Supplementary Information

Single Molecule Diffusion and its Heterogeneity during the Bulk Radical Polymerization of Styrene and Methyl Methacrylate

Beate Stempfle,[a] **Maren Dill,**[a] **Martin J. Winterhalder,**[a] **Klaus Müllen**[b] and **Dominik Wöll***[a,c]

[a] Faculty of chemistry, University of Konstanz, Universitätsstrasse 10, 78464 Konstanz, Germany.

[b] Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany.

[c] Zukunftskolleg, University of Konstanz, Universitätsstrasse 10, 78464

Table of contents

1. Difference in reactivity

Rate constants for polymerization (k_p) at 20 °C were calculated according to [S1], termination rate constants (k_t) were taken from reference [S2].

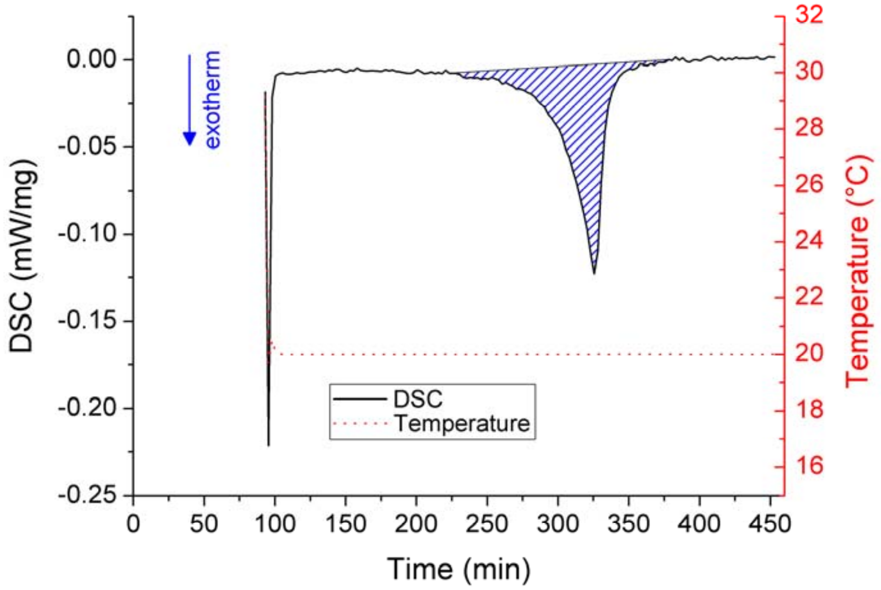
Table S1: Rate constants for the polymerization of methyl methacrylate and styrene in bulk.

	k_p / l mol^{-1}s^{-1}	k_t / l mol^{-1}s^{-1}
MMA	277	3.9×10^{7}
ST	69	7.8×10^{7}

We assume that monomer concentration, initiator concentration, and cleavage rate and efficiency of the initiator are comparable in both systems. If this is the case, the ratio of polymerization rates r is only determined by the values of k_p and k_t:

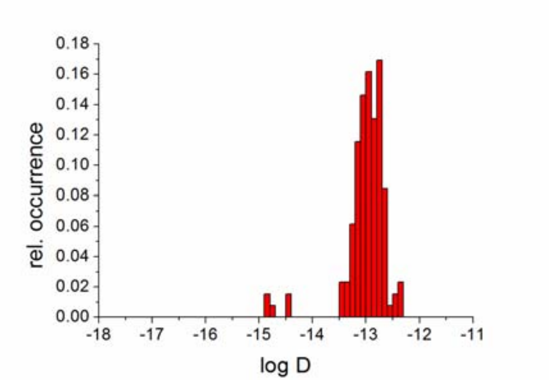
$$\frac{k_{p,MMA}}{k_{t,MMA}^{0.5}} \Big/ \frac{k_{p,ST}}{k_{t,ST}^{0.5}} = 5.68$$

2. Differential Scanning Calorimetry

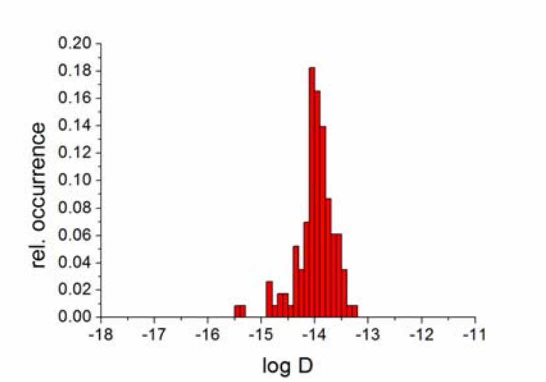


The degassed MMA polymerization mixture (13.7 mg) was filled into an aluminum pan and sealed with an aluminum lid under oxygen-free atmosphere. The sample was placed into a DSC (Netzsch Phoenix 204 F1), and the heat flow at isothermal conditions (20 °C) was measured against an empty sample pan.
The start of the DSC experiment is not equal to the start of the polymerization, as the used thermal initiator cleaves at room temperature. Therefore the polymerization reaction takes place already during the preparation of the experiment. The time delay between the start of the reaction and the start of the DSC experiment was appox. 90 min.

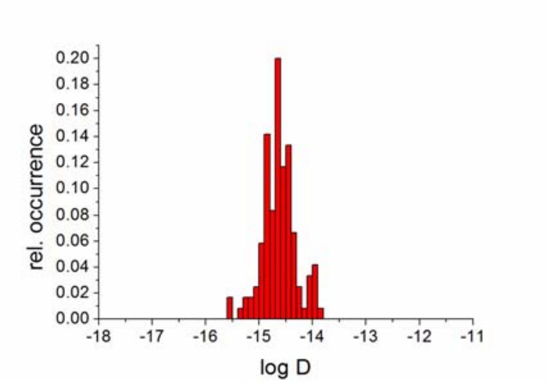
3. Distribution of the diffusion coefficients for dye 1 during the polymerization of styrene



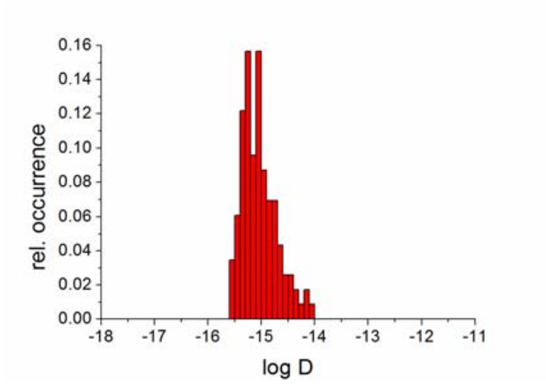
conversion: 73%
average D: 1×10^{-13} m^2s^{-1}



conversion: 76%
average D: 1×10^{-14} m^2s^{-1}

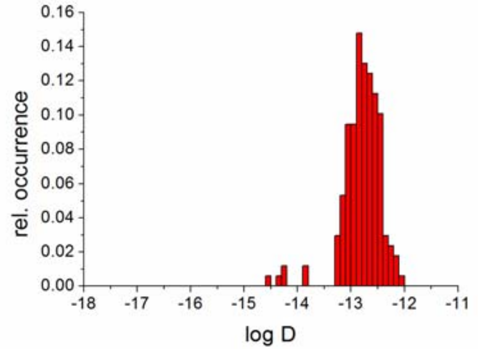


conversion: 79%
average D: 1×10^{-15} m^2s^{-1}

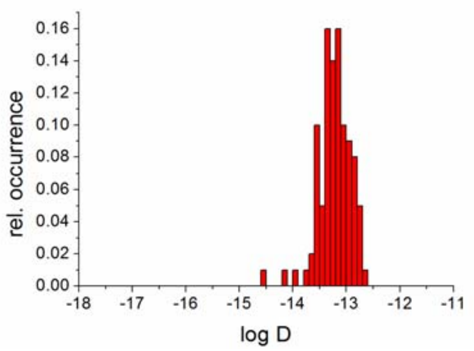


conversion: 83%
average D: 1×10^{-16} m^2s^{-1}

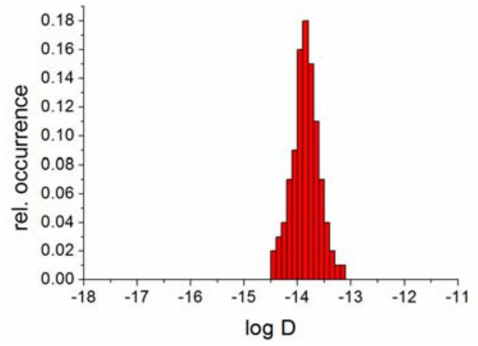
4. Distribution of the diffusion coefficients for dye 1 during the polymerization of MMA



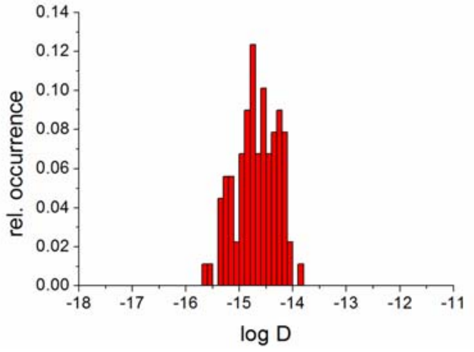
conversion: 55%
average D = 2×10^{-13} m^2s^{-1}



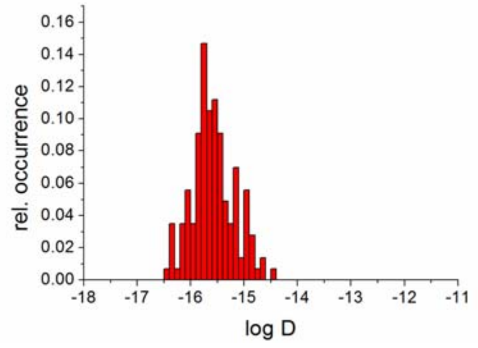
conversion: 58%
average D = 4×10^{-14} m^2s^{-1}



conversion: 60%
average D = 1×10^{-14} m^2s^{-1}

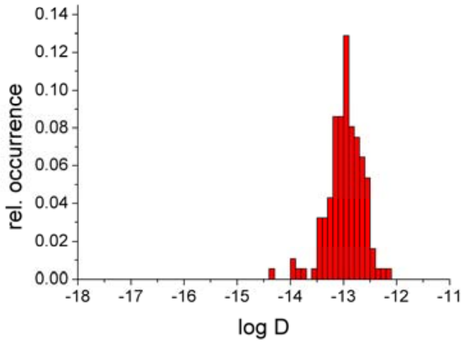


conversion: 63%
average D = 2×10^{-15} m^2s^{-1}

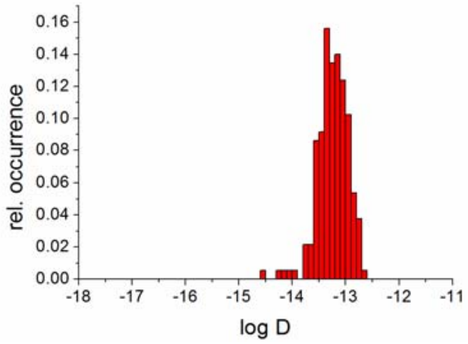


conversion: 73%
average D = 1×10^{-16} m^2s^{-1}

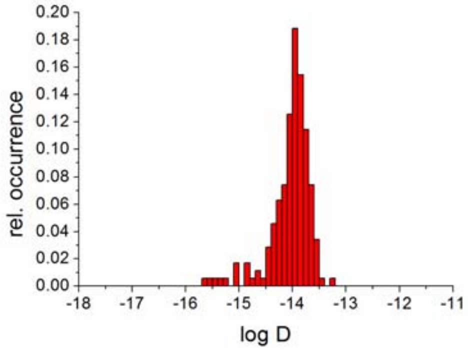
5. Distribution of the diffusion coefficients for dye 2 during the polymerization of styrene



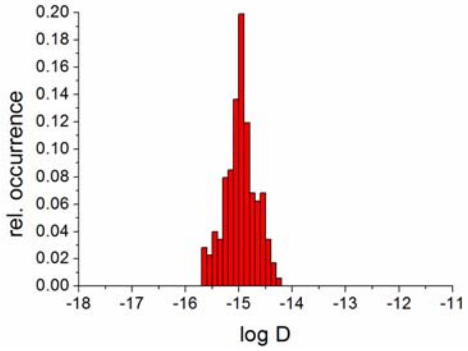
conversion: 40%
average D = 1×10^{-13} m^2s^{-1}



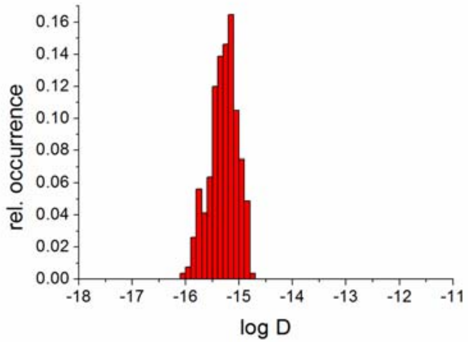
conversion: 56%
average D = 7×10^{-14} m^2s^{-1}



conversion: 65%
average D = 1×10^{-14} m^2s^{-1}

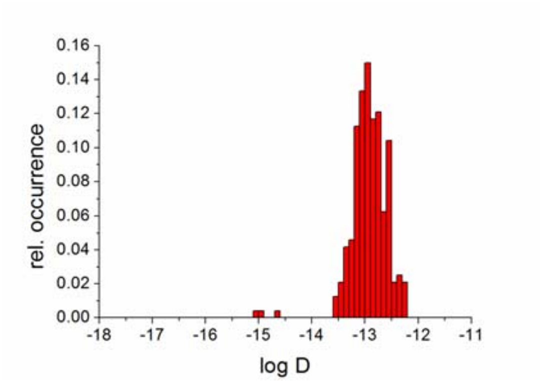


conversion: 70%
average D = 1×10^{-15} m^2s^{-1}

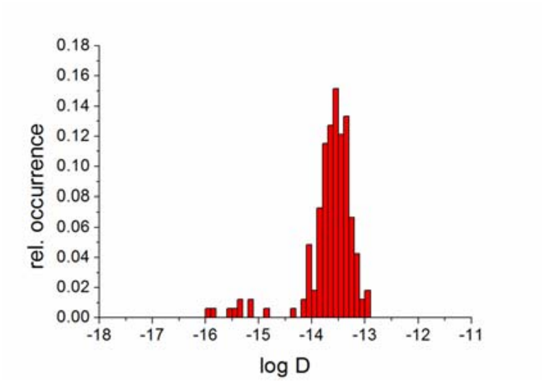


conversion: 78%
average D = 2×10^{-16} m^2s^{-1}

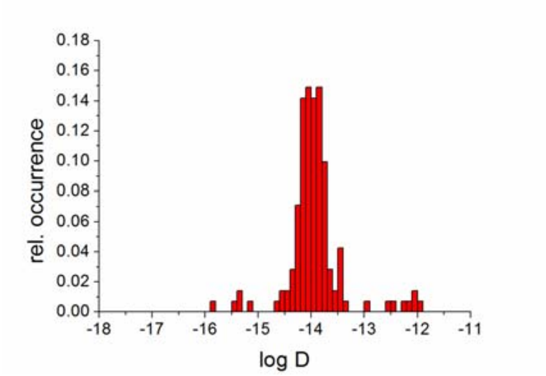
6. Distribution of the diffusion coefficients for dye 2 during the polymerization of MMA



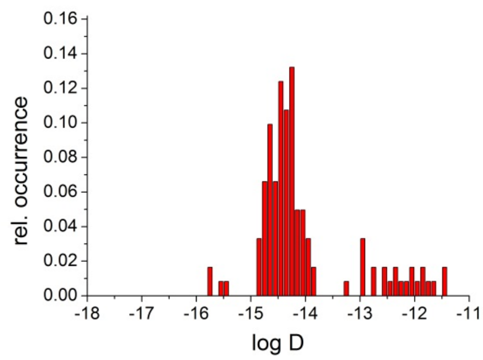
conversion: 30%
average D = 2×10^{-13} m^2s^{-1}



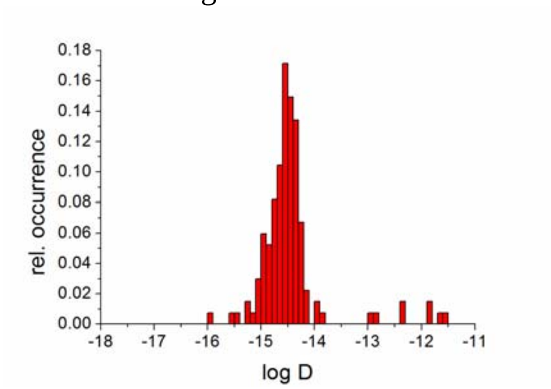
conversion: 41%
average D = 3×10^{-14} m^2s^{-1}



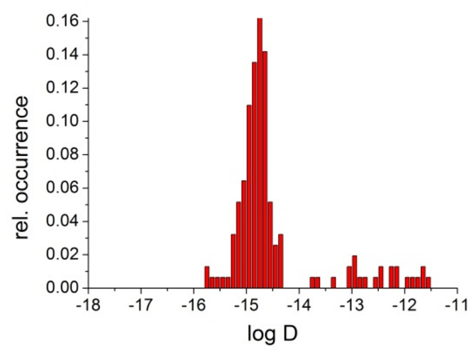
conversion: 45%
average D = 1×10^{-14} m^2s^{-1}



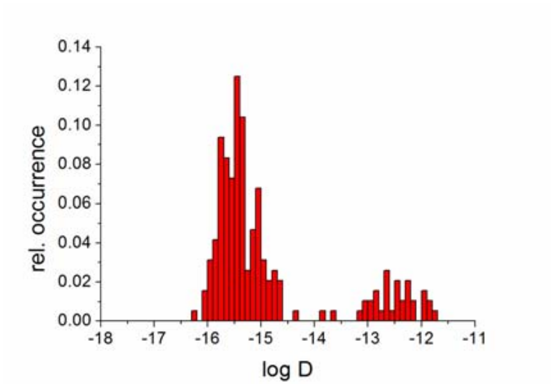
conversion: 48%
average D = 3×10^{-15} m^2s^{-1}



conversion: 50%
average D = 1×10^{-15} m^2s^{-1}



conversion: 52%
average D = 5×10^{-16} m^2s^{-1}



conversion: 56%
average D = 1×10^{-16} m^2s^{-1}

7. Mark-Houwink coefficients (taken from ref [S3])

		styrene / PS	**MMA / PMMA**
Mark-Houwink coefficient	**K** (for PS / Toluene) / ml g^{-1}	0.0105	
Mark-Houwink coefficient	**K** (for PMMA / EtOAc) / ml g^{-1}		0.011
Mark-Houwink coefficient	**a** (for PS / Toluene)	0.73	
Mark-Houwink coefficient	**a** (for PMMA / EtOAc)		0.69
weight-averaged molar mass	$\mathbf{M_w}$ / g mol^{-1}	54000	180000
overlap concentration	**c*** / g ml^{-1}	0.050	0.032
overlap conversion	**x*** / g ml^{-1}	0.048	0.027
radius of gyration	$\mathbf{R_g}$ / nm	7.5	13.0

8. Sample Movies

Movies taken during the polymerization of MMA

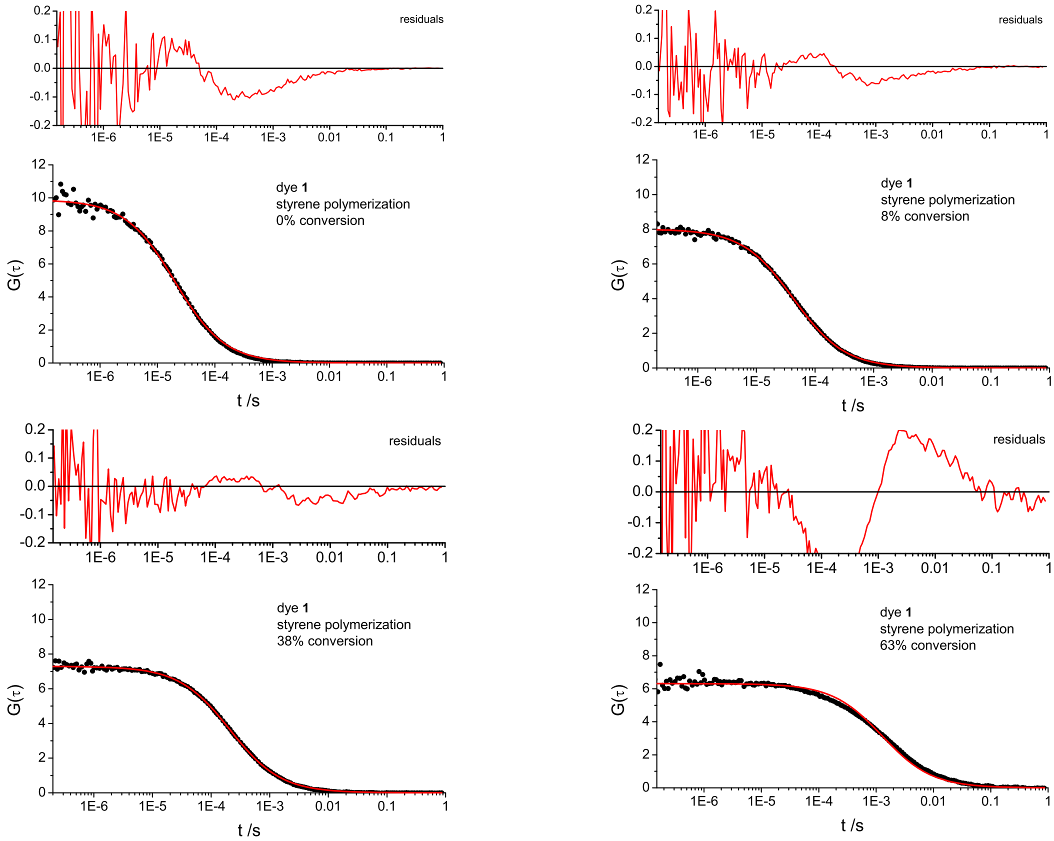
MMA_dye2_conv30:	Motion of dye **2** during the polymerization of MMA at 30% conversion, integration time per frame 0.029 s, unprocessed movie.
MMA_dye2_conv41:	Motion of dye **2** during the polymerization of MMA at 41% conversion, integration time per frame 0.029 s, unprocessed movie.
MMA_dye2_conv45:	Motion of dye **2** during the polymerization of MMA at 45% conversion, integration time per frame 0.029 s, unprocessed movie.
MMA_dye2_conv50:	Motion of dye **2** during the polymerization of MMA at 50% conversion, integration time per frame 0.029 s, unprocessed movie.
MMA_dye2_conv56:	Motion of dye **2** during the polymerization of MMA at 56% conversion, integration time per frame 0.029 s, unprocessed movie.

Movies taken during the polymerization of styrene

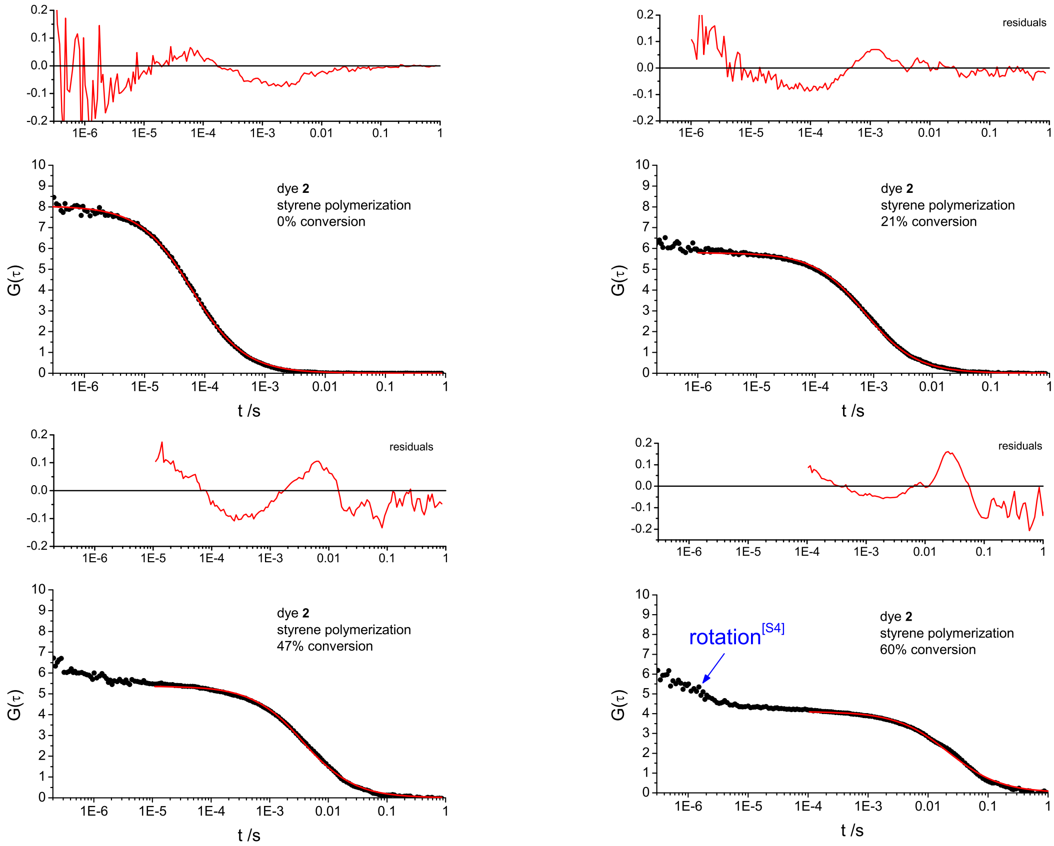
St_dye2_conv40:	Motion of dye **2** during the polymerization of styrene at 40% conversion, integration time per frame 0.029 s, unprocessed movie
St_dye2_conv56:	Motion of dye **2** during the polymerization of styrene at 56% conversion, integration time per frame 0.030 s, unprocessed movie
St_dye2_conv65:	Motion of dye **2** during the polymerization of styrene at 65% conversion, integration time per frame 0.040 s, unprocessed movie
St_dye2_conv70:	Motion of dye **2** during the polymerization of styrene at 70% conversion, integration time per frame 0.040 s, unprocessed movie
St_dye2_conv78:	Motion of dye **2** during the polymerization of styrene at 78% conversion, integration time per frame 0.040 s, unprocessed movie

9. Typical FCS curves and their fits

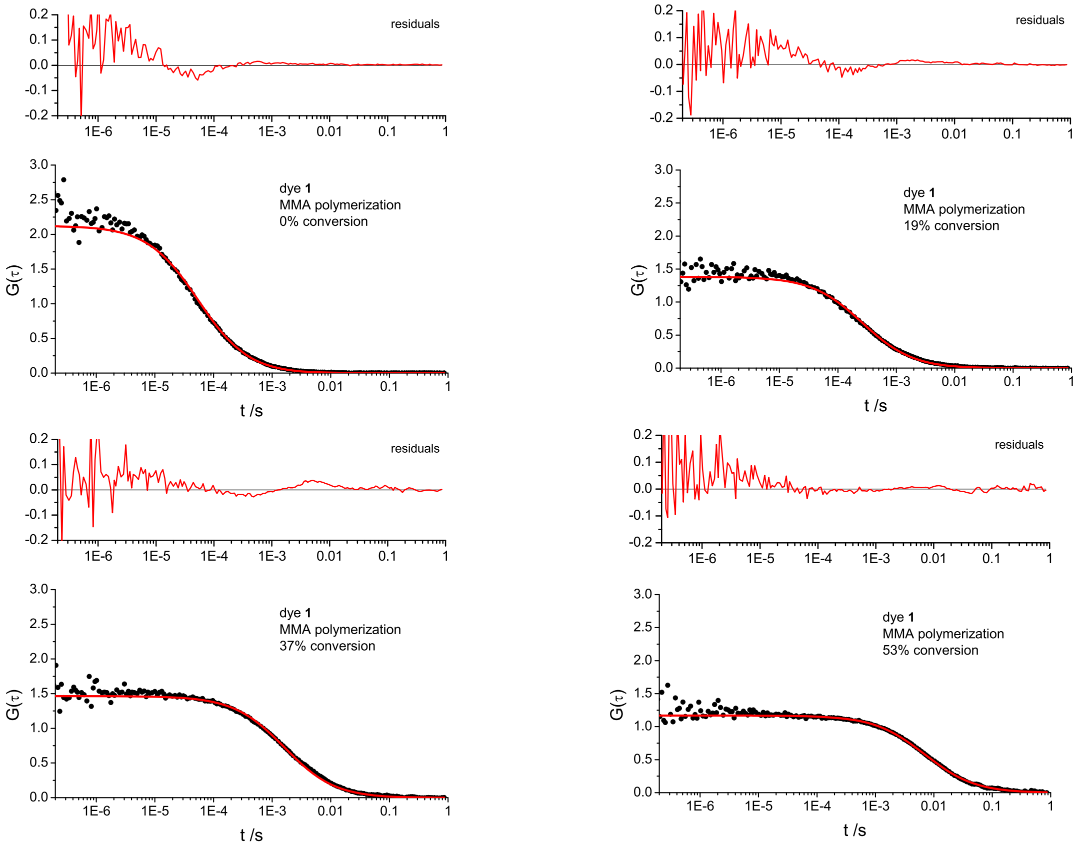
Dye 1 during the polymerization of styrene



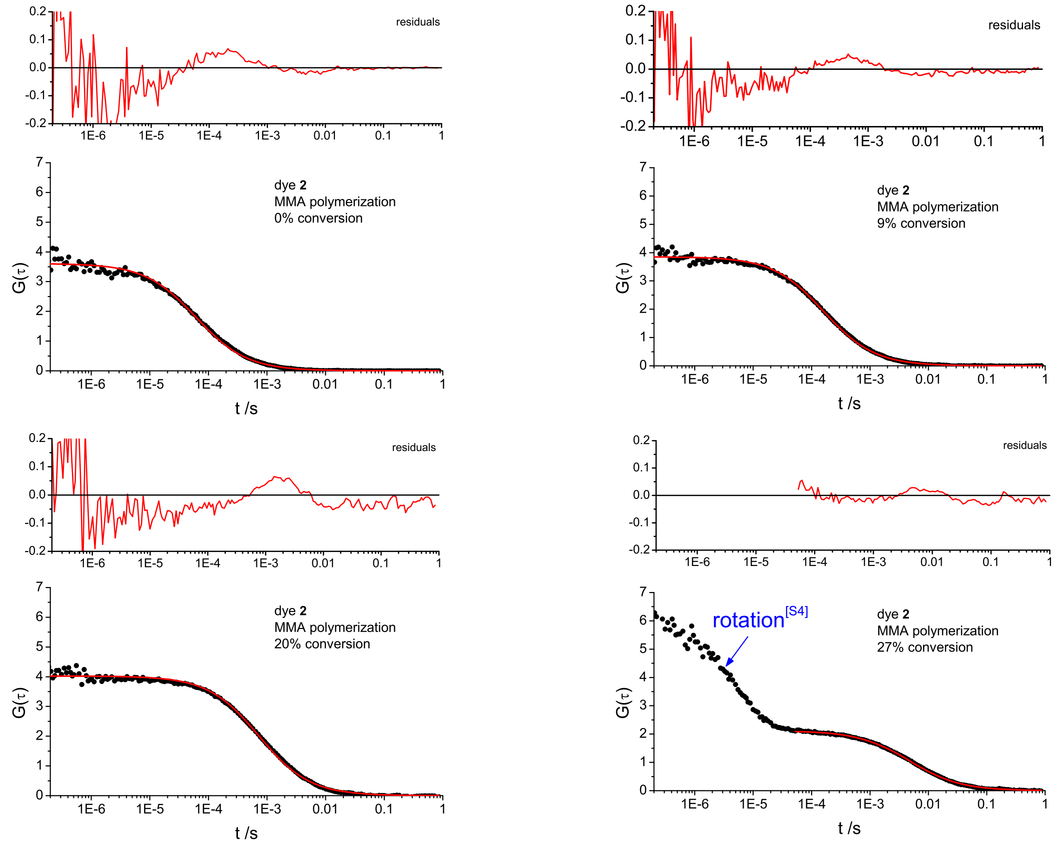
Dye 2 during the polymerization of styrene



Dye 1 during the polymerization of MMA

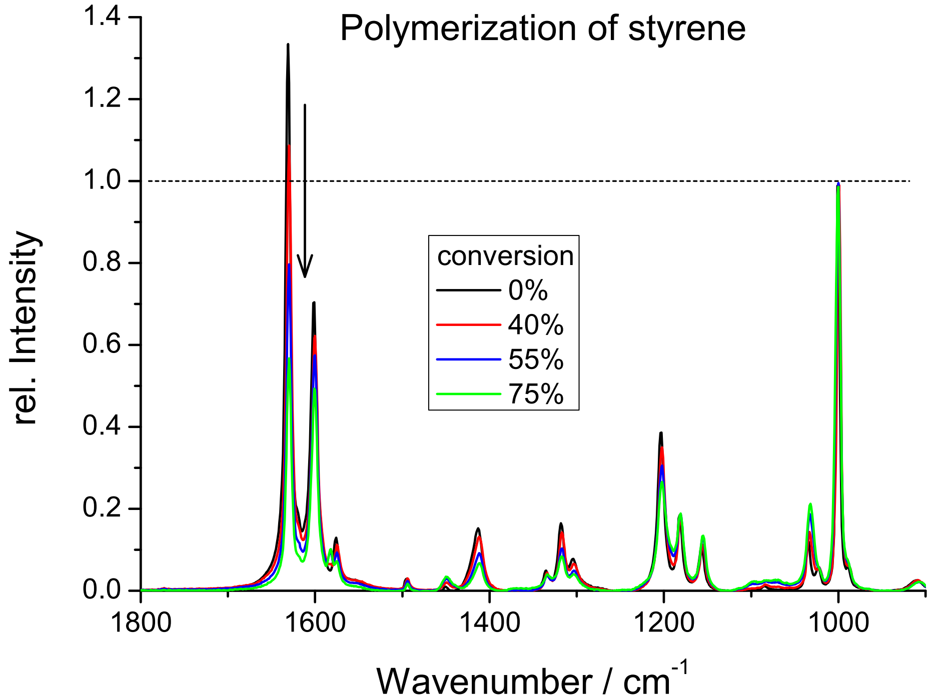


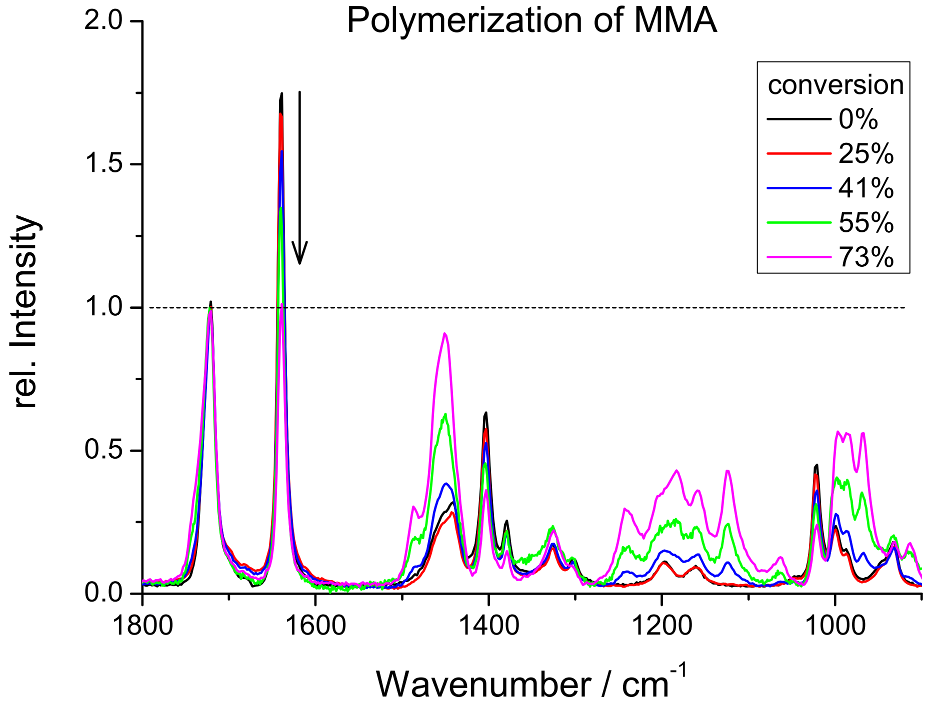
Dye 2 during the polymerization of MMA



10. Raman spectra used for determination of conversion

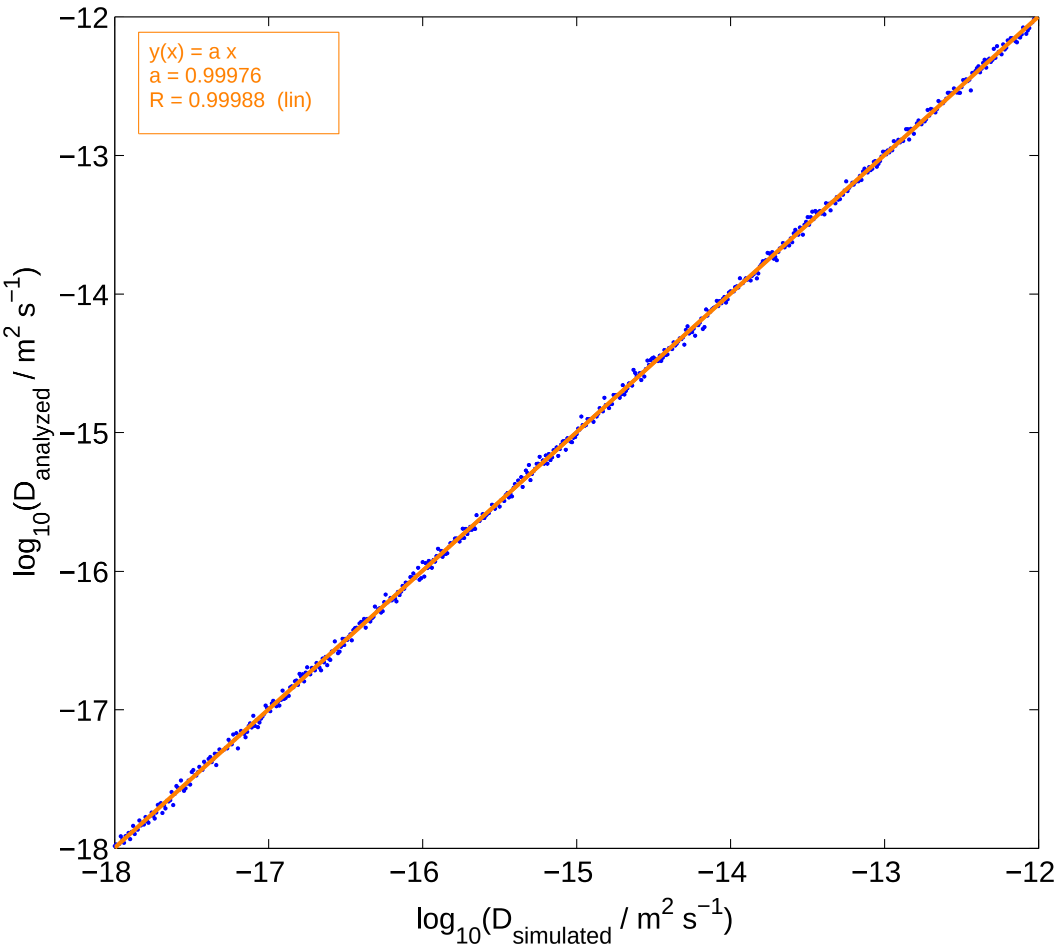
Monomer-to-polymer conversion was monitored by Raman spectroscopy.[S5] For the polymerization of styrene, the ratio of intensities between the C=C-stretching vibration at 1630 cm^{-1} and a ring vibrational mode at ca. 1000 cm^{-1} was determined. For the polymerization of MMA, the ratio of intensities between the C=C-stretching vibration at 1640 cm^{-1} and the C=O-stretching vibration at 1720 cm^{-1} was determined. From the ratios, the conversions were calculated using a calibration with solutions of known concentration. Note that the relation of the peak intensities is not linear with conversion, as reported in [S5].





11. Verification of the relation $R_T^2\pi \cdot s^{-1} \approx 2.12 \times D$ between track radius and diffusion coefficient

Monte Carlo Random Walk simulations were performed to elucidate the relation between track radius R_T and diffusion coefficient D. For this, 100 trajectories with 100 steps each were simulated using diffusion coefficients between 10^{-18} and 10^{-12} m^2s^{-1}. The diffusion coefficients obtained using the track radius analysis described in this paper for all 100 trajectories with the same diffusion coefficients were averaged and plotted versus the ground truth diffusion coefficients as used for the corresponding simulation. The good correlation between simulated and analyzed diffusion coefficients is shown in the figure below. It verifies the relation $\boldsymbol{R_T^2\pi \cdot s^{-1} \approx 2.12 \times D}$.



Literature

[S1] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer, A. M. vanHerk, *Macromol. Chem. Phys.* **1997**, *198*, 1545-1560.

[S2] O. F. Olaj, I. Schnöll-Bitai, *Eur. Polym. J.* **1989**, *25*, 635-641.

[S3] J. E. Mark (Ed.), *Physical Properties of Polymers Handbook*, 2nd Edition, Springer, **2007**.

[S4] M. Dorfschmid, K. Müllen, A. Zumbusch, D. Wöll, *Macromolecules* **2010**, *43*, 6174-6179.

[S5] B. Chu, G. Fytas, G. Zalczer, *Macromolecules* **1981**, *14*, 395-397.