

Supporting information for

In Situ Stabilizer Formation from Methacrylic Acid Macromonomers in Emulsion Polymerization

Ingeborg Schreur-Piet^a and Johan P.A. Heuts^{a*}

^a *Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands, e-mail: j.p.a.heuts@tue.nl*

Characteristics of *t*-BMA and/or MAA macromonomers

To characterize the macromonomers SEC, NMR and MALDI analysis have been performed. A short overview of the results are given below.

SEC

In Fig. S1 Overview plot of the MMD of all three *t*-BMA macromonomers is given.

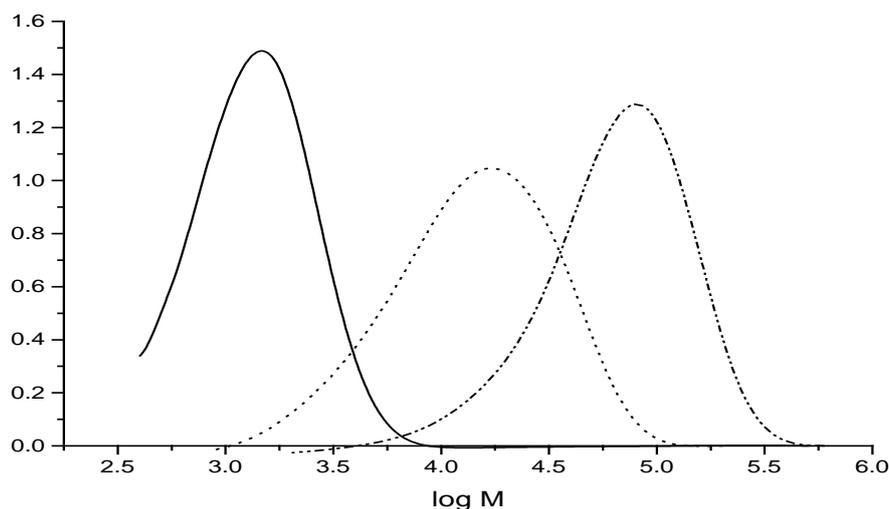


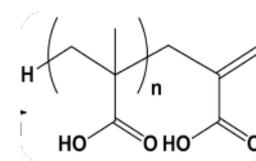
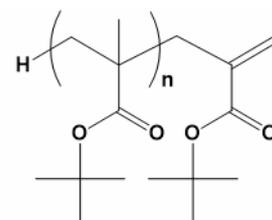
Fig. S1 Molar mass distribution of *t*-BMA-macromonomers MM₁₆ (-); MM₈₀(..) and MM₃₅₀(-.) by SEC .

¹H NMR

The characteristic shifts in NMR are mentioned in Table S1.

Table S1 *t*-BMA and MAA macromonomers for NMR

Shift (ppm)	number H	group
<i>t</i> -BMA MM		
0.9-2.6	1	H end group
	9n	CH ₃ of butyl acrylate group
	3n	CH ₃ on polymer backbone
	2n	CH ₂ on polymer backbone
		different shift for CH ₂ in macromonomer
5.4 - 6.1	2	CH ₂ cis-trans terminal C=C for <i>t</i> -BMA MM
MAA-MM		
0.9-2.6	1	H end group
	3n	CH ₃ on polymer backbone
	2n	CH ₂ on polymer backbone
		different shift for CH ₂ in macromonomer
5.6 - 6.2	2	CH ₂ cis-trans terminal C=C for MAA MM
11.0	1n	H of acid group (only visible when protonated)



Calculation DP_n from NMR

For the calculation of DP_n for *t*-BMA macromonomer first a correction for rest monomer is made, by subtracting the intensity of the monomer H's from the total intensity. The remaining NMR intensity is

the intensity of the macromonomer end group (2 H) plus the intensity of the rest of the polymer (14n+11+1 H).

$$I_{\text{total}} = 2 + (14n + 12) = I_{\text{end}} + I_{\text{rest}} \quad DP_n = n+1$$

A comparable calculation can be done for MAA macromonomer, the proton on the acid was not taken into account because the acid is deprotonated in methanol.

$$I_{\text{total}} = 2 + (5n + 3) = I_{\text{end}} + I_{\text{rest}} \quad DP_n = n+1$$

In Fig. S2 an overlay the NMR spectra of *t*-BMA and MAA is shown. Clearly the absence of the intensity peak of the butyl acrylate group (1.4 ppm) after acidolysis of the polymer can be seen. The peak at 3.3 ppm is due to the solvent MeOD. In this case the water HDO peak (4.8 ppm) is suppressed, because it deformed the peaks of the macromonomer end group.

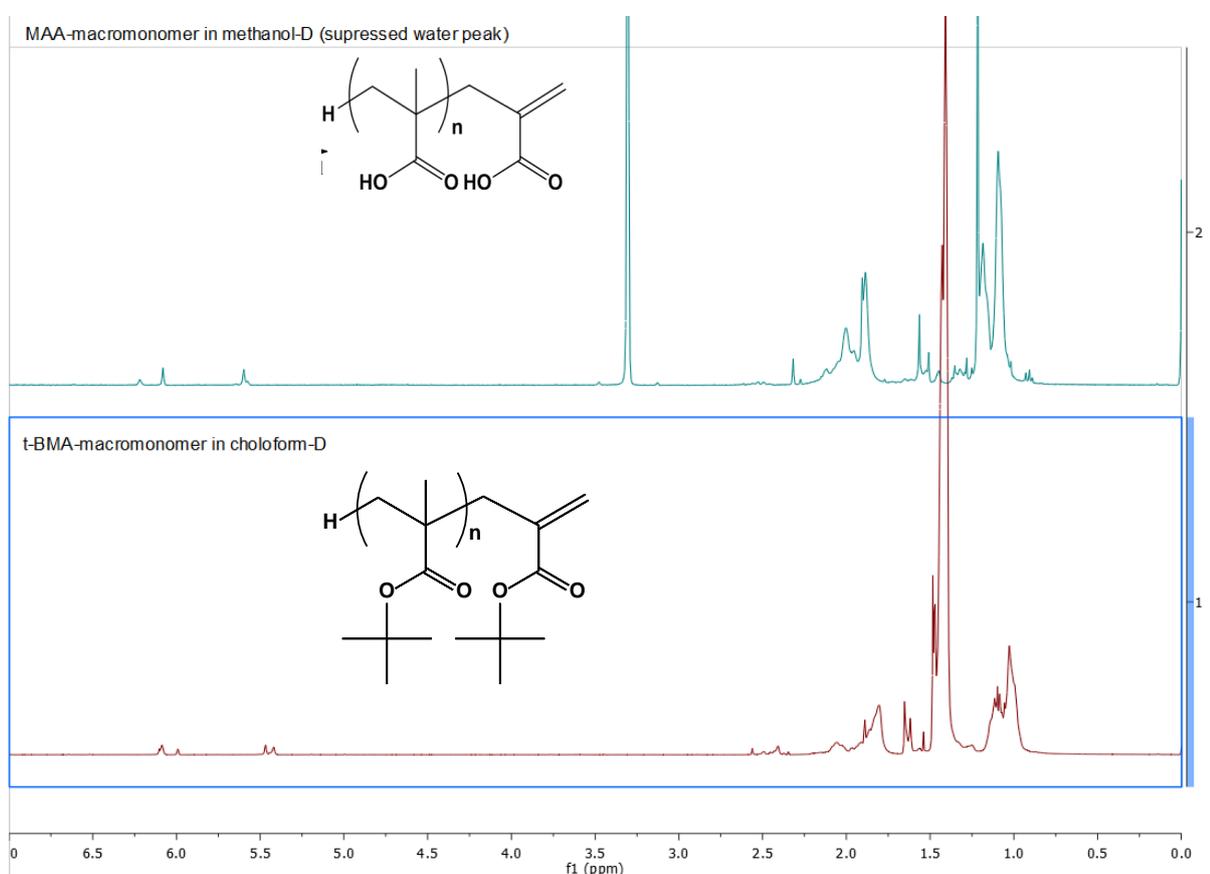


Fig. S2 ¹H NMR of *t*-BMA macromonomer (bottom) and of MAA macromonomer (top)

In Fig. S3 to S5 the NMR spectra of the *t*-BMA macromonomer and the according MAA spectra are shown.

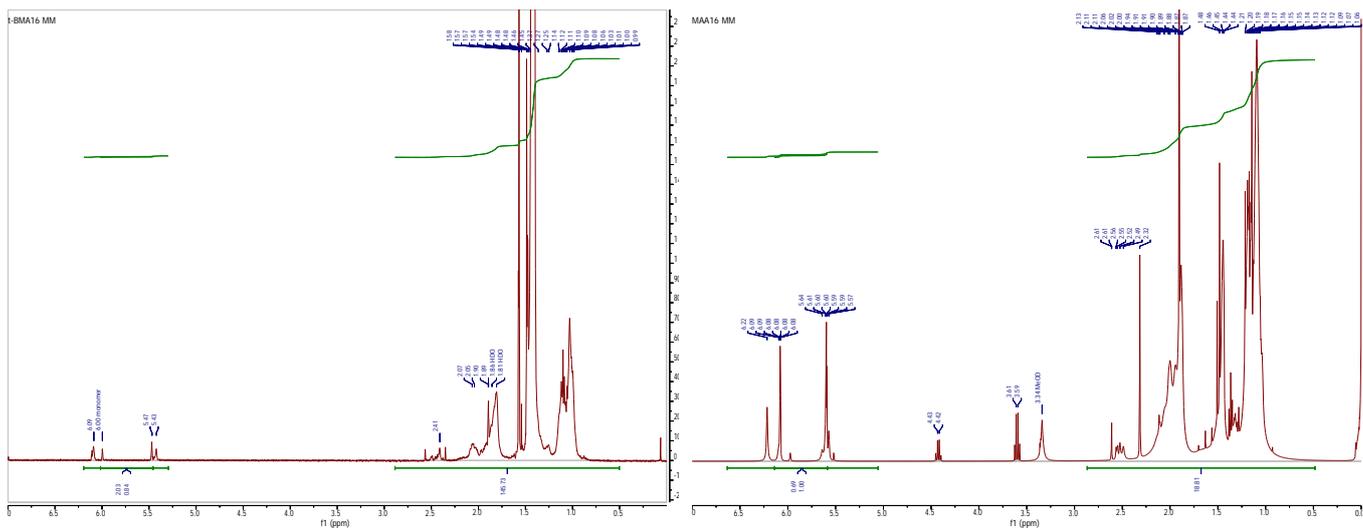


Fig. S3 ^1H NMR of *t*-BMA₁₆-MM (left) and MAA₁₆-MM (right).

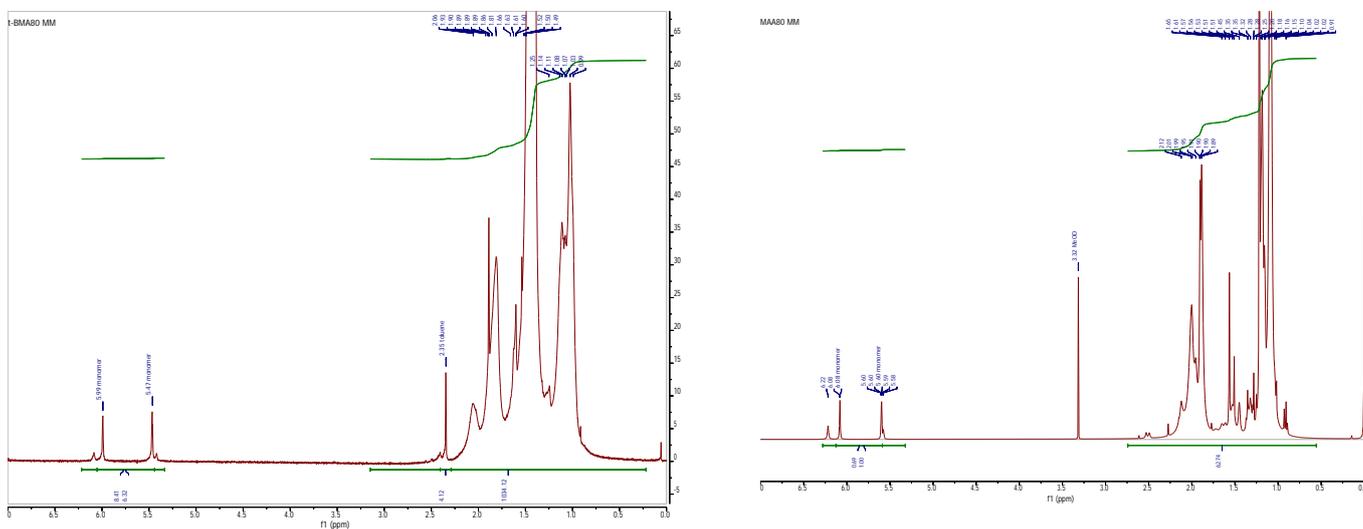


Fig. S4 ^1H NMR of *t*-BMA₈₀-MM (left) and MAA₈₀-MM with HDO suppression (right).

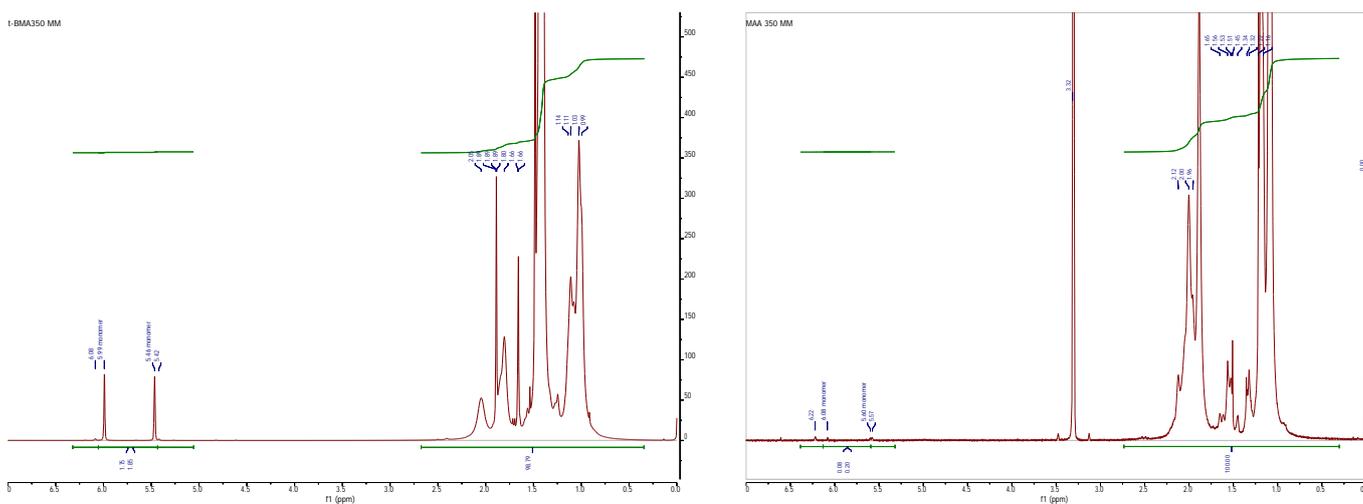


Fig. S5 ^1H NMR of *t*-BMA₃₅₀-MM (left) and MAA₃₅₀-MM with HDO suppression (right).

Batch emulsion polymerization of MMA with MAA₈₀ and MAA₃₆₀

In Fig. S6 the conversion time curves for the batch emulsion polymerizations with MM are given.

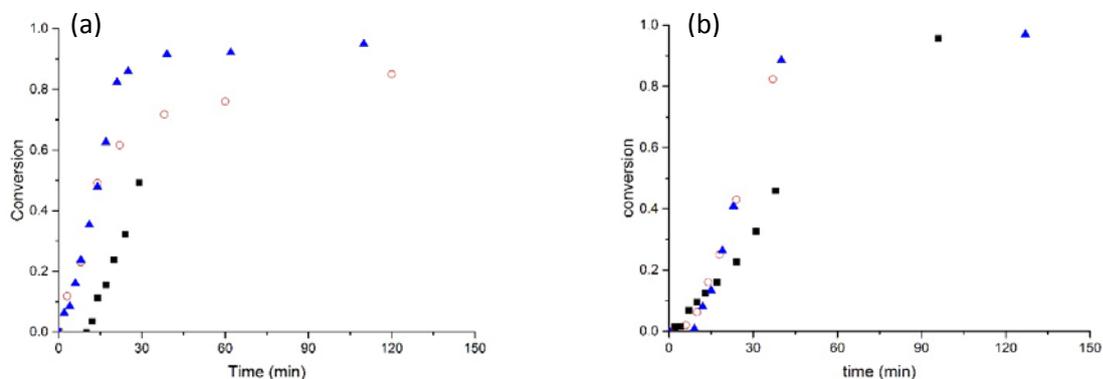


Fig. S6 Batch emulsion polymerization of MMA with 4 pphm macromonomer: (a) MAA₁₆ and (b) MAA₃₅₀ with variable amounts of SDS. Concentration SDS: (■) 0.5 pphm; (○) 1 pphm and (▲) 1.5 pphm.

Table S2 Particle diameters of pMMA latexes stabilized by SDS and 4 pphm MAA-MM.

	SDS (pphm)	Conversion ^a	DLS	
			D_n (nm)	<i>Pdl</i>
MAA ₁₆	0.5	0.5	76	0.1
	1.0	0.8	93	0.8
MAA ₈₀	0.5	0.6	78	0.1
	1.0	0.8	77	0.1
MAA ₃₅₀	0.5	1.0	56	1.2
	1.0	0.8	91	0.1

^a Conversion latex DLS measurement

Semi-batch emulsion copolymerization of MMA and BA with MAA₈₀

In Fig. S7 the conversion time curves for the semi-batch emulsion copolymerizations of MMA and BA are shown for different monomer feed compositions using 5 and 15 ppm of MAA₈₀.

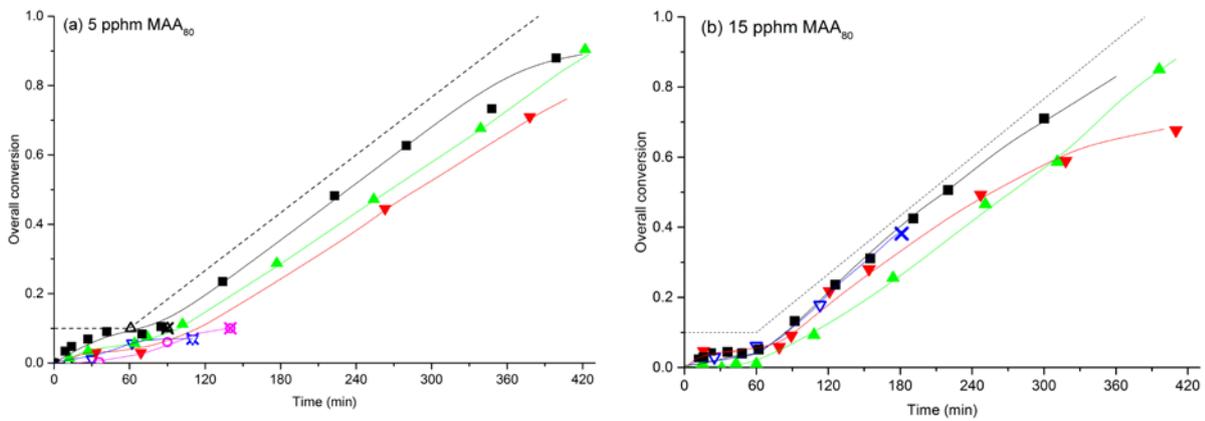


Fig. S7 Semi-batch copolymerization of BA and MMA with 5 and 15 ppm MAA₈₀, no SDS. $w_{BA}=1$ (■); $w_{BA}=0.5$ (▲); $w_{BA}=0.3$ (▼); $w_{BA}=0.2$ (△); $w_{BA}=0.1$ (○) and $w_{BA}=0.05$ (▽). The dotted line indicates the addition profile of the semi-batch reaction. Crosses indicate major coagulation.

Batch and semi-batch emulsion polymerization of BMA and EA with MAA80.

In Fig. S8 and S9 the conversion time curves for emulsion polymerization of EA and BMA in batch and semi-batch processes with the particles size distributions are shown.

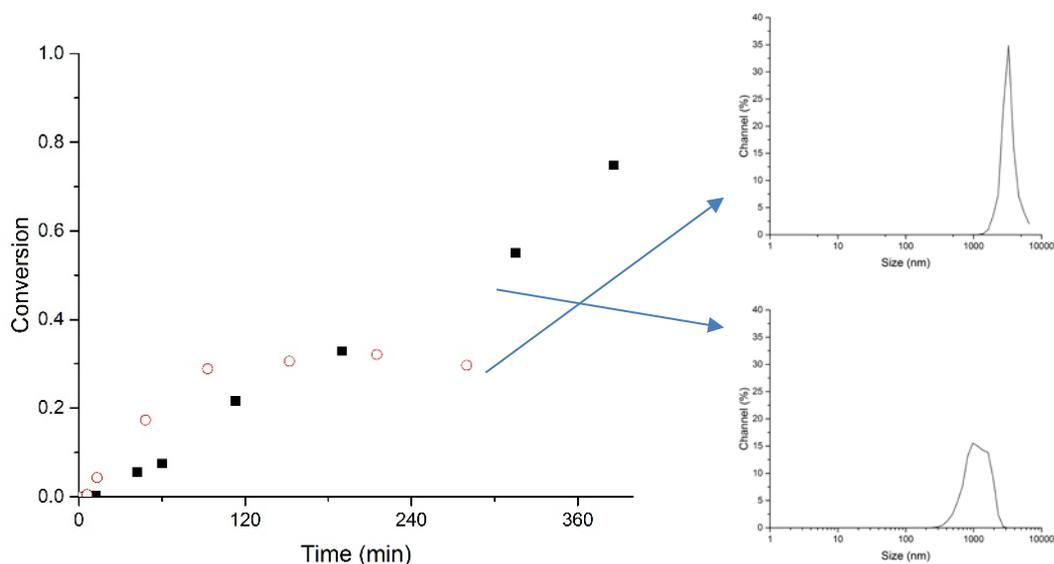


Fig. S8 Conversion time curve of the emulsion polymerization of ethyl acrylate with 5 ppm MAA₈₀ in (○) batch and (■) semi-batch process and corresponding particle size distributions: batch (top) and semi-batch (bottom).

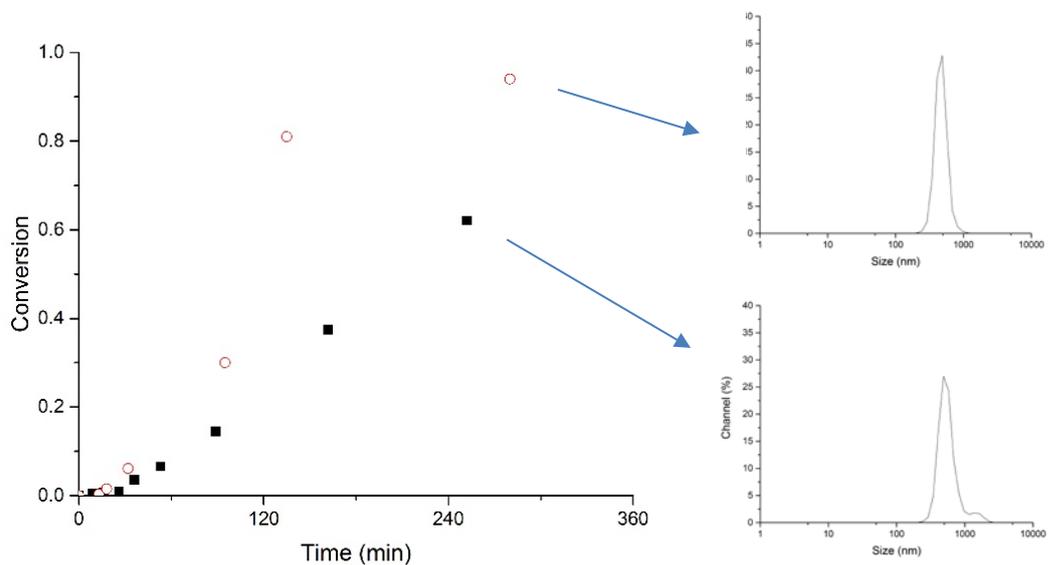


Fig. S9 Conversion time curve of the emulsion polymerization of butyl methacrylate with 5 ppm MAA₈₀ in (○) batch and (■) semi-batch process, and corresponding particle size distributions.

MALDI-ToF MS of MAA macromonomer

In Fig. S10 the MALDI-ToF MS spectrum of MAA-macromonomer is shown. On top the measured spectrum; below a simulation with Na^+ and K^+ , respectively, as cationating agent and on the bottom an overlay of all three graphs. Clearly can be seen that both Na^+ and K^+ ions are present, the intensity of the K^+ signal, however, is always lower than of the Na^+ signal.

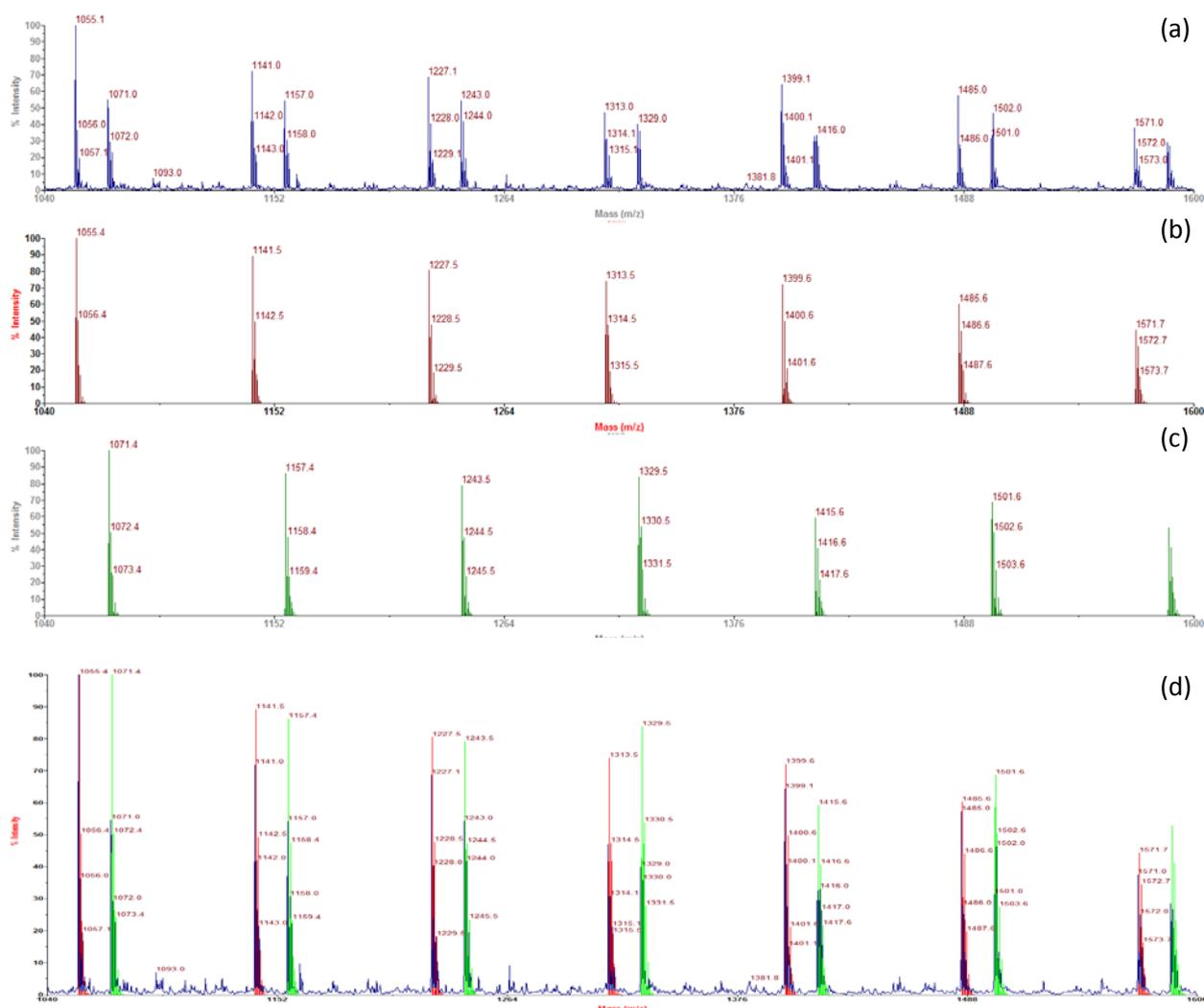


Fig. S10 MALDI-ToF MS spectrum of MAA-macromonomer. (a) Measured spectrum; (b) simulation with Na^+ as cationating agent; (c) simulation with K^+ as cationating agent and (d) an overlay of all three graphs. Used end groups for calculation: H and a vinylic group.

SEM, TEM and Cryo TEM images of p(BA-co-MMA) latexes with MAA₈₀

In Fig. S11 to S14 the SEM or (Cryo)TEM images of p(BA-co-MMA) latexes with the corresponding particle size distributions (PSD) as determined by DLS are given.

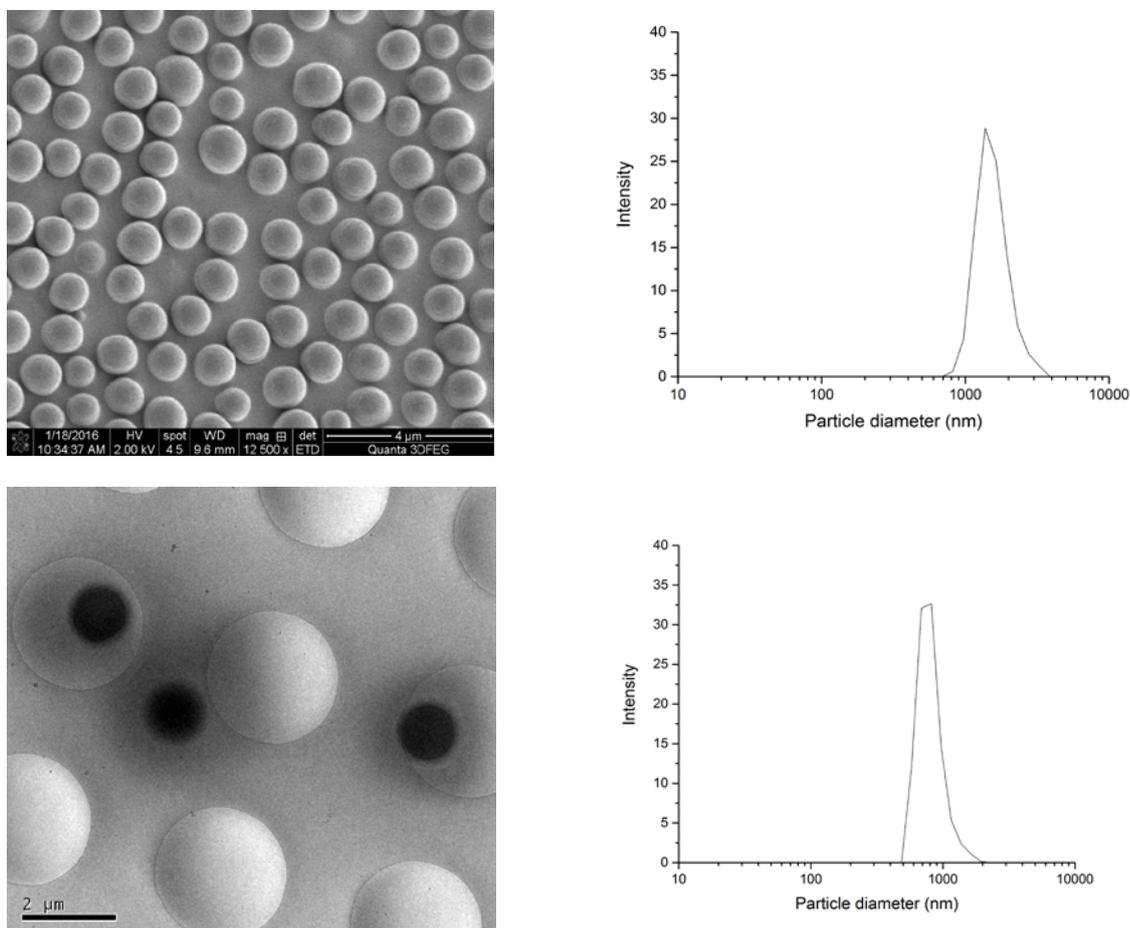


Fig. S11 SEM and Cryo TEM images respectively of BA latexes in batch process with 5 and 10 ppm MAA₈₀ with corresponding PSD as obtained by DLS.

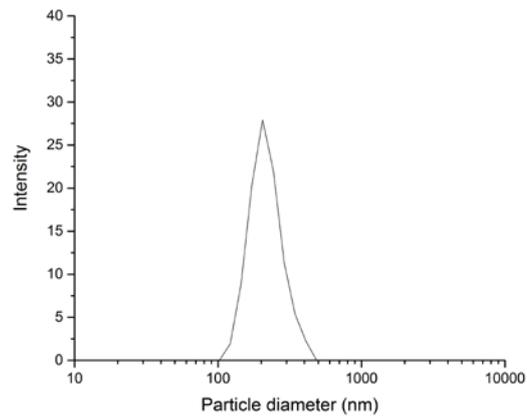
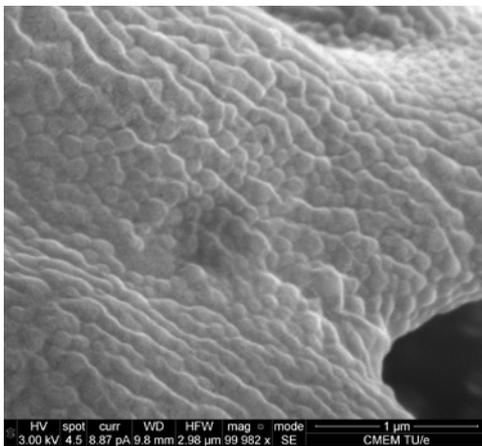
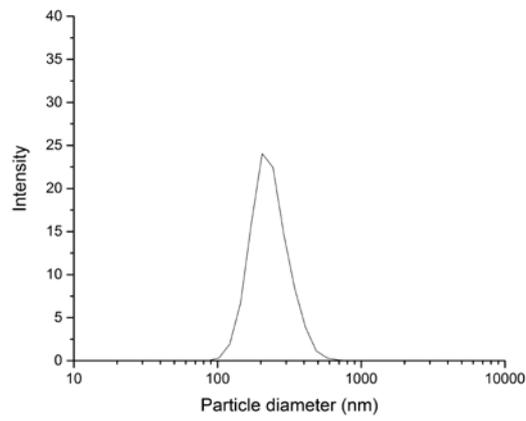
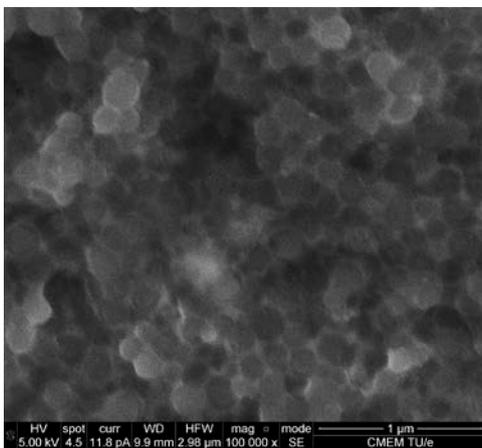
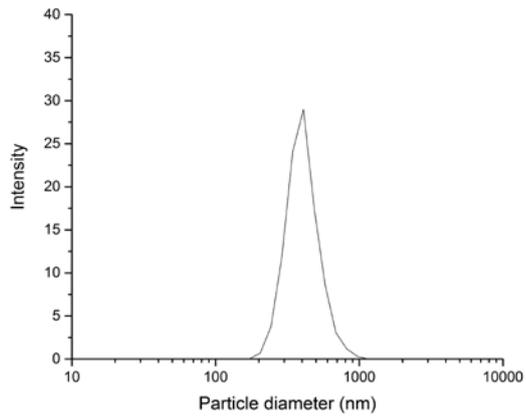
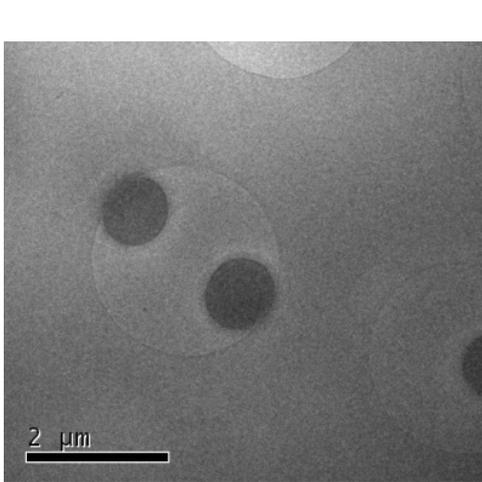


Fig. S12 Cryo TEM and SEM images of BA latexes in semi-batch process with 5, 10 and 15 pphm MAA₈₀ with corresponding PSD as obtained by DLS.

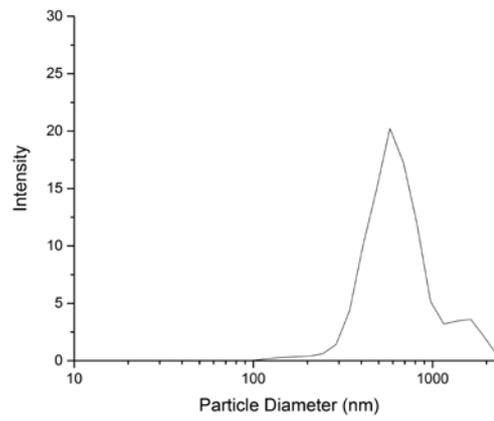
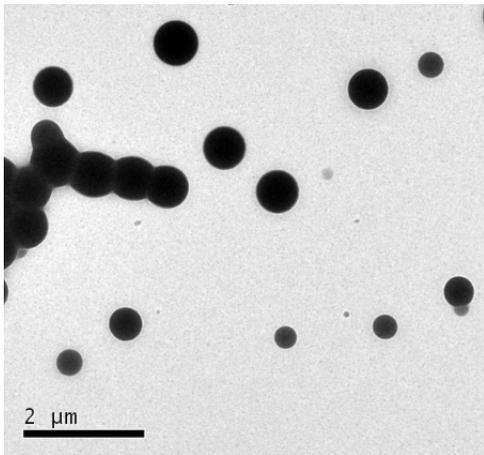
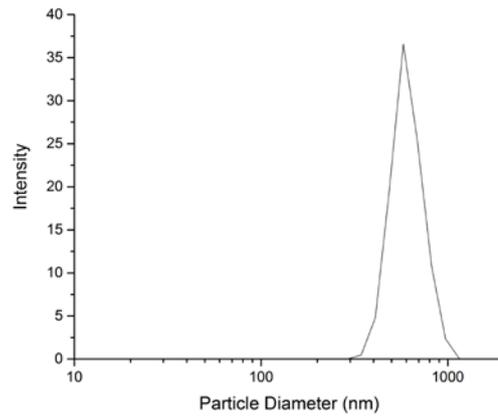
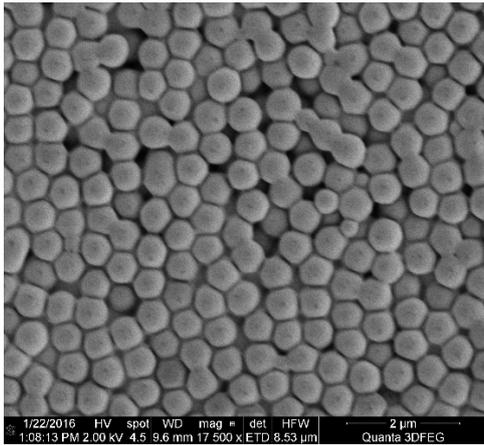


Fig. S13 SEM and TEM image of BA-co-MMA latexes ($w_{BA} = 0.5$) in semi-batch process with 5 and 10 pphm MAA₈₀ with corresponding PSD as obtained by DLS.

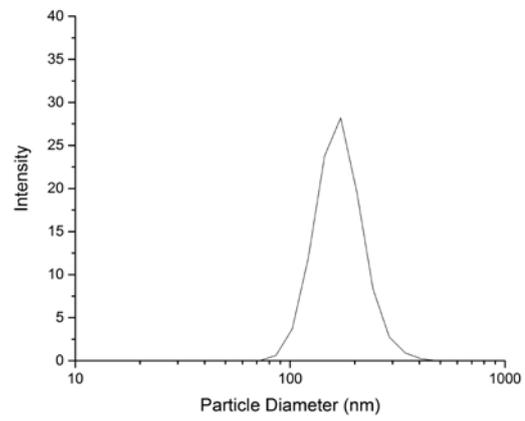
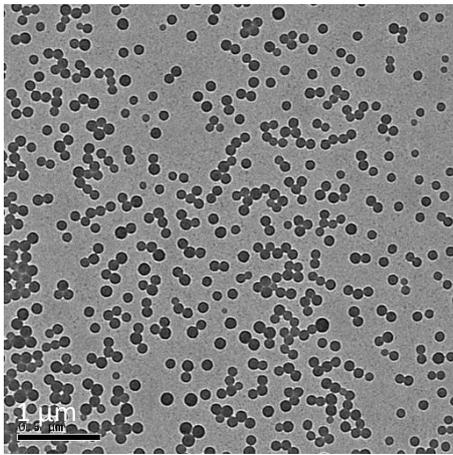
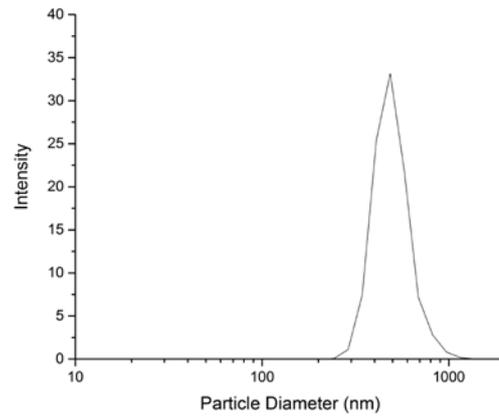
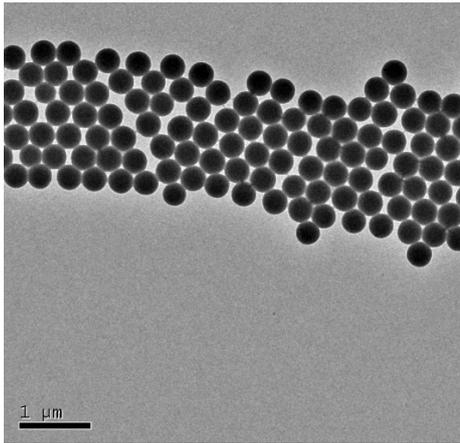
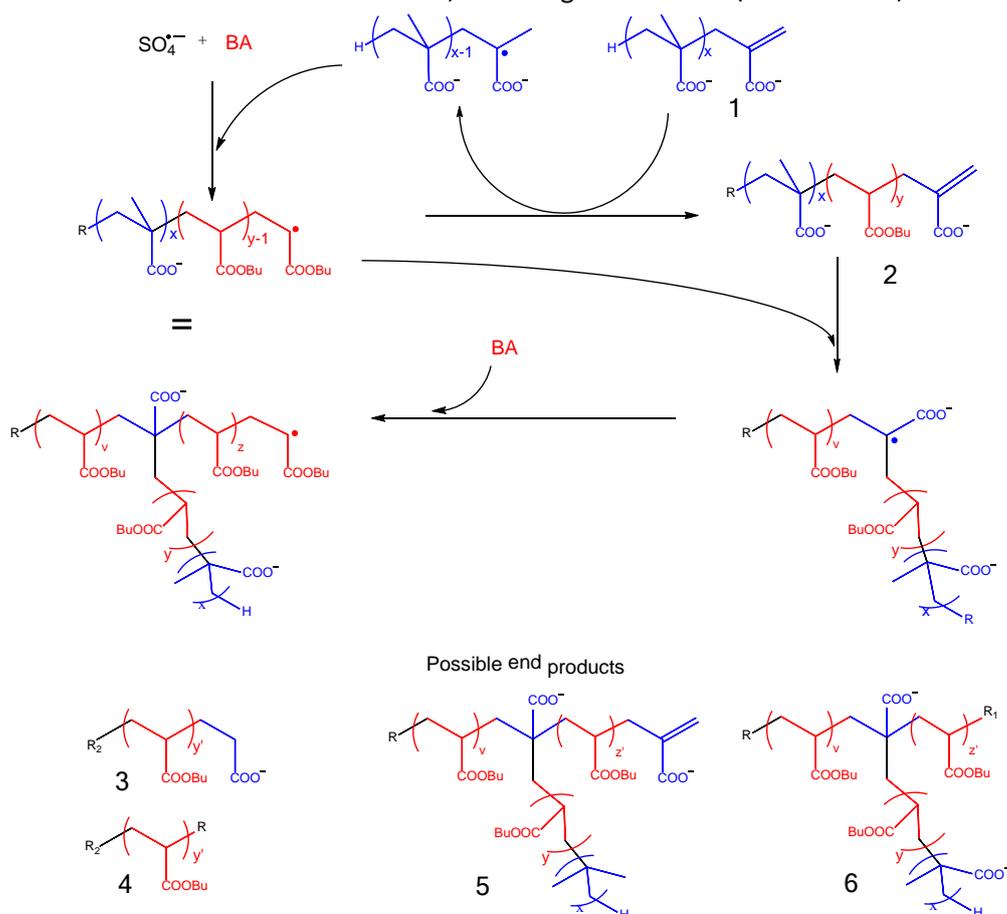


Fig. S14 TEM images of BA-co-MMA latexes ($w_{BA} = 0.3$) in semi-batch process with 10 and 15 pphm MAA₈₀ with corresponding PSD as obtained by DLS.

MALDI–ToF MS of the initially formed oligomers in emulsion polymerization of BA with MAA₈₀

Because of the use of THAP–DAC matrix-salt combination, both Na⁺ as K⁺ ions can be seen in the spectrum as cationating ion. The MALDI spectrum of MAA macromonomer (see Fig. S10) shows for this mass range always a larger peak with Na⁺ ions than with K⁺ ions, in Table S3 only Na⁺ peaks are mentioned, the mass of K⁺ is 38.9637, which gives a $\Delta m/z$ of +15.9739. The end groups used in the calculations are hydrogen, sulfate, hydroxyl, and a vinylic end group of MAA. No end groups from the dissociation of AIBN were taken into account in the MALDI spectrum, because the MALDI spectrum of MAA macromonomer shows only a hydrogen end group.

In Scheme S1 possible pathways to potential end products are given. With this scheme in hand the peaks from the MALDI spectrum of the initially formed products were identified. The measured and calculated m/z values are shown in Table S3. Most of the measured oligomers are graft (or block) copolymers (**6**) of MAA and BA; in rare cases also macromonomers (thus terminated with H and vinyl group) (**5**) were formed. Still some of the unreacted macromonomer (**1**) seems to be present, although it should be noted that the m/z of this structure is the same as that of copolymer structure **6**. We also observe a small number of peaks from the termination by recombination reaction of two smaller pMAA radicals (**1^T**). The intermediate reaction product of a growing pBA chain with one MAA macromonomer (**3**) was observed with an OH end group. The OH group comes from the decomposition of the persulphate initiator. Structure 5 is a macromonomer of BA and MAA, and is a special form of 6. In the MAA chain also an exchange of one or more H⁺ with Na⁺ can occur, this will give a rise in m/z of 21.9820, indicated with *.



Scheme S1 Possible pathways for *in situ* formation of amphiphilic copolymers, R = H, OH or SO₄⁻; R₁ = H, OH, SO₄⁻, MAA_{C=C}, R₂ = OH or SO₄⁻; y ≥ 1.

Table S3 Elaboration of a part of the MALDI-TOF-MS spectrum of oligomers at start of semi-batch emulsion polymerization of BA with 15 ppm MAA₈₀ as stabilizer. T= 60 °C, 350 rpm, 0.25 ppm KPS.

m/z		Type ^a	Number monomer units		End group			
measured	calculated ^c	#	x ^b	y ^b	MAA _{C=C}	H	OH	SO ₄
1055.2	1055.4	1	11	0	1	1		
	1055.5	6	9	2		2		
1057.1	1057.4	1 ^T	12	0		2		
1060.7	1060.5	5	4	4	1			1
1077.1	1077.4	1 [*]	11	0	1	1		
	1077.5	6 [*]	9	2		2		
1079.2	1079.4	1 ^T	12	0		2		
1099.1	1099.5	6	11	1		2		
1101.0	1101.4	1 ^{T*}	12	0		2		
1121.4	1121.5	6 [*]	11	1		2		
1141.2	1141.5	1	12	0	1	1		
	1141.5	6	10	2		2		
1143.1	1143.5	1 ^T	13	0		2		
1149.2	1149.7	3	0	8	1		1	
1163.1	1163.5	1 [*]	12	0	1	1		
	1163.5	6 [*]	10	2		2		
1177.5	1177.7	5	2	7	1	1		
1185.1	1185.5	6	12	1		2		
1207.1	1207.5	6 [*]	12	1		2		
1227.1	1227.5	1	13	0	1	1		
	1227.6	6	11	2		2		
1229.1	1229.5	1 ^T	14	0		2		
1249.1	1249.5	1 [*]	13	0	1	1		
	1249.5	6 [*]	11	2		2		
1251.1	1251.5	1 ^T	14	0		2		
1271.1	1271.6	6	13	1		2		
1272.1	1272.6	5	2	7	1			1
1293.1	1293.5	6 [*]	13	1		2		
1313.2	1313.5	1	14	0	1	1		
	1313.6	6	12	2		2		

^a Structure according to scheme S1. ^b x = total number of MAA units and y = total number of BA units. ^c Molar masses used for calculations in g/mol: BA=128.0838; MAA=86.0368; MAA_{C=C}=85.0290; Na⁺=22.9898; H=1.0078; SO₄⁻=95.9517; OH⁻=17.0027. Na⁺ is applied as cationating agent. * Exchange of 1 H⁺ with 1 Na⁺ in the pMAA chain; 1^T terminated PMAA chain by recombination. Accuracy for m/z of the mass analyzer after calibration is ca. ± 0.5.

