SUPPLEMENTAL MATERIAL

I.   MODEL AND PARAMETER

A.   Model

In our work, a bead-spring model is adapted for polymer chain structure maintenance of both the probed chain and polymeric crowders. The connection between beads is implemented by an finite extensible nonlinear elastic (FENE) interaction, which stipulates a restricted maximum bond length between consecutive beads. Such a restricted maximum bond length enables us to avoid occasional intersections between chain bodies. This intersection implies an unphysical picture in the current non-chemical reaction simulation, i.e. the chemical bond can be broken and crossed by other molecules and then form again. To be specific, in our model system, there exist basically three types of interaction functions of energy, including non-bond interaction $U_{\mathrm{non-bond}}$ between arbitrary pair of sites (HS crowders, polymer crowder beads, probed chain beads), bond-connection interaction $U_{\mathrm{bond-connection}}$ between consecutive beads of both crowding and probed chains, and the bond-angle interaction $U_{\mathrm{bond-angle}}$ for particularly rod-like polymer crowders.

We assume the non-bond interaction energy $U_{\mathrm{non-bond}}$ between sites i and j follows the Weeks-Chandler-Anderson (WCA) potential in form of:

$$U_{\mathrm{non-bond}} = \sum_{i,j} \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \frac{1}{4} \right] \qquad \textbf{S.1}$$

where ϵ_{ij} is the interaction strength, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. r_{ij} denotes the distance between the pair of sites. The energy is truncated at $r_{ij} = 2^{1/6}\sigma_{ij}$.

The bond-connection interaction energy $U_{\mathrm{bond-connection}}$ between consecutive beads m and n is prescribed to be the finite extensible nonlinear elastic (FENE) potential given by

$$U_{\mathrm{bond-connection}} = \sum_{m,n} -\frac{\kappa r_f^2}{2} \ln \left[1 - \left(\frac{r_{mn}}{r_f} \right)^2 \right], \quad r_{mn} < r_f \qquad \textbf{S.2}$$

where κ is the connection strength and r_f denotes the maximum bond length.

In addition, for rod-like polymer, the bond-angle interaction energy $U_{\mathrm{bond-angle}}$ follows:

$$U_{\mathrm{bond-angle}} = \sum_{\mathrm{angle}} k_{\mathrm{angle}} (\theta_{\mathrm{angle}} - \pi)^2 \qquad \textbf{S.3}$$

where θ_{angle} refers to the bond angle between two consecutive bonds on the rod-like polymer chain. k_{angle} is the interaction strength.

B.   Parameter

$k_B T$ is set to the energy unit with k_B being the Boltzmann constant and T the system temperature. In our simulation, we fixed the probed chain length equal to 100. Denoting the probed chain site as p, crowder site as c, the non-bond interaction strength $\epsilon_{ij} = 4k_B T$ for all c-c site pairs as well as all p-p site pairs, while $\epsilon_{ij} = 10k_B T$ for all p-c site pairs. For bond-interaction, $\kappa = 30k_B T/\sigma^2$ and $r_f = 1.5\sigma_i$ where $i = p, c$. For simplicity, the probed chain bead mass m_p and diameter σ_p are chosen as the mass and length units, m and σ respectively. Then, time is scaled by $\tau = \sqrt{m\sigma^2/k_B T}$.

The entire system is enclosed in a periodic boundary cube box of a large volume, with its side length $l = 40\sigma$. A Langevin thermostat is employed to maintain temperature with a friction coefficient along with a corresponding random force exerted on arbitrary sites. The friction coefficient ζ_p exerted on the beads of probed chain is set to be $0.1m\tau^{-1}$. According to the relation of Stokes-Einstein where friction coefficient is proportional to size, the friction coefficient ζ_c exerted on crowder sites c is then determined through $\zeta_c = \zeta_p \frac{\sigma_c}{\sigma_p}$. The simulation integration time step $\Delta\tau = 0.001\tau$. After initial equilibration for $10^3\tau$ of simulated system, simulation is then run for $\sim 10^8$ time steps ($\sim 10^5\tau$) and data is obtained every 2500 steps. The entire simulation is repeated $20-30$ times with different random choices of initial system conformations for a smooth statistics of results.

II.   FINITE SIZE EFFECT CHECK

Before the simulation , we have to ensure that the simulation box is large enough to make the finite size effects negligible. To this aim, we run simulations for the probed chain with enlarged box side length l/σ, ranging from 40 (which has been adopted in the manuscript) to 60. We consider the three types of crowding system with the specific choice of parameters: for hard sphere crowders, the diameter is $\sigma_c = 40^{1/3}$, for flexible and rod-like crowders, the chain length is $N = 40$. The volume fraction is identical to be $\phi = 0.18$. We evaluate the gyration radius R_g of the probed chain as a function of simulation box side length. Results are plotted in Fig. S 1 below. It is clear that R_g remains nearly unchanged with increasing l, which demonstrates that the finite size effect in our simulation has been safely avoided.

III.   EVIDENCE OF EQUILIBRATION

Because the crowder discussed in our work involves a rod-like type, which could possibly introduce long-range as well as long-time correlation of configurations of the simulation sys-
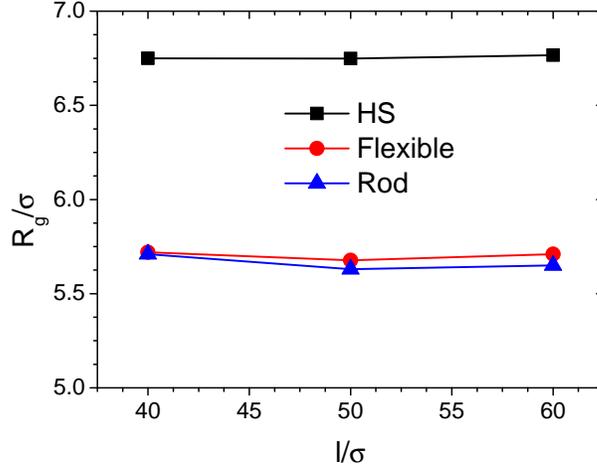
Fig. S 1: Gyration radius of the probed chain R_g under compaction of three types of crowders as a function of simulation box length l, at $\phi = 0.18$.

tem, care must be taken to ensure that the system is well equilibrated before data recording. To provide explicit evidence that our results are obtained from full equilibration, we resort to intermediate dynamic scattering function F of the probed chain, which gives the density-density correlation in Fourier space at wave vector $\mathbf{q}$ that enables us to inspect whether the simulated system relaxes from an initial configuration. This scattering function F can be evaluated according to

$$F(\mathbf{q}, t) = \frac{1}{N}\langle \rho_{-\mathbf{q}}(t')\rho_{\mathbf{q}}(t'+t)\rangle = \frac{1}{N}\sum_{i,j}\langle e^{-i\mathbf{q}\cdot\mathbf{r}_i(t')}e^{i\mathbf{q}\cdot\mathbf{r}_j(t'+t)}\rangle_{t'} \qquad \textbf{S.4}$$

where $\mathbf{r}_i(t)$ denotes the position of probed chain site i at time t. $\rho_{\mathbf{q}}(t') = \sum_i \int d\mathbf{r}e^{i\mathbf{q}\cdot\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}_i(t)) = \sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i(t)}$ is the number density of sites in Fourier space, which gives the holo-information of position configuration of the probed chain. Note that on the one hand computational cost of $F(\mathbf{q}, t)$ is terrifically huge even for a specific $\mathbf{q}$; on the other hand, the existence of anisotropy is not negligible. Here we chose three typical $\mathbf{q} = (2\pi/R_g^0, 0, 0), (0, 2\pi/R_g^0, 0), (0, 0, 2\pi/R_g^0)$ as a trade off, where $R_g^0 = 7.32\sigma$ is the gyration radius of chain in absence of crowders. We chose $2\pi/R_g^0$ as the norm of $\mathbf{q}$ in order to inspect the relaxation of probe chain configuration on the scale of the chain size. The results of normalized modulus of intermediate dynamic scattering function $|F(\mathbf{q}, t)| / |F(\mathbf{q}, 0)|$ are shown in Fig. S 2. The results show the configuration of probed chain in the rod-like crowding environment is approximately relaxed within a time scale of $\sim 10^3\tau$, which is nearly two orders of magnitude less than the time length of trajectories used to sample data, thus ensuring that the sampling under in our work gives converged results.
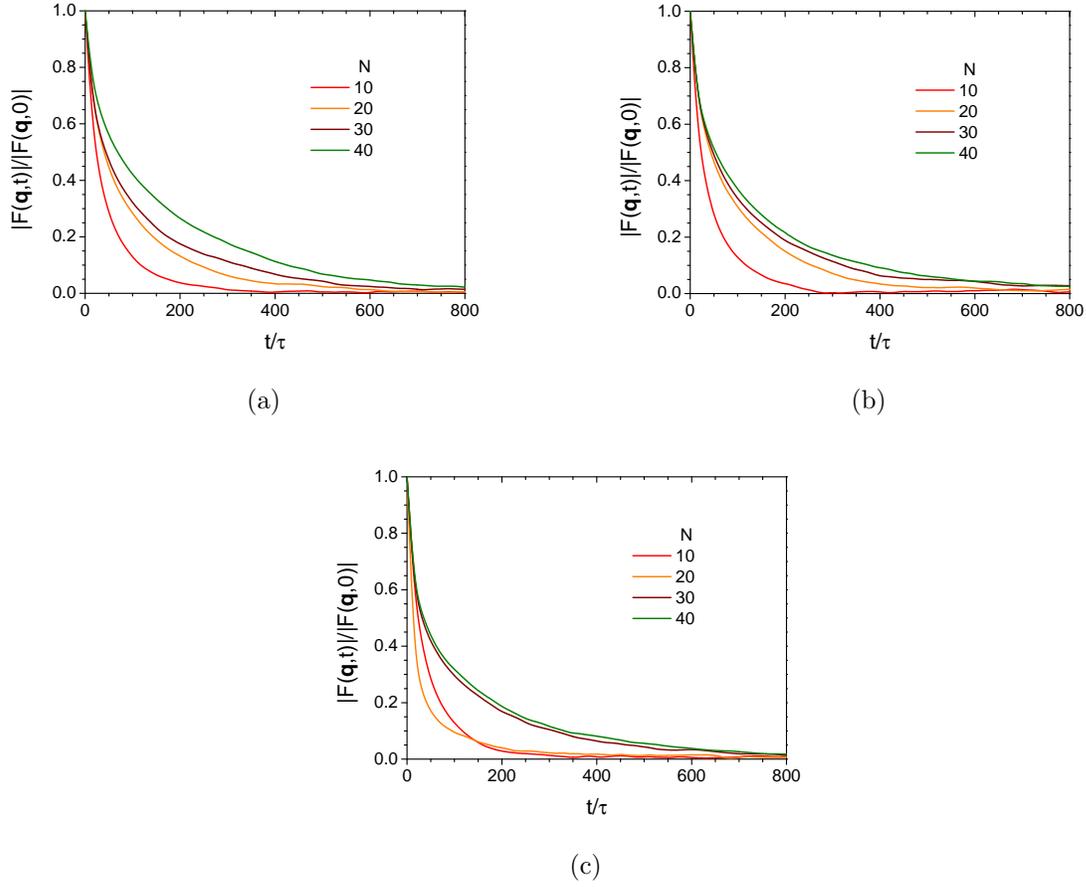
Fig. S 2: Normalized modulus of intermediate dynamic scattering function $|F(\mathbf{q}, t)| / |F(\mathbf{q}, 0)|$ in rod-like crowder system for $\mathbf{q} = (2\pi/R_g^0, 0, 0)$ (a), $\mathbf{q} = (0, 2\pi/R_g^0, 0)$ (b), $\mathbf{q} = (0, 0, 2\pi/R_g^0)$ (c) with varied crowder chain length N at volume fraction $\phi = 0.18$.

IV. SHAPE PARAMETERS

To investigate the shape of the probed chain conformation, shape parameters S are introduced. S is rotationally invariant in space and defined base on the inertia tensor $\mathbf{T}$, the component of which is defined as:

$$T_{\alpha\beta} = \frac{1}{2N_p^2} \sum_{i,j=1}^{N_p} (r_{i\alpha} - r_{j\alpha})(r_{i\beta} - r_{j\beta}) \qquad \textbf{S.5}$$

where N_p is the number of beads on the probed chain. $r_{i\alpha}$ is the αth component of the position of bead i, $\alpha, \beta = x, y, z$. Denoting the eigenvalues of tensor $\mathbf{T}$ by e_k ($k = 1, 2, 3$)

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and $\bar{e} = \left(\sum\limits_{k=1}^{3} e_k \right) / 3$, we have the required S:

$$S = 27 \frac{\left[\prod\limits_{k=1}^{3} (e_k - \bar{e}) \right]}{(3\bar{e})^3} \qquad \textbf{S.6}$$