047.43	3333.86	8.1053	1.087
AZ-PLP-94	160	250	89.9	0.002754442	1.053357556	4.906110781	21559	39621	63559	3282.07	3015.87	3225.35	8.0962	1.088
AZ-PLP-95	90	500	99.8	0.002681325	1.043659912	4.860943102	40435	83122	125716	3494.78	3592.11	3621.85	8.1590	0.973
AZ-PLP-96	90	250	99.8	0.002681325	1.043659912	4.860943102	40028	81818	121659	3459.57	3535.76	3504.96	8.1489	0.978
AZ-PLP-97	180	500	99.8	0.002681325	1.043659912	4.860943102	21944	40435	66963	3793.28	3494.78	3858.41	8.2410	1.085
AZ-PLP-98	180	250	99.8	0.002681325	1.043659912	4.860943102	21752	39824	65685	3759.94	3441.97	3784.74	8.2322	1.092
AZ-PLP-99	20	500	-0.2	0.003663675	1.141615912	5.317182282	19641	35974	61439	344.86	315.83	359.59	5.8431	1.092
AZ-PLP-100	20	250	-0.2	0.003663675	1.141615912	5.317182282	19641	35571	57851	344.86	312.29	338.59	5.8431	1.104
AZ-PLP-101	25	500	10	0.003531697	1.1316244	5.270645886	20982	40028	64834	464.58	443.15	478.51	6.1411	1.048
AZ-PLP-102	25	250	10.1	0.00353045	1.131526444	5.270189646	21752	38402	63983	481.66	425.18	472.28	6.1772	1.133
AZ-PLP-103	30	500	20.2	0.003408897	1.121632888	5.224109489	22717	43093	71027	608.98	577.59	634.67	6.4118	1.054
AZ-PLP-104	30	250	20.2	0.003408897	1.121632888	5.224109489	23105	41864	69527	619.36	561.13	621.27	6.4287	1.104

3. Density Measurements

The temperature-dependent density measurement of AAEMA was performed on an Anton Paar DMA 5000 M density meter with a precision of 10^{-2} °C and $5 \cdot 10^{-6}$ g·mL^{-1}. MeHQ was added during the measurement to the solution to inhibit any polymerization.

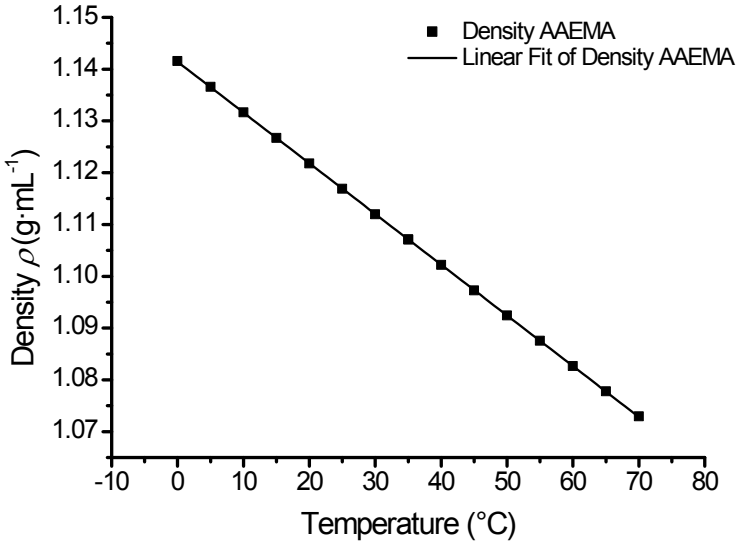

Figure S5: Density ρ of AAEMA vs. temperature.

4. Reactivity Ratio

a. Copolymer Synthesis

A total amount of 0.02 mol of monomer (40 wt%), MMA (1.8 g, 0.018 mol) and AAEMA (0.43 g, 0.002 mol), was dissolved in 60 wt% ethyl 3-ethoxypropionate (EEP) (3.5 mL). The solution was degassed with argon and heated to 75 °C. Samples were taken every 15 – 30 min in order to follow the conversion by 1H NMR. The copolymer was precipitated in cold MeOH (-20 °C) and analysed by DSC. Copolymerizations were performed from 10 – 90 % MMA content.

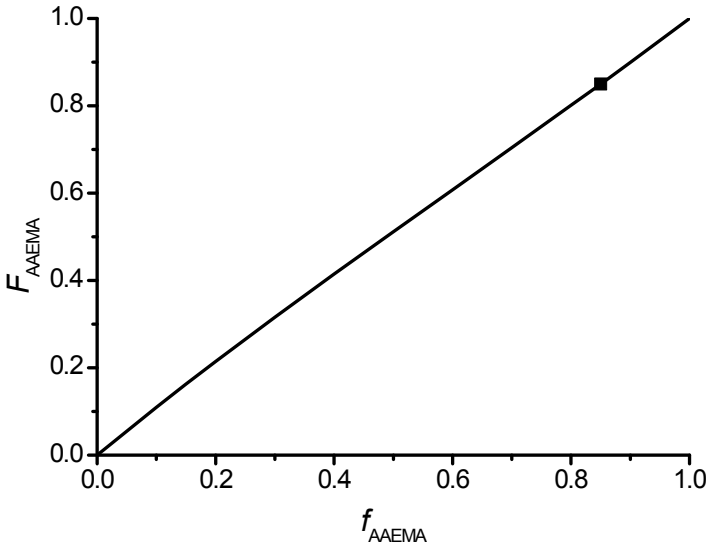

Figure 6: Instantaneous copolymerization behavior F_{AAEMA} vs. f_{AAEMA} (straight line)) with crossover point (reactangle).

$$F_1 = \frac{r_1 f_1^2 + (f_1 f_2)}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$
$$\text{with,} \quad f_1 = \frac{[M_1]}{[M_1] + [M_2]} \tag{1}$$

Table S4: Experimental conditions of synthesis of PMMA-co-PAAEMA

m_{MMA}	m_{AAEMA}	$mol\%_{\mathrm{MMA}}$	$mol\%_{\mathrm{AAEMA}}$	$wt\%_{\mathrm{Monomer}}$	n_{AIBN}	m_{AIBN}	m_{EEP}	V_{EEP}	T_g
g	g	-	-	-	mol	g	g	mL	°C
1.80216	0.42842	0.9	0.1	0.4	0.0002	0.0322	3.346	3.52	83
1.40168	1.28526	0.7	0.3	0.4	0.0002	0.0322	4.030	4.24	52
1.0012	2.1421	0.5	0.5	0.4	0.0002	0.0322	4.715	4.96	34
0.60072	2.99894	0.3	0.7	0.4	0.0002	0.0322	5.399	5.68	17
0.20024	3.85578	0.1	0.9	0.4	0.0002	0.0322	6.084	6.40	8
0.10012	4.06999	0.05	0.95	0.4	0.0002	0.0322	6.255	6.58	

0.30036	3.64157	0.15	0.85	0.4	0.0002	0.0322	5.913	6.22

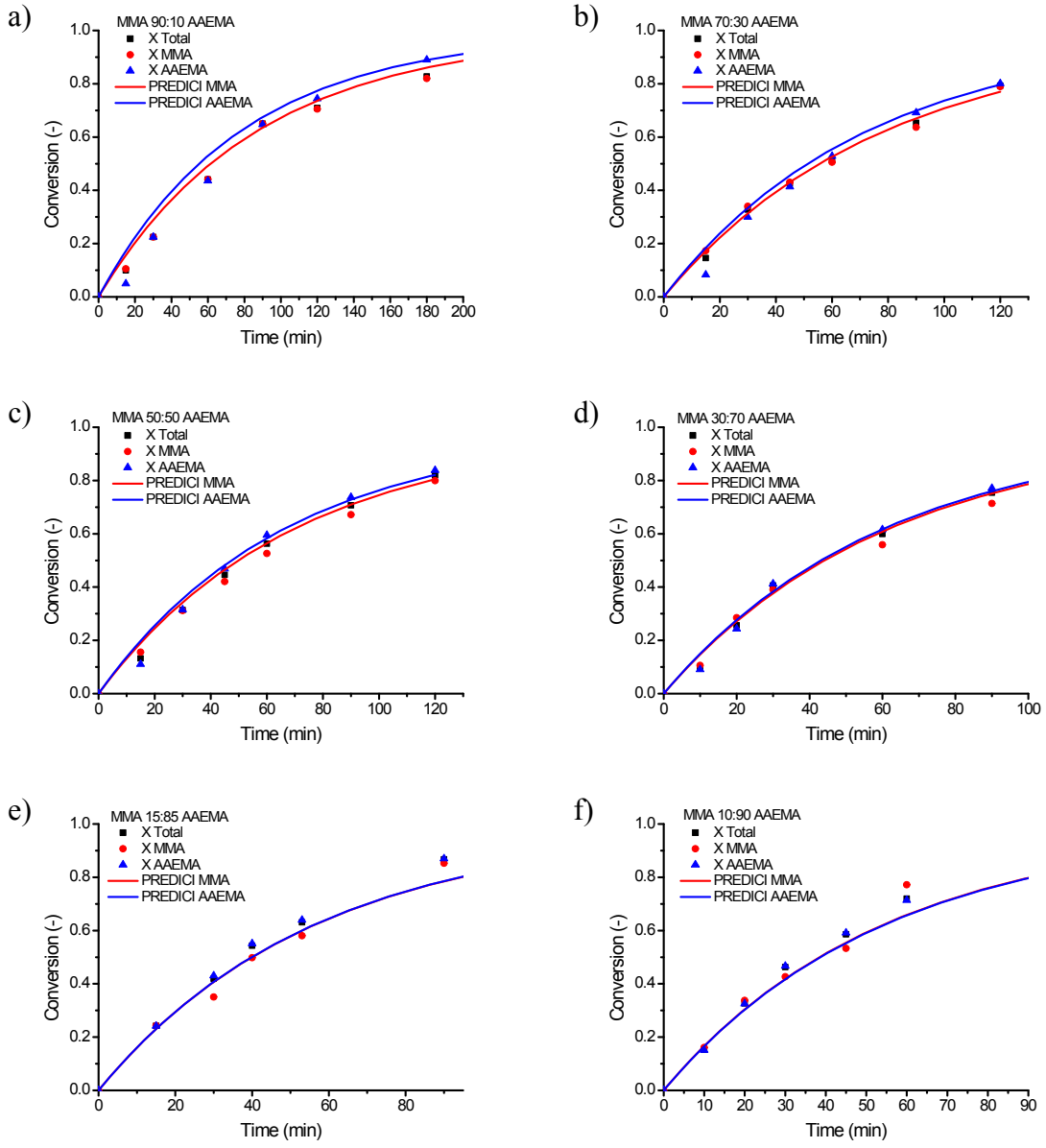

Figure S7: Experimental (symbols) and simulated (lines) conversion *vs*. time plot for overall monomer (black squares), MMA (exp.: red circles; sim.: red straight line) and AAEMA (exp.: blue triangles; sim.: blue dashed line) for a) 90 mol% MMA and 10 mol% AAEMA b) 70 mol% MMA and 30 mol% AAEMA c) 50 mol% MMA and 50 mol% AAEMA d) 30 mol% MMA and

70 mol% AAEMA e) 15 mol% MMA and 85 mol% AAEMA f) 10 mol% MMA and 90 mol% AAEMA initiated with 1 mol% AIBN.

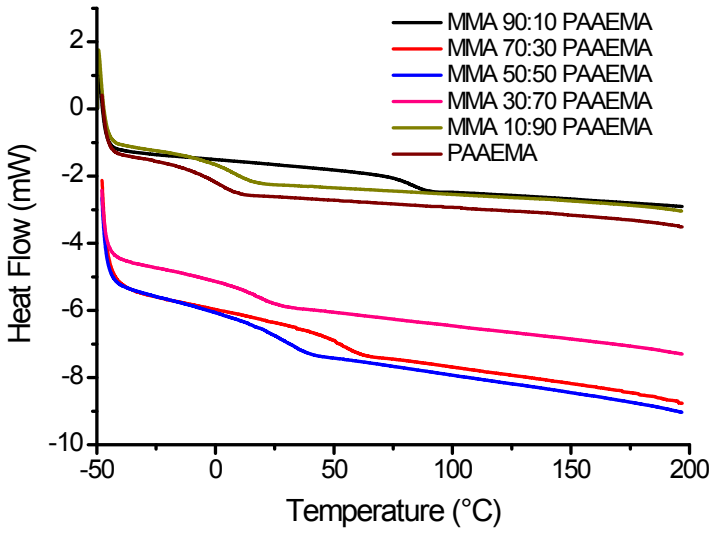

Figure S8: Differential scanning calorimetry (DSC) traces of PAAEMA and PMMA-co-PAAEMA.

b. PREDICI simulation

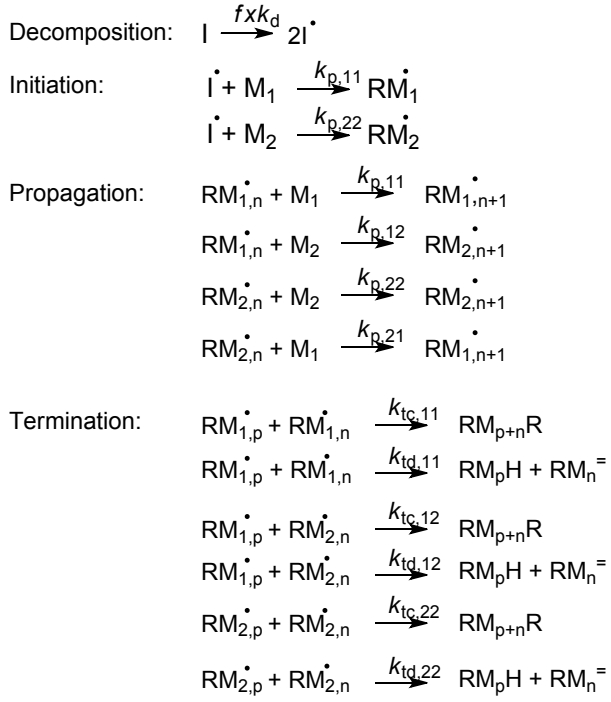

Figure S9: Scheme of a classical radical polymerization with I=AIBN, R=Decomposition Component, M_1=MMA, M_2=AAEMA radicals are denoted with a dot. Reactions used for PREDICI simulation of copolymerization for reactivity ratio.

Table S5: Parameters for PREDICI simulation of copolymerization for reactivity ratios at 75 °C.

Coefficient	Value	
	k_0 (L·mol^{-1}·s^{-1})	E_a (kJ·mol^{-1})
k_d	2.89E+15	130.2
f	7.00E-01	
k_{p11}	2.67E+06	22.36
k_{p22}	2.13E+06	19.69
$k_{p12} = k_{p11}/r_{12}$	8.90E-01	

$k_{p21} = k_{p22}/r_{21}$	9.80E-01	
k_{tc11}	6.55E+07	5.89
k_{td11}	1.33E+08	5.89
k_{tc21}	6.55E+07	5.89
k_{td21}	1.33E+08	5.89
k_{tc22}	6.55E+07	5.89
k_{td22}	1.33E+08	5.89

5. Copolymerization with BPO/Amine

a. Copolymer Synthesis

1 mol% BPO (0.306 g, 0.0009467 mol) was dissolved in a mixture of MMA (9 g, 0.09 mol) and ECEMA (1 g, 0.00467 mol) and degassed with argon for 10 min. DHEPT (0.185 g, 0.0009467 mol) was dissolved in MMA (taken from the initially 9 g) and added in equimolar concentration with respect to BPO to the solution and the temperature profile was recorded by using a pico TC-08 data logger and type K thermocouple. The experiment was performed with comonomer ratios ranging from 0 wt% - 100 wt%. Each experiment was analysed by 1H NMR and DSC.

Table S6: Experimental conditions of synthesis of PMMA-co-PAAEMA

m_{BPO} (75%)	n_{BPO}	m_{DHEPT}	n_{DHEPT}	m_{AAEMA}	n_{AAEMA}	m_{MMA}	n_{MMA}	T_g	t_{max}
g	mol	g	mol	g	mol	g	mol	°C	s
0.32	0.001	0.195	0.001	0	0	10	0.1	101	2570
0.306	0.0009467	0.185	0.0009467	1	0.00467	9	0.09	91	1550
0.271	0.00084	0.164	0.00084	3	0.014	7	0.07	76	650
0.237	0.000734	0.143	0.000734	5	0.0234	5	0.05	41	375

0.151	0.000467	0.091	0.000467	10	0.0467	0	0	2	205

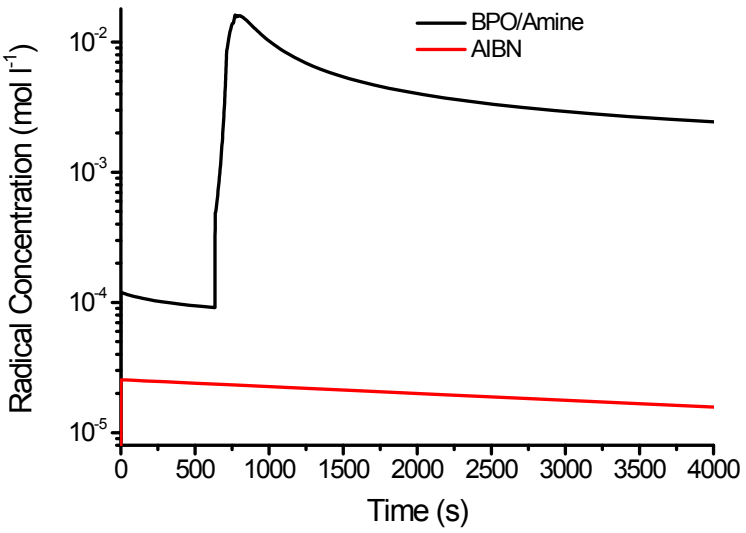

Figure S10: Simulated radical concentration *vs*. time profiles for BPO/amine (black) and AIBN (red) initiation.

b. PREDICI simulation

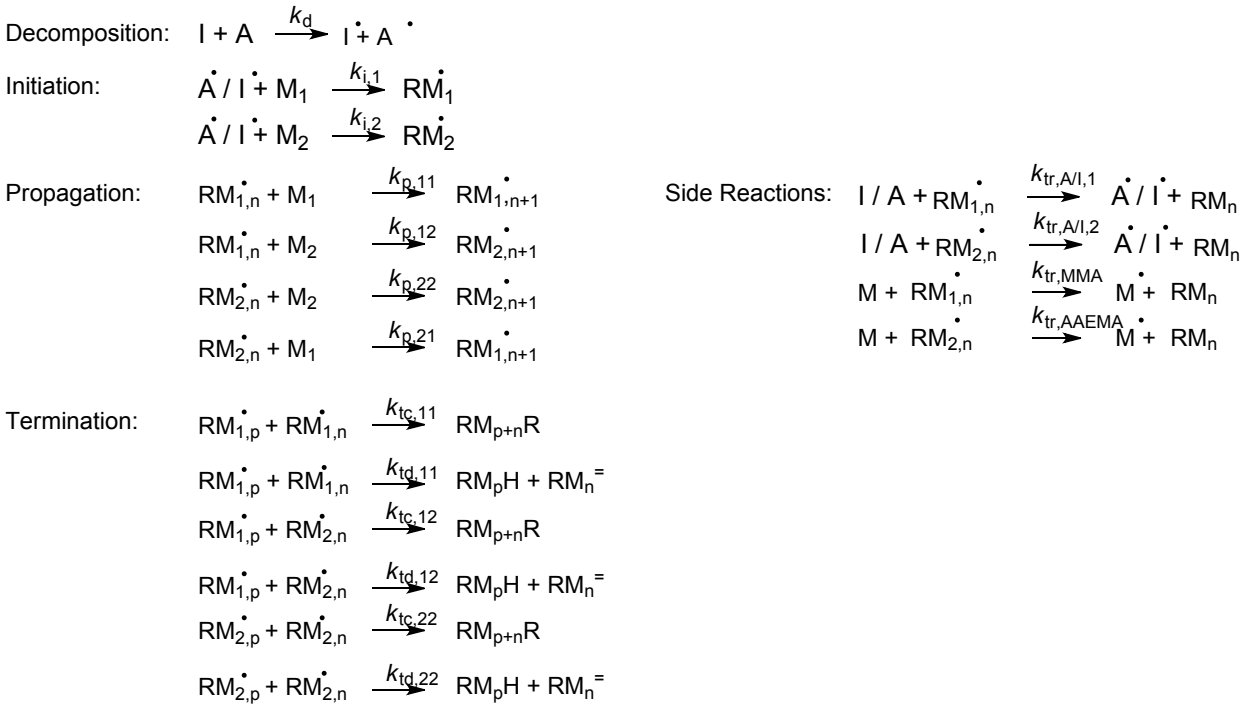

Figure S11: Scheme of a "bicomponent" radical polymerization with I=BPO, A=DHEPT, R=Decomposition Component, M_1=MMA, M_2=AAEMA radicals are denoted with a dot. Reactions used for PREDICI simulation of copolymerization for BPO/DHEPT.

Table S7: Parameters for PREDICI simulation of copolymerization with BPO/DHEPT at 25 °C.

Coefficient	Value		Coefficient	Value	
	k_0 (L·mol^{-1}·s^{-1})	E_a (kJ·mol^{-1})		k_0 (L·mol^{-1}·s^{-1})	E_a (kJ·mol^{-1})
k_{d0}	7.40E+03	3.34E+01	$alpha_m$	1.23E-03	
f_1	3.00E-01		$alpha_p$	2.10E-04	
k_{i1}	1.76E+08		T_{gm}	-1.26E+02	
k_{i2}	9.70E+05		T_{gp}	1.14E+02	
k_{p0}	2.67E+06	2.24E+01	D_{m0}	8.00E-08	
k_{t0}	1.98E+08	5.89E+00	D_{p0}	1.00E-03	
delta	6.70E-01		$gamma_m$	7.63E-01	

t_{21}	2.75E+01	sigma	5.85E-10
t_{22}	3.50E+01	N_A	6.02E+23
t_{31}	1.50E+01	$gamma_t$	3.88E+00
t_{32}	1.00E+01	j_c	7.00E+01
t_{41}	2.80E+01	alpha	6.99E-09
t_{42}	2.66E+01	n	2.00E+00
C_{MMA0}	5.00E-05	$gamma_I$	4.10E-01
C_{A0}	1.50E-01	$C\text{-}D_{I0}$	1.00E-05
C_{BPO0}	6.00E-02	k_I	1.00E+07
C_{tp01}	1.00E+00	k_{p0_AAEMA}	2.13E+06 1.07E+01
C_{tp02}	1.00E+00	r_{MMA}	8.90E-01
v_m	1.06E-06	r_{AAMEA}	9.80E-01
v_p	8.47E-07		

i. Coefficient Calculations (.fun files)

Initiation rate coefficient k_d:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
Vfm=0.025+getkp("alpham")*(gettemp("Reactor_1")-getkp("Tgm"))
Vfp=0.025+getkp("alphap")*(gettemp("Reactor_1")-getkp("Tgp"))
ev=(getkp("vm")-getkp("vp"))/getkp("vm")
jp=xMMA*(1-ev)/(1-xMMA*ev)
rp=getkp("sigma")/2
Vf8=Vfm*(1-jp)+jp*Vfp
result1=getkp("kd0")
result2=(getkp("f1")/(1+getkp("C-DI0")/exp(-getkp("gammaI")/Vf8)))
```

Propagation rate coefficient MMA $k_{p,MMA} = k_{p11}$:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
ev=(getkp("vm")-getkp("vp"))/getkp("vm")
kp0=getkp("kp0")*10^-3
Vfm=0.025+getkp("alpham")*(gettemp("Reactor_1")-getkp("Tgm"))
Vfp=0.025+getkp("alphap")*(gettemp("Reactor_1")-getkp("Tgp"))
rp=getkp("sigma")/2
jp=xMMA*(1-ev)/(1-xMMA*ev)
Vf8=Vfm*(1-jp)+jp*Vfp
Dm=getkp("Dm0")*exp(-getkp("gammam")/Vf8)
a=4*3.14159*getkp("NA")*rp*Dm
oneoverkp=1/a+1/kp0
kp=1/oneoverkp*1000
result1=kp
result2=xMMA
```

Propagation rate coefficient AAEMA $k_{p,AAEMA} = k_{p22}$:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
ev=(getkp("vm")-getkp("vp"))/getkp("vm")
kp0=getkp("kp0_AAEMA")*10^-3
Vfm=0.025+getkp("alpham")*(gettemp("Reactor_1")-getkp("Tgm"))
Vfp=0.025+getkp("alphap")*(gettemp("Reactor_1")-getkp("Tgp"))
```

```
rp=getkp("sigma")/2
jp=xMMA*(1-ev)/(1-xMMA*ev)
Vf8=Vfm*(1-jp)+jp*Vfp
Dm=getkp("Dm0")*exp(-getkp("gammam")/Vf8)
a=4*3.14159*getkp("NA")*rp*Dm
oneoverkp=1/a+1/kp0
kp=1/oneoverkp*1000
result1=kp
```

Termination rate coefficient $k_{t,11} = k_{t,22} = k_{t,12}$:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
if (xMMA<0.35)
kt=getkp("kt0")*(1-xMMA)
result1=kt
if ((xMMA<0.5) && (xMMA>=0.35))
kt=exp(getkp("t21")-getkp("t22")*xMMA)
if ((xMMA<0.78) && (xMMA>=0.5))
kt=exp(getkp("t31")-getkp("t32")*xMMA)
if ((xMMA<1) && (xMMA>=0.78))
kt=exp(getkp("t41")-getkp("t42")*xMMA)
delta=getkp("delta")
ktc=kt*(1-delta)
ktd=kt*delta
result1=ktc
result2=ktd
```

Transfer reaction from polymer to monomer rate coefficient $k_{tr,MMA}$ resp. $k_{tr,AAEMA}$:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
ev=(getkp("vm")-getkp("vp"))/getkp("vm")
kp0=getkp("kp0")*10^-3 resp. kp0=getkp("kp0_AAEMA")*10^-3
Vfm=0.025+getkp("alpham")*(gettemp("Reactor_1")-getkp("Tgm"))
Vfp=0.025+getkp("alphap")*(gettemp("Reactor_1")-getkp("Tgp"))
rp=getkp("sigma")/2
jp=xMMA*(1-ev)/(1-xMMA*ev)
Vf8=Vfm*(1-jp)+jp*Vfp
Dm=getkp("Dm0")*exp(-getkp("gammam")/Vf8)
a=4*3.14159*getkp("NA")*rp*Dm
oneoverkp=1/a+1/kp0
kp=1/oneoverkp*1000
result1=kp*getkp("CMMA0")
```

Transfer reaction from polymer to initiator rate coefficient $k_{tr,Amine}$ resp. $k_{tr,BPO}$:

```
monomer=getco("MMA")+getco("AAEMA")
polymer=getmy("PMMA",1)+getmy("PMMA*",1)+getmy("PAAEMA*",1)
xMMA=polymer/(polymer+monomer)
ev=(getkp("vm")-getkp("vp"))/getkp("vm")
kp0=getkp("kp0")*10^-3 resp. kp0=getkp("kp0_AAEMA")*10^-3
Vfm=0.025+getkp("alpham")*(gettemp("Reactor_1")-getkp("Tgm"))
Vfp=0.025+getkp("alphap")*(gettemp("Reactor_1")-getkp("Tgp"))
rp=getkp("sigma")/2
```

jp=xMMA*(1-ev)/(1-xMMA*ev)

Vf8=Vfm*(1-jp)+jp*Vfp

Dm=getkp("Dm0")*exp(-getkp("gammam")/Vf8)

a=4*3.14159*getkp("NA")*rp*Dm

oneoverkp=1/a+1/kp0

kp=1/oneoverkp*1000

result1=kp*getkp("CBPO0") *resp.: getkp("CA0")*