

Structure of a single polymer chain confined in a dense array of nanoposts

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Control of polymer conformations in heterogeneous confinement plays an important role in natural and engineering processes. We present a simulation study on the conformational structure and dynamics of a single, flexible polymer in a dense array of nanoposts with different sizes and separations, especially, when the volume of the interstitial space formed between four nanoposts is less than the size of the polymer chain. When a polymer is placed in the array of nanoposts, the size of polymer increases compared with that in the absence of nanoposts due to the confinement effect. It is shown that when a polymer is confined in the array of nanoposts the chain is elongated in the direction parallel to the nanoposts. As the interstitial volume between four nanoposts decreases either by increasing the nanopost diameter or by decreasing the separation between nanoposts, the chain elongation becomes more pronounced. On the contrary, the polymer size varies in a non-monotonic fashion, with an initial elongation followed by a chain contraction, as the interstitial volume is reduced both by increasing the nanopost diameter and decreasing the separation at the same time while keeping constant the width of the passageway between two nanoposts. The simulation analysis shows that the non-monotonic dependence of polymer size is determined by interplay between the chain alignment along the nanoposts in each interstitial volume and the chain spreading through passageways over several interstitial volume.

Key Words : confinement, nanopost, elongation

Introduction

The structural control of polymer chains plays an important role in regulating the physicochemical properties of polymers in natural and engineering processes. Thermal conductivity or charge mobility in a single polymer chain is lost in bulk due to the disordered arrangement of polymer chains, which is yet enhanced when the polymer chains are aligned in 1-dimensional nanostructures in comparison with that in bulk^{1,2}. The ability to precisely control the polymer conformation in near future will provide more opportunities to develop new functional material that does not work efficiently in disordered bulk phase but attain the efficiency in their function when arranged in a specific order.

Here, we investigate the structure and dynamics of a single polymer chain confined in a dense array of nanoposts. At first, we employ the Edison program “Analysis of DNA structure in nano-channel” and “the structure and dynamic of the confined polymer”. However, we want to analysis in more advanced system, so we design the polymer in a densely packed array of nanoposts. Moreover, recent advances in the nanofabrication enabled the preparation of the array of nanoposts with a range of dimensions and morphologies. The volume of interstitial space among nanoposts can be reduced down to a dimension only available for small

molecules. Therefore, the motivation of this work is to understand the confinement effect of the array of nanoposts on the arrangement of polymer chains when their interstitial volume is less than size of polymer chains.

The confinement of polymer chains in a 1-dimensional nano-channel has been widely investigated using theoretical and computational methods as well as in experiments. The size of polymer chains increases in the channel direction to the extent determined by the polymer size and channel height. The confinement effect in the dense array of nanopost in this work is more complicated than that in a 1-dimensional channel due to the spatial connectivity between interstitial spaces among nanoposts. Unlike the confinement in a channel, polymer chains can still spread over several interstitial spaces. In earlier works, it was reported that in 2 dimension the confinement of polymer chains by the presence of immobile obstacles can induces the further spreading of the polymer chains through the interstitial spaces among the obstacles. In a 3-dimensional dense array of nanoposts of this work, however, we show that the polymer chains arrange in the direction parallel to the nanoposts. We show how the change in the interstitial volume of the nanopost array induces the structural and dynamical properties of polymer chains.

Theory and Computational Method

We use a flexible polymer modeled as a bead-spring chain and the number of segments (N) is 128. Each polymer segments interacts with other segments by repulsive Lennard-Jones potential in Eq (1)

$$U_r(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon & 0 < r < r_c \\ 0 & \text{elsewhere} \end{cases} \quad (1)$$

where σ is a diameter of polymer segments and used as a unit of length hereafter. The cut-off distance r_c is set to $2^{1/6} \sigma$. Bonded segments in a polymer chain interact with a combination of finite extension nonlinear elastic (FENE) potential in Eq (2) and the repulsive Lennard-Jones potential given in Eq (1)

$$U_b(r) = \frac{1}{2} k_b R_b^2 h \left[1 - \left(\frac{r}{R_b} \right)^2 \right] \quad (2)$$

where $k_b = 30k_B T / \sigma^2$ and $R_b = 1.5\sigma$ to prevent bonds in polymers from crossing each other³.

In the system, a polymer chain is placed a regular array of nanoposts. The nanoposts are separated by a distance of S_p from the nearest neighbor, as shown in figure 1 (a), and the diameter of nanoposts is D_p . The volume of the interstitial space formed between four nanoposts is V_i . The values of S_p and D_p are varied between 6 and 14 and between 4 and 12, respectively. System size ranges between 48 and 56 to accommodate 4 to 8 nanoposts in one direction, as shown in figure 2. Polymer segments with nanoposts by repulsive Lennard-Jones potential of the form for $r_0 < r < r_0 + r_c$ and $U_r(r)=0$ for $r > r_0 + r_c$. Here, r_0 defines the size of nanoposts such that $D_p = 2r_0 + \sigma$. ϵ is set to $k_B T$ and $r_c = 2^{1/6} \sigma$ as before.

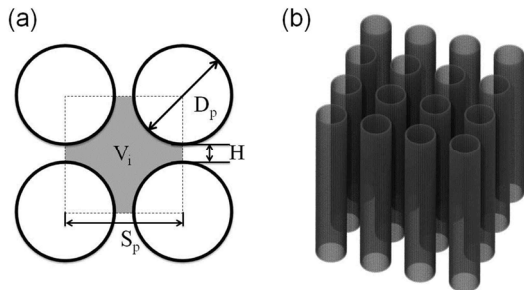


FIG. 1. Definition of parameters of the nanopost array (a) The centers of the two nearest nanoposts are separated by a distance of S_p , the diameter of the nanoposts is D_p and the gap distance between two

nearest nanoposts is H . S_p and D_p are given in unit of σ , the diameter of chain monomers. The volume of an interstitial site surrounded by four nanoposts (shaded in the figure) is called the interstitial volume, V_i . (b) A snapshot of polymer in the nanopost array with $(S_p, D_p)=(12, 8)$.

Brownian dynamics (BD) simulations are run to mimic the solvent-induced stochastic dynamics of polymer chains. The statistical properties are calculated by averaging over 20 different simulations starting from independent initial configurations. Conventional Brownian dynamics⁴ without hydrodynamic interactions is performed by GROMACS 4.5.4 with a use of tabulated interaction functions^{5,6}. τ_{BD} is the unit of time of BD simulation and a time step is $10^{-4} \tau_{BD}$. Each simulation is computed 1×10^9 time steps ($1 \times 10^5 \tau_{BD}$) and total simulation time is more than 50 times longer than the correlation time of the end-to-end vector of a polymer chain in the absence of nanoposts.

To get the size of the polymer, we calculate a radius of gyration of the polymer (R_g) in Eq (5)

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (R_i - R_{cm})^2 \quad i = 1, \dots, N \quad (5)$$

where R_i is the position vector of the i th monomer of the polymer chain and R_{cm} is the chain center of mass position vector. As the polymer is stretched along the nanopost, the chain size in parallel direction to nanopost corresponds in Eq (6)

$$R_{g,\parallel}^2 = \frac{1}{N} \sum_{i=1}^N (z_i - z_{cm})^2 \quad i = 1, \dots, N \quad (6)$$

because the nanopost is parallel to z-axis. To obtain the average values of the equilibrium polymer, we calculated the average R_g , $R_{g,\parallel}$ of each set after 4×10^8 time steps, when the conformation of polymer reaches equilibrium. Then, we calculate again the average and standard deviation of the average of R_g , $R_{g,\parallel}$ independent 20 sets from earlier. Moreover, the shape properties of polymer chain can be characterized by the gyration tensor (S). The gyration tensor is defined as

$$S_{ij} = \frac{1}{N} \sum_{n=1}^N (x_{n,i} - x_{cm,i})(x_{n,j} - x_{cm,j}) \quad i, j = 1, \dots, 3 \quad (7)$$

where $x_{n,k}$ is the k th component of n th particle's position vector, and $x_{cm,k}$ is the k th component of the center of mass of the polymer. The eigenvalues of S are calculated numerically⁷ as λ_1 , λ_2 , and λ_3 . Then,

the deviation of the cluster shape from a sphere is estimated as the cluster asphericity⁸⁻¹⁰ (A) defined by

$$A = \frac{\sqrt{(\lambda_1 - \lambda_2)^2 + (\lambda_2 - \lambda_3)^2 + (\lambda_3 - \lambda_1)^2}}{2\sqrt{(\lambda_1 + \lambda_2 + \lambda_3)^2}} \quad (8)$$

A is zero for a sphere and deviates from zero for a non-spherical object up to unity in case of a rod. The asphericity is also averaged using previous method. Dynamic property of the polymer between nanoposts is investigated by the number of the occupied interstitial site (N_{ov}). We set the criteria, which is the polymer occupies one interstitial site if the total number of monomers in this site is 5 or more.

In our simulation, a road from one interstitial site to another adjacent interstitial site exists and this is simply notated as a gap. In some cases, the polymer escapes the trapped space since the number of allowed polymer conformations in one interstitial site is less than the polymer spreading over 2 or more interstitial sites¹¹. Moreover, if the gap is enough wide, the environment is similar to free-nanopost system. R_g in this system is approaching that in the absence of nanoposts in figure 2. In addition, focusing the shade region with the gap distance to nearest nanoposts (H), is defined as $S_p - D_p$, has 2, R_g dependent of interstitial volume is non-monotonic.

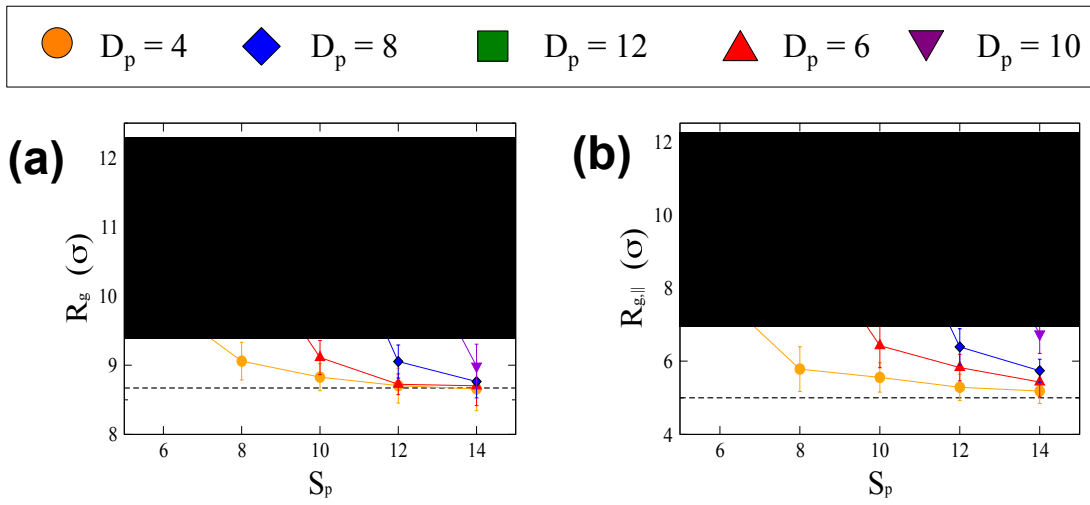


FIG. 2. Size of a polymer as a function of the distance between the centers of the two nearest nanoposts (S_p) (a) The square root of the mean square radius of gyration, $\langle R_g^2 \rangle^{1/2}$. (b) The square root of the mean square radius of gyration parallel to the nanopost, $\langle R_{g,\parallel}^2 \rangle^{1/2}$. Symbols represent different diameters of nanoposts and the dashed line is the size of a polymer in the absence of nanoposts. The shaded region emphasizes the non-monotonic dependence of polymer size for the separation of $S_p - D_p = 2$.

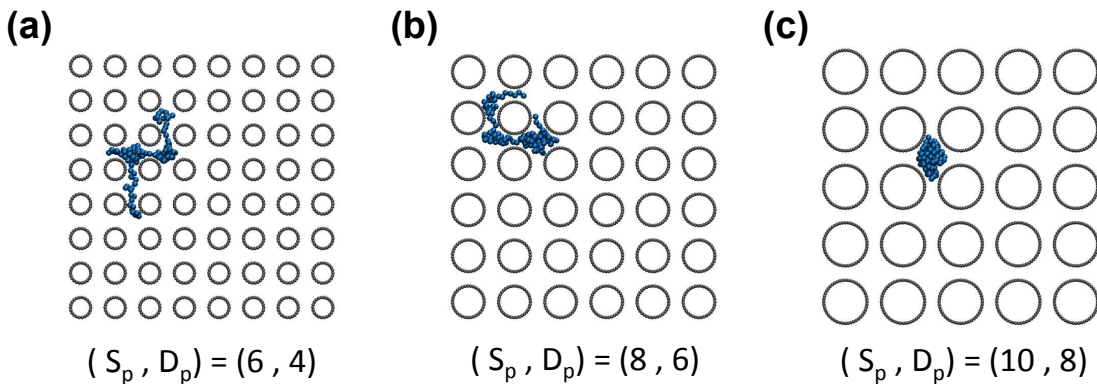


FIG. 3. Arrangement of the nanopost array with different parameters S_p and D_p

The result shows R_g of the polymer is the biggest value when $(S_p, D_p) = (10, 8)$. In case of $(S_p, D_p) = (6, 4)$, the interstitial volume is so small for polymer to stay in one interstitial volume and the polymer escapes to another interstitial site. This is favorable because the conformational entropy is increased while the polymer stretches out and has more available conformations¹¹. In addition, the gap volume and interstitial volume are similar, so free energy in both regions is not so different. Thus, the snapshot (a) in figure 3 indicates that the polymer move and spread over many interstitial sites. Whereas, in the enough interstitial volume, the polymer, $(S_p, D_p) = (10, 8)$, the gap volume and interstitial volume are far different and free energy barrier is too high to pass from one interstitial site to another interstitial site¹². Also, in this case, the road to z direction along the nanoposts is wider than other directions, so the polymer is elongated along the

nanoposts. Over the interstitial volume in $(S_p, D_p) = (10, 8)$, the polymer mostly stay in one interstitial site.

From the asphericity in figure 5, we investigate the shape of the polymer. When S_p or D_p is fixed, the asphericity has the similar trend with results in figure 2. As interstitial volume decreases, the shape of the polymer becomes the rod. While $R_{g,||}$ has highest value in $(S_p, D_p) = (10, 8)$, the peak of asphericity is in $(S_p, D_p) = (12, 10)$ as shown in figure 5 (b). In the figure 6 (c) and (d), the probability that the polymer in $(S_p, D_p) = (10, 8)$ is occupied 2 or more interstitial sites is more than that in $(S_p, D_p) = (12, 10)$ because the interstitial volume is smaller. When the polymer in $(S_p, D_p) = (10, 8)$ is spread over two interstitial sites, they has larger radius of gyration to x and y direction. Therefore, the shape is relatively close to sphere shape and the asphericity in $(S_p, D_p) = (10, 8)$ is smaller than that in $(S_p, D_p) = (12, 10)$.

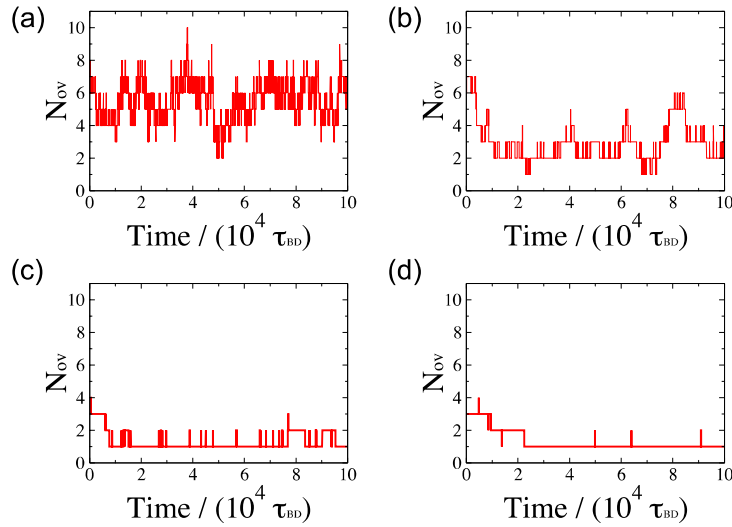


FIG. 4. Dynamics of polymer spreading over the number of interstitial sites. The number of occupied interstitial volumes (N_{ov}) is presented as a function of time (in unit of $10^4 \tau_{BD}$). Parts (a)-(d) are taken for $S_p - D_p = 2$ in order of $(S_p, D_p) = (6, 4), (8, 6), (10, 8),$ and $(12, 10)$, respectively.

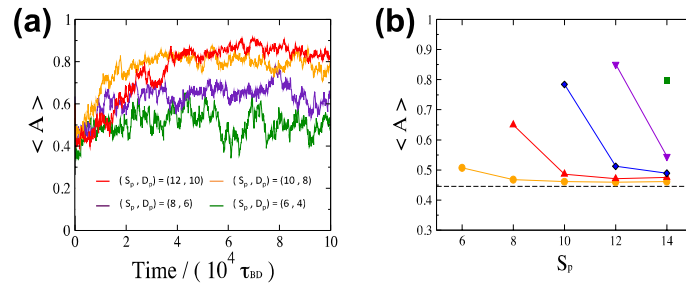


FIG. 5. Asphericity as a criterion of the polymer shape (a) parts are taken for $S_p - D_p = 2$ in order of $(S_p, D_p) = (6, 4), (8, 6), (10, 8),$ and $(12, 10)$, respectively and (b) asphericity as a function of the distance between the centers of the two nearest nanoposts (S_p).

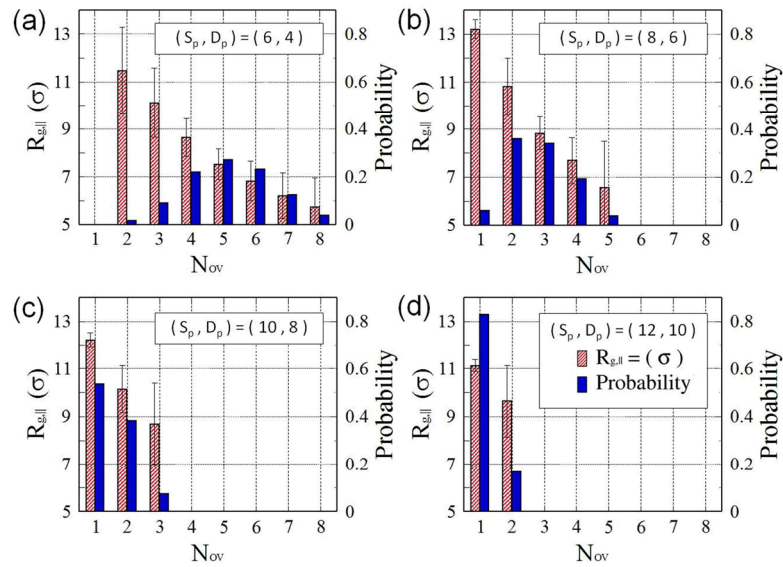


FIG. 6 The red part is $R_{g,||}$ and the blue part is the probability by the number of the occupied sites (N_{ov}). (a)-(d) are taken for $S_p - D_p = 2$ in order of $(S_p, D_p) = (6, 4)$, $(8, 6)$, $(10, 8)$, and $(12, 10)$, respectively.

Discussion

In summary, we have studied the conformation of the polymer confined in an array of the nanoposts changing the interstitial volume and gap distance between the nanoposts. We explain the size of the polymer is increasing as the interstitial volume is decreasing. Due to loss of the number of allowed polymer conformation, however, the polymer dislikes to stay in one interstitial site and spreads to all x, y and z directions, so the size of the polymer becomes smaller. Thus, the polymer size is determined by interplay between these two effects and the R_g and $R_{g,||}$ by S_p and D_p has the non-monotonic result. When the volume is less than the interstitial volume in $(S_p, D_p) = (10, 8)$, polymer escapes to one interstitial volume and spreads several interstitial volumes. In the bigger volume than that, there is enough space for the polymer to shrink and stay inside one interstitial volume mainly. From these results, in conclusion, the interstitial volume by the array of nanoposts affects the size and shape of the polymer.

Acknowledgments

This research was supported by the EDISON Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Science, ICT & Future Planning (No. NRF-2012-M3C1A6035357). It was also supported by Samsung

Science and Technology Foundation under Project Number SSTF-BA1401-13.

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