Supplementary Information

Nanoscale study of polymer dynamics

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Contents

Polymer contour length

The labelled polymer contour length, L, was calculated by using a histogram of the polymer length during the measurement time. Starting from the longest length and considering the time at which the polymer had this length and checking the fitted image we extract the polymer length as the longest length in the histogram where the chain is entirely in the focal plane, Fig. S1.
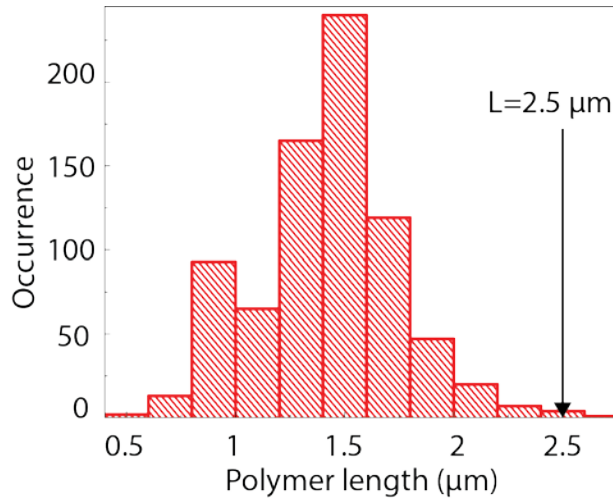

Figure S1| The contour length of the polymer. Histogram of the polymer length during measurement time.

Persistence length

In order to obtain the persistence length of the labelled polymer we plotted the occurrence of end-to-end distance extracted from real-time fluorescence images, Fig. S2. To avoid the surrounding chains effect this experiment was done in the diluted matrix (concentration=3 mg/ml). As can be seen in the figure S2 our data fits well with a Gaussian and follows an ideal chain model. Within this model we calculated the polymer persistence length as follows[1]:

$$P(\vec{R}) = (\frac{3}{2\pi L l_p})^{1/2} \exp(\frac{-3R^2}{2Ll_p})$$

Where R is the end-to-end distance, L and l_p are the contour and persistence length of the labelled polymer, $l_p = 120 \pm 30$ nm^2.
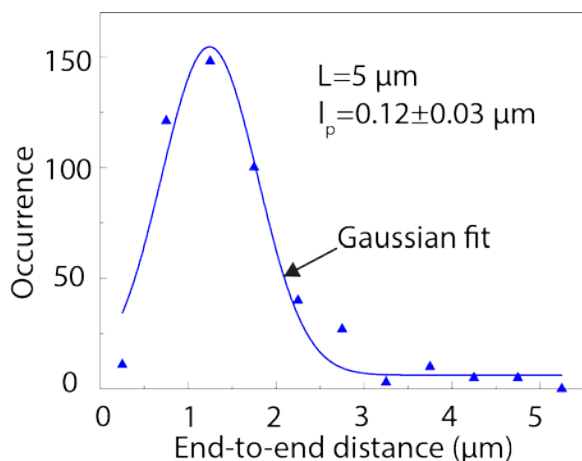

Figure S2| Polymer persistence length. Calculating the persistence length (l_p) of the labelled L,D-PIAA in a diluted matrix (3 mg/ml) using Gaussian end-to-end distribution function.

Additional data on extracting parameters of the confined polymer motion

Analogous to Fig. 3 in the manuscript, figures S3a and S4a, are the snapshots of the motion of the labelled L,D-PIAA chain in a concentrated solution of unlabelled L,D-PIAA (see movie#5 and movie#3) and clearly show the constrained motion of the polymers.

In figures S3b and S4b we plotted the superimposed conformations of the labelled polymer for the entire movie from t=0 to t=70 s, S3b, and t=0 to t=80 s, S4b, and estimated the tube diameter to be a=150±30 nm and a=160±30 nm. The imaginary tubes demonstrated in figure S3a and S4a can be seen clearly in figure S3b and S4b. When the tubes do not have any overlap then we can approximately determine the disentanglement time to be τ_d=70 s and τ_d=83 s, respectively.

In figure S3 c and d we extracted the Rouse time, τ_R=1.0±0.1 s and the tube diameter, a=140±20 nm using the same procedure as described in figure 5 in the manuscript.

In order to extract the Rouse time and the tube diameter (a=140±30 nm) for the chain in figure S4c and d, we applied the same procedure as figure 5 in the manuscript as well. For this data the disentanglement time, τ_d, was longer than our measurement time and we were not able to observe reptation regime thus, the Rouse time could not be extracted.
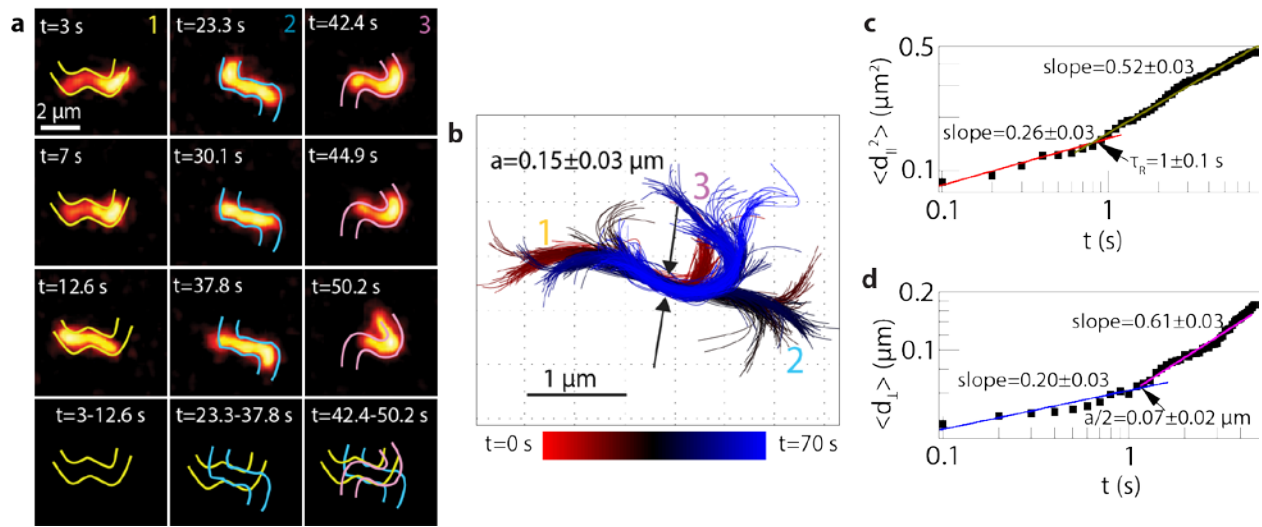

Figure S3| movie analysis. a, Snapshots of the worm-like motion of a single chain in a concentrated matrix. The imaginary tube is marked in each snapshot and superimposed with increasing time in the last row. The columns (1 to 3) indicate changes occurred in the tube shape during time. **b,** Superimposed chain configuration for the entire movie. The colour code indicates the time. The corresponding changes in the tube shape that is shown with the numbers in the snapshots can be seen here clearly (1 to 3). **c,** $\langle d_\parallel^2 \rangle$ as a function of lag time, indicating the regimes of local reptation (exponent = 0.26 ± 0.03) and reptation(exponent = 0.52 ± 0.03). The time between the two regimes is the Rouse time τ_R = 1 ± 0.1 s. **d,** perpendicular displacement versus lag time for a labelled chain in the concentrated matrix. Two regimes can be distinguished from the change in the slope of the fits (solid lines). The tube radius is extracted to be $a/2$ = 0.07 ± 0.02 µm from the crossing point of the fits.
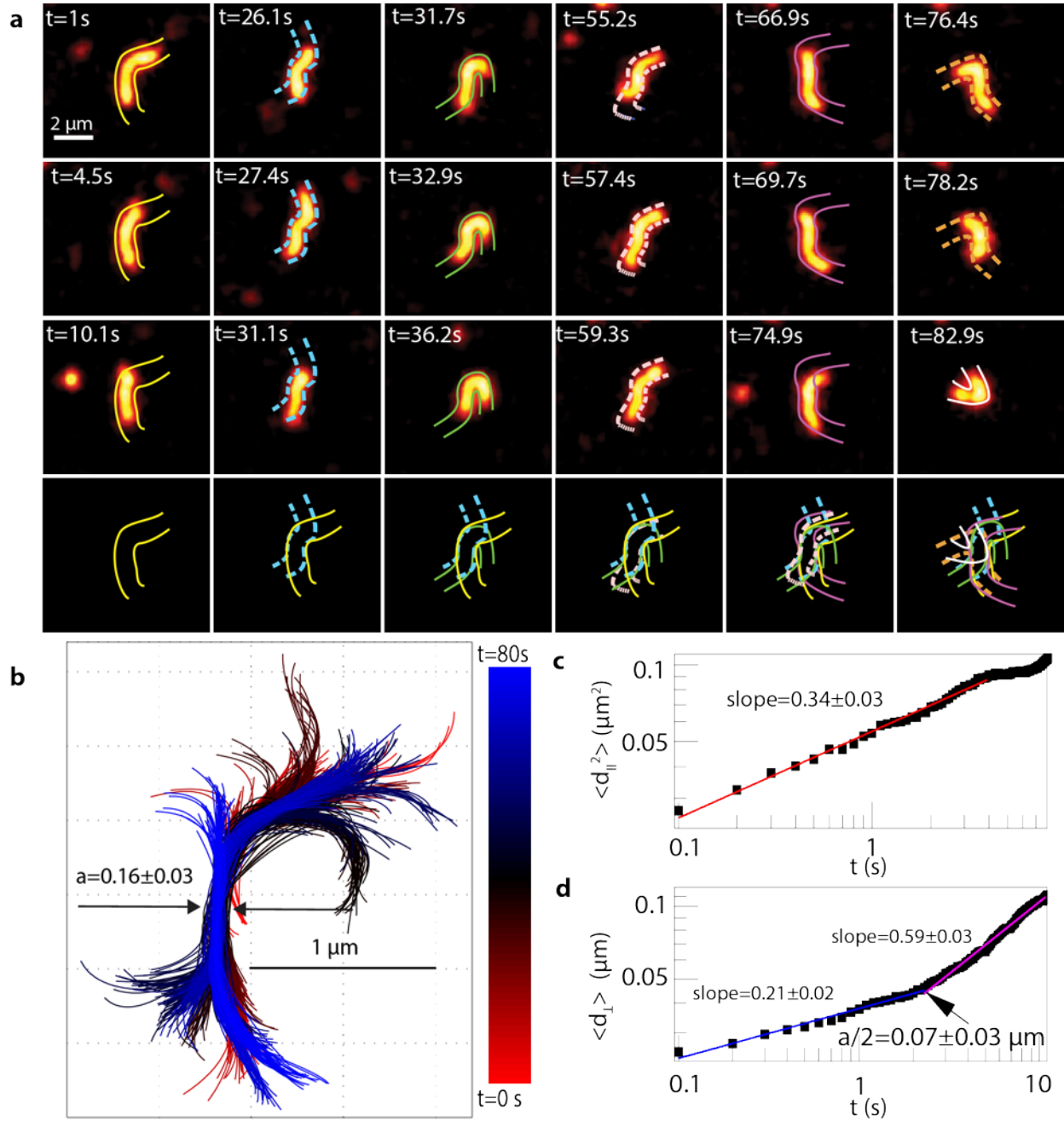
Figure S4| movie analysis. a, Snapshots of the worm-like motion of a single chain in a concentrated matrix. The imaginary tube is marked in each snapshot and superimposed with increasing time in the last row. The columns indicate changes occurred in the tube shape during time. **b,** Superimposed chain configuration for the entire movie. The colour code indicates the time. **c,** $\langle d_{\parallel}^2 \rangle$ as a function of lag time. **d,** Average perpendicular displacement versus lag time for a labelled chain in the concentrated matrix. Two regimes can be distinguished from the change in the slope of the fits (solid lines). The tube diameter is extracted to be a=140±30 nm from the crossing point of the fitted lines.

References

1   Doi, M. & Edwards, S. F. *The Theory of Polymer Dynamics*. (Oxford University Press Inc., 1986).

2   van Buul, A. M. *et al.* Stiffness versus architecture of single helical polyisocyanopeptides. *Chemical Science* **4**, 2357, doi:10.1039/c3sc50552a (2013).