Supplementary Information

Real-time monitoring of photoinduced atom transfer radical polymerization by time-resolved diffusion NMR

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Experimental Details

Materials

All chemicals were purchased from commercial sources and used as received unless otherwise noted. Tris(2-pyridylmethyl)amine (TPMA, >98%), 2-hydroxyethyl 2-bromoisobutyrate (HOBiB, >97%), copper bromide(II) ($CuBr_2$, >98%) and Eosin Y disodium salt (>90%) were purchased from TCI. Poly(ethylene glycol) monomethyl ether methacrylate (n ≈ 9, average M_n = 500, $OEOMA_{500}$) stabilized with MEHQ, was purchased from TCI and passed through a column of basic alumina to remove inhibitor prior to use. Phosphate-buffered saline (PBS, 10X, pH = 7.4) was purchased from Thermo Scientific. DMSO and deuterium oxide (D_2O) were purchased from Carl Roth GmbH and Armar Isotopes, respectively.

Instrumentation

Nuclear Magnetic Resonance (NMR)

T1 measurement

The polymer sample of DP_T = 600 (84% monomer conversion) was used to establish the T_1 relaxation value of the systems. The measurement was performed on a Bruker AVANCE Neo 300 MHz spectrometer equipped with a BBI 300 MHz W1 5 mm z-gradient probe with a BVT-3000 temperature controller. The sequence used was t1ir with time points in range 0.01-2 s, ns = 4, d1 = 5 s, at 313 K. The T1 value was fitted using TopSpin's built-in T_1T_2 tool. The resulting longitudinal relaxation value was 0.33 s. The surprisingly low value for a polymer is due to the presence of Cu^{2+}/TPMA complex in the system.

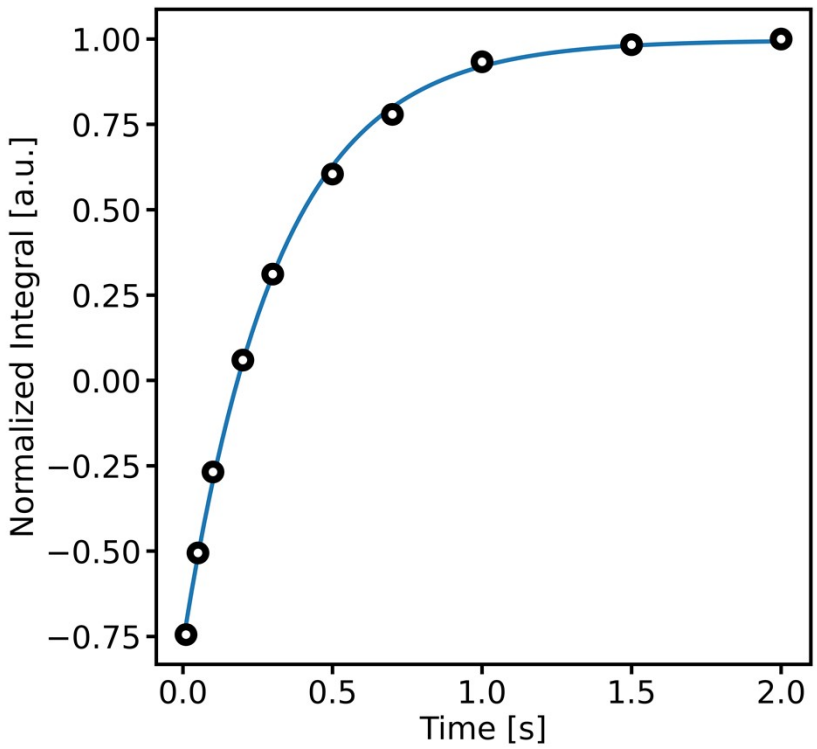

Figure S1. T_1 relaxation curve of DP_T 600 sample.

Supplementary Information

The effect of Cu^{2+}/TPMA concentration on the monomer polymer ratio

To make sure that the Cu^{2+} induced increased relaxation will not change the integral ratio, we have studied the DP_T 600 sample with 84% conversion ratio with multiple Cu^{2+} concentrations. Each sample was studied with a zg sequence, ns = 32, d1 = 5 s, at 313 K temperature. The spectra processing and signals integration were performed using TopSpin software. Integrals are in the range 4.52-4.44 ppm (monomer) and 4.4-4.2 ppm (polymer). The resulting ratio is gathered in the Table below:

Cu^{2+} concentration [mg/ml]	Mono/Poly integrals
0.067	0.1885
0.084	0.1805
0.084 (TPMA 0.262 + 0.065)	0.1954
0.1508 (TPMA 0.262 + 0.065)	0.1822

NMR in situ illumination setup

Green light illumination was provided by a 530 nm (30 nm FWHM) fiber-coupled LED (M530F2) purchased from Thorlabs. The maximum power of 9.6 mW at the end of the optical fiber was measured at a 1000 mA maximum current, using 1 m of FT400EMT Ø400 μm core, 0.39 NA multimode fiber. During monitoring experiments, 3 m length FT1000UMT (Thorlabs) Ø1000 μm core, 0.39 NA multimode fiber was used. The optical fiber tip was polished using sandpaper to illuminate the sample more homogeneously. The LED current was set to 200 mA using a T-cube LED driver (LEDD1B), purchased from Thorlabs. The optical fiber was inserted into the PhotoNMR Sampling Device-5mm (New-ERA)[1] tube for sample illumination. An Arduino module controlled the illumination setup by connecting to the LED driver BNC port and using the driver's trigger mode.

NMR experiments during reaction monitoring were performed on a Bruker AVANCE II 300 MHz spectrometer equipped with a BBI 300 MHz W1 5 mm z-gradient probe with a BVT-3000 temperature controller. Experiments for dispersity estimation were performed on a Bruker AVANCE II 500 MHz spectrometer equipped with a Diff30 probe. The spectrometers were controlled using TOPSPIN software (versions 3.2 and 2.1, respectively).
Polymerization monitoring experiments were performed at 313K, while dispersity measurements were performed at 298K.

Interleaved acquisition

During monitoring of the polymerization, standard ^{1}H experiments were interleaved with stebpgp1s1d pulse sequences for the acquisition of TR-DNMR. The acquisition parameters for standard ^{1}H experiments were: pulse length: 13 μs, relaxation delay: 5 s, number of scans: 4. For TR-DNMR parameters were: Δ: 150 ms, δ: 0.2 ms, pulse length: 13 μs, relaxation delay: 5 s, number of scans: 4. A series of 16 gradient values, logarithmically spaced from 0.0253 to 0.4813 T/m, was randomly chosen and permuted. This series was then repeated for subsequent experiments. The light source was active throughout the process and was turned off only when the monomer conversion reached its target of 90% or 70%.

Dispersity measurements

After the polymerization process was monitored, the sample tube was transported to a second spectrometer. A series of stebpgp1s1d pulse sequences was performed with the following parameters: Δ: 100 ms, δ: 8 ms, pulse length: 9.5 μs, relaxation delay: 2.2 s. The gradient strengths were adjusted to cover the range where the sample's dispersity behavior deviates significantly from that of a low dispersity sample. The gradient ranged from 0.0841 to 0.7988

T/m. However, the upper limit was lowered for low molecular weight polymers as they produced no detectable signal at the highest gradient strengths. Each dispersity measurement consisted of 19 experiments. To maintain a consistent signal-to-noise ratio, experiments with higher gradients had more scans, as dispersity is more visible at higher gradients. The number of scans ranged from 16 at the lowest gradient strength to 256 at the highest. After the acquisition, each gradient spectrum is normalized by the number of scans to keep the integrals' values independent of the scans. The data were then fitted to the Gamma model using equation (4), and the dispersity was calculated using equation (5).

Data analysis

For processing the acquired data, the JupyterLab environment was used with the following packages: nmrglue[1], NumPy[2], SciPy[3], and Matplotlib.

All data were imported with nmrglue. Each spectrum was zero-filled to 32768 points, weighted exponentially, and Fourier transformed. Standard experiments were weighted by 10 Hz, TR-DNMR experiments by 2 Hz, and experiments for dispersity analysis by 1 Hz.

Standard ^{1}H experiments were used for calculating conversion by fitting two Lorentzian functions to the peaks of monomer (4.5 ppm) and polymer (4.33 ppm), integrating both, and dividing the integral of the polymer peak by the sum of their integrals.

Inverse Laplace Transform versus two-exponential fit.

The diffusion coefficients can be extracted from TR-D experiments either using a two-exponential fit (as used in this work) or with the Inverse Laplace Transform. The second approach is free of the assumption of the signal and therefore in theory more prone to disturbance. To check if this assumption is correct we have processed the TR-D experiment of the DP_T 200 sample with both methods. The ILT was performed with TRAIN[4] (500 iterations, termination factor 1.03, 1024- point logarithmic grid from 1e-13 to 1e-8). The comparison between two approaches is shown in Figure S2. This clearly shows that the ILT approach is more prone to disturbance.

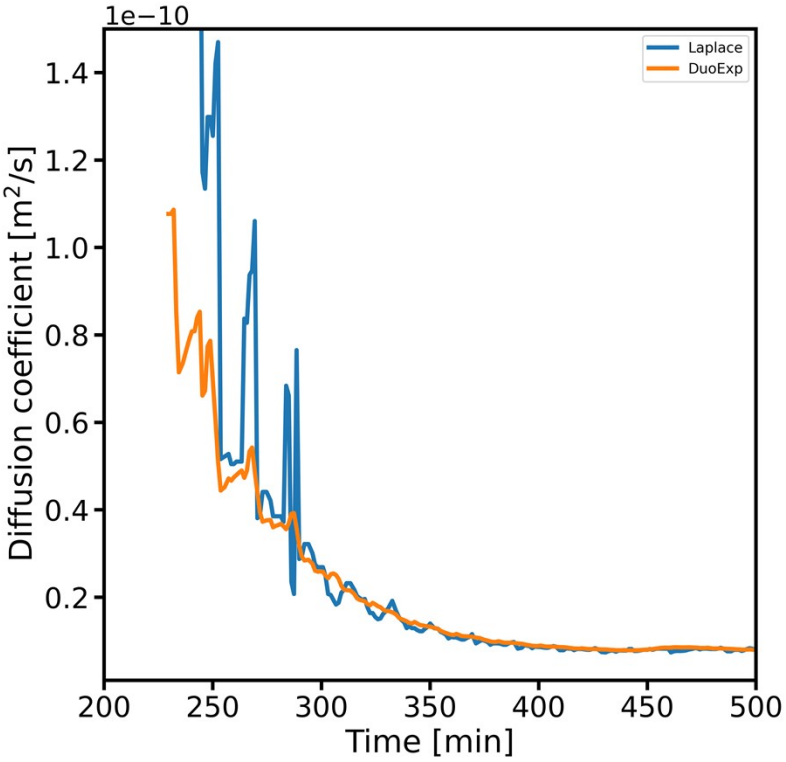

Figure S2. Comparison between the Diffusion coefficient of the polymer calculated with ILT (Laplace) and two-exponential fit (DuoExp).

Viscosity change during the polymerization

To check how much the polymerization affects the viscosity of the system we have repeated the reaction monitoring for DP_T 200 with an addition of TMSP (3-(trimethylsilyl)propionic acid sodium salt). The TMSP signal was used to follow the change in the diffusion coefficient during the process.

Experiment with TMSP was performed on a Bruker AVANCE III 500 MHz spectrometer equipped with a TBI probe. The spectra were processed using TopSpin software. Integration of the TMSP signal, 0.2-0.1 ppm, was performed in the JupyterLab.

The resulting diffusion dependence of TMSP on conversion of the reaction is presented in the Figure S3.

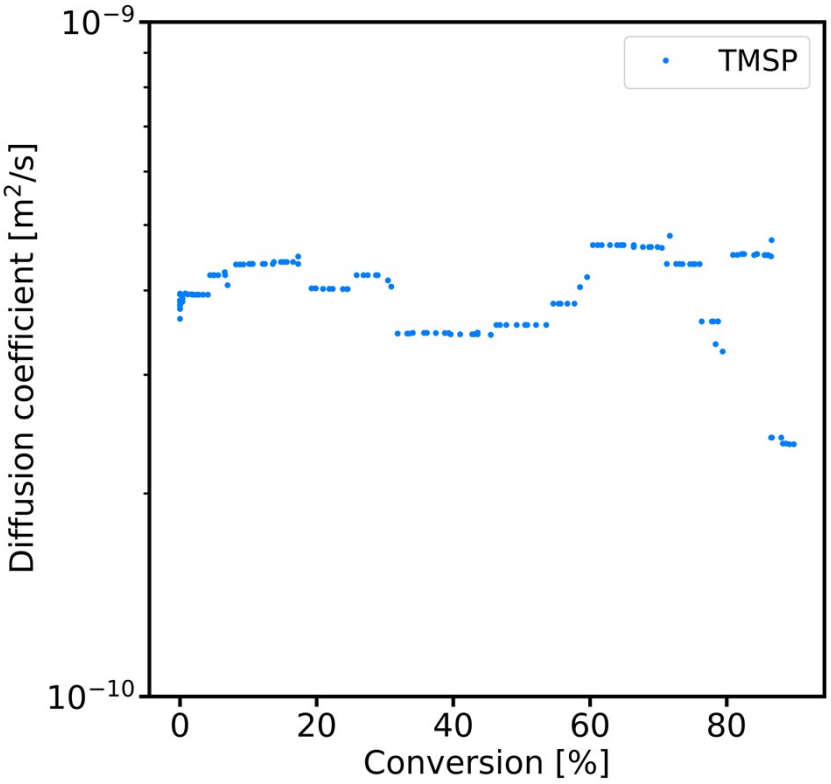

Figure S3. Diffusion coefficients of TMSP as a function of conversion of polymerization.

The figure clearly states that the viscosity change in the system is negligible. The relatively large fitting error of the TMSP is due to the fact that the gradient sampling in TR-D experiment was designed for polymer analysis and TMSP peak was only visible for 3 lowest gradients.

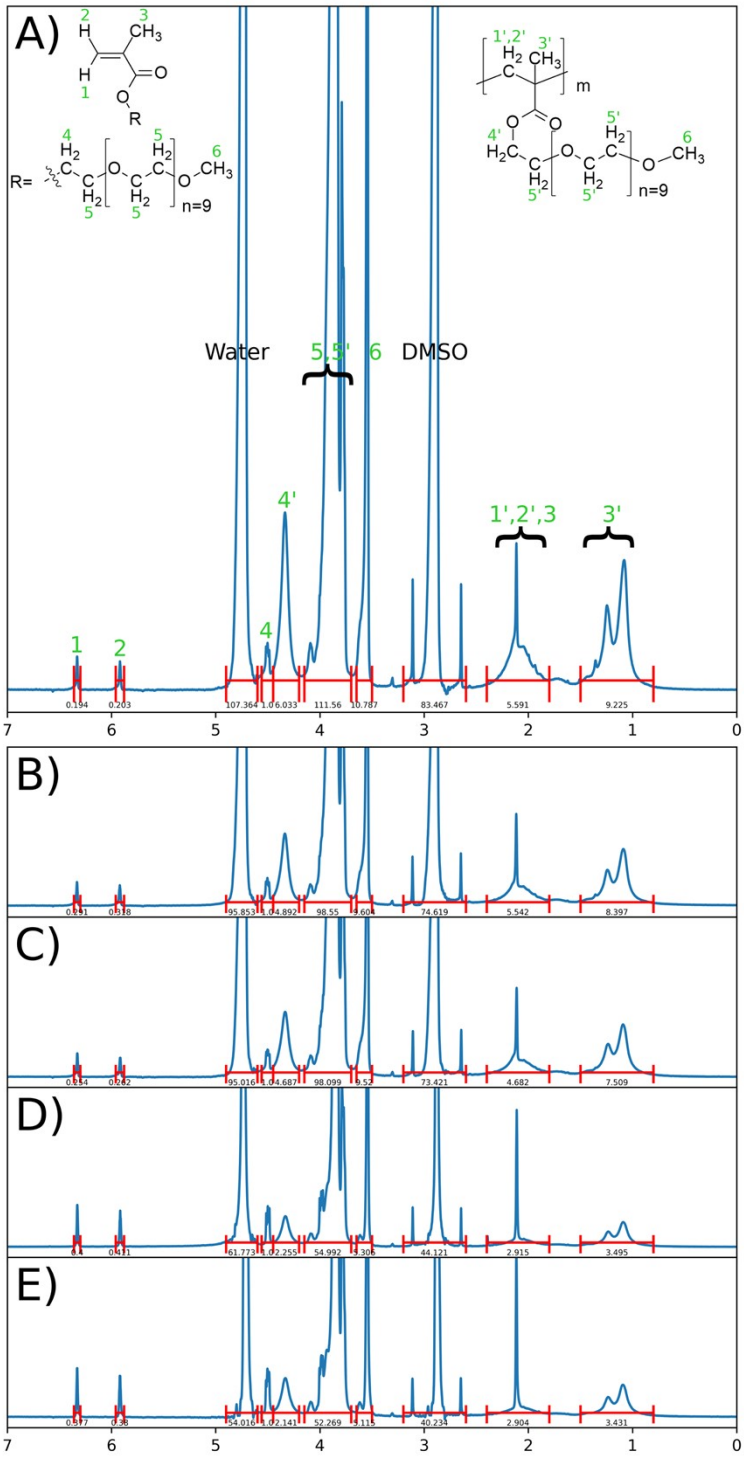

Figure S4. The ^{1}H proton spectra of the reaction mixture were taken at the end of the polymerization process. The spectra of the samples: A) DP_T = 50, B) DP_T = 100, C) DP_T = 200, D) DP_T = 400, E) DP_T = 800. In part A), the signals are assigned to the monomer and polymer hydrogen groups. The processing of the spectra was performed in the TopSpin software, and the integrals were calculated using JupyterLab. The integrals here are just values of the integrals from one point to another, so the monomer to polymer conversion taken from the values of 4 and 4' may differ from calculations described in the data analysis section, as those signals overlap.

Supplementary Information

Size Exclusion Chromatography with Multi-Angle Light Scattering (SEC-MALS)

SEC measurements of p($OEOMA_{500}$) (DP_T of 50, 100 and 200) were performed using an Agilent SEC system (Agilent, 1260 Infinity II) coupled with MALS detector (Wyatt Technology, USA). Measurements were performed using PSS columns (Styrogel 10^5 , 10^3, and 10^2 Å) with DMF as an eluent at 50 °C and the flow rate of 1 mL/min. The injection volume was 100 µL.

Size Exclusion Chromatography (SEC)

SEC measurements of p($OEOMA_{500}$) (DP_T of 400 and 800) were performed using a Shimadzu (Kyoto, Japan) modular system equipped with a CBM-40lite system controller, DGU-403 degassing unit, SIL-40 automatic injector, the RID-20A differential refractive-index detector. Measurements were performed using PSS columns (2x GRAM 3000 Å and GRAM 100 Å) with DMF as an eluent at 40 °C and the flow rate of 1 mL/min. The injection volume was 100 µL. Linear poly(methyl methacrylate) standards were used for calibration (Mp = 1 591 000, 1 020 000, 538 500, 273 600, 156 200, 60 300, 32 340, 13 630, 6940, 1980, 1015 and 535 g/mol).

ATRP polymerization procedure

Prior to polymerization, the following stock solutions were prepared: HOBiB (300 mM, 63.2 mg in 1.0 mL DMSO, used for DP_T = 50) - this solution was further diluted to concentrations of 150, 75, 37.5, 25, and 18.8 mM, corresponding to target DP_T values of 100, 200, 400, 600, and 800, respectively; $CuBr_2$ (33.5 mg in 20.0 mL DMSO), TPMA (13.1 mg in 1.0 mL DMSO), Eosin Y disodium salt ($EYNa_2$, 10.4 mg in 10 mL H_2O).

The ATRP reaction mixture was prepared in a 1.0 mL volumetric flask by weighing 150 mg of $OEOMA_{500}$ and sequentially adding DMSO (20 µL) and the following stock solutions: $CuBr_2$ (40 µL), TPMA (20 µL), HOBiB at the appropriate concentration for the target DP (20 µL), $EYNa_2$ (10 µL), PBS (100 µL). The flask was then filled to the mark with D_2O.
The final concentrations in the mixture were: [$OEOMA_{500}$] = 300 mM, [HOBiB] = 0.375-6.0 mM (depending on the target DP_T), [$CuBr_2$] = 0.30 mM, [TPMA] = 0.90 mM, [$EYNa_2$] = 0.015 mM. The mixture was vortexed to ensure homogeneity, and 500 µL of it was then transferred into an NMR tube.

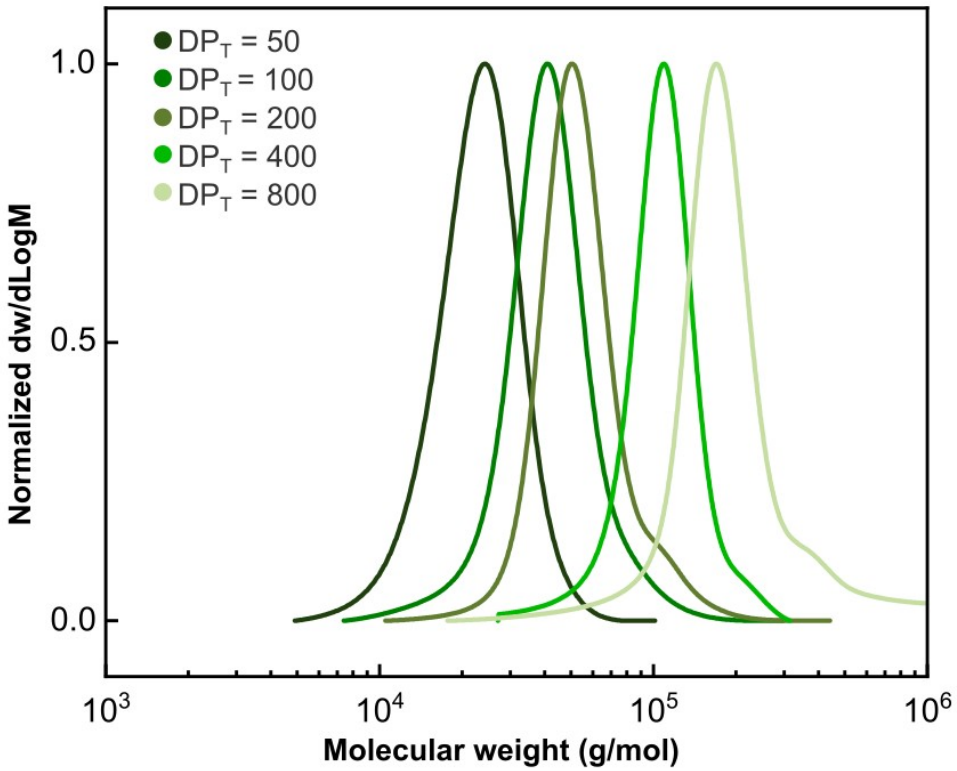

Figure S5. SEC analysis of p(OEOA$_{500}$) with varying targeted DP$_T$.

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