Closed-loop multi-target optimization for discovery of new emulsion polymerization recipes

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Electronic Supplementary Information

1. MOAL algorithm

1.1 Definition of the input variables

Reaction conditions:

- reaction temperature
- feeding time 1
- feeding time 2
- post-processing time (time of the reaction to continue after feeding time has finished)
- P (ratio of initiator solution fed in the reactor during feeding time 1 and 2)

Starting material:

- amount of water
- amount of initiator solution (7% concentrated)
- amount of seed (30% solid content)

Feeding:

- amount of surfactant solution (15% concentrated)
- amount of CTA
- amount of styrene
- amount of butyl-acrylate
- amount of water for initiator solution which get fed into the reactor
- amount of initiator which needs to get solubilized in the water

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The highly dimensional decision space of fourteen variables was chosen to allow the discovery of new recipes for the target of high conversion and particle size of 100 nm. The fourteen variables were relaxed as much as possible to allow the discovery of new recipes with the MOAL algorithm. However, only physical constraints were made to obtain feasible recipes, as for the amount of surfactant and initiator the water solubility was taken into account or another example for the reaction temperature the activation temperature of the initiator and the boiling point of water were taken into account.

1.2 Definition of constraints for variables

The following are the reaction settings (input variables for the model considered):

- M^1_I, M^2_I, I_I, E_I, and W_I are the initial amounts of monomers, initiator, emulsifier and water respectively. T is the reaction temperature, CTA is the amount of chain transfer agent and P_0 is the amount of polymer in seed.
- M^1_F, M^2_F, E_F, I_F are the fed amounts of monomers, emulsifier and initiator respectively. WE_F and WI_F are emulsifier and initiator solutions in feed. WI_F is split into two parts pWI_F and $(1 - p)WI_F$ (where $p \in (0, 1)$) and is added in two stages.
- F^1_t, F^2_t are feeding times for adding pWI_F and $(1 - p)WI_F$ respectively and P_t is the post feeding time. The total reaction duration is the sum of F^1_t, F^2_t and P_t.

The ranges of the variables and constraints are:

1. $M^1_I = M^2_I = 1 \cdot 10^{-10}$g and $E_I = E_F = 1 \times 10^{-4}$g. These are kept constant for all recipes.
2. $W_I, WE_F, WI_F \in (0, 1500\text{g}]$ and $225 \leq WI + WE_F + WI_F \leq 1500$.
3. $I_I \in (0, 0.2WI)$ and $I_F \in (0, 0.2WI_F)$.
4. $F^1_t, F^2_t, P_t \in (0, 180\text{min}]$ and $30 \leq F^1_t + F^2_t \leq 180$.
5. $T \in [65, 95]$ in degrees Celsius, $CTA \in (0, 20\text{g}]$ and $P_0 \in [5, 30\text{g}]$.
6. $M^1_F, M^2_F \in (0, 1500\text{g}]$ and $150 \leq M^1_F + M^2_F \leq 1500$.
7. The final constraint is that the overall volume of the ingredients must not exceed the capacity of the reactor (3L).

2. ***In silico* optimization using a physical model of emulsion copolymerisation**

In silico optimisation using a physical model of emulsion copolymerisation revealed 18 feasible recipes within 84 experiments.

Table S1: Given recipes from the MOAL algorithm to gain the target of full conversion and 100 nm particle sizes during the simulations.

Exp. No.	T (°C)	water[2] (g)	initiator[3] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[4] (g)	CTA[5] (g)	SDBS solution[6] (g)	water for initiator feed (g)	P[7]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
1	89.44	175.2272	64.0193	12.18	31.38	98.44	28.94	19.30	189.8698	984.95	0.96	95.6137	171.63	437.80
2	92.47	1185.0349	310.8302	30.02	4.98	122.17	23.94	14.86	19.6229	19.93	0.17	2.8144	53.44	103.00
3	67.91	885.8431	112.3602	5.94	73.09	68.68	24.14	15.90	72.7057	154.94	0.45	20.0282	835.92	75.00
4	85.39	172.4091	8.2065	100.54	1.44	105.35	10.60	15.03	226.4839	334.62	0.70	59.6225	790.75	90.70
5	69.48	465.1882	47.3156	37.05	106.95	63.00	9.91	5.02	54.2950	16.02	0.35	2.6613	516.80	388.26
6	73.58	897.2619	136.5438	8.74	5.74	95.54	24.48	18.68	38.0844	145.10	0.47	0.3454	98.14	454.54
7	74.34	148.8983	35.8536	45.42	16.56	134.67	16.26	1.68	171.7285	528.14	0.15	87.2294	873.37	0.26
8	78.28	347.2282	0.6437	119.52	23.21	15.20	14.99	5.20	11.0042	1.19	0.91	0.0431	73.66	135.18
9	91.08	530.1331	30.7381	98.26	20.95	92.38	15.05	1.52	104.1213	40.68	0.18	1.9522	35.42	726.52
10	93.34	416.2814	56.2345	60.93	11.57	140.45	14.74	4.83	175.5282	24.99	0.13	4.7076	828.75	36.59
11	72.04	554.5336	3.4167	6.16	19.66	131.71	21.19	9.02	66.0478	16.21	0.74	0.6125	197.67	324.07
12	83.77	98.9564	36.7875	71.25	32.74	80.42	12.66	10.17	572.4899	448.34	0.79	57.7748	536.55	66.37
13	75.52	1245.7895	274.1516	72.42	10.58	54.22	16.77	4.61	148.9677	5.35	0.23	0.1827	193.44	77.94
14	92.70	142.9581	51.7440	77.66	11.03	46.45	15.22	11.90	165.3393	280.45	0.71	12.4379	91.53	127.64
15	77.73	74.6142	7.8340	4.39	135.39	131.46	17.22	11.57	189.3298	279.24	0.96	30.5385	197.67	320.65
16	94.60	419.7988	66.8845	34.63	9.24	145.63	9.50	16.47	12.1369	9.83	0.54	1.9035	97.83	60.71
17	81.00	753.5780	274.9433	2.30	7.51	173.61	14.26	11.64	120.3905	30.53	0.53	3.6921	747.55	58.79

[2] Amount of water used in the reactor as starting material

Exp. No.	T (°C)	water[8] (g)	initiator[9] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[10] (g)	CTA[11] (g)	SDBS solution[12] (g)	water for initiator feed (g)	P[13]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
18	83.87	655.0419	40.0829	147.45	10.56	111.44	12.37	1.69	66.2844	56.82	0.76	10.5528	244.29	50.60
19	92.86	274.1051	80.3030	29.23	24.99	34.70	12.17	6.05	372.4776	240.80	0.93	41.5467	513.92	24.82
20	73.76	142.7280	47.2565	104.35	49.27	169.91	7.94	13.16	121.2492	8.03	0.90	0.3706	82.45	366.35
21	84.81	476.9154	187.5606	91.78	10.22	156.19	24.58	2.94	48.9056	85.51	0.52	19.2582	280.87	76.59
22	66.63	816.0207	225.3879	76.78	1.55	171.41	6.64	4.22	162.5487	38.81	0.78	3.4212	299.03	45.50
23	66.72	818.1133	226.1891	77.45	2.26	171.69	6.84	4.14	162.3188	43.07	0.78	2.5460	301.00	42.37
24	94.35	1305.2877	267.1772	59.25	40.69	151.53	8.05	5.02	12.2650	13.48	0.69	3.0595	197.34	208.11
25	76.29	257.2994	62.5430	101.75	29.97	164.92	13.91	0.52	31.1544	461.69	0.96	68.1298	372.37	21.01
26	82.49	388.9864	50.8130	13.85	62.12	165.37	13.56	6.45	242.8972	131.39	0.63	24.3324	263.23	119.17
27	92.79	678.2930	104.4728	20.42	9.27	117.23	6.65	2.97	284.1747	49.87	0.38	3.1411	370.16	8.42
28	88.11	106.6388	29.5456	30.56	29.21	120.89	16.94	12.33	31.1767	15.54	0.83	3.7097	158.43	227.35
29	90.88	442.8715	177.8230	133.62	20.48	149.92	5.98	11.83	958.1551	3.42	0.11	0.0920	324.33	72.58
30	92.89	207.2628	14.3615	35.24	6.78	79.65	7.15	12.21	4.1564	291.10	0.80	14.7623	435.79	23.82
31	73.21	570.1065	180.0786	42.00	0.72	174.46	8.02	2.85	45.8876	6.64	0.68	0.1352	116.03	223.58
32	94.89	837.1270	244.6972	111.24	2.37	171.08	20.99	7.62	30.5690	28.51	0.02	0.9960	425.02	11.71
33	79.28	177.4819	9.7503	32.22	17.38	105.14	15.21	0.02	1023.9904	126.70	0.99	22.2270	223.89	74.50
34	88.62	213.0711	8.2343	148.95	0.60	164.63	20.31	9.29	36.5067	542.40	0.77	90.3888	330.92	90.43
35	79.71	437.7618	49.1669	3.21	21.72	149.99	13.54	6.80	44.5403	359.46	0.87	0.7212	312.63	0.83
36	93.11	217.8358	41.6004	37.55	0.42	147.20	13.59	3.38	66.3183	142.81	0.46	25.5331	296.71	78.18
37	94.28	854.0755	330.0775	0.70	0.65	175.71	13.76	8.95	36.3154	13.35	0.47	1.4960	326.82	106.84

[8] Amount of water used in the reactor as starting material
[9] Amount of initiator used in the reactor as starting material
[10] 15% solid content, particle size 70 nm
[11] Chain transfer agent
[12] 15% surfactant solution
[13] Ratio of initiator solution fed in the reactor during feeding time 1 and 2

Exp. No.	T (°C)	water[14] (g)	initiator[15] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[16] (g)	CTA[17] (g)	SDBS solution[18] (g)	water for initiator feed (g)	P[19]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
38	85.20	174.7768	14.3027	2.59	30.58	100.05	18.90	1.18	333.9396	123.05	0.67	20.7425	397.49	8.37
39	90.81	450.3442	174.8398	134.19	18.72	150.30	6.18	11.83	965.7990	1.89	0.11	0.0920	322.72	75.72
40	94.74	826.4459	244.3046	111.52	2.96	172.73	21.16	7.59	31.7338	31.78	0.01	0.9960	427.13	21.46
41	89.06	693.3275	76.5548	74.20	8.70	117.26	9.34	2.35	187.0076	53.22	0.55	5.8331	321.46	22.42
42	93.16	237.8954	30.2966	37.72	8.00	97.68	7.56	13.12	28.5434	219.80	0.74	11.8335	351.73	14.66
43	90.69	430.9316	173.1961	132.55	15.11	152.88	5.71	11.59	974.0777	17.07	0.10	0.2891	328.05	81.40
44	85.45	222.2561	20.5037	135.64	9.98	165.07	18.90	7.23	39.9115	537.13	0.81	82.8460	333.12	66.60
45	90.61	187.5799	31.9343	25.94	13.72	130.74	15.49	2.63	154.4909	120.55	0.54	22.9320	362.80	35.65
46	94.56	1191.2621	280.1312	43.40	28.89	156.85	9.35	6.12	16.0850	2.35	0.64	5.7987	234.03	192.77
47	90.27	442.1393	177.6721	133.69	22.16	150.77	5.94	11.48	972.0900	22.58	0.11	0.7007	297.59	54.48
48	91.25	468.7852	172.5955	134.34	18.77	153.14	6.27	11.92	955.3610	24.63	0.12	0.4082	334.09	74.05
49	94.18	309.2587	31.4047	33.61	9.95	111.53	8.38	14.06	6.7672	167.22	0.66	5.5580	292.93	60.24
50	90.85	460.1536	181.5803	134.67	16.83	146.39	5.97	11.97	965.0930	37.34	0.11	4.7451	303.95	53.93
51	82.83	118.9617	31.2128	55.90	36.88	142.93	13.46	12.81	68.6244	6.79	0.84	3.4610	143.62	279.11
52	90.66	635.6163	91.8040	46.52	9.58	113.06	7.71	2.60	236.2932	56.37	0.47	4.2662	362.63	15.63
53	86.57	652.6904	52.4649	118.37	14.67	110.91	10.77	2.16	125.2874	76.94	0.67	0.2237	262.94	84.18
54	89.77	665.6025	219.3979	102.26	7.45	165.24	22.67	5.42	31.2581	70.09	0.26	7.9809	351.97	42.84
55	81.11	433.0410	51.7649	6.97	41.44	157.52	13.45	6.50	137.4849	253.08	0.76	12.6945	289.95	42.79
56	79.50	249.8846	45.8414	115.19	22.40	162.38	15.47	2.72	43.2920	488.85	0.92	77.8887	328.46	49.80
57	90.61	501.0354	180.7299	134.65	22.33	151.23	5.80	11.99	943.3967	13.04	0.09	1.7629	322.28	55.11

[14] Amount of water used in the reactor as starting material
[15] Amount of initiator used in the reactor as starting material
[16] 15% solid content, particle size 70 nm
[17] Chain transfer agent
[18] 15% surfactant solution
[19] Ratio of initiator solution fed in the reactor during feeding time 1 and 2

Exp. No.	T (°C)	water[20] (g)	initiator[21] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[22] (g)	CTA[23] (g)	SDBS solution[24] (g)	water for initiator feed (g)	P[25]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
59	94.42	1452.9348	243.1767	81.38	54.98	143.50	6.05	4.06	12.7069	6.17	0.79	5.3161	152.91	246.24
60	83.42	370.3859	49.0708	15.47	78.73	172.37	13.50	6.55	302.5737	28.61	0.55	31.2722	271.71	167.69
61	93.16	416.4112	58.8484	32.84	8.51	100.77	7.07	8.34	119.0493	164.98	0.58	6.6379	376.40	12.55
62	94.53	858.3950	282.7818	59.95	2.52	173.91	17.86	8.46	35.3106	39.34	0.22	2.1792	368.58	47.64
63	65.32	881.1546	232.9378	82.79	2.14	170.79	6.20	4.30	188.4662	49.29	0.81	2.4904	348.02	12.15
64	91.13	456.2079	178.3100	138.49	18.46	149.88	5.80	11.18	935.1139	29.58	0.08	6.3430	335.44	32.40
65	90.62	482.1062	178.4476	135.26	20.31	145.31	5.81	11.93	951.1348	51.62	0.10	6.5174	322.78	57.91
66	89.85	447.3698	181.4941	138.58	16.33	144.96	5.87	11.87	962.9662	43.68	0.08	2.1428	333.22	56.80
67	90.38	451.6224	178.0494	134.31	17.37	150.67	6.00	12.58	960.6667	26.22	0.10	6.4494	331.02	36.24
68	92.08	332.1611	67.0774	46.51	6.68	129.10	12.90	9.37	38.7123	135.58	0.58	11.8720	288.05	69.98
69	94.39	226.6916	18.7218	25.42	4.80	126.51	9.48	8.23	35.7054	156.47	0.54	18.1945	309.99	90.72
70	90.94	448.4880	178.0838	133.18	16.54	148.15	5.19	12.06	956.5289	2.41	0.11	1.0993	307.97	40.53
71	90.30	712.5391	289.3471	22.48	6.16	169.56	16.83	6.70	11.6623	52.89	0.53	7.8271	313.15	109.08
72	92.42	331.3071	45.1083	28.78	8.75	91.17	7.03	9.85	83.1369	237.62	0.67	10.9768	386.90	9.92
73	68.73	744.6765	209.3359	66.83	0.91	174.43	6.91	3.53	149.6054	49.85	0.76	4.2339	249.45	121.03
74	91.19	475.6729	175.0724	136.70	21.21	150.31	5.67	12.16	939.4443	37.91	0.09	1.8902	318.54	78.13
75	85.93	274.6160	52.5205	61.02	24.34	156.29	9.57	14.88	68.5551	14.34	0.70	4.1577	111.97	216.87
76	90.94	433.0572	174.4790	128.70	16.76	151.08	6.19	11.89	965.8527	17.60	0.09	1.5152	305.85	39.44
77	92.84	523.2731	82.8404	28.74	9.16	114.31	6.90	6.79	204.9247	85.53	0.50	4.4831	352.10	3.68
78	93.32	353.7939	48.7460	34.43	7.67	101.20	7.05	9.77	111.1732	166.28	0.64	10.3229	387.02	8.81

[20] Amount of water used in the reactor as starting material
[21] Amount of initiator used in the reactor as starting material
[22] 15% solid content, particle size 70 nm
[23] Chain transfer agent
[24] 15% surfactant solution
[25] Ratio of initiator solution fed in the reactor during feeding time 1 and 2

Exp. No.	T (°C)	water[26] (g)	initiator[27] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[28] (g)	CTA[29] (g)	SDBS solution[30] (g)	water for initiator feed (g)	P[31]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
79	82.73	256.5203	34.9808	126.40	15.66	162.97	17.24	4.89	70.3426	499.55	0.86	81.6503	342.98	50.15
80	90.08	681.8076	82.0161	57.30	7.46	114.89	8.72	2.45	217.7809	45.97	0.51	3.7445	356.05	31.48
81	85.68	1099.8902	215.0590	66.13	31.86	155.42	7.41	3.65	46.8603	6.61	0.74	5.3913	139.61	231.59
82	94.00	281.5141	11.7123	22.35	3.97	104.19	5.42	9.18	30.4506	199.86	0.57	2.5861	379.05	1.52
83	84.21	324.2543	36.9627	14.02	19.05	144.99	14.53	5.04	113.2485	263.60	0.74	11.2069	321.05	3.25
84	88.83	652.8495	69.5469	79.81	12.82	110.83	8.93	2.54	166.8276	62.98	0.54	5.2433	288.50	79.80

[26] Amount of water used in the reactor as starting material
[27] Amount of initiator used in the reactor as starting material
[28] 15% solid content, particle size 70 nm
[29] Chain transfer agent
[30] 15% surfactant solution
[31] Ratio of initiator solution fed in the reactor during feeding time 1 and 2

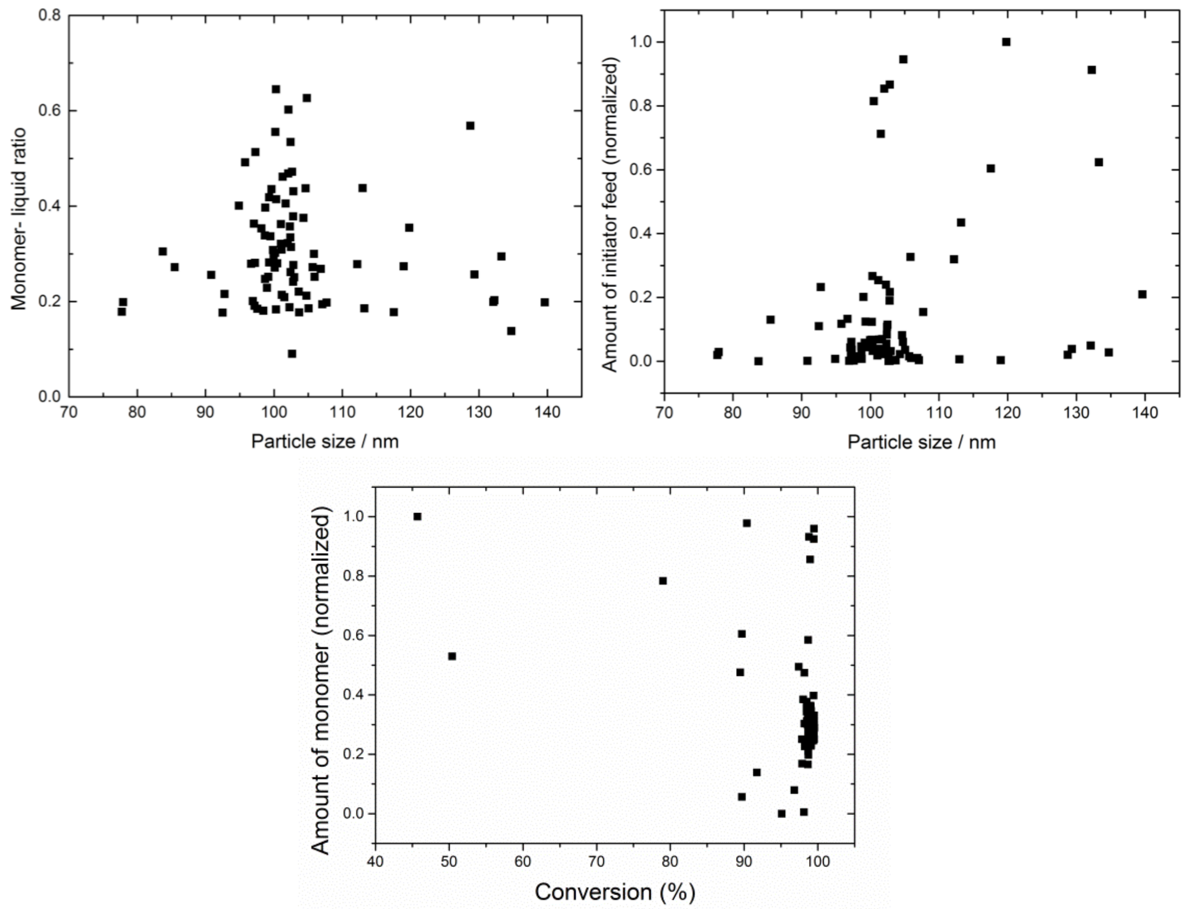


Figure S1. Results of the simulation of the emulsion polymerization model with the MOAL algorithm: the figures show a) monomer-liquid ration to the particle size; b) the correlation of the amount of initiator feed to particle size; c) the behaviour of conversion and amount of monomer.

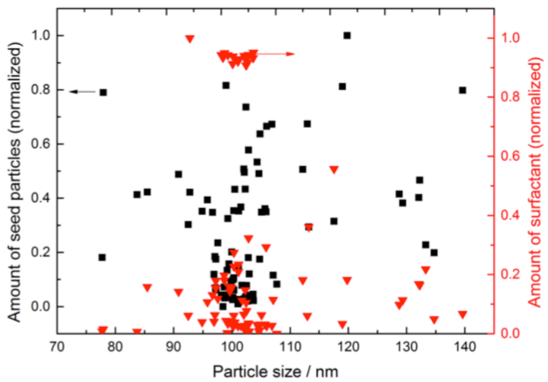


Figure S2. Results of the simulation of the emulsion polymerization model with the MOAL algorithm: shows the behaviour of the amount of surfactant on particle size and the amount of seed particles on the particle size.

Table S2. Results of conversion and particle size of *in silico* optimisation using a physical model of emulsion copolymerisation.

Exp. No.	Particle diameter	Conversion	Exp. No.	Particle diameter	Conversion
1	119.80	0.90	44	102.82	0.99
2	77.93	0.95	45	102.25	0.99
3	139.63	0.46	46	104.74	0.99
4	133.28	1.00	47	98.73	0.99
5	134.73	0.90	48	103.60	0.99
6	118.99	0.50	49	99.16	0.99
7	132.25	0.99	50	99.30	0.99
8	83.72	0.90	51	105.06	0.99
9	128.73	0.79	52	100.30	0.99
10	132.09	0.99	53	97.57	0.99
11	112.98	0.89	54	102.38	0.98
12	117.57	0.99	55	96.67	0.99
13	90.85	0.92	56	100.48	0.99
14	85.48	0.97	57	101.00	0.99
15	112.19	0.98	58	102.44	0.99
16	77.75	0.98	59	102.33	0.99
17	129.33	0.99	60	105.84	0.99
18	92.48	0.99	61	101.72	0.99
19	113.22	0.97	62	104.29	0.99
20	107.06	0.98	63	98.69	0.99
21	98.98	0.98	64	100.10	0.99
22	97.28	0.99	65	101.28	0.99
23	97.18	0.99	66	102.07	0.99
24	102.94	0.99	67	100.17	0.99
25	101.51	0.99	68	99.30	0.99
26	101.15	0.99	69	102.79	0.99
27	100.33	0.99	70	98.44	1.00
28	102.11	0.99	71	104.60	0.99
29	102.65	0.99	72	102.50	0.99
30	107.69	0.99	73	99.63	0.99
31	96.91	0.98	74	102.66	1.00
32	105.93	0.98	75	97.08	0.99
33	92.78	0.98	76	98.16	0.99
34	104.81	0.98	77	98.66	0.99
35	94.88	0.99	78	102.41	0.99
36	100.29	0.99	79	102.00	0.99
37	105.66	0.99	80	101.12	0.99
38	102.82	0.99	81	99.86	0.99
39	102.79	0.99	82	101.02	1.00
40	106.85	0.99	83	95.80	0.99

41	97.23	0.99	84	99.48	0.99
42	100.19	0.99			
43	103.66	1.00			

Table S3. Results of the validation of the *in silico* recipes.

Experiment	Conversion (%)	Particle size (nm)
Val. Exp.1	99.5	135
Val. Exp.2	12.2	-
Val. Exp.3	99.9	309
Val.Exp.4	42.2	214
Val.Exp.5	50.9	-
Val.Exp.6	65.3	49900
Val.Exp.7	91.1	178
Val.Exp.8	-	-
Val.Exp9	86.8	-
Val.Exp10	63.0	-
Val.Exp.11	84.0	1910
Val.Exp.12	48.7	4504

3. Experimental closed-loop optimization

3.2 Reaction setup

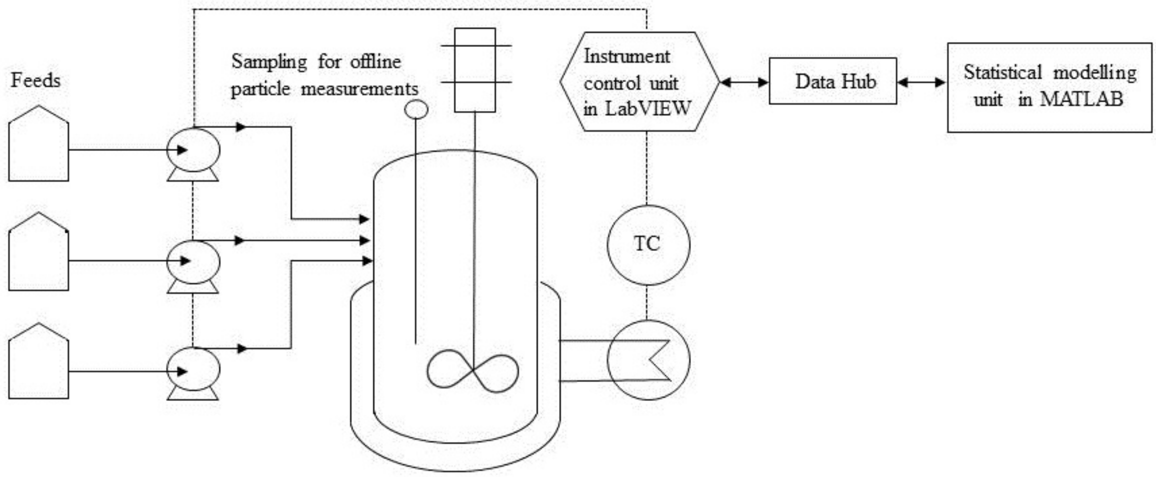


Figure S3. Automated semi-batch system incorporated feedback for discovery new recipes for emulsion polymerization reactions.

3.3 Emulsion polymerization recipe:

General composition of the system for copolymerization of styrene and butyl acrylate:[1]

Butyl acrylate: 77 g

Styrene: 7 g

$K_2S_2O_8$: 0.6 g

$NaHCO_3$: 0.03g

Aerosol MA80: 3.6 g

Aerosol 22N: 0.7

H_2O: variable to feed rate

Table S4. Given recipes from the MOAL algorithm to gain the target of full conversion and 100 nm particle size experimentally.

Exp. no.	T (°C)	water[32] (g)	initiator[33] (g)	feeding time 1 (min)	feeding time 2 (min)	post-processing time (min)	seed[34] (g)	CTA[35](g)	SDBS[36] (g)	water for initiator feed (g)	P[37]	amount of initiator in feed (g)	styrene (g)	butyl acrylate (g)
1	81.41	1395.06	43.9758	168.07	3.65	144.05	8.55	8.44	46.4872	3.39	0.96	0.4444	168.11	27.90
2	85.36	885.16	69.4367	21.97	75.09	5.73	11.92	0.92	29.7184	227.47	0.69	14.4263	49.35	707.62
3	76.45	955.06	35.6950	46.10	37.07	127.69	23.87	5.52	167.1877	51.61	0.16	1.2283	789.67	11.27
4	82.56	383.42	19.5616	74.03	28.39	172.67	18.68	2.77	18.9519	27.81	0.84	1.4143	304.23	878.20
5	75.50	119.43	14.7149	35.52	54.40	105.35	18.74	18.34	101.8241	192.64	0.75	14.6575	69.52	126.17
6	85.54	147.33	20.9479	96.05	22.63	178.89	1.71	0.96	59.0770	11.32	0.20	1.0594	157.98	0.67
7	73.23	227.02	29.5471	127.13	6.35	103.04	2.59	2.24	0.3336	2.43	0.36	0.0254	133.33	2.52
8	65.03	97.74	2.6074	1.39	14.41	170.24	7.52	0.18	46.0400	41.76	0.24	7.5326	203.89	0.26
9	94.29	78.43	2.1167	1.97	27.22	131.05	4.52	0.39	109.7996	5.23	0.12	1.2643	177.47	22.05
10	66.99	132.74	9.2963	12.81	55.51	95.04	4.26	0.50	14.5027	0.54	0.09	0.0696	236.21	1.94
11	66.98	179.66	24.4615	2.62	22.06	167.81	8.11	2.16	103.8970	19.82	0.03	2.4006	47.77	14.12
12	71.91	175.92	21.1791	29.79	0.08	173.61	3.58	3.97	0.5594	0.03	0.08	0.2161	142.14	52.62
13	72.84	204.25	18.2128	14.08	53.70	143.67	3.58	0.72	3.1579	0.35	0.16	0.1457	145.54	24.20
14	65.92	197.34	22.4066	118.79	3.86	176.34	13.21	0.20	58.4129	13.12	0.03	0.5869	84.56	10.75
15	65.76	198.95	21.8410	118.55	4.33	174.86	13.04	0.15	54.9401	12.60	0.03	0.2885	85.59	12.89
16	67.05	144.09	8.0615	69.33	45.50	146.14	6.33	0.69	146.0732	3.50	0.32	0.2929	26.85	64.41
17	71.99	258.65	1.6127	10.84	44.69	177.91	11.63	0.50	52.1584	3.76	0.49	1.1670	59.78	11.91
18	72.23	252.94	1.7877	9.63	46.32	177.39	11.39	0.46	54.8137	2.36	0.49	0.4100	61.74	14.50
19	66.68	131.15	2.4491	56.05	0.74	145.25	4.51	1.22	73.0387	16.87	0.17	2.2665	170.10	0.66
20	66.41	131.53	2.0953	56.80	0.74	146.62	4.54	1.24	72.4129	14.64	0.18	2.0335	172.87	0.67

[32] Amount of water used in the reactor as starting material
[33] Amount of initiator used in the reactor as starting material
[34] 15% solid content, particle size 70 nm
[35] Chain transfer agent
[36] 15% surfactant solution
[37] Ratio of initiator solution fed in the reactor during feeding time 1 and 2

Table S5. Performance of the experimental optimization of the recipe with MOAL algorithm. In red the unfeasible experiments are marked.

Exp. No .	Particle size (nm)	Conversion	Feasibility
1	169	0.99	1
2	0	0.00	-1
3	156.75	0.98	1
4	537	0.70	1
5	0	0.00	-1
6	263.3	0.73	1
7	303.75	0.53	1
8	192	0.97	1
9	0	0.00	-1
10	175.6	0.27	1
11	70	1.00	1
12	301.3	0.57	1
13	268.2	0.62	1
14	151.25	1.00	1
15	133.75	1.00	1
16	65.52	1.00	1
17	107.7	1.00	1
18	92.52	1.00	1
19	115.15	0.98	1
20	105.75	0.98	1

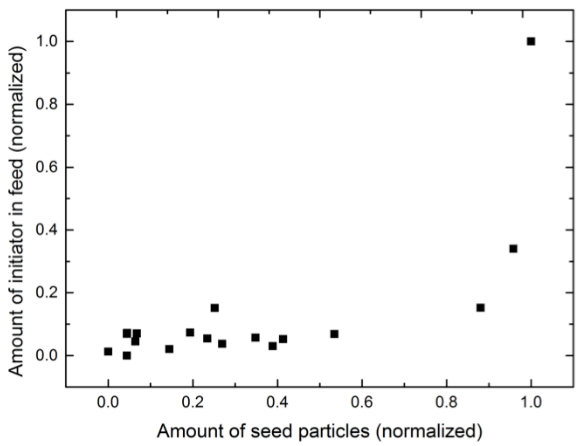


Figure S4. Results of the experiment of the emulsion polymerization model with the MOAL algorithm: the figures show the correlation of the amount of initiator feed to the amount of seed particles.

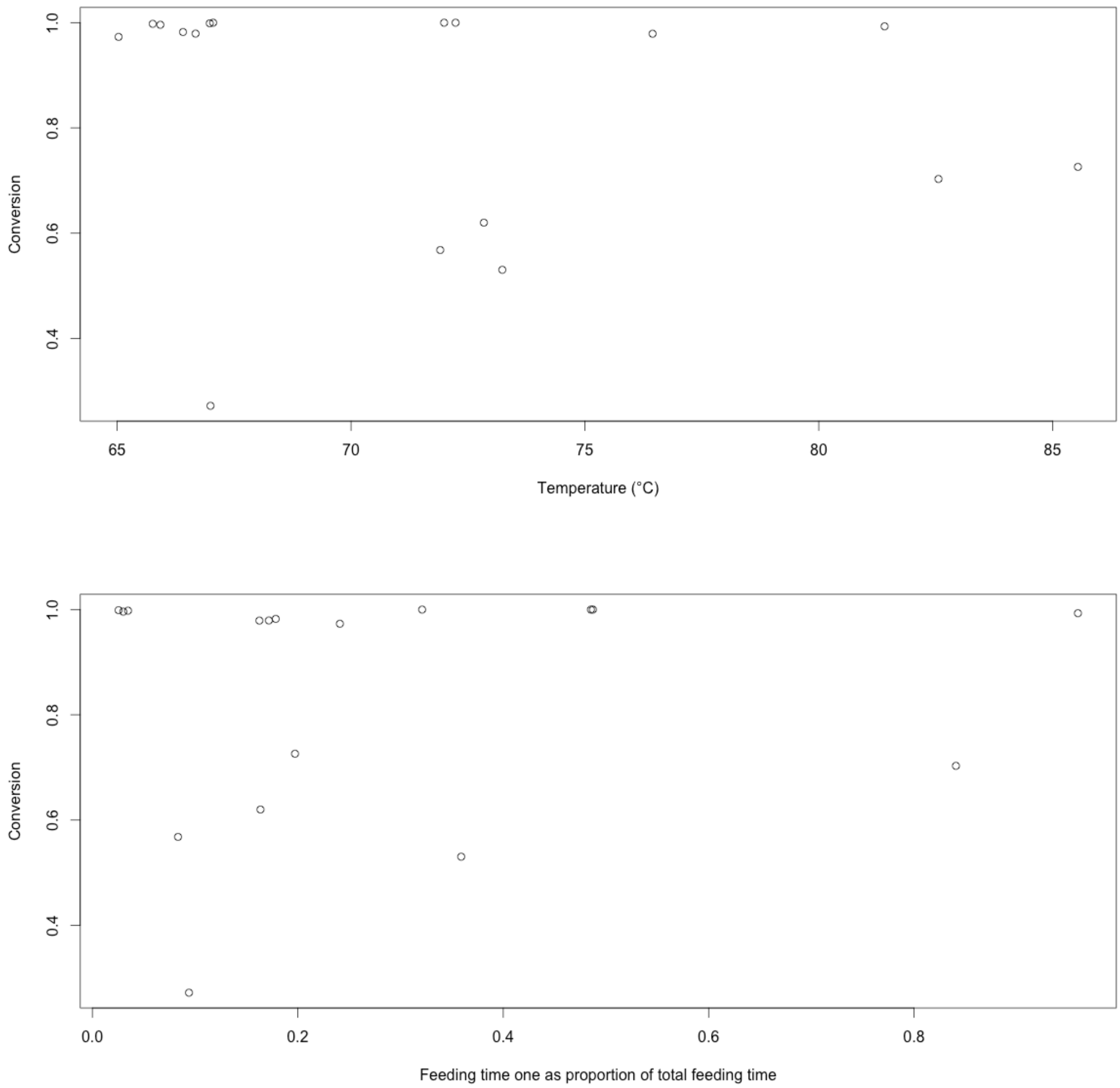
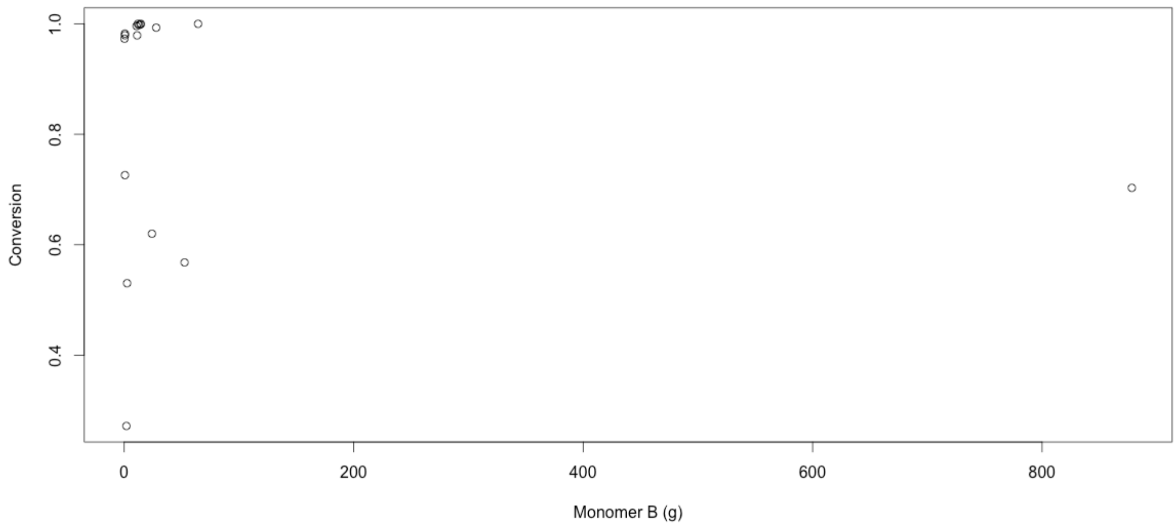


Figure S5. Each plot shows the correlation of one of the fourteen variables with conversion. In none of these plots a trend can be seen. Due to the low number of experiments and only three experiments which fulfilled the targets, it is not surprising that no trend can be obtained.



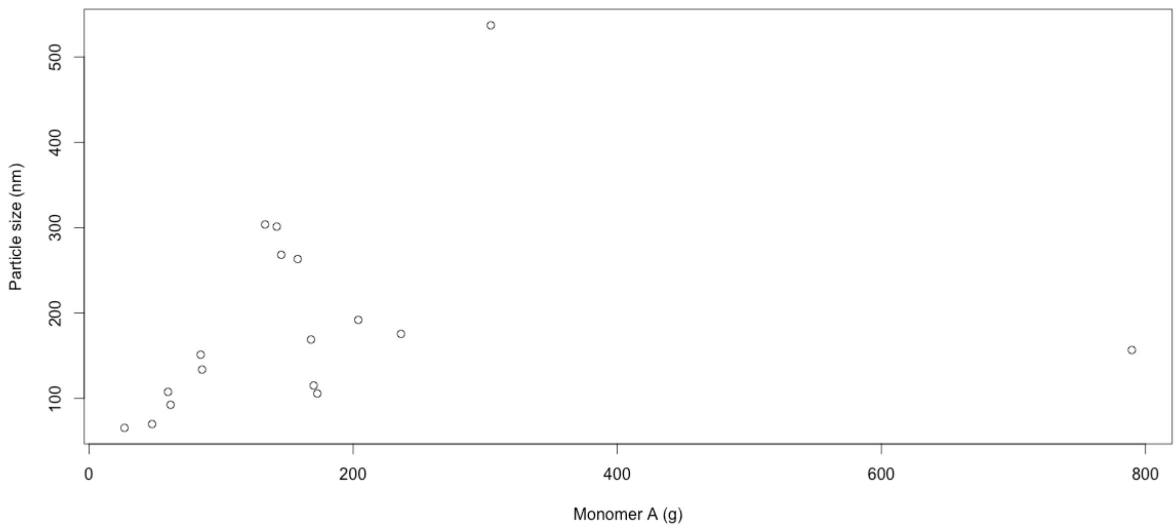


Figure S6. Pair-wise correlation of the fourteen variables regarding particle size. Although the correlation of particle size with monomer, surfactant and initiator is known, this trend cannot be obtained from the low number of experiments.

Reference:

[1] A. Cruz-Rivera, L. Rios-Guerrero, C. Monnet, B. Schlund, J. Guillot, C. Pichot, *Polymer.* **1989**, *30*, 1872–1882.