Supplementary Information (SI) for Polymer Chemistry.

Electronic Supplementary Information

Group Transfer Polymerization by Argon Droplet Flow for Continuous, Consistent Production of Well-defined Polymers

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Materials

All reagents were commercially available, and used as received without any purification. 2-Methoxypropyl-1-acetate (PEGMEA) was purchased from Nippon Nyukazai.

Analysis

Monomer conversion determination by Gas Chromatography (GC)

GC analysis was performed on a Shimadzu GC-2014 instrument equipped with an FID detector to determine monomer conversions of methyl methacrylate (MMA) and butyl methacrylate (BMA). A small amount of benzaldehyde as an internal standard was added to a polymer containing solution, and diluted in *n*-methylpyrrolidone for sample preparation. For monomer conversions of MMA, an Agilent DB-FFAP column was used under the following conditions: the initial oven temperature was 60 °C, and then the temperature was increased to 180 °C at 15 °C/min. For monomer conversions of BMA, a Shimadzu CBP10-M25-025 column was used under the following conditions: the initial oven temperature was 60 °C, and then the temperature was increased to 250 °C at 10 °C/min.

Molecular weight determination by Gel Permeation Chromatography (GPC)

The number-average molecular mass (M_n) and polydispersity index ($Đ$) of obtained polymers were determined by means of GPC analysis, using polystyrene as a standard. A polymer containing solution was dissolved in tetrahydrofuran (THF). A Waters Separation module e2695 and Waters

Refractive index detector 2414 were used with the combination of Straygel HR1, 2, 4 as the separation columns. THF was used as the mobile phase at a flow rate 1.0 mL/min at 35 °C.

Procedures for polymerization

General procedure for group transfer polymerization (GTP) in batch reactors (entry 1, 2 in table 1)

MMA and PEGMEA were dried over molecular sieves overnight before use. Dried MMA (2.88 g, 28.7 μmol), dried PEGMEA (6.86g), dimethyl ketene methyl trimethylsilyl acetal (MTS, 0.10 g, 0.574 μmol), and 0.8 M 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (P_4-*t*-Bu) solution in hexane (0.62 mg, 0.0006 μmol) were added to a 30 mL test tube, and then it was immersed in a 40 °C oil bath for 10 min while stirring. The same amount of methanol as MTS (0.10 g) was added, and the reaction mixture was kept while stirring for 1 min to quench the polymerization. The obtained viscous reaction mixture was analyzed for monomer conversions by GC, and M_n and $Đ$ by GPC without any work-up. For the large-scale batch reaction, a 100 mL flask was used instead of the 30 mL test tube, and the amount of each reagent was changed as follows: MMA: 17.26 g, 172.4 μmol, MTS: 0.60 g, 3.448 μmol, PEGMEA: 41.20 g, P_4-*t*-Bu solution in hexane: 3.71 mg, 0.0034 μmol.

General procedure for GTP in fully continuous flow (entry 3 in table 1)

PFA tubes with different internal diameter (i.d.) were purchased through Flon Chemical. A PFA tube was put together in a circle shape with ties, and immersed in an oil bath (Figure 6 and Figure S1). An exemplified procedure is written as below for the fully continuous flow (entry 3) in Table 1, whose reaction conditions were $[MMA]_0/[MTS]_0/[P_4\text{-}t\text{-Bu}] = 50/1/0.001$, $[MMA]_0 = 3.8$ mol/L in PEGMEA, (MMA+MTS)/(PEGMEA) = 30/70 in weight. A solution of MTS (5.00 g, 0.0287 mmol) and dried MMA (143.85 g, 1.44 mmol) was prepared in a bottle. In the other bottle, a solution of P_4-*t*-Bu solution in hexane (31.0 mg, 0.0287 µmol) and dried PEGMEA (343.00 g) was prepared. HPLC pumps (Intelligent Pump UI-22-410P, Flom, Inc.) were connected to the MTS and MMA solution, the P_4-*t*-Bu and PEGMEA solution, respectively. The flow rates were set 0.85 and 1.97 mL/min for the MTS and MMA solution and the P_4-*t*-Bu and PEGMEA solution, respectively. The two flows were mixed through MiChs α600 with i.d. of 0.6 mm, and then went to PFA tubes immersed in a 40 °C oil bath resulting in the total flow rate of 2.82 mL/min. The length and volume of the PFA tube with i.d. of 2.0 mm in the oil bath were 9.0 m and 28.2 mL, and the residence (reaction) time was 10 min. A flask with methanol (0.30 g) with a stirring bar was placed in the end of the flow reactors to quench polymerization. The first 30 min-elute was discarded, and the samples were taken for 10 min. For the extend operating time reaction, the samples were further taken for every 10 min during 11-110 min operating time (1st sample: 11-20 min, 2nd sample 21-30 min, …., last sample: 101-110 min).

General procedure for GTP in droplet flow (entry 4 in table 1)

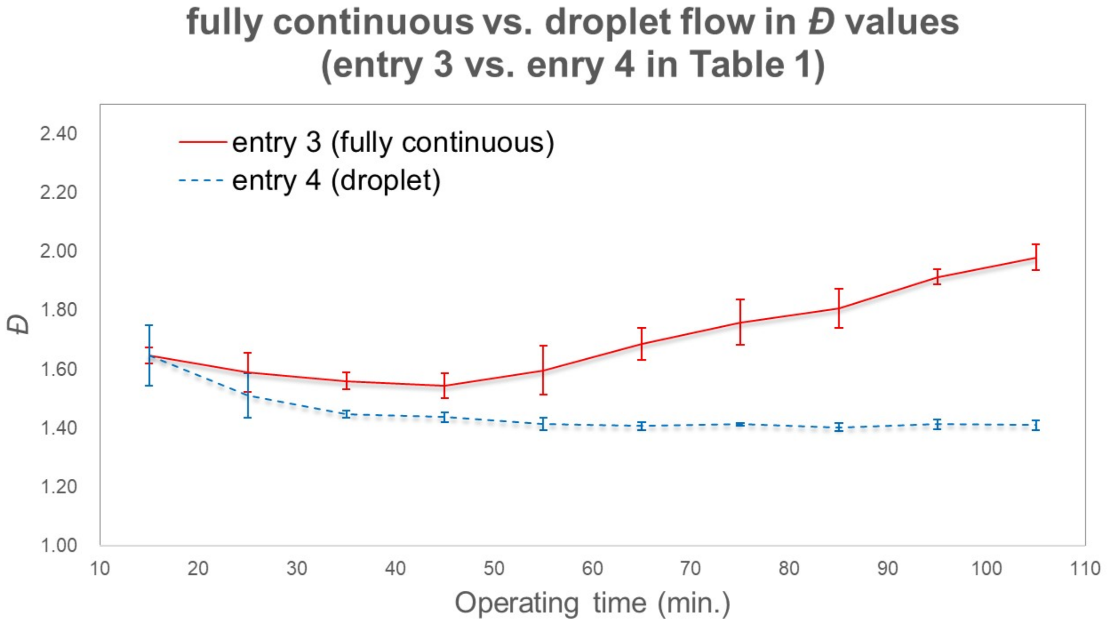
The flow rates of each mixture, MMA and MTS, P_4-*t*-Bu and PEGMEA, were as halved (0.42, 0.99 mL/min) as in the fully continuous flow above, and approximately the same volume of argon as the liquid phase was incorporated so that the liquid phase and the argon phase alternately appeared in a short period. The pressure of argon was 0.2 MPa, and the amount of argon was adjusted by Swagelok Stainless Steel Low Flow Metering Valve, 1/4 in. (SS-SS4-VH), which was connected to the argon pump. The total flow of the reaction mixture liquid was 1.41 mL/min. The length of the liquid droplet was approximately 2-10 mm, depending on i.d. of flow reactors and flow rates.□As Corrigan et al. reported, calculation of the amount of gas which should be incorporated for a target residence time of the liquid phase is very difficult because of variable volume of gas, argon.[a] Volume of argon in flow reactors can change by i) temperature, ii) system pressure and pressure drop, iii) gas solubitily to the liquid phase. Therefore, the amount of argon was roughly adjusted by appearance first, and then further adjusted for a target residence time by measuring the speed of the droplet. Several TIPS for making gas-liquid droplet in flow reactors available in S.I. of their work. Pictures of gas-liquid droplet can be seen in Figure 6 and Figure S1.

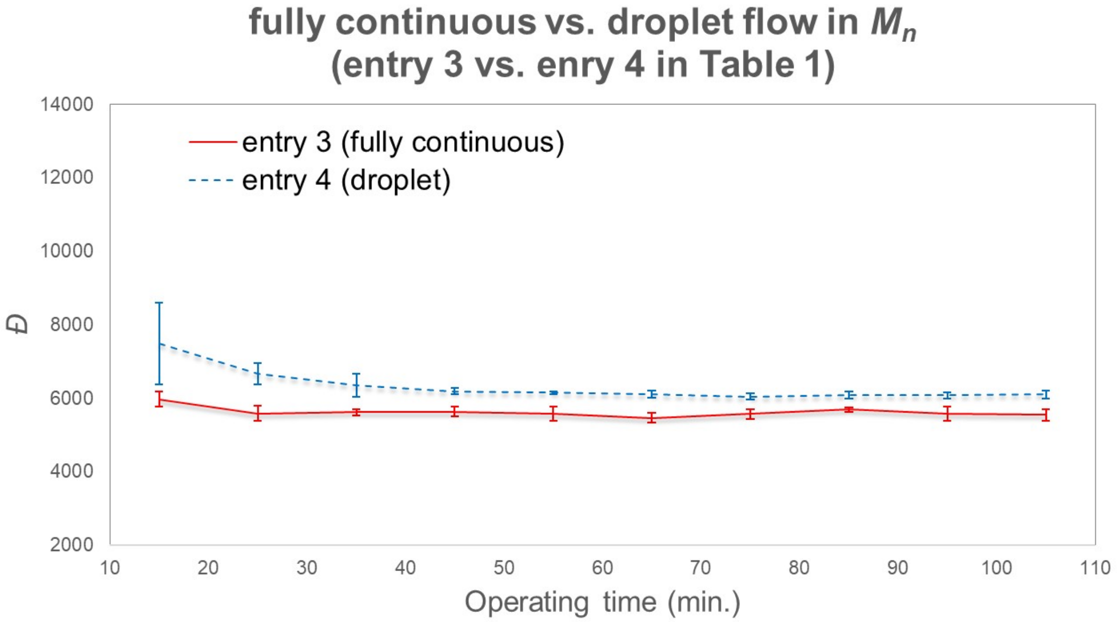
Figure S1. A picture of droplet flow.

A procedure for GTP of poly(MMA-b-BMA) in droplet flow

Circle-shaped 4.5 and 9.5 m PFA tubes with i.d. of 2.0 mm were prepared for the 1st block MMA and for the 2nd block BMA polymerization, respectively (Figure 6). The reactions condition was $[\mathrm{MMA}]_0/[\mathrm{BMA}]_0/[\mathrm{MTS}]_0/[\mathrm{P}_4\text{-}t\text{-Bu}]$ = 50/10/1/(0.001+0.001) with theoretical molecular weight = 6530, and (MMA+BMA+MTS)/(PEGMEA) = 30/70/60 in weight. A solution of MTS (5.00 g, 0.0287 mmol) and dried MMA (143.85 g, 1.44 mmol) was prepared in the 1st bottle. In the 2nd bottle, a solution of P_4-*t*-Bu solution in hexane (31.0 mg, 0.0287 μmol) and dried PEGMEA (343.00 g) was prepared. In the 3rd bottle, a solution of P_4-*t*-Bu solution in hexane (31.0 mg, 0.0287 μmol), dried BMA (40.86 g, 0.287 mmol), and dried PEGMEA (89.53 g) was prepared. UI-22-410P HPLC pumps were connected to each bottle, and the flow rates were set 0.21, 0.50 and 0.19 mL/min for the 1st, 2nd and 3rd bottles, respectively. The mixtures in the 1st and 2nd bottles were mixed through MiChs α600 with i.d. of 0.6 mm, and then went to 4.5 m PFA tubes immersed in a 40 °C oil bath for the 1st block MMA polymerization. The total flow rate of the liquid reaction mixture was 0.71 (0.21+0.50) mL/min, and approximately the same volume of argon was incorporated a T-shaped mixer with i.d. of 2.0 mm to make droplet. The volume of the PFA tube in the oil bath was 14.1 mL^3, and the residence (reaction) time was 10 min. The mixture (P_4-*t*-Bu, BMA and PEGMEA) in the 3rd bottles was incorporated into the reaction mixture flow through a T-shaped mixer with i.d. of 2.0 mm in the end of flow reactors of the 1st block MMA polymerization. The total flow rate of the liquid reaction mixture was 0.90 mL/min without changing the volume of argon in flow reactors. The volume of the PFA tube in the oil bath was 29.8 mL, and the residence (reaction) time was 19 min for the 2nd block BMA polymerization. A flask with methanol (0.20 g) with a stirring bar was placed in the end of the flow reactors to quench polymerization. The first 29 (10+19) min-elute was discarded, and the samples were taken for every 29 min during 30-319 min operating time (1st sample: 30-58 min, 2nd sample 59-87 min, …., last sample: 291-319 min).

Detailed experimental data





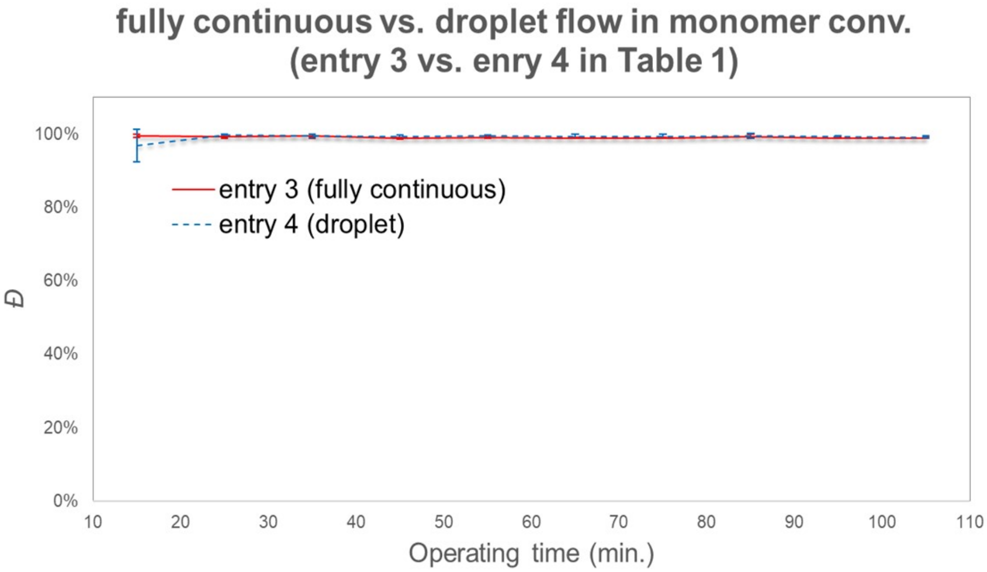


Figure S2. M_n, $Đ$ values, and monomer conversions for the fully continuous (entry 3) and droplet flow (entry 4) in Table 1. Reactions were carried out three times, and the standard deviations are described in the error bars.

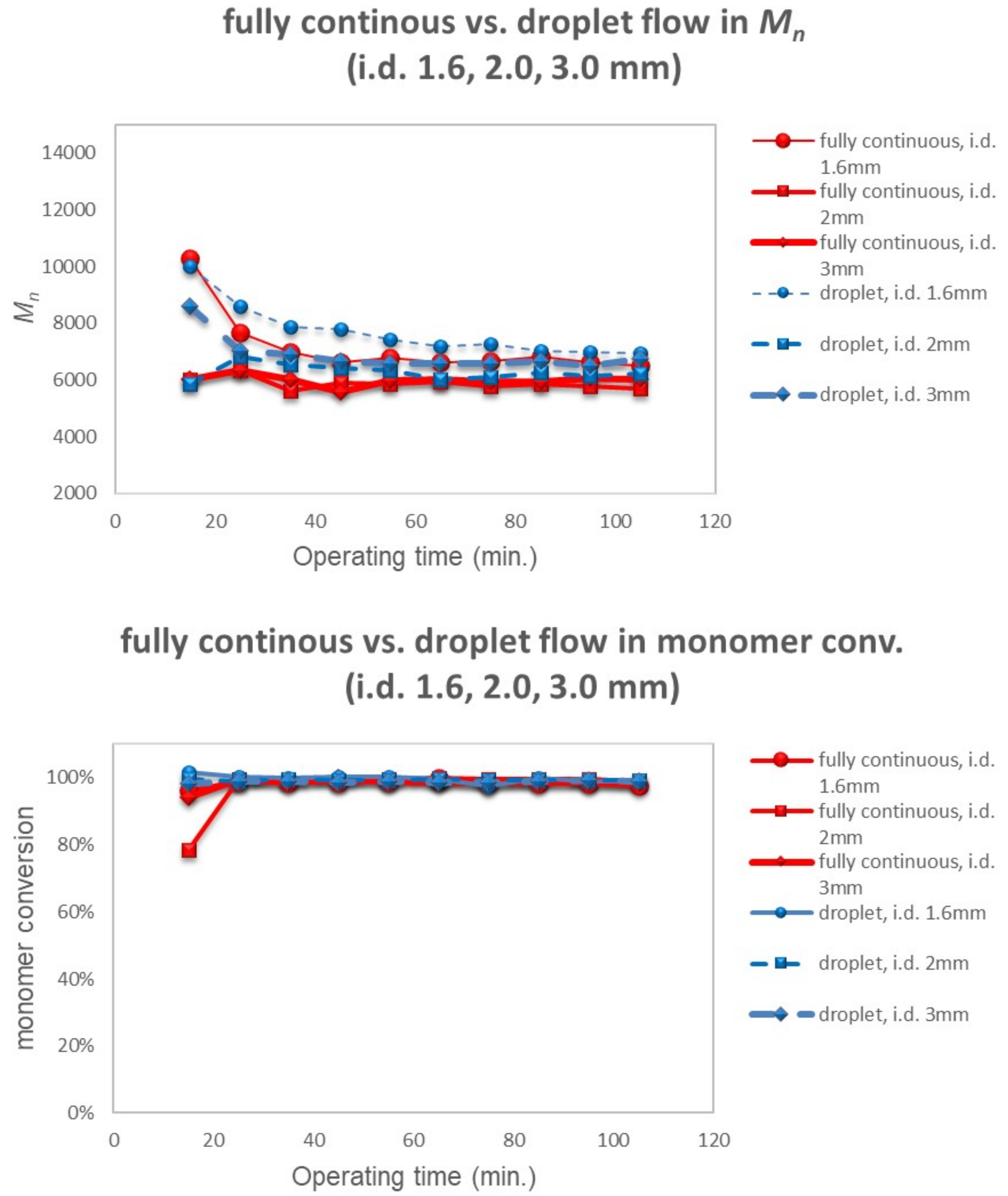


Figure S3 M_n and monomer conversions for the fully continuous and droplet flow in case of (a) $[MMA]_0/[MTS]_0/[P_4\text{-}t\text{-Bu}]$ = 50/1/0.001, (MMA+MTS)/(PEGMEA) = 30/70 in weight, flow length: 9.0 m with i.d. of 1.6, 2.0, and 3.0 mm in Figure 4.

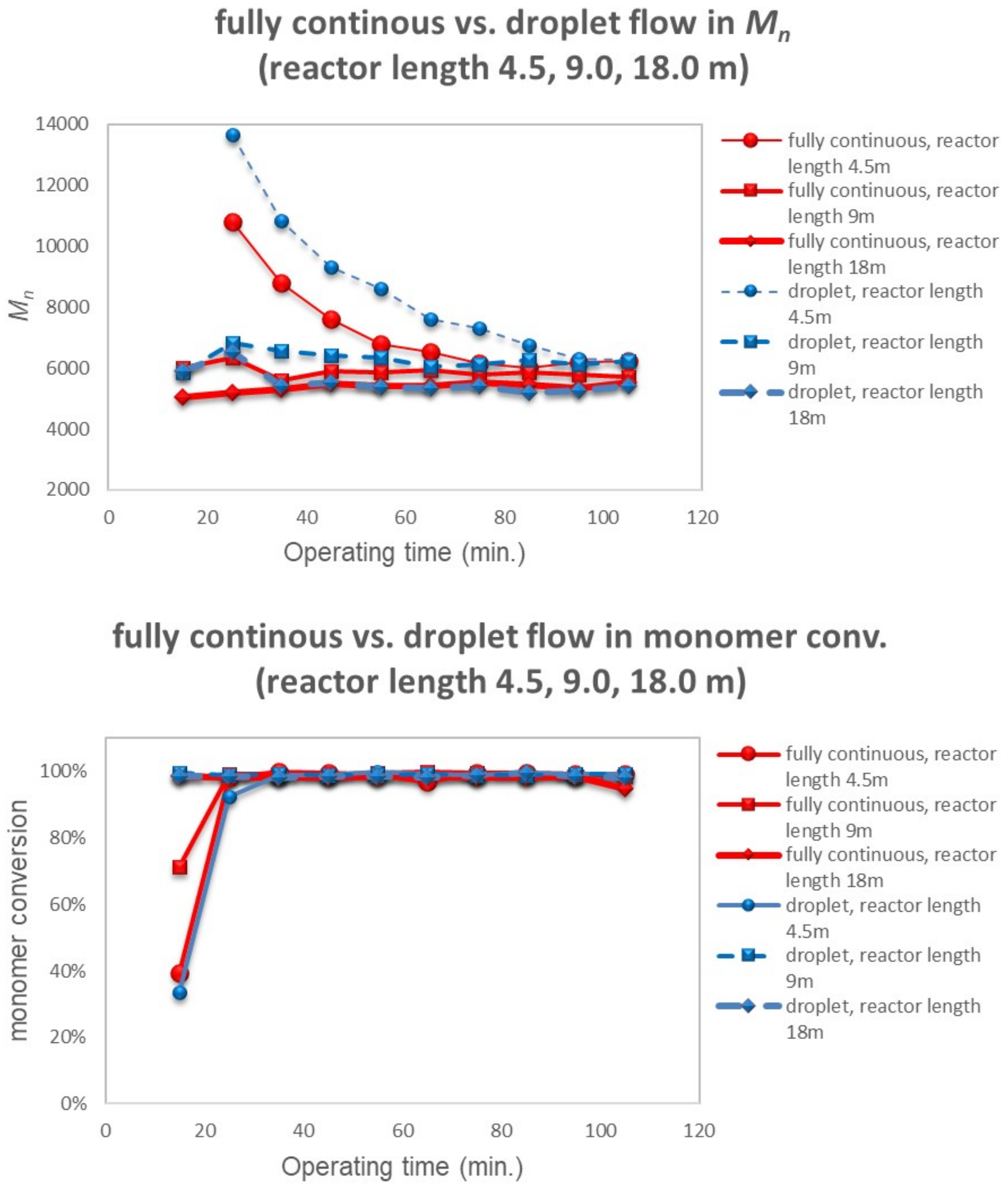
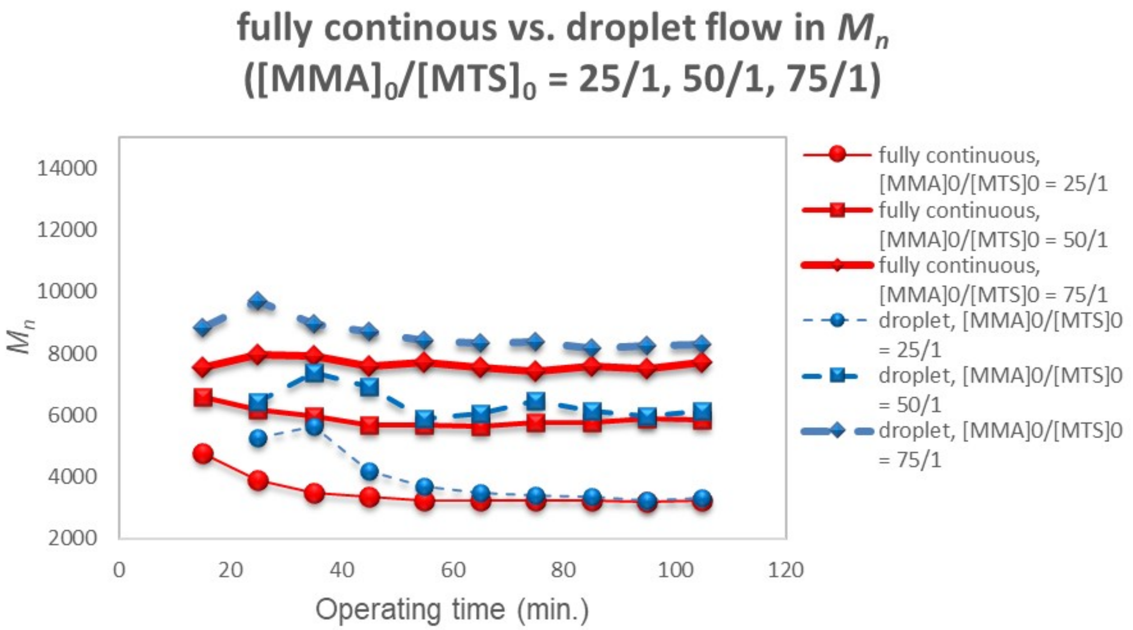


Figure S4 M_n and monomer conversions for the fully continuous and droplet flow in case of (b) $[\mathrm{MMA}]_0/[\mathrm{MTS}]_0/[\mathrm{P}_4\text{-}t\text{-Bu}]$ = 50/1/0.001, (MMA+MTS)/(PEGMEA) = 30/70 in weight, flow length: 4.5, 9.0, and 18.0 m with i.d. of 2.0 mm in Figure 4.



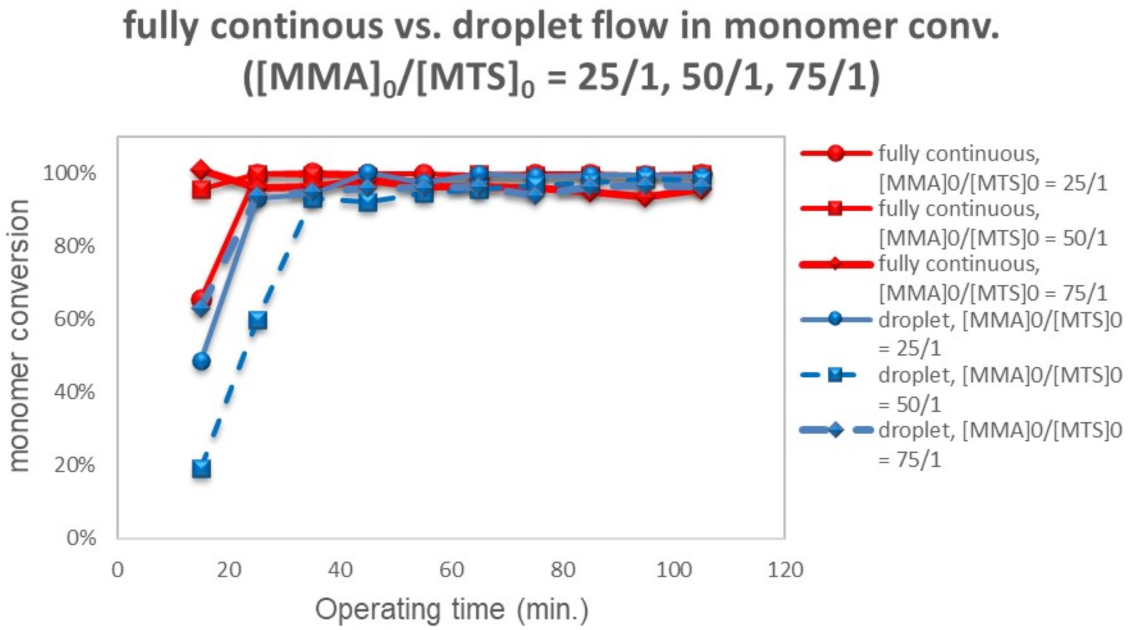


Figure S5 M_n and monomer conversions for the fully continuous and droplet flow in case of (c) *The reaction was conducted at 60 °C instead of 40 °C. [MMA]$_0$/[MTS]$_0$/[P$_4$-*t*-Bu] = 25/1/0.001, 50/1/0.001, and 75/1/0.001, (MMA+MTS)/(PEGMEA) = 30/70 in weight, flow length: 9.0 m with i.d. of 2.0 mm in Figure 4.

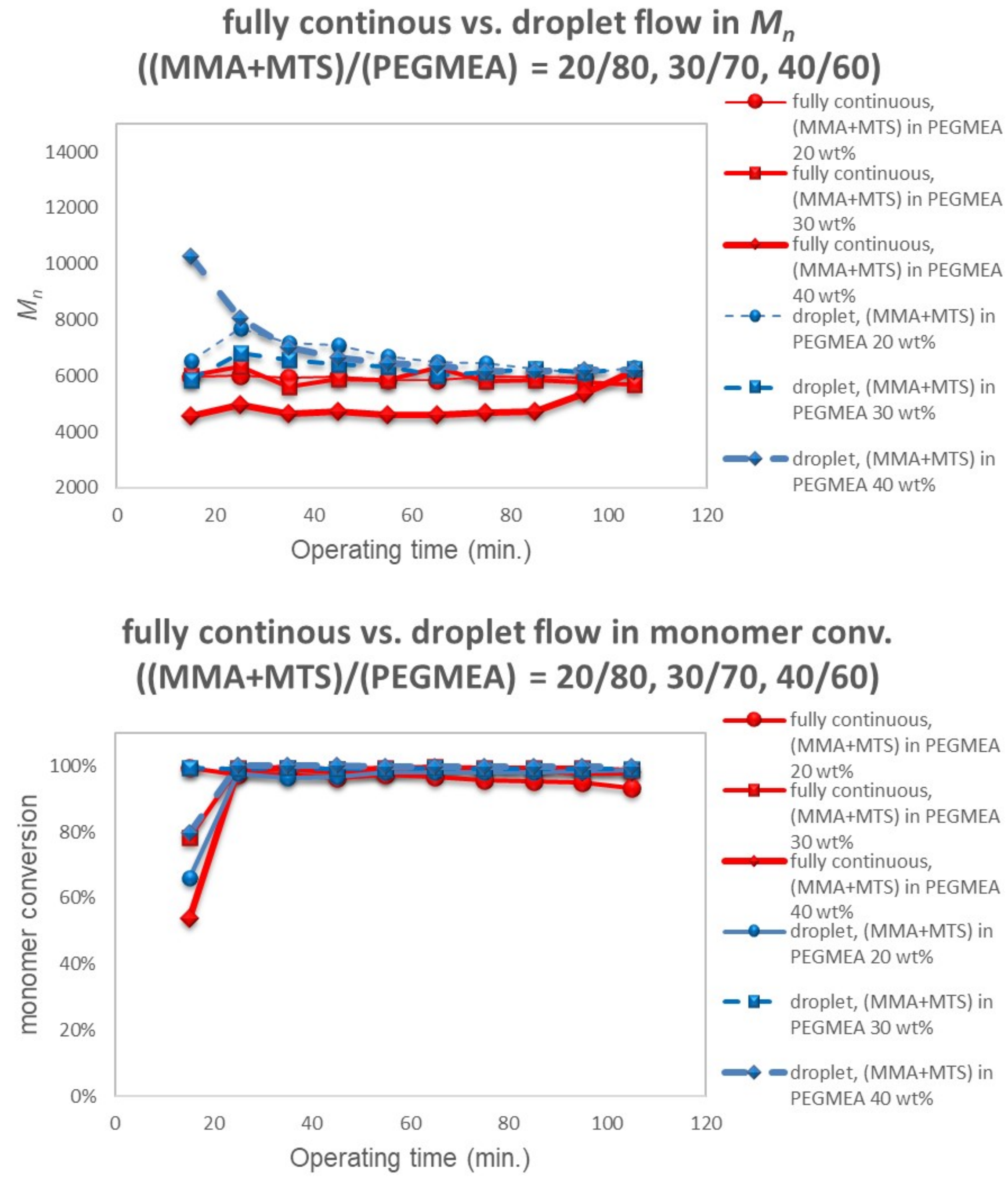


Figure S6 M_n and monomer conversions for the fully continuous and droplet flow in case of (d) $[MMA]_0/[MTS]_0/[P_4\text{-}t\text{-Bu}]$ = 50/1/0.001, (MMA+MTS)/(PEGMEA) = 20/80, 30/70, and 40/60 in weight, flow length: 9.0 m with i.d. of 2.0 mm in Figure 4.

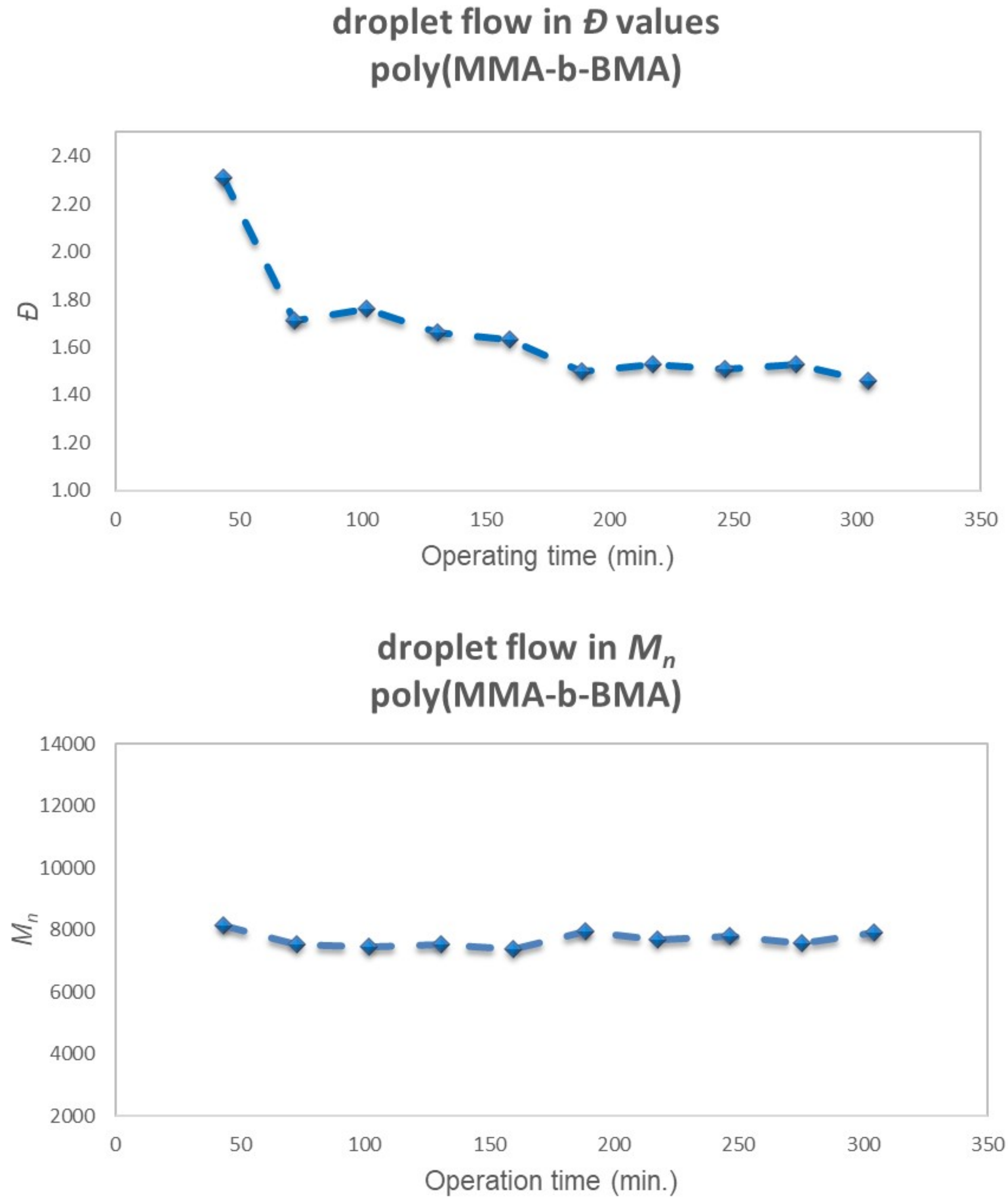


Figure S7 *Đ* values and M_n of poly (MMA-b-BMA) in droplet flow with different sampling times in Scheme 1.

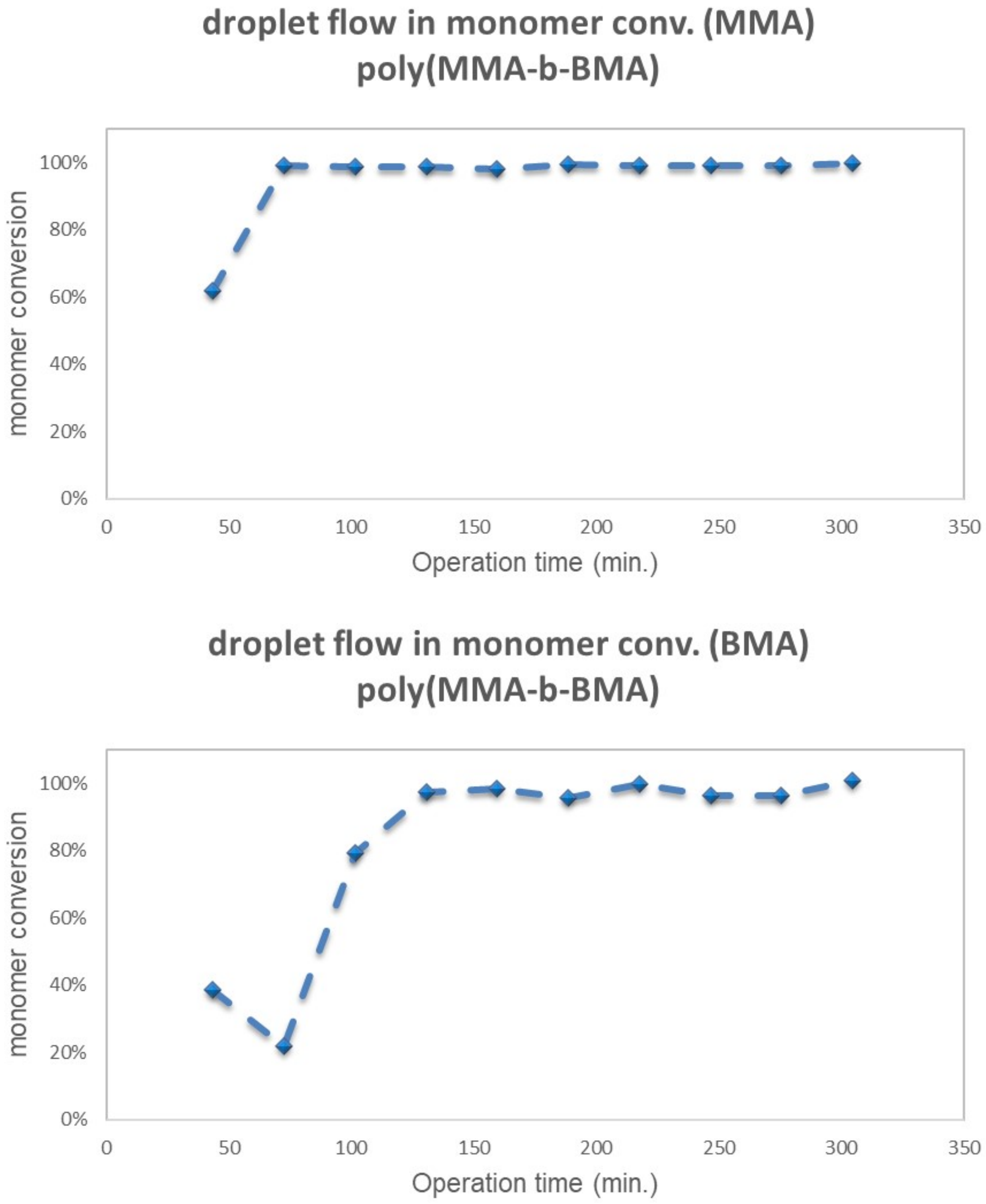


Figure S8 monomer conversions (MMA, BMA) of poly (MMA-b-BMA) in droplet flow with different sampling times in Scheme 1.

Reference

(a) N. Corrigan, L. Zhernakov, M. H. Hashim, J. Xu and C. Boyer, *React. Chem. Eng.*, 2019, **4**, 1216–1228.