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

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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.

<table>
<thead>
<tr>
<th></th>
<th>$k_p / \text{l mol}^{-1}\text{s}^{-1}$</th>
<th>$k_t / \text{l mol}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>277</td>
<td>3.9×10⁷</td>
</tr>
<tr>
<td>ST</td>
<td>69</td>
<td>7.8×10⁷</td>
</tr>
</tbody>
</table>

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 $k_t$:

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

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 approx. 90 min.
3. Distribution of the diffusion coefficients for dye 1 during the polymerization of styrene

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

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

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

conversion: 83%
average D: $1 \times 10^{-16}$ m$^2$s$^{-1}$
4. Distribution of the diffusion coefficients for dye 1 during the polymerization of MMA

- Conversion: 55%
  - Average $D = 2 \times 10^{-13}$ m$^2$s$^{-1}$

- Conversion: 58%
  - Average $D = 4 \times 10^{-14}$ m$^2$s$^{-1}$

- Conversion: 60%
  - Average $D = 1 \times 10^{-14}$ m$^2$s$^{-1}$

- Conversion: 63%
  - Average $D = 2 \times 10^{-15}$ m$^2$s$^{-1}$

- Conversion: 73%
  - Average $D = 1 \times 10^{-16}$ m$^2$s$^{-1}$
5. Distribution of the diffusion coefficients for dye 2 during the polymerization of styrene

- Conversion: 40%
  - Average $D = 1 \times 10^{-13} \text{ m}^2\text{s}^{-1}$

- Conversion: 56%
  - Average $D = 7 \times 10^{-14} \text{ m}^2\text{s}^{-1}$

- Conversion: 65%
  - Average $D = 1 \times 10^{-14} \text{ m}^2\text{s}^{-1}$

- Conversion: 70%
  - Average $D = 1 \times 10^{-15} \text{ m}^2\text{s}^{-1}$

- Conversion: 78%
  - Average $D = 2 \times 10^{-16} \text{ m}^2\text{s}^{-1}$
6. Distribution of the diffusion coefficients for dye 2 during the polymerization of MMA

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

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

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

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

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

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

conversion: 56%
average $D = 1 \times 10^{-16}$ m$^2$s$^{-1}$
7. Mark-Houwink coefficients (taken from ref [S3])

<table>
<thead>
<tr>
<th></th>
<th>styrene / PS</th>
<th>MMA / PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mark-Houwink coefficient</td>
<td>K (for PS / Toluene) / ml g⁻¹</td>
<td>0.0105</td>
</tr>
<tr>
<td>Mark-Houwink coefficient</td>
<td>K (for PMMA / EtOAc) / ml g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Mark-Houwink coefficient</td>
<td>a (for PS / Toluene)</td>
<td>0.73</td>
</tr>
<tr>
<td>Mark-Houwink coefficient</td>
<td>a (for PMMA / EtOAc)</td>
<td></td>
</tr>
<tr>
<td>weight-averaged molar mass</td>
<td>M_w / g mol⁻¹</td>
<td>54000</td>
</tr>
<tr>
<td>overlap concentration</td>
<td>c* / g ml⁻¹</td>
<td>0.050</td>
</tr>
<tr>
<td>overlap conversion</td>
<td>x* / g ml⁻¹</td>
<td>0.048</td>
</tr>
<tr>
<td>radius of gyration</td>
<td>R_g / nm</td>
<td>7.5</td>
</tr>
</tbody>
</table>
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 1: styrene polymerization, 0% conversion
- Dye 1: styrene polymerization, 6% conversion
- Dye 1: styrene polymerization, 38% conversion
- Dye 1: styrene polymerization, 63% conversion

**Dye 2 during the polymerization of styrene**

- Dye 2: styrene polymerization, 0% conversion
- Dye 2: styrene polymerization, 21% conversion
- Dye 2: styrene polymerization, 47% conversion
- Dye 2: styrene polymerization, 63% conversion
**Dye 1 during the polymerization of MMA**

![Graph 1](image1)

**Dye 2 during the polymerization of MMA**

![Graph 2](image2)
10. Raman spectra used for determination of conversion

Monomer-to-polymer conversion was monitored by Raman spectroscopy.\textsuperscript{[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 $10^{-12}$ m²s⁻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 $R_T^2 \pi \cdot s^{-1} \approx 2.12 \times D$.

![Graph showing the correlation between simulated and analyzed diffusion coefficients.](image)

**y(x) = a x**  
$a = 0.99976$  
$R = 0.99988$ (lin)

**Literature**


