Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Online Tracing of Molecular Weight Evolution during Radical Polymerization via high-resolution FlowNMR spectroscopy

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Materials

The monomer methyl acrylate (MA, Alfa Aesar, 99%) were deinhibited over a column of activated basic alumina before polymerization. The initiator azobisisobutyronitrile (AIBN, Acros Organics, 98%) was recrystallized from methanol prior to use. The radical inhibitor hydroquinone (HQ, Acros Organics, 99%) was used without further purification. The reversible addition-fragmentation chain transfer (RAFT) agent 2-(Dodecylthiocarbonothioylthio)propionic acid (DoPAT) was synthesized following literature procedure.[1] The solvents toluene (VWR, ≥99.9%, HPLC grade), tetrahydrofuran (VWR, 99.5%) and methanol (VWR, ≥99.9%, HPLC grade) were used as received.

Experimental

Polymerization procedure For polymerization of MA with thermal RAFT a solution of MA, DoPAT and AIBN in toluene was prepared (DoPAT : AIBN : MA 1 : 0.15 : 100/250/500) with a monomer concentration of 1M in a total volume of 150 mL. The solution was filtered through a 0.45µm filter and deoxygenated by purging the solution with argon for 30 minutes. A homemade PEEK flow-reactor (1/16" OD, 0.75 mm ID, SGE Analytical Science) with an internal volume of 5 mL and backpressure regulator (100 psi, Upchurch Scientific) was placed in an oil bath heated to 85 °C. The solution was pumped through the reactor using a peristaltic pump (Vapourtec SF-10) and cooled to 4 °C after exiting the reactor. Residence times were screened by varying the flowrate of the reagent stream. The flow reactor was connected directly to the NMR spectrometer using the same 1/16" PEEK tubing. After waiting 1.5 times the residence time a proton nuclear magnetic resonance (^{1}H-NMR) measurement for conversion determination was performed. For diffusion ordered NMR spectroscopy (DOSY) the sample flow was diluted by using an additional peristaltic pump to mix the solution with toluene at a higher flowrate after exiting the reactor (targeting a 1/10 dilution). The sample flow was diverted from the NMR spectrometer with a bypass valve prior measurements to ensure static measurement conditions. Samples were collected in a solution of hydroquinone in methanol to inhibit further polymerization and were measured on SEC-MALLS. A schematic overview of the set-up is given in Figure S1 and details of the NMR measurements are given in the following paragraph.

NMR All NMR data were acquired on a Bruker AVIII 500 MHz spectrometer equipped with a Prodigy cryoprobe, using an InsightMR flow tube. Quantitative ^{1}H NMR spectra were acquired with the zg30 pulse program, a d1 delay of 10 s, and 32 scans. DOSY spectra were acquired using a convection compensated dstebpgp3s pulse sequence. The gradient pulse was a smooth rectangle with gradient strength 6 – 57 G cm^{-1}. For each DOSY spectrum, 16 diffusion experiments each with 32 scans were performed, in a linear ramp. A diffusion delay, d20, of 80 ms and a gradient pulse length, p30, of 1.2 ms (Δ = 2.4 ms) were used for most polymers. For some higher molecular weight polymers, d20 and p30

were set to 80 ms and 1.6 ms respectively. After phase and baseline correction in TopSpin, diffusion data were processed in Dynamics Center to obtain diffusion coefficients.

SEC-MALS Polymer size distributions were measured using a Tosoh EcoSEC HLC-8320GPC consisting out of an autosampler and a PSS guard column SDV (50 × 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 μm, 300 × 7.5 mm), a differential refractive index detector (Wyatt Optilab TrEX RI detector) and MALS detector (Wyatt Heleos Dawn II multiangular light scattering). The weight average molecular weight of the polymers was determined via Astra V using a dn/dc value of 0.068 mL·g^{-1} for pMA polymers.[2]

Experimental setup

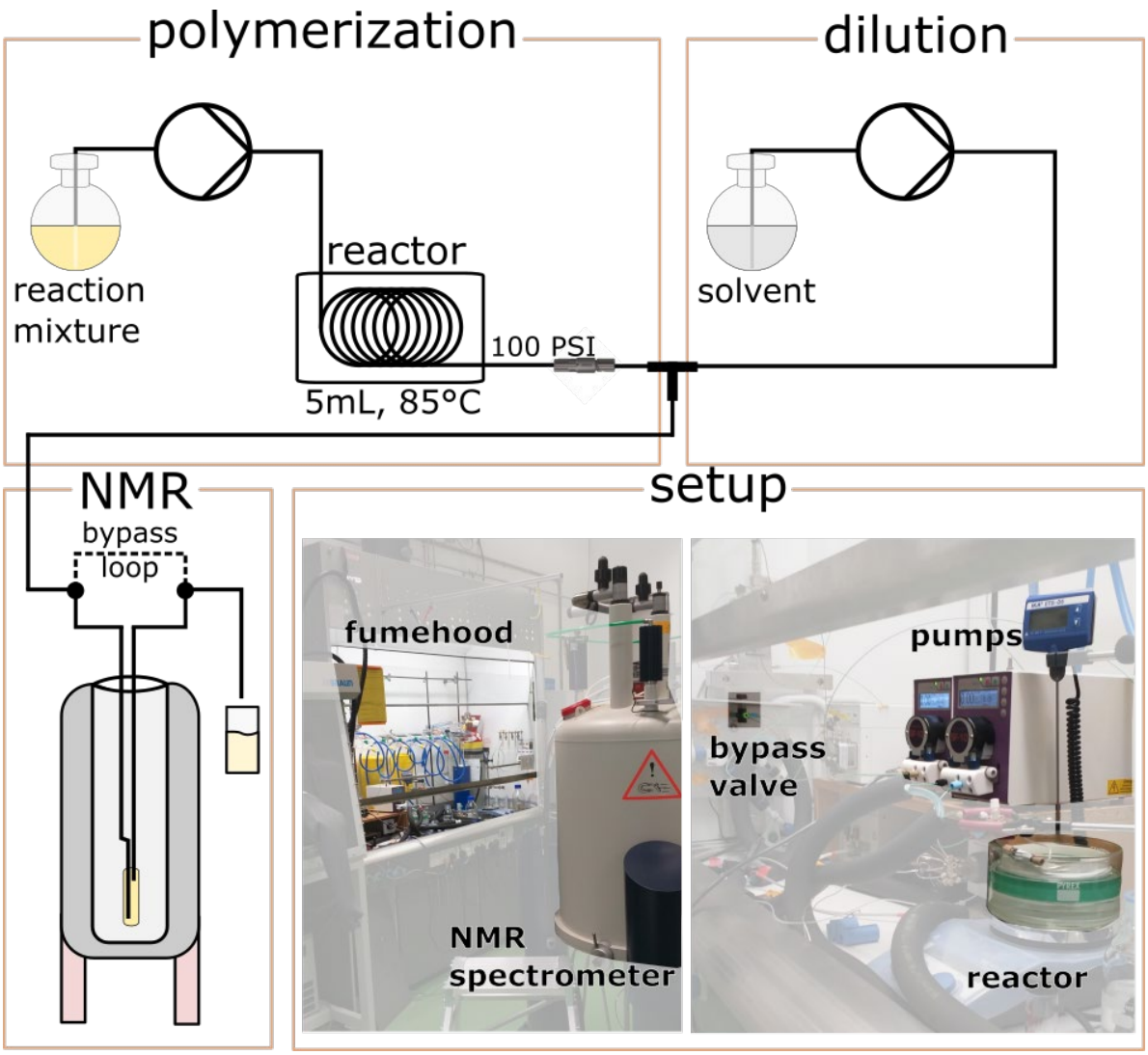


Figure S1: Schematic overview of the setup for measurement of monomer conversion and diffusion coefficient.

Supporting Results

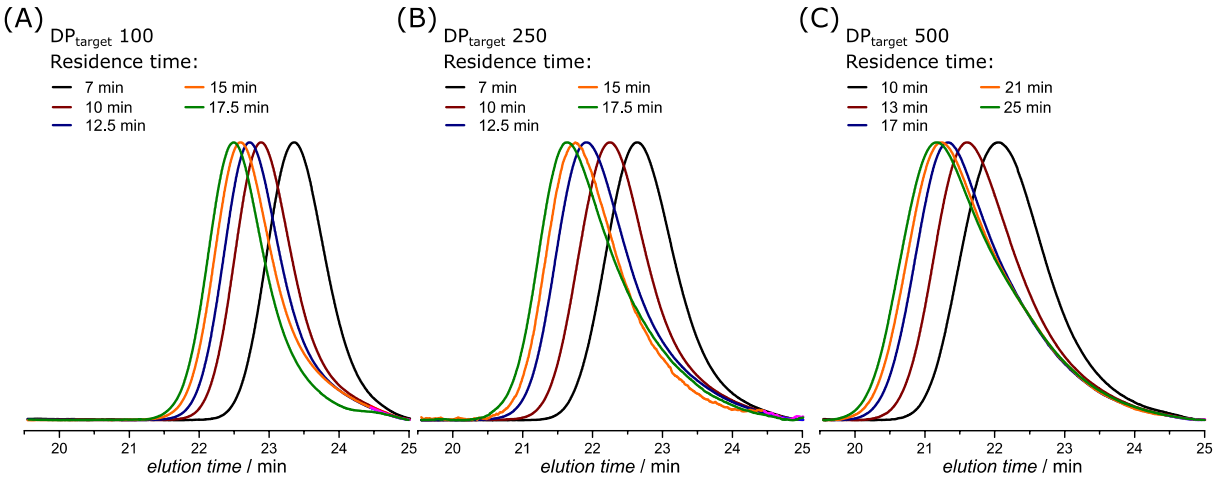


Figure S2: SEC traces for the synthesized polymers *via* RAFT polymerization of MA for various residence times in a continuous flow reactor and for targeted degrees of polymerization (DP$_{target}$) of (A) 100, (B) 250 and (C) 500.

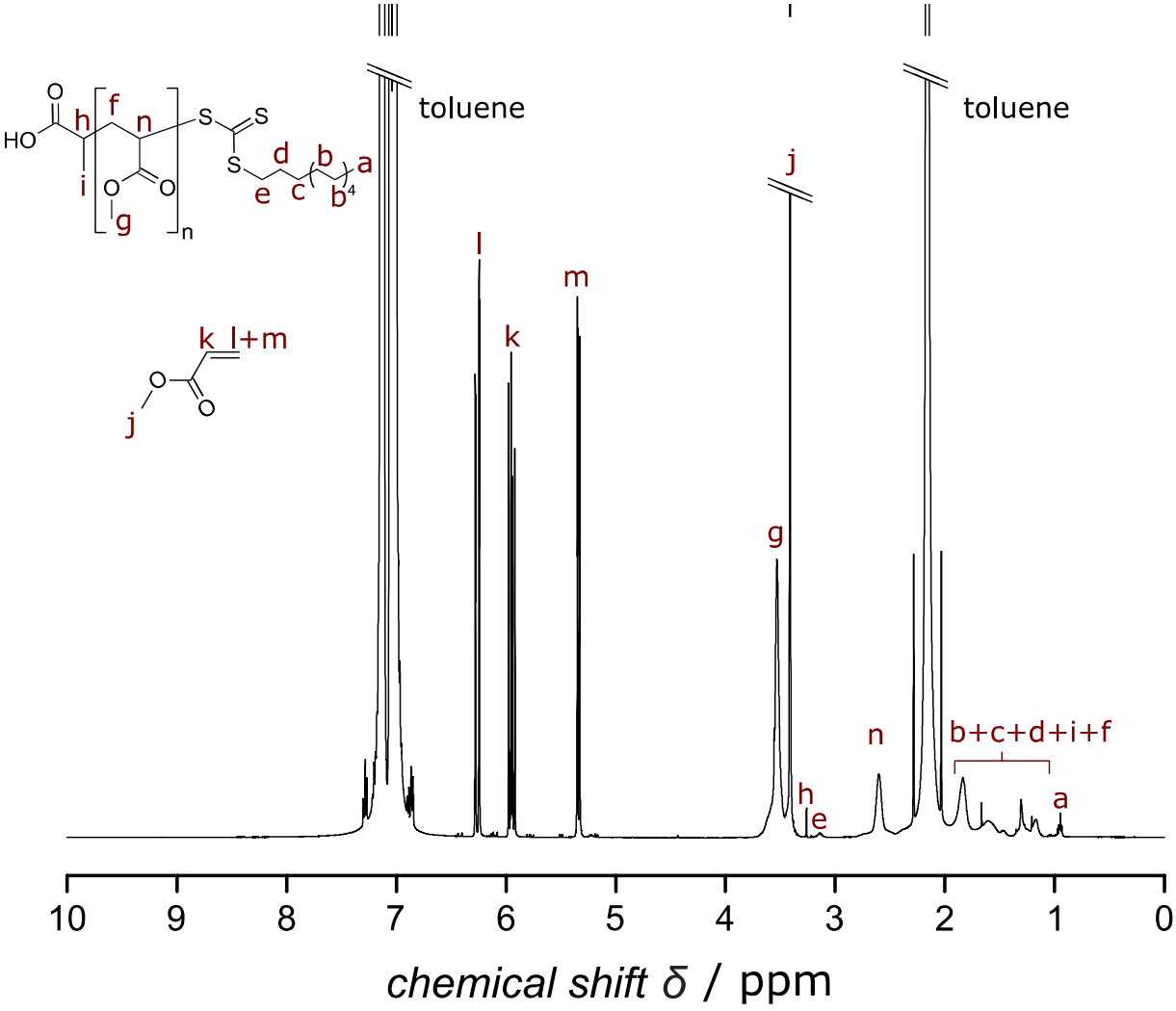
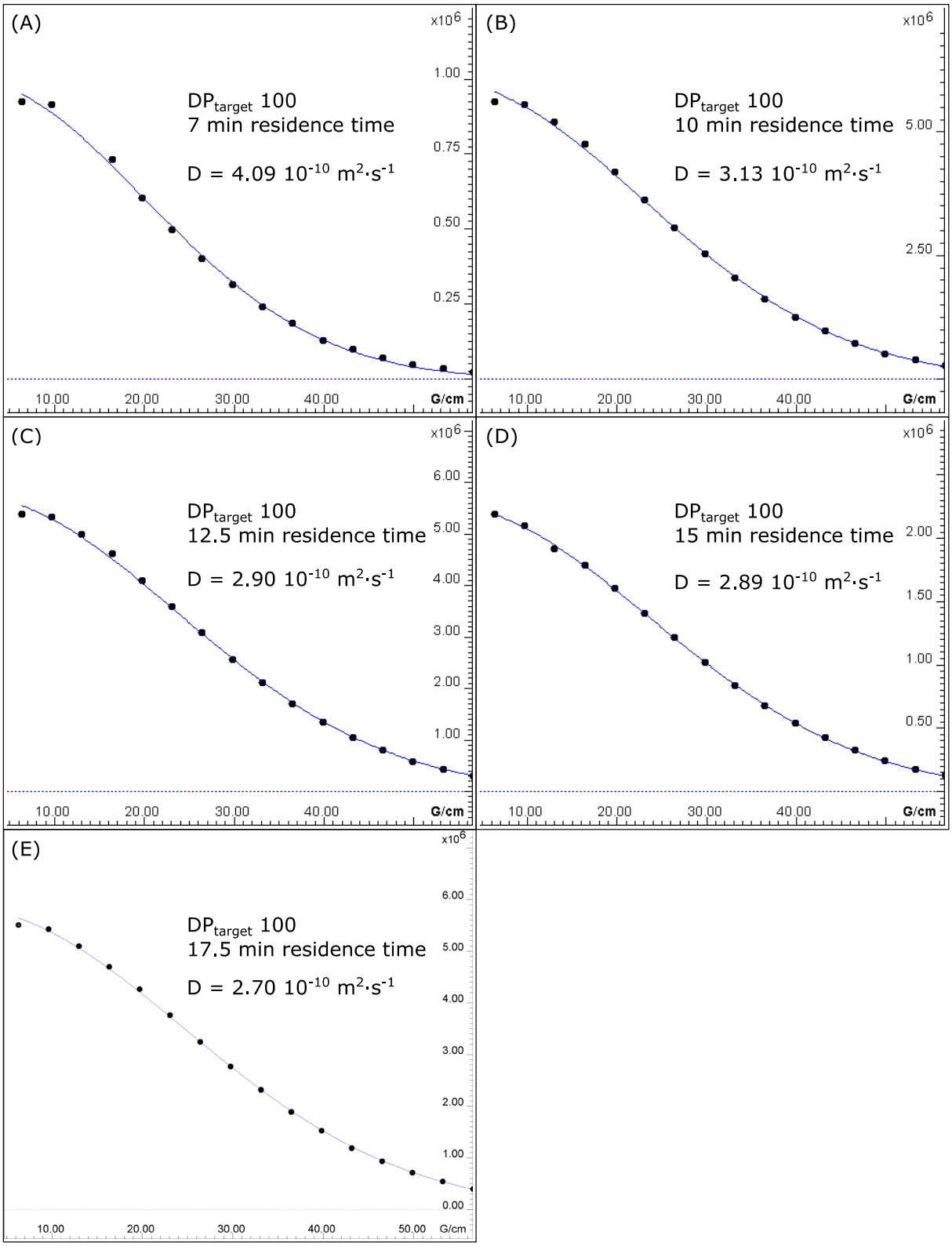


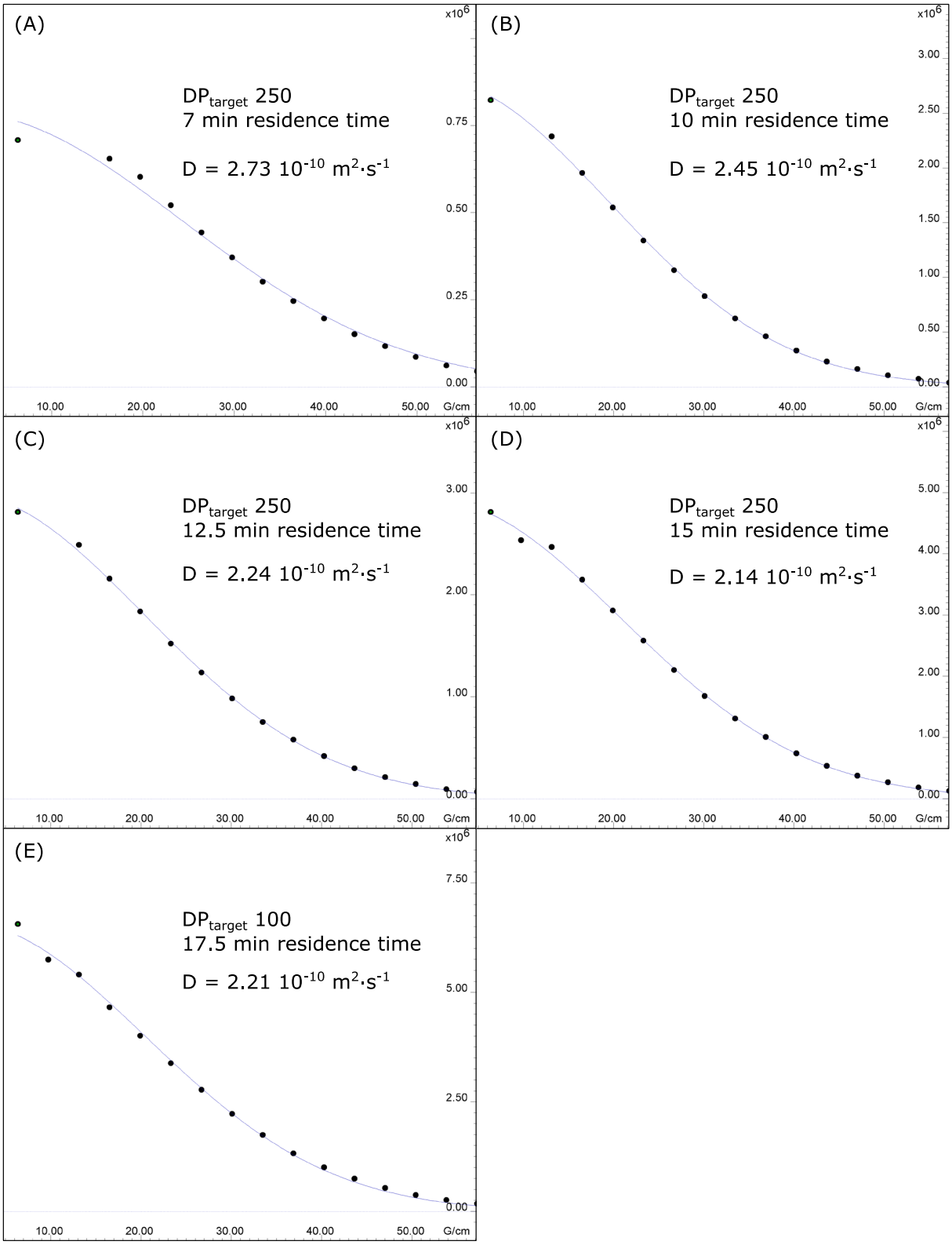
Figure S3 Assigned ^{1}H-NMR spectrum of polymethyl acrylate polymer and methyl acrylate monomer measured in toluene and synthesized in continuous flow *via* RAFT.

Table S1: Monomer conversion and SEC-MALLS data for polymers synthesized *via* RAFT polymerization in continuous flow reactors.

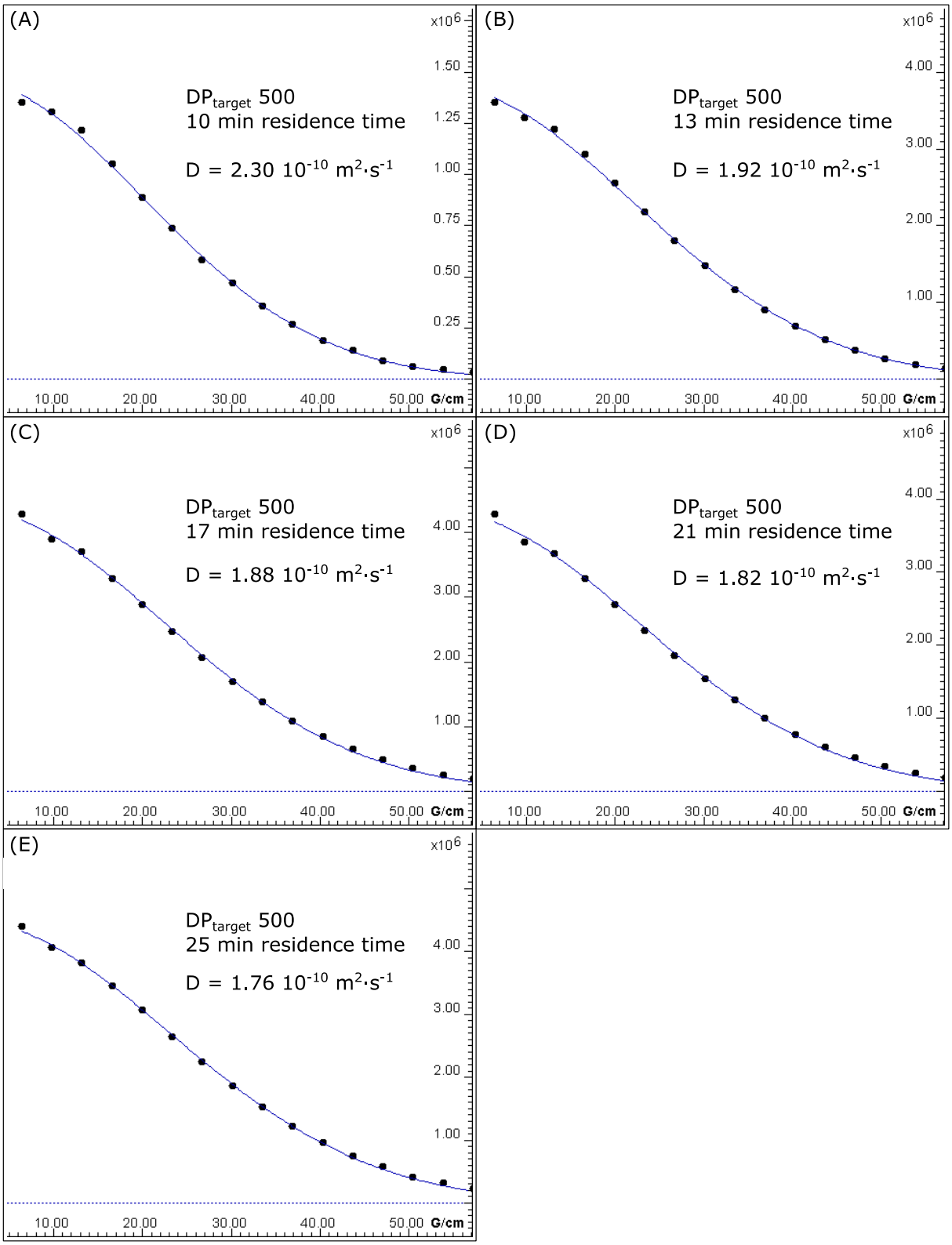
DP_{target}	Residence time (min)	Monomer Conversion	$M_{w,\ MALLS}$ ($g \cdot mol^{-1}$)	$M_{n,\ MALS}$ ($g \cdot mol^{-1}$)	$Đ_{MALS}$
100	7.0	25%	2640	2410	1.10
100	10.0	35%	3650	3340	1.10
100	12.5	42%	4020	3610	1.11
100	15.0	47%	4570	4090	1.12
100	17.5	52%	5800	5340	1.09
250	7.0	22%	4440	3870	1.15
250	10.0	30%	5840	5140	1.14
250	12.5	35%	7690	6700	1.15
250	15.0	41%	8900	8400	1.06
250	17.5	45%	9330	8450	1.10
500	10.0	20%	6930	6040	1.15
500	13.0	24%	8880	7240	1.23
500	17.0	32%	11250	9840	1.15
500	21.0	37%	12580	11280	1.12
500	25.0	40%	11820	8660	1.37



Figures S4: Fits of DOSY data on polymers synthesized by MA polymerization *via* RAFT in continuous flow reactors with a targeted degree of conversion of 100 for residence times of (A) 7 min, (B) 10 min, (C) 12.5 min, (D) 15 min and (E) 17.5 min. The methyl sidegroups of polymerized methyl acrylate (δ 3.7-3.46 ppm, Figure S3 g) is used to determine the diffusion coefficient of the polymer with DOSY.



Figures S5: Fits of DOSY data on polymers synthesized by MA polymerization *via* RAFT in continuous flow reactors with a targeted degree of conversion of 250 for residence times of (A) 7 min, (B) 10 min, (C) 12.5 min, (D) 15 min and (E) 17.5 min. The methyl sidegroups of polymerized methyl acrylate (δ 3.7-3.46 ppm, Figure S3g) is used to determine the diffusion coefficient of the polymer with DOSY.



Figures S6: Fits of DOSY data on polymers synthesized by MA polymerization *via* RAFT in continuous flow reactors with a targeted degree of conversion of 500 for residence times of (A) 10 min, (B) 13 min, (C) 17 min, (D) 21 min and (E) 25 min. The methyl sidegroups of polymerized methyl acrylate (δ 3.7-3.46 ppm, Figure S3g) is used to determine the diffusion coefficient of the polymer with DOSY.

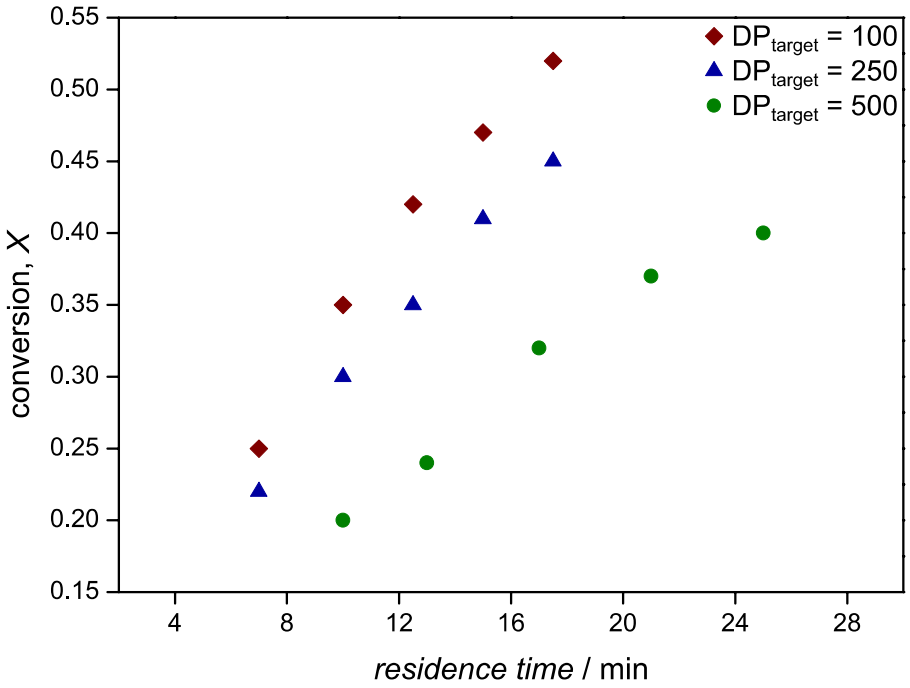


Figure S7: Monomer conversion as a function of residence time in a continuous flow process for MA RAFT polymerization.

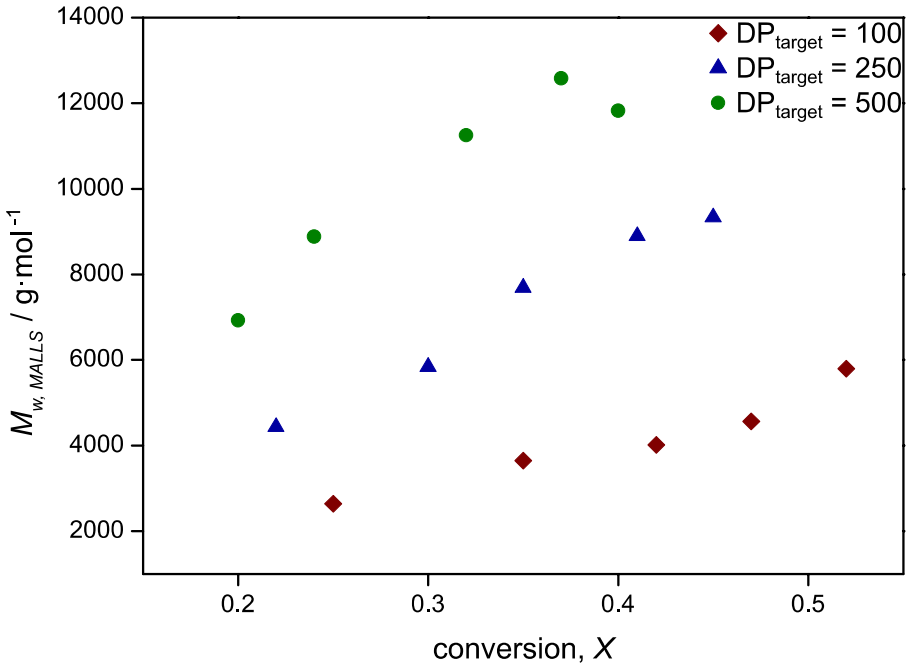


Figure S8 Weight-average molecular weight as benchmarked by SEC-MALLS in function of monomer conversion for MA RAFT polymerizations with varying target degree of polymerization.

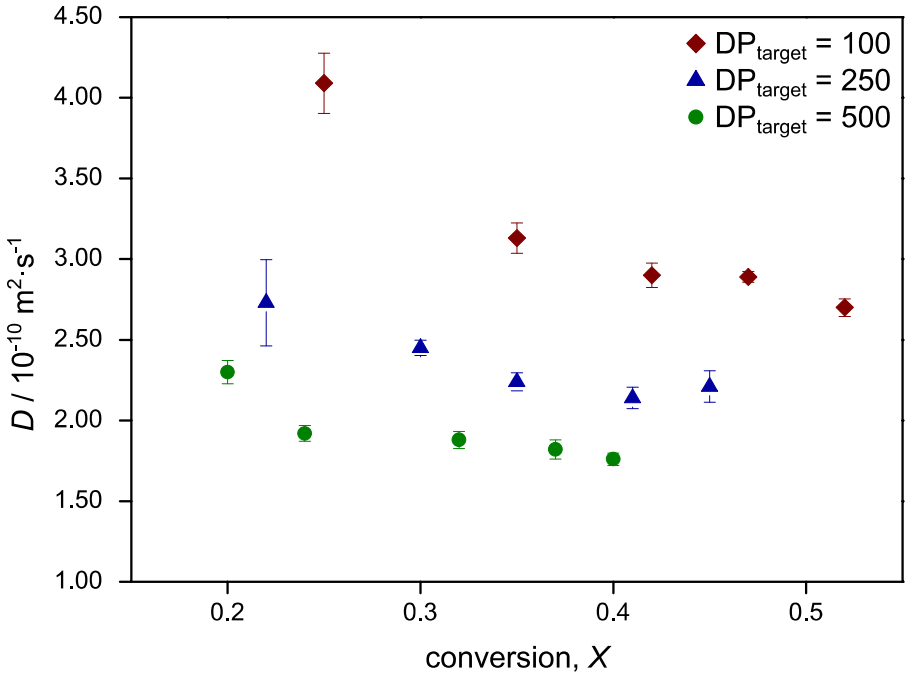


Figure S9: Diffusion coefficient determined by DOSY as a function of monomer conversion for MA polymerization via RAFT in a continuous flow process.

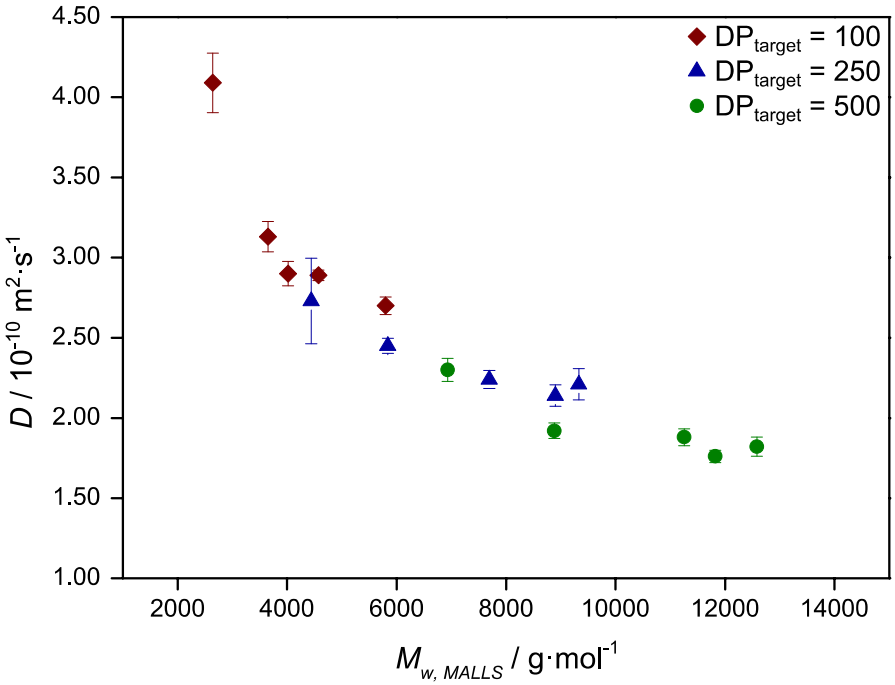


Figure S10 Diffusion coefficients determined by DOSY as a function of weight-average molecular weight as benchmarked by SEC-MALLS for MA RAFT polymerizations with varying target degree of polymerization.

References

1 C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such and B. S. Hawkett, *Macromolecules*, 2005, **38**, 2191-2204.
2 T. Junkers, M. Schneider-Baumann, S. S. Koo, P. Castignolles and C. Barner-Kowollik, *Macromolecules*, 2010, **43**, 10427-10434.