SUPPLEMENTAL MATERIAL

Model: We used a bead-spring model for the flexible polymers. A large spring constant is chosen so that the distance between two successive monomers remains approximately a constant. We chose Weeks-Chandler-Anderson (WCA) potential for excluded volume interactions between monomers, and soft-sphere potential for crowder-crowder and crowder-monomer.

The energy function for the system consisting of the self-avoiding walk (polymer) and soft spherical crowders is

$$H_{tot} = H_B + H_{m-m} + H_{m-c} + H_{c-c}. \qquad (1)$$

Here $H_B = K\sum_{i=1}^{N-1}\left(|\vec{r}_{i+1}-\vec{r}_i|-l_0\right)^2/l_0^2$ is the bond potential along the polymer chain, K is the spring constant with l_0 being the bond length. We used the WLC potentials for soft-core repulsion, so that $H_{m-m} = \sum_{i<j}^{N}\epsilon\left[(\frac{\sigma_{ij}}{r_{ij}})^{12}-(\frac{\sigma_{ij}}{r_{ij}})^{6}\right]\Theta\left(\frac{\sigma_{ij}}{r_{ij}}-1\right)$ with $\Theta(\ldots)$ being a Heaviside step function. ϵ is Lennard-Jones energy constant controlling the strength of the excluded volume interaction, and σ_{ij} is the distance between two particles in direct contact, given by $\sigma_{ij} = \sigma_i + \sigma_j$ with σ_i being the radius of a bead, where i and j are either the index for monomers in polymer chain or for crowding particles. Lastly, $H_{m-c} = \sum_i^N\sum_j^{n_c}\epsilon\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}$ and $H_{c-c} = \sum_{i<j}^{n_c}\epsilon\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}$ are the monomer-crowder and crowder-crowder repulsions, respectively. We simulated for N =50, 100, and adjusted n_c to achieve the range of crowder volume fraction ($\phi = n_c\times\frac{4}{3}\pi\sigma_c^3/V$, where $V = L_x\times L_y\times L_z$ is the volume of periodic box) between 0 and 0.4. In order to investigate the effect of the size of crowders, we used $N = 100$ with $\sigma_c = 3.6\sigma_m$.

In order to compare our results with the results obtained from simulations with implicit crowders [10], we chose the same parameters used in Ref [10]. In particular, the number of monomers is $N = 50$ and $\sigma_m = 5\sigma_c$. Other simulation parameters are listed in Table I.

Simulation details: In order to obtain adequate sampling of the conformational space of the system, we performed low friction Langevin dynamics (LFLD) [23]. We followed the same simulation procedure described in detail elsewhere [24]. The data for analysis were collected after 2×10^5 time steps for equilibration. The number of crowders varies according to chain conformation with the average value being $\sim 10^4$ for $\phi = 0.3$.

Expression of $P(R_g)$ from scaling argument: Based on the argument that the radius of gyration R_g strongly decreases for $R_g < N^{1/d}$ and $R_g > N$ and that the distribution of the end-to-end distance x decays as $P(x)\sim e^{-x^\delta}$ [29], Lhuillier has proposed $P(R_g)$ of SAW in d dimension as follows [28], which we slightly modified for our analysis,

$$P_N(R_g)\sim\exp\left\{-N\left[\left(\frac{N}{R_g^d}\right)^\alpha+\left(\frac{R_g}{N}\right)^\delta\right]\right\}. \qquad (2)$$

The first term in the exponent arises from the repulsion energy and the second term corresponds to elastic energy, which renders $P_N(R_g)\to 0$ when R_g is either too small or too large. When $P(R_g)$ is written in terms of the dimensionless variable $t = R_g/\overline{R}_g = R_g/bN^\nu$, then $P(t)\sim\exp\left[-(bt)^{-d\alpha}N^{1+\alpha(1-\nu d)}-(bt)^\delta N^{\delta(\nu-1)+1}\right]$. Noting the property that $P(t)$ is independent of N, we can determine $\alpha = (\nu d-1)^{-1} = 5/4$ and

K	l_0	k_BT	Δt	ζ_m	ζ_c
1500ϵ	$1.11\ \sigma_m$	$0.6\ \epsilon$	$0.01\ \tau$	$0.05m\tau^{-1}$	$\zeta_m\left(\frac{\sigma_c}{\sigma_m}\right)$

TABLE I: Parameters characterizing the model. Lennard Jones energy constant ϵ, the diameter of monomer σ_m and $\tau = \sqrt{\frac{m\sigma_m^2}{\epsilon}}$ are used as the unit energy, the unit length and the unit of time, respectively. K is a spring constants for a chain connectivity between monomers, l_0 is a bond length between monomers of a chain, k_BT is a temperature, Δt is a simulation time step, ζ_m and ζ_c are the friction coefficients for monomer and crowding particles, respectively.

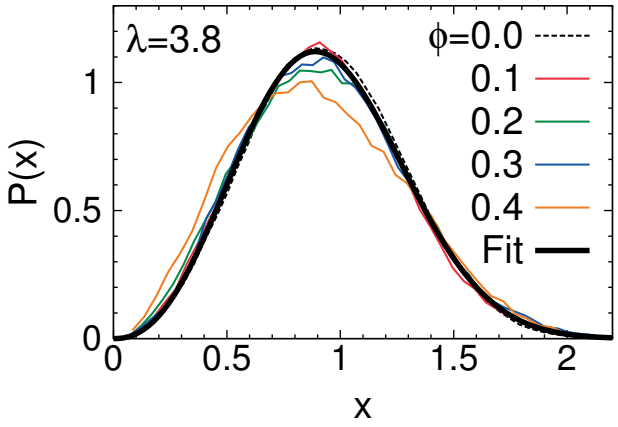

FIG. S1: The end-to-end distance (R_{ee}) distribution of a SAW scales as $P(x)\sim x^g$ at $x\to 0$ and $P(x)\sim e^{-x^\delta}$ at $x\gg 1$ where $x = R_{ee}(\phi)/\overline{R}_{ee}(\phi)$ with $\overline{R}_{ee}\sim N^\nu$ and $\delta = (1-\nu)^{-1}$ [29]. All the $P(R_{ee})$s with varying $\phi = 0.0-0.4$ are collapsed onto $P(x) = \mathcal{N}x^{g+2}\exp\left[-bx^\delta\right]$ with $\mathcal{N} = 3.68$, $g = 0.30$, and $b = 1.23$ with $\delta = 2.5$ fixed. Note that $g\approx(\gamma-1)/\nu = 0.283$ ($\nu = 0.588$, $\gamma = 7/6$) [29]. As the perturbation (ϕ) increases, we observe an increasing deviation from $P(x)$ with $\phi = 0$.

$\delta = (1-\nu)^{-1} = 5/2$, which leads to Eq.1 in the main text.

Size of PEG: In PEG-6000, 6000 corresponds to the polymer molecular weight (M_w (g/mol)). The average radius of gyration of PEG with M_w is $\sigma_c = 0.0215 \times M_w^{0.583}$ nm [25]. Since molecular weight of PEG monomer is ≈ 44 g/mol, we can convert the expression of σ_c in terms of molecular weight into the one in terms of the degree of polymerization P: $\sigma_c \approx 0.195 \times P^{0.583}$ nm.