Supporting Information

Functional Prototyping of 3D Printed Reactors for Continuous Emulsion Polymerization

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To Section 3.1 3D Printing of the Reactors

X 4 and SMX geometry	
cross bars	4x2 mm
length	340 mm
diameter	25 mm

X4 mixing element (continuous in both reactor halfs)

SMX Mixing element (identical in each half of reactor)

Figure S1. Details of static mixing elements X4 and SMX as used in reactors b and c, respectively.

To Section 3.2 Determination of temperature profiles and steady state

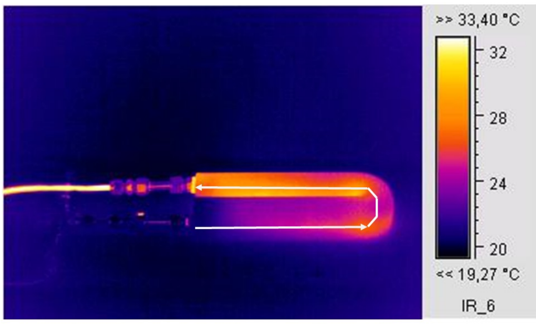

Figure S2. Details of determination of temperature profiles from IR camera figures: the data was evaluated following the white line (the software IC-Report DuoVision 1.07.35S only allowed evaluation along straight lines).

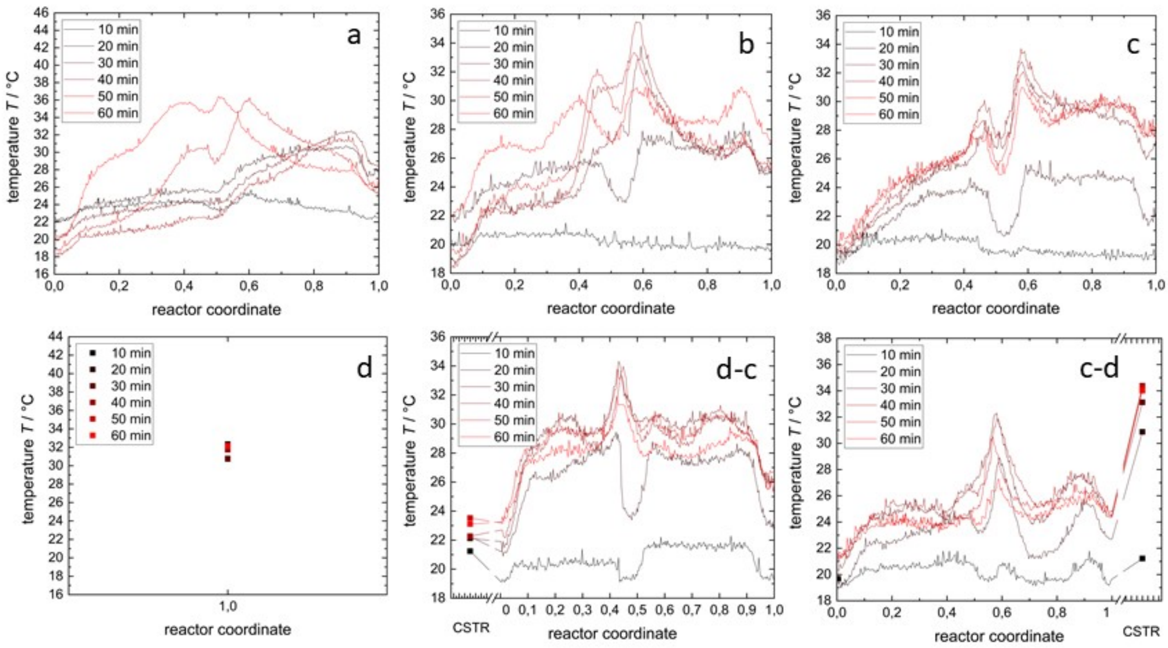

Figure S3. Temperature profiles along the reactor axis based on thermal images of the investigated reactors (a) empty tubular reactor, (b) tubular reactor with X4 mixing, (c) tubular reactor with SMX mixing, (d) continuously stirred tank reactor, (e) reactor combination of (c) and (d) for τ = 10 min.

To Section 3.3 Comparing polymerizations in single reactors

Looking at the MWD of the TR SMX mixing elements and the CSTR (Figure S4c and d), almost no shifting of the center of the curves in the stationary state is observed. These results agree with the constant product properties observed in the previous evaluations.

Contrary, the tubular reactor without mixing elements had a significant shift in the center of the MWD curve to higher molar masses in the course of the experiment (Figure S4a). The parabolic velocity profile in the laminar flow regime of a tubular reactor causes a broad residence time distribution.[39] Subsequentially, also the molecular mass distribution broadens. Even more important, the significant increase of the molecular weight is a typical sign of polymer aggregation and agglomeration typical for fouling.[40] Since agglomeration and fouling can crucially affect the process and the product, it is assumed to be the most explicit explanation for the fluctuations during the experiments. The MWD of the CSTR (Figure S4d) shows an additional plateau of the curve. The primary maximum is located at about 10^5 g mol^{-1}, while the additional plateau is found at higher molecular masses of about 10^6 g mol^{-1}.

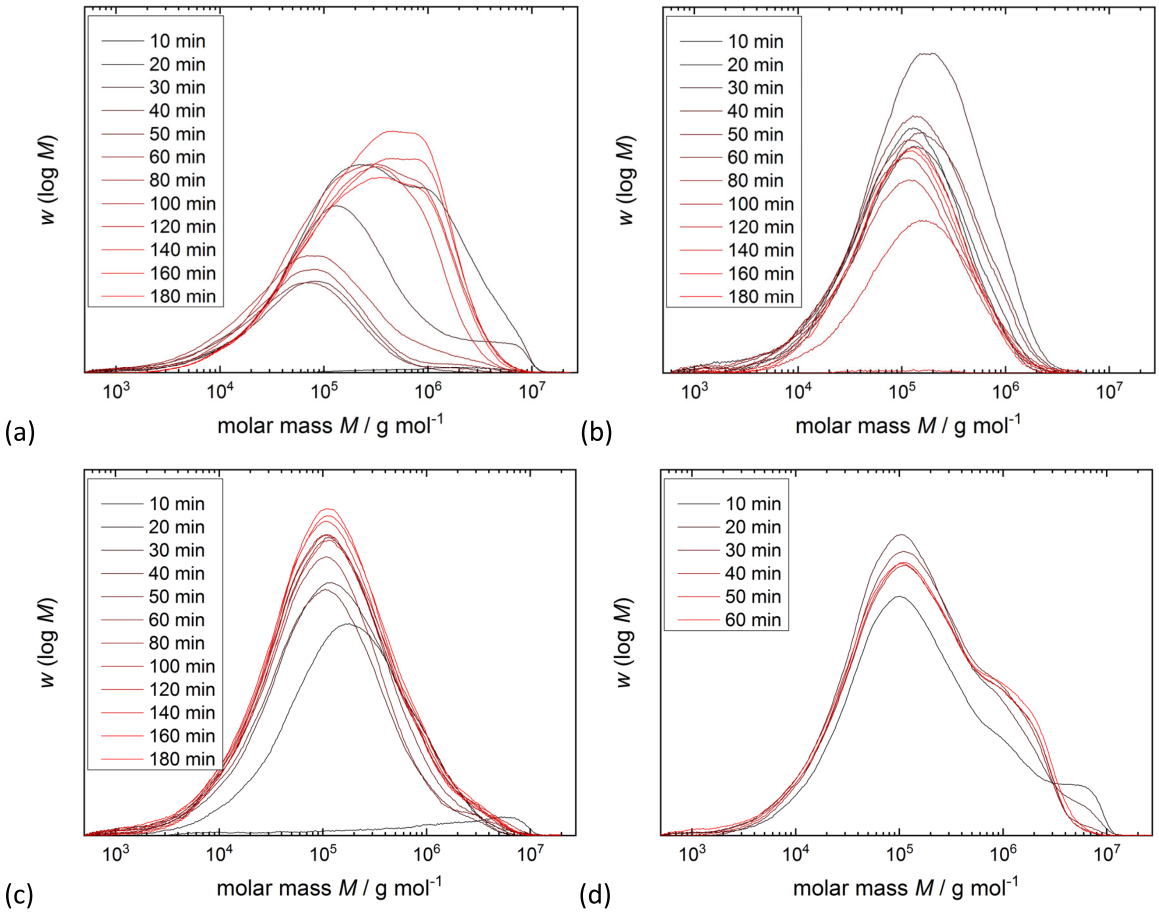

Figure S4. Molecular weight distribution of S/BA-copolymer in dependency of the time obtained by polymerization in the tubular reactor without mixing elements (a), with X 4mm mixing elements (b), with SMX mixing elements (c) and the CSTR (d).

The reactor b was not cleaned but only drained after a reaction day. Afterwards, the reactor was dried for 65 days under a moderately compressed air stream to determine the polymer mass of the fouling most exactly. After being dried, the polymer mass was 33.74 g. Furthermore, the main areas of fouling were localized by cutting the reactor open after the drying process. Figure S5 shows the fouling on the inside of the inlet and the outlet of the PLA reactor. Figure S6 shows the bend of the reactor in a close-up. While the inlet is free from fouling, in the other locations polymer was found. The most polymer was located at the bottom of the bend, where no mixing elements are placed. Also, polymer deposits are visible between the static mixing elements, but less than in the other mentioned locations. The mixing elements seem to counteract deposition of the polymer but cannot wholly prevent it. To investigate this in more detail, extensive experiments with the different reactor types, flow rates and operating hours could be performed.

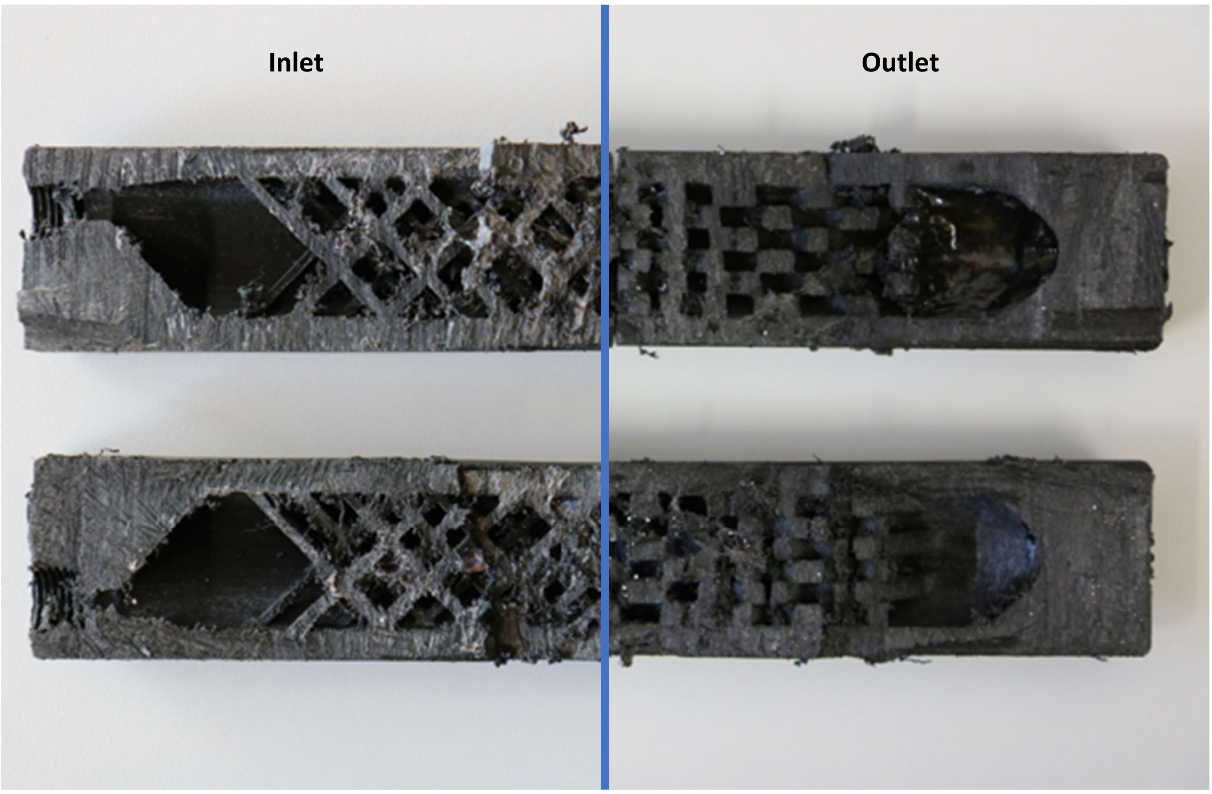

Figure S5. Fouling at the inlet (left) and outlet (right) of the reactor with X 4 mm mixing elements. The inlet was cut vertically, the outlet horizontally.

Figure S6. Close-up of the fouling at the bend of the PLA reactor with X 4 mm mixing elements.

To Section 3.4 Polymerizations in dual reactor combinations

The MWD of the polymer was uniform throughout the processes of both modular set-ups (Figure S7). Proceeding from the previous results, especially (1) TR (SMX) and (2) CSTR showed highly consistent MWDs. After more substantial fluctuations of the distribution during the process start-up also the set-up (1) CSTR and (2) TR SMX stabilized after ca. 3 τ. Furthermore, the products of both modular set-ups seem not affected by fouling according to the GPC results. Compared to the single CSTR (compare Figure S4d), no remarkable plateaus at higher molecular masses are found which indicates a more uniform residence time distribution of the latex particles in the reactors.

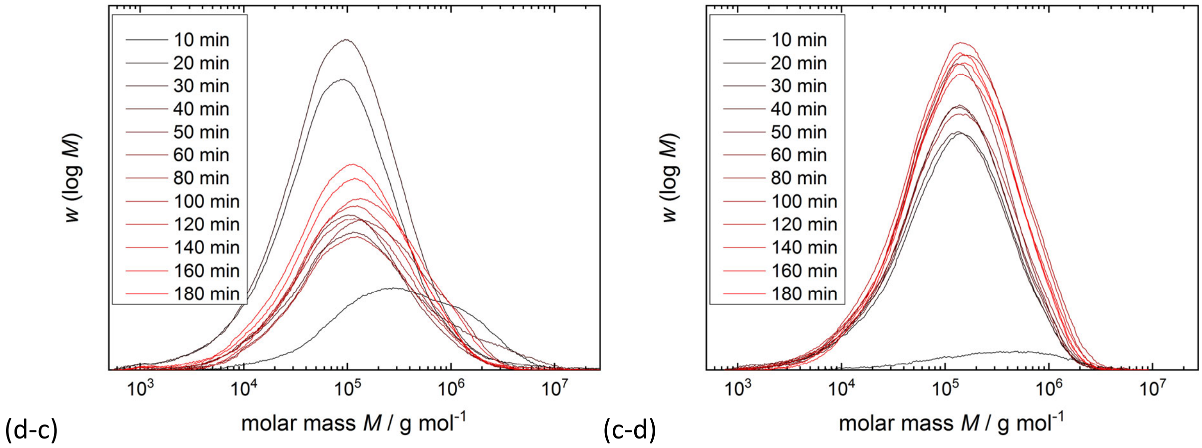

Figure S7. Molecular weight distribution of S/BA-copolymer in dependency of the time for the investigated reactor combinations d-c and c-d.

References

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