Supporting Information

to

Stochastic dynamics of hairballs in single-polymer growth

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A. Waiting time distribution, $F_0(t)$

The waiting time distributions of hairball unravelling event, $F_0(t)$, are obtained from the Inverse Laplace transform of $\tilde{F}_0(s)$ in Eq.(3a) which is given by

$$F_0(t)$$

$$= \frac{b\,k\,e^{-\frac{1}{2}(k+\alpha+\beta+A)t}}{2A\left[b^2 + k\,\beta - b(k+\alpha+\beta)\right]}\left[\{b(k+\alpha-\beta) + \beta(-k+\alpha+\beta)\}(1-e^{A\,t}) \right.$$

(S.1)

where $A = \sqrt{(k+\alpha+\beta)^2 - 4\,k\,\beta}$ and $b = \dfrac{a}{m}$. In the limit of $\alpha = 0$ and $\beta = 0$, the hairball cannot access the stable states (n^*) and the resulting probability distribution is

$$F_0(t) = \frac{bk}{b-k}(e^{-k\,t} - e^{-b\,t})$$

(S.2)

This clearly indicates that in the absence of the stable configurations the waiting time follows a single exponential behaviour which is not consistent with the experimentally observed non-exponential distributions.

B. Calculation of jump length distribution

We defined the Laplace transform of first passage probability distribution $P_l(t)$ by

$$\tilde{P}_l(s) = \int_0^\infty P_l(t)e^{-st}dt$$

. After talking the Laplace transform of Eqs. (4) in main text, we obtain

$$(s+b)\tilde{P}_0(s) = b\tilde{P}_m(s);$$

(S.3a)

$$(s + a + \alpha + k)P_l(s) = aP_{l+1}(s) + \alpha P_{l*}(s); \qquad m \le l \le n - 1 \tag{S.3b}$$

$$(s + \beta)P_{l*}(s) = \beta P_l(s); \qquad m \le l \le n - 1 \tag{S.3c}$$

$$(s + a + \alpha + k)P_n(s) = \alpha P_{n*}(s) + k \tag{S.3d}$$

$$(s + \beta)P_{n*}(s) = \beta P_n(s); \tag{S.3e}$$

These linear equations can be easily solved for the function $P_0(s)$, yielding

$$P_0(s) = \frac{bk}{a(s + b)}\left(\frac{a(s + \beta)}{(s + a + \alpha + k)(s + \beta) - \alpha\beta}\right)^{n + m - 1},$$
$$\tag{S.4}$$

which is equivalent to Eq. (5) in the main text.

C. Analytical determination of the minimum number *m*

Apart from extracting the minimum number *m* required for formation of globules from the experimentally available data as discussed in the main text, it can also be determined theoretically. We utilized the force-extension curve equation[1] of the classic worm-like chain model

$$\frac{pF}{k_B T} = \frac{1}{4}\left(1 - \frac{\Delta z}{L_0}\right)^{-2} - \frac{1}{4} + \frac{\Delta z}{L_0} \tag{S.5}$$

to determine the relative extension $\Delta z/L_0$ where Δz is the extension and L_0 corresponds to the polymer's contour length. In the above equation, p is the persistence length of a polymer (~0.71 nm for poly-NB and ~0.88 nm for poly-CO)[2], F is the applied magnetic force, T is the temperature and k_B is the Boltzmann constant. At room temperature, we obtained the extension length Δz for poly-NB and poly-CO subjected to known magnetic force and using their respective lengths L_0 as ~0.62 nm and ~0.9 nm.[2] Since in experiments, all jumps smaller than 10 nm were rejected owing to measurement errors, we finally obtained a theoretical minimum number $m = 10/\Delta z$ for all cases.

Parameter	F= 17 pN [NB] = 1M	F= 4.5 pN [NB] = 1M	F= 17 pN [NB] = 0.1M	F= 17 pN [CO] = 1M
	m= **23**	*m*=**42**	*m*=**23**	*m*=**15**
a (s⁻¹, Expt.)	2.334	3.973	1.636	0.48
k ($\times 10^{-3}$ s⁻¹)	6.7	5.6	6.16	2.82

| α ($\times 10^{-3}$ s⁻¹)	4.23	31.49	14	4.78
β ($\times 10^{-3}$ s⁻¹)	3.21	17.15	7.63	3.17

Table S1: Theoretical parameters used to compare our results with existing experimental data extracted from Ref. 2 for different cases. The rate constant *a* provided in Ref. 2 was used whereas other rate constants are the best fit values. Here, m corresponds to the minimum number of monomers required to form an entangled hairball which is determined theoretically as discussed in the Supporting Information's text.

In Fig. S1, while using the *m* values indicated in Table S1, we compare existing experimental data jump length distributions with the function $P(n)$ obtained in our analytical Eq. (6a) in the main text to determine the best-fit parameter k as presented in Table S1. Our results fit well with the existing experimental data as shown in Fig. S1, thereby, supporting this approach. The best-fit k values are then used in Eq. (S.1) to compare function $F_0(t)$ with the experimentally available data: see Figure S2 and we observe good quantitative agreements.
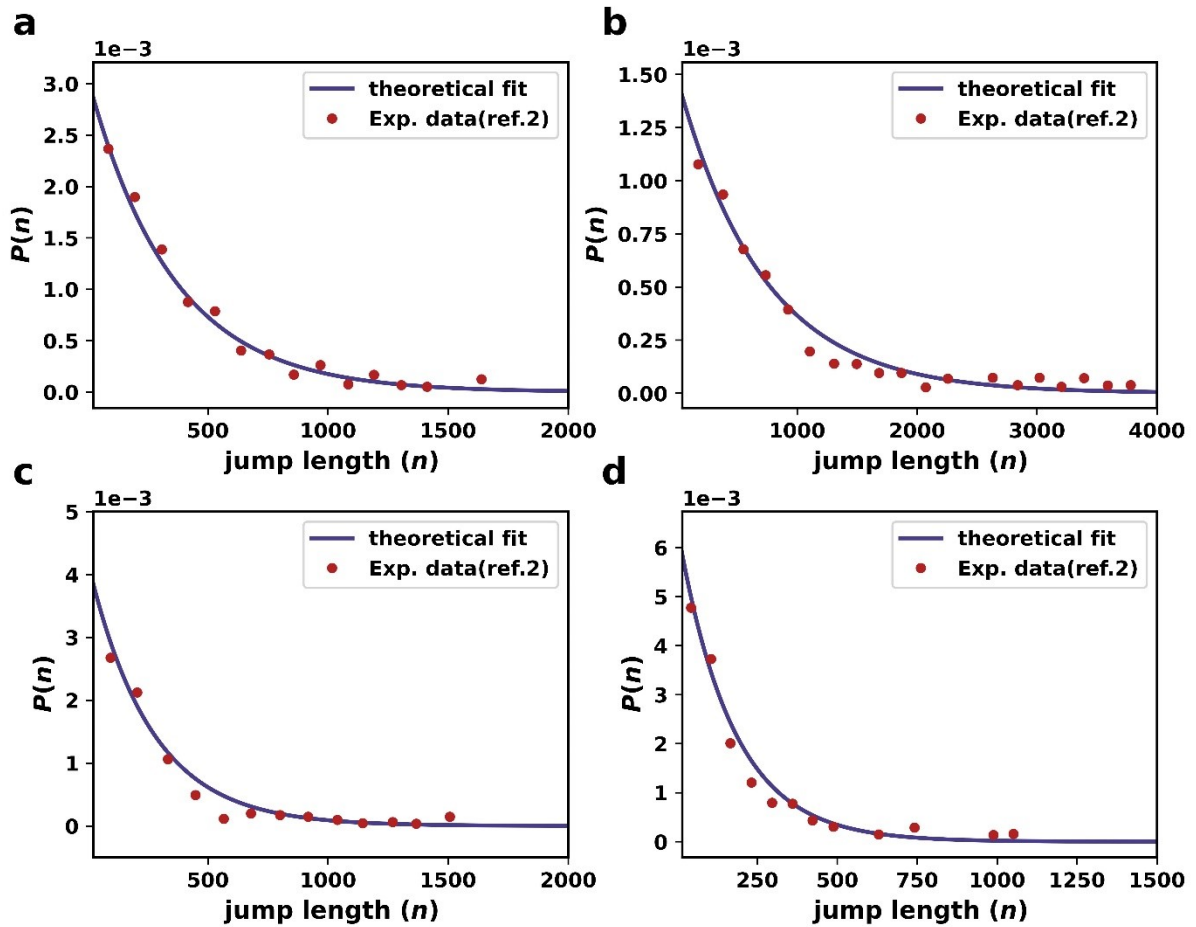
Figure S1: Jump distributions, $P(n)$, compared with the experimental data in Ref. [2] when (a) F = 17 pN, [NB] = 1M, (b) F = 4.5 pN, [NB] = 1M, (c) F = 17 pN, [NB] = 0.1M and (d) F = 17 pN, [CO] = 1M. Here, F is the applied force along the polymer, [NB] and [CO] are respective

norbornene and cyclooctene concentrations. The theoretical curves are plotted using Eq. (6a) of the main text with the parameters presented in Table S1 and the dots are experimental data taken from ref. [2]
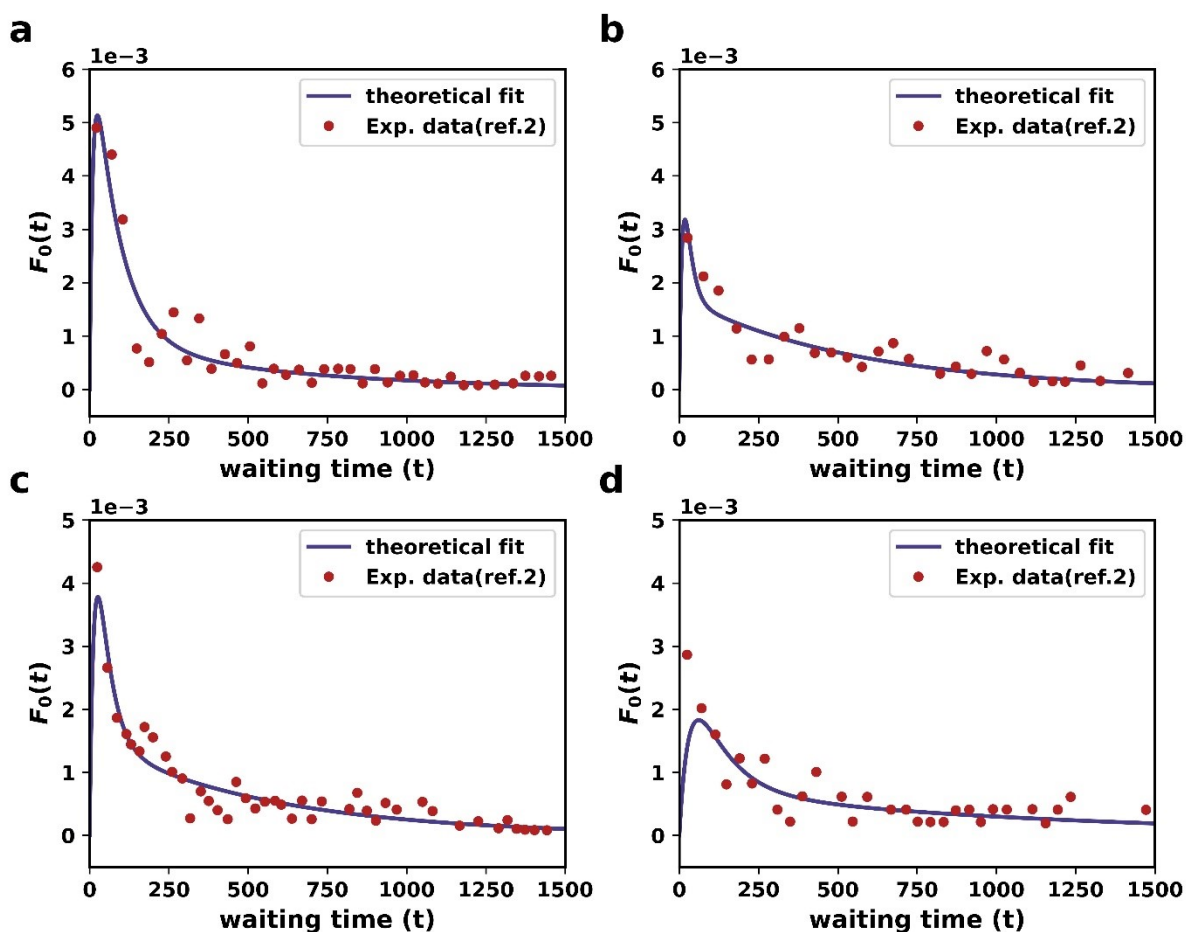
Figure S2: Wait-time distributions, $F_0(t)$, determined from the inverse Laplace transform of Eq. (3) compared with the experimental data in Ref. [2] when (a) F = 17 pN, [NB] = 1M, (b) F = 4.5 pN, [NB] = 1M, (c) F = 17 pN, [NB] = 0.1M and (d) F = 17 pN, [CO] = 1M. Here, F is the applied force along the polymer, [NB] and [CO] are respective norbornene and cyclooctene concentrations. The theoretical curves are plotted using Eq. (S.1) considering the parameters presented in Table S1 and the dots are experimental data taken from ref.[2]

D. Simulations of jump length and waiting time

To simulate the wait-and-jump process according to our theoretical approach, we used standard Gillespie algorithm.[3] Initially the polymer hairball was in state 0 where no monomer formed the hairball. After addition of minimum m number of monomers, the hairball in any state $n \geq m$ was allowed to either jump by rate constant k, add one more monomer with rate a or reach the stable configuration (n^*) with rate α. From the stable configuration the hairball can return to configuration n with rate β. The process gets completed after first jump process is observed and corresponding waiting time and jump length are recorded.

In order to consider the possibility of partial jumps in our simulations, the hairball in any state $n \geq m$ was allowed to jump to any randomly selected state $n^{'} (m \leq n' < n)$ or it may fully unravel. The simulations were stopped if a jump event occurs and the corresponding waiting time and jump length were recorded.

For simulating the possibility of multiple hairballs, we considered the simplest case where two hairballs have formed during the polymerisation. Two hairball case can be viewed as a combination of partial unravelling of hairball and existence of two hairballs. After partial unravelling of hairball according to previous case, the remaining hairball can form a secondary hairball at some position and newly added monomers form a new hairball at different position. In this case the secondary hairball and newly growing hairball can jump randomly leading to wait-and-jump event. These events were recorded according to the same procedure as described above.

We simulated a sequence of 50 wait-and-jump events for a single Monte-Carlo iteration and Pearson's correlation coefficient was determined for all three cases. Using the approach described above, 3000 iterations were simulated, and their values of correlation coefficient were used to generate the distribution as shown in Fig. (4b, 4d, 4f) of the main text.

References:

1.   Bouchiat, C.; Wang, M. D.*, et al.*, Estimating the Persistence Length of a Worm-Like Chain Molecule from Force-Extension Measurements. *Biophysical Journal* **1999**, *76*, 409-413.
2.   Liu, C.; Kubo, K.*, et al.*, Single polymer growth dynamics. *Science* **2017**, *358*, 352-355.
3.   Gillespie, D. T., Exact stochastic simulation of coupled chemical reactions. *The Journal of Physical Chemistry* **2002**, *81*, 2340-2361.