Supporting Information

Universality of Time-Temperature Scaling Observed by Neutron Spectroscopy on Bottlebrush Polymers

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**Method**

**Samples**

The samples used for quasi-elastic neutron scattering (QENS) experiments, were PDMS-g-PDMS bottlebrush polymer with varying side chain length, $M_n^{side\,chain} = 298, 1800, 11500$ g/mol, and similar backbone length, $M_n^{backbone} = 16500, 13500$ g/mol, synthesized based on anionic ring opening polymerization and characterized by Gel Permeation Chromatography (GPC), and Nuclear Magnetic Resonance (NMR). A more detailed description of the synthesis can be found in Jakobi et al.$^{S1}$

**Neutron Scattering Experiments**

Dynamical studies, based on the intermediate scattering function, $S_{inc}(Q,t)$, on these samples have been performed by QENS and have been published in Bichler et al.$^{S5}$ Hereby, a combination of three different spectrometers has been used to capture a time range of three orders of magnitude, i.e., $t = 1$ ps to $t = 1$ ns. The short times were covered by the time-of-flight spectrometer Pelican$^{S2}$ and the long times by the backscattering spectrometer EMU$^{S3}$, both located at ANSTO, Sydney, Australia. For the intermediate times, the time-of-flight backscattering instrument IRIS$^{S4}$, at the spallation source ISIS, Didcot, UK was used. Transforming the data into the time domain, results in the incoherent intermediate scattering function, $S_{inc}(Q,t)$. This allows a combination of the data of the three instruments and subsequently enables the combined analysis of $S_{inc}(Q,t)$ based on the different relaxation processes.$^{S5}$ The time dependence of $S_{inc}(Q,t)$ for all temperatures measured and for all three samples can be found in Bichler et al.$^{S5}$
Supporting Analysis Steps for the example PDMS-g-PDMS with $M_n^\text{side chain} = 11500$ g/mol

Mean-Square Displacement Analysis

The mean-square displacement (MSD) analysis is based on the cumulative serial expansion of the incoherent intermediate scattering function, $S_{\text{inc}}(Q,t)$, following equation (1) in the main text. Hereby, $\ln(S_{\text{inc}}(Q,t))$ is represented as a function of $Q^2$ for selected time values, $t$. Describing this representation with equation (1) leads to two fit parameters, the non-Gaussian parameter, $\alpha_2(t)$, and the mean-square displacement, $MSD \left(\langle r^2(t)\rangle\right)$, both depending on time, $t$. This analysis way is illustrated in Fig. S1 exemplarily for 8 different time values. For the main text, this analysis has been done for 31 different times values, resulting in 31 values for $\alpha_2(t)$ and for the mean-square displacement, $MSD$. Both are illustrated in Fig. 1b and Fig. 2a, of the main text, respectively.

![Fig. S1](image.png)

**Fig. S1.** Analysis of the experimental intermediate scattering function, $S_{\text{inc}}(Q,t)$, with the cumulant series expansion. Intermediate scattering function, $S_{\text{inc}}(Q,t)$, represented in the common logarithm vs. $Q^2$ for eight different time values in picoseconds, as indicated, at the temperature $T = 300$ K. Dashed lines are the description with equation (1) from the main text.
Adjustment for Fast Vibrations

In order to adjust the mean-square displacement of the methyl group and the segmental dynamics for fast vibrations, the atomistic mean-square displacement has been used. It is included in the Debye-Waller Factor and obtained from the incoherent intermediate scattering function analysis. These values have been subtracted from the respective temperatures of the original mean-square displacement data (Fig. 2a) to gain the single process mean-square displacement. The resulting temperature dependence of the atomistic mean-square displacement is shown in Fig. S2 including a dashed line, which serves as a guide for the eye.

**Fig. S2.** Atomistic mean-square displacement of the PDMS-g-PDMS with $M_n^{side\ chain} = 11500$ g/mol. (a) Atomistic mean-square displacement, $MSD$, vs. temperature, $T$, for the PDMS-g-PDMS bottlebrush polymer. Dashed line is a guide for the eye. (b) Mean square displacement, $MSD$, vs. time, $t$, for the methyl group rotations. Dashed lines represent the time-independent atomistic mean square displacement at the respective temperatures as indicated.
Shift Parameter

To create the mean-square displacement of the single processes, time, $a_T$, and displacement, $b_T$, scaling has been applied. Hereby, for the methyl group mean-square displacement shift factors for both directions have been used, while for the segmental mean-square displacement only the time axis has been scaled. In case of the methyl group, time shift factor, $a_T$, and relaxation time, $\tau_\ell$, show a similar temperature scaling, which points to a time-temperature superposition principle (purple squares in Fig. S3a). The temperature dependence can be described with an Arrhenius law, with the activation energy, $E_A$, being the same as obtained for the temperature dependence of the relaxation times, $\tau_\ell$.

$$a_T = a_0 \cdot \exp \left( \frac{E_A}{RT} \right) \quad \text{(S1)}$$

The shift factors, $b_T$, show a linear relationship with temperature as illustrated in Fig. S3b, which is described by

$$b_T = m \cdot T + b_0 \quad \text{(S2)}$$

The associated fit parameter, describing the temperature dependence for both shift factors are summarized in Table S1.

The mean-square displacement for the segmental dynamics needs only to be shifted along the time axis. The shift parameters used follow the Vogel-Fulcher-Tammann (VFT) behavior known from dielectric spectroscopy experiments on this sample.
**Fig. S3. Temperature dependence of the obtained shift parameters for the methyl group mean-square displacement.** (a) Shift parameter, $a_T$, vs. $1000/T$. Solid purple line is the best description with the Arrhenius law, equation (S1). Grey symbols and dashed grey lines are the temperature dependence of the relaxation times, $\tau_\ell$, obtained for the methyl group rotation and included for comparison. (b) Shift parameter, $b_T$, vs. temperature, $T$. Solid line is the best description with the linear relationship and parameters defined in equation (S2).

**Table S1. Fit parameters for the temperature dependencies.** Temperature dependence of the shift factors, $a_T$ and $b_T$ as described by equations (S1), and (S2), respectively. Errors are the standard deviations of the respective quantity.

|        | $a_0$                 | $E_A$ (kJ/mol) |
|--------|-----------------------|----------------|
| $a_T$  | $(4.2 \pm 0.6) \cdot 10^{-5}$ | $(5.8 \pm 0.4)$ |
| $b_T$  | $(0.006 \pm 0.001)$   | $(0.7 \pm 0.1)$ |
Parametrization of the Pure Segmental Mean-Square Displacement

To simplify the summation of the pure methyl group mean-square displacement and the pure segmental mean-square displacement, the latter one was interpolated by the mathematical expression

\[
\langle r^2(t) \rangle = at^b + a_1 t^{b_1} + a_2 t^{b_2}
\]  

(S3)

with \(a = 502\), \(b = 0.6\), \(a_1 = -800\), \(b_1 = 0.7\), \(a_2 = 324\), and \(b_2 = 0.74\) as illustrated in Fig. S4.

The aim was to find a parametrization of the segmental mean-square displacement for further data treatment, allowing to create the master curve of the segmental mean-square displacement in the same time range with exactly the same points as obtained for the methyl group mean-square displacement master curve. This allows easier pointwise addition of the partial mean-square displacements, resulting in the overall mean-square displacement (Fig. 4b).

![Graph showing parametrization of pure segmental dynamics mean-square displacement.](image)

**Fig. S4.** Parametrization of the pure segmental dynamics mean-square displacement. Mean-square displacement, \(MSD\), vs. time, \(t\), at the reference temperature \(T_{ref} = 250\) K. Solid line is the parametrization with equation (S3).
Experimental verification of the approach used for creating the final mean-square displacement.

**Fig. S5.** Experimental verification of the approach used for creating the final mean-square displacement. Mean-square displacement, $MSD$, vs. time, $t$, for the single methyl group rotation (solid green circles), for the single segmental dynamics (solid blue squares), for the original mean-square displacement, as obtained from the intermediate scattering function (solid cyan stars) and the combined mean-square displacement of methyl group and segmental dynamics (solid orange circles) without the atomistic mean-square displacement.
Fig. S6. Supporting data for the PDMS-g-PDMS bottlebrush polymer with $M_n^{side\ chain} = 1800$ g/mol. (a) Mean-square displacement, $MSD$, vs. time, $t$, as obtained from the intermediate scattering function, $S(Q, t)$, by using the cumulant series expansion, equation (1) from the main text. (b) Atomistic mean-square displacement, $MSD$, vs. temperature, $T$. Dashed line is a guide for the eye. (c) Mean-square displacement, $MSD$, vs. time, $t$, for the single methyl group rotation (solid green circles), for the single segmental dynamics (solid blue squares), for the original mean-square displacement, as obtained from the intermediate scattering function (solid cyan stars) and the combined mean-square displacement of methyl group and segmental dynamics (solid orange circles) without the atomistic mean-square displacement.
Supporting Data for PDMS-g-PDMS bottlebrush polymers with $M_n^{side\ chain} = 293$ g/mol

**Fig. S7.** Supporting data for the PDMS-g-PDMS bottlebrush polymer with $M_n^{side\ chain} = 293$ g/mol. (a) Mean-square displacement, $MSD$, vs. time, $t$, as obtained from the intermediate scattering function, $S(Q,t)$, by using the cumulant series expansion, equation (1) from the main text. (b) Atomistic mean-square displacement, $MSD$, vs. temperature, $T$. Dashed line is a guide for the eye. (c) Mean-square displacement, $MSD$, vs. time, $t$, for the single methyl group rotation (solid green circles), for the single segmental dynamics (solid blue squares), for the original mean-square displacement, as obtained from the intermediate scattering function (solid cyan stars) and the combined mean-square displacement of methyl group and segmental dynamics (solid orange circles) without the atomistic mean-square displacement.
Additional Figures on the example of PDMS-g-PDMS with $M_n^{side\ chain} = 11500$ g/mol

**Fig. S8:** Illustration of the time scales of the three different neutron spectrometers. Mean-square displacement, $MSD$, vs. time, $t$, as obtained from the intermediate scattering function, $S(Q, t)$, by using the cumulant series expansion, equation (1). Shaded areas indicate the time scales of the different spectrometer. Short times: Pelican, intermediate times: IRIS, and long times: EMU.
References:

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