Supporting information for:

Modelling and Control of the Microstructure of MAA-co-PEGMA Water Soluble Copolymers

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Assessment of Starved Semibatch Conditions:

As discussed in the paper starved conditions in semibatch copolymerisation with monomers with widely different reactivity ratios is achieved running the polymerisation at high overall instantaneous conversion (> 85%); namely at high polymerisation rates. In order to find out these conditions several experiments were carried out. Figure S1 (a and b) show the conversion evolution of the instantaneous overall conversion and the cumulative copolymer composition for these experiments. All the reactions were conducted at MAA/PEGMA = 3/1 and the effect of initiator concentration, temperature and solids content on the instantaneous overall conversion and cumulative copolymer composition was studied. It can be seen that the increase of initiator concentration together with the increase in the temperature from 70 ºC to 90 ºC had only a minor effect in the instantaneous conversion. On the other hand, the effect of increasing of the solids content on the rate of polymerisation was significant. When experiments were run at 10 wt% solids content high instantaneous conversion (X_{inst} > 85%) was not achieved. At 20 wt% SC the reaction achieved starved condition at 70% of overall conversion. On the other hand, reasonable starved conditions were achieved at 30 wt% SC, 2% initiator concentration (wbom), and at 90 ºC with 8 hours of feeding. At this condition, almost 80% of the polymer was produced with the desired copolymer composition (Figure S1 b).

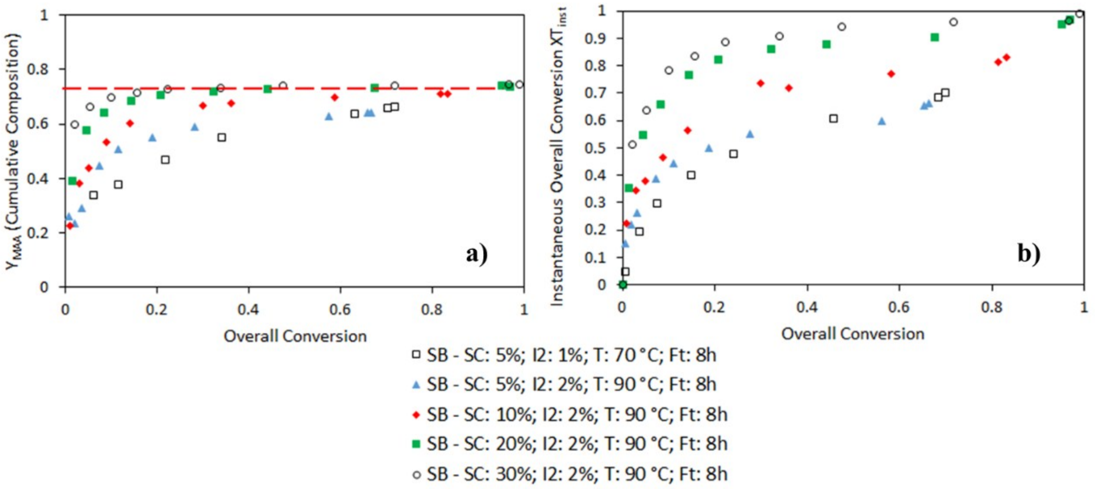

Figure S1. a) Conversion evolution of the instantaneous conversion. b) Conversion evolution of the cumulative copolymer composition for experiments carried out at the operation conditions indicated in the legend: (SB: Semibatch; SC: solids content; I2: Initiator (bwom); T: Temperature; Ft: Feed time).

Kinetics Scheme and General Kinetic Parameters:

The detailed mathematical model was developed based on the kinetic scheme of the copolymerisation of MAA and PEGMA**5** presented in Scheme S1 using Predici$^{®}$ commercial software(1). The kinetic scheme contains the conventional steps for free radical copolymerisation: initiation, propagation chain transfer to monomer and termination reactions. In Table S1 the kinetic parameters taken from the literature are presented.

Scheme S1. Kinetic mechanism of the copolymerisation of MAA/PEGMA5. *M_1*: MAA monomer; *M_2*: PEGMA5 monomer; *I*: Initiator; *$R_{i,1}$*: Chain end radical of monomer 1 with length i; *$R_{i,2}$*: Chain end radical of monomer 2 with length i; *Pi*: Dead polymer with length i; *f*: Initiator efficiency; *cd*: Ratio between termination by disproportionation and termination by combination.

Initiation:

$$I \xrightarrow{k_d} 2fR_0$$

$$R_0 + M_1 \xrightarrow{k_{i1}} R_1$$

$$R_0 + M_2 \xrightarrow{k_{i2}} R_2$$

Propagation:

$$R_{i,1} + M_1 \xrightarrow{kp_{11}} R_{i+1,1}$$

$$R_{i,2} + M_2 \xrightarrow{kp_{22}} R_{i+1,2}$$

$$R_{i,1} + M_2 \xrightarrow{kp_{12}} R_{i+1,2}$$

$$R_{i,2} + M_1 \xrightarrow{kp_{21}} R_{i+1,1}$$

Chain Transfer to Monomer:

$$R_{i,1} + M_1 \xrightarrow{ktrm_{11}} P_i + R_1$$

$$R_{i,2} + M_2 \xrightarrow{ktrm_{22}} P_i + R_2$$

$$R_{i,1} + M_2 \xrightarrow{ktrm_{12}} P_i + R_2$$

$$R_{i,2} + M_1 \xrightarrow{ktrm_{21}} P_i + R_1$$

Termination by Disproportionation:

$$R_{i,1} + R_{j,1} \xrightarrow{cd * kt_{11}} P_i + P_j$$
$$R_{i,2} + R_{j,2} \xrightarrow{cd * kt_{22}} P_i + P_j$$
$$R_{i,1} + R_{j,2} \xrightarrow{cd * kt_{12}} P_i + P_j$$

Termination by Combination:

$$R_{i,1} + R_{j,1} \xrightarrow{(1-cd) * kt_{11}} P_{i+j}$$
$$R_{i,2} + R_{j,2} \xrightarrow{(1-cd) * kt_{22}} P_{i+j}$$
$$R_{i,1} + R_{j,2} \xrightarrow{(1-cd) * kt_{12}} P_{i+j}$$

Table S1. Kinetic parameters used in the developed mathematical model of the MAA/PEGMA5 copolymerisation gathered from literature. 1 refers to MAA and 2 refers to PEGMA. The pre-exponential factors are in s^{-1} or in L·mol^{-1}·s^{-1}.

Rate Coefficient	Reference
$kd = 8.0\,x\,10^{15} exp^{(-\frac{135.0}{RT})}$ $f = 0.6$	(2)
$kp_{22} = k_{i2} = exp^{(16.58 - \frac{2.1\,x\,10^4}{8.3144T} - 1.86\,x\,10^{-2} W_{\%PEGMA})}$	(3)
$kp_{11} = k_{i1} = (\frac{1}{kp_1^0 \exp(-Bw_{M,MAA})} + \frac{1}{K_D C_E^{\beta}})$ $C_E = 2(\frac{w_{NaOH}}{MW_{NaOH}} + \frac{w_{NaHCO3}}{MW_{NaHCO3}} + \frac{w_{M,MAA}}{MW_{MAA}})$ $kp_1^0 = 2.5 \times 10^5 exp(-1880.0/T)$ $B = 1.92$ $\beta = 2.18$ $K_D = 201$	(4), (5)
$kp_{12} = \frac{kp_{11}}{r_1}$ $r_1 = 0.07 + b_1 \cdot W_{M,MMA}$ $kp_{21} = \frac{kp_{22}}{r_2}$ $r_2 = 9.89 + 117.21 \cdot W_{M,MMA}$	(6)
$ktrm_{11} = 0.353\ at\ 50°C\ for\ non\ ionized\ MAA$	(7)
$ktrm_{22} = 2.0\,x\,10^{15} exp^{(-\frac{46.1}{RT})}\ for\ MMA$ $ktrm_{12} = ktrm_{21} = \sqrt{ktrm_{11} x\ ktrm_{22}}$	(8)
$kt_{11} = kt_{12} = kt_{22} = \frac{1}{\frac{1}{k_{SD}} + \frac{\eta_r}{k_{TD}^0}}$ $\eta_r = exp^{(C_\eta x)}\ x{:}weight\ fraction\ of\ polymer$ $cd = 0.8$ $k_{TD}^0 = 1 \times 10^9$	(9)

Model Validation:

Figure S2 shows the experimental evolution of the instantaneous conversion of MAA and PEGMA5 in semibatch starved reactions and different monomer ratios and the model prediction.

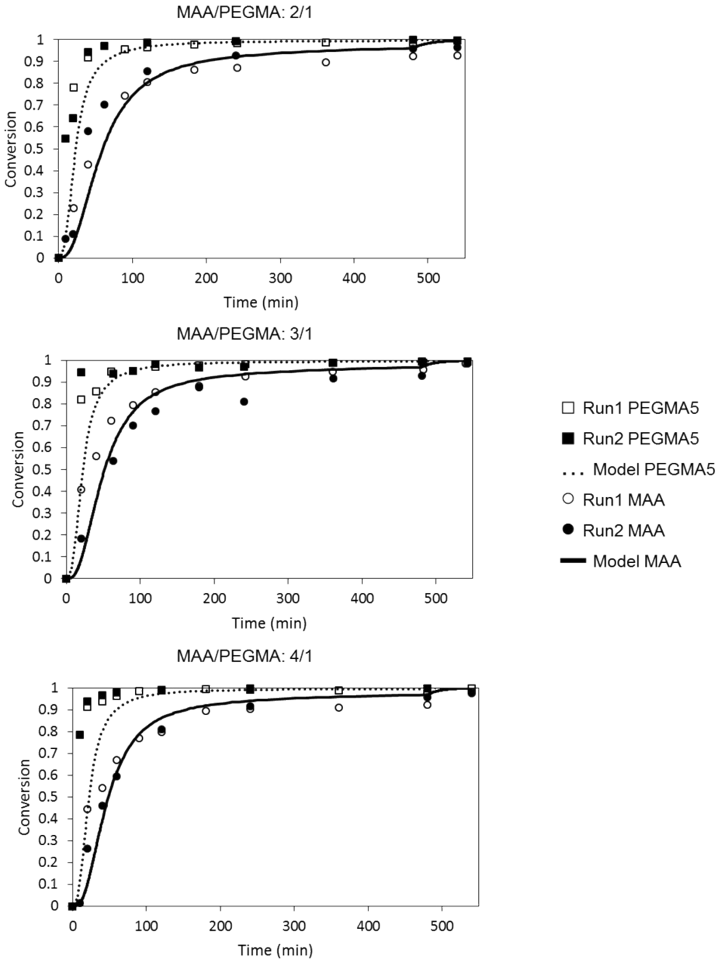

Figure S2. Instantaneous conversion evolution of MAA and PEGMA5 monomers in monomer starved semibatch experiments. Dots are experimental data and lines (solid (MAA) dashed (PEGMA5)) model predictions.

Optimal Addition Strategy:

Table S2. Recipe for the synthesis of the reactions with different comonomer ratio employing optimal monomer addition strategy.

Reaction	**Optimal (2/1)**			**Optimal (3/1)**			**Optimal (4/1)**		
Ingredients	**IC (g)**	**FMAA (g)**	**FPEGMA (g)**	**IC (g)**	**FMAA (g)**	**FPEGMA (g)**	**IC (g)**	**FMAA (g)**	**FPEGMA (g)**
MAA	19.70	45.95		25.00	58.33		28.90	67.41	
PEGMA	8.80		105.52	8.20		88.60	8.80		74.85
H_2O	340.76	48.38		317.24	61.39		301.71	70.97	
NaOH	6.12	20.04		11.48	25.44		13.20	29.40	
$NaHCO_3$	1.08			1.13			1.11		
KPS	3.59			3.61			3.60		
Total	380.05	114.37	105.52	366.66	145.16	88.60	357.32	167.78	74.85

Figure S3 shows the evolution of the jacket and reactor temperature as well as the evolution of heat released during the reaction performed using and optimal addition strategy to produce a homogeneous copolymer with MAA/PEGMA5 4/1. The evolution of heat released during the first minutes of the reaction was easily controlled by the control system of the reactor and temperature only deviated in the first few minutes of the polymerisation. Indeed after the first 20 minutes of the polymerisation the reactor was heated in order to maintain at the desired reaction temperature of 90 ºC.

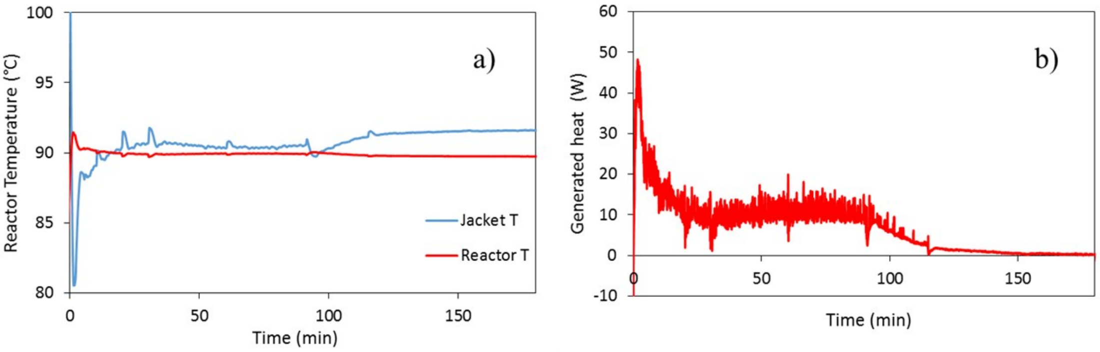

Figure S3.a) Time evolution of the jacket and reactor temperatures during the synthesis of optimal MAA/PEGMA5 = 4/1 copolymer. b) Time evolution of the generated heat for the optimal MAA/PEGMA5 = 4/1 reaction.

Measurements of the sequence distribution along the reaction

In order to verify that homogeneous composition copolymers were produced along the reaction the monomer sequence distribution was analysed to samples withdrawn from the reactor at different monomer conversions for the MAA/PEGMA5 = 3/1 reaction employing ^{13}C-NMR. Figure S4 and Table S3 show the multiplicity of the carbonyl peak of the MAA units in the chains and the calculated fractions of triads after deconvolution of the signal into pentads, respectively. Also in Table S3 the ideal random copolymerisation triads are presented for comparison with those produced in the optimal experiments.

Note that the ideal triad fraction at different times is not exactly the same due to the experimental deviation from the targeted value. However, the experimental and ideal values of the triads are very close between them, which is and indication that the homogeneity of the copolymer is maintained during the whole process of the reaction.

Table S3. Fraction of the triads obtained from the ^{13}C-NMR measurements and the ideal fractions of triads (random copolymerisation) for the optimal addition experiment MAA/PEGMA5 = 3/1 at different reaction times. A is MAA unit and B is PEGMA5 unit.

	Experimental			Ideal*		
	Triad			Triad		
Reaction	(AAA)	(AAB)	(BAB)	(AAA)	(AAB)	(BAB)
MAA/PEGMA5: 3/1 (t20)	0.346	0.300	0.070	0.367	0.291	0.057
MAA/PEGMA5: 3/1 (t60	0.397	0.288	0.041	0.383	0.288	0.054
MAA/PEGMA5: 3/1 (tfinal)	0.410	0.282	0.050	0.408	0.284	0.049

*Calculated using a Bernoullian model. Y_{MAA} is the composition referred to MAA monomer.

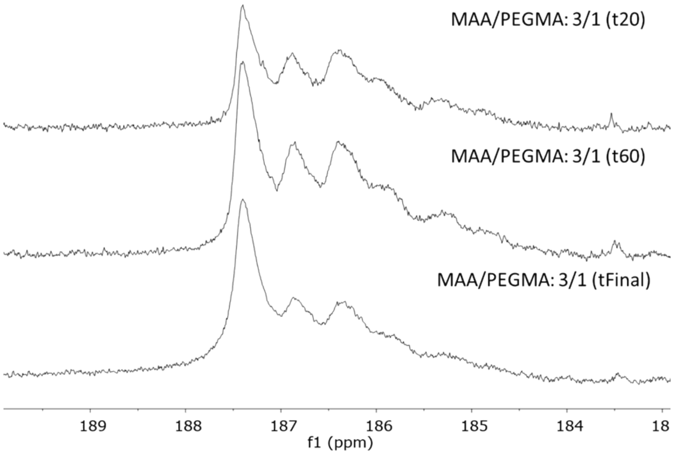

Figure S4. ^{13}C-NMR spectra of the carbonyl area corresponding to the carboxylic monomer of the copolymers MAA/PEGMA5 = 3/1 synthesized employing optimal addition policies at different times of the reaction.

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