

Supplementary Information for

## Catalytic assembly of symmetric diblock copolymers in a thin film: A dissipative particle dynamics simulation study

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### DPD Algorithm

Dissipative particle dynamics is a mesoscopic coarse-grained simulation method for soft materials, which is a suitable and efficient method for simulating the self-assembly of BCPs.<sup>1,2</sup> In DPD simulation, a particle represents the center of mass of a cluster of atoms, and the mass, length, and time scales are all unity. In our simulations, the time evolution of interacting coarse-grained (CG) beads is governed by Newton's equations of motion,

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i$$

Particles  $i$  and  $j$  interact with each other via a pairwise additive force, and thus the total force on particle  $i$  is given by,

$$\vec{F}_i = \sum_{i \neq j} \vec{F}_{ij}^C + \vec{F}_{ij}^D + \vec{F}_{ij}^R$$

where  $\vec{F}_{ij}^C$  is a conservative force,  $\vec{F}_{ij}^D$  is a dissipative force, and  $\vec{F}_{ij}^R$  is a random force between particles. All forces are nonzero within a cutoff  $r_c$ . Specifically, in our simulation,

$$\vec{F}_{ij}^C = a_{ij}\omega(r_{ij})\hat{r}_{ij}$$

$$\vec{F}_{ij}^D = -\gamma\omega^2(r_{ij})(\hat{r}_{ij} \cdot \vec{v}_{ij})\hat{r}_{ij}$$

$$\vec{F}_{ij}^R = -\sigma\omega(r_{ij})\alpha_{ij}(\Delta t)^{-1/2}\hat{r}_{ij}$$

where  $a_{ij}$  is a maximum repulsion between particles  $i$  and  $j$ ,  $r_{ij}$  is the distance between them, with the corresponding unit vector  $\hat{r}_{ij}$ ,  $\vec{v}_{ij}$  is the vector difference in velocities of the two particles,  $\gamma$  is the friction coefficient and  $\sigma$  is noise strength, which are coupled by  $\sigma^2 = 2\gamma k_B T$ ; the unit of energy  $k_B T$  is set to 1, the value  $\sigma = 3.0$  and  $\gamma = 4.5$  are used to study the catalytic assembly, and  $\alpha_{ij}$  is a Gaussian random number with zero mean and unit variance.

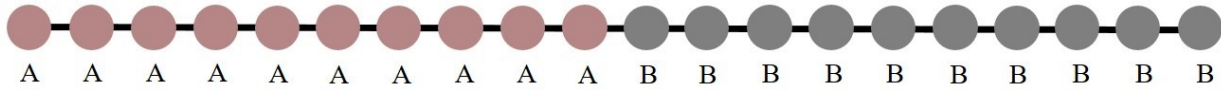
The weighting factor  $\omega(r_{ij})$  is given by,

$$\omega(r_{ij}) = \begin{cases} 1 - \frac{r_{ij}}{r_c}, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases}$$

And all the variables are nondimensionalized in the DPD simulations.

## DPD models

symmetric diblock copolymer  $A_{10}B_{10}$



catalytic molecule



wall



Fig. S1 DPD model of copolymer  $A_{10}B_{10}$ , catalytic molecule C, and wall W.

As shown in Figure S1, a diblock copolymer molecule is represented by a coarse-grained model. For the sake of simplicity, each copolymer molecule is built by 10 hydrophilic particles (A and B) on each side; i.e.  $A_{10}B_{10}$ . Molecule C served as catalytic molecule is added into the system. And solvent particles (denoted by W) are included explicitly in the simulations; however, they are not shown in the following figures.

The copolymer  $A_{10}B_{10}$  is constructed by joining consecutively particles with harmonic spring force. The spring force is given by,

$$F_{ij}^S = k_s \left(1 - \frac{r_{ij}}{r_s}\right) \hat{r}_{ij}$$

where  $k_s$  is the spring constant set to 4.0 and the equilibrium bond length  $r_s = 0.85$ .

Catalytic assembly of the diblock copolymers can be controlled by changing the conservative (repulsive) parameters between particles. Following Laradji and Kumar<sup>3,4</sup>, the repulsive parameter between two particles is set to  $a_{ij} = 25.0$ . For the interaction between two segment of polymer particles, we have chosen the value  $a_{AB} = 40.0$  such that the two types of particles are in the strong segregation regime. In order to prevent escape of copolymers and catalytic molecules escape from the system, two dense walls with fixed position are constructed and placed on the top and bottom boundary of the box along with  $z$ -axis. Each of the wall consists of frozen W particles; and the nearest distance between W particles is set to 0.25. The W particles is neutral, i.e. nonselective for

A, B and C particles; and the interaction between walls and other particles are set as 25.0. The C particles represent the catalytic molecule C and is nonselective for A and B, i.e.  $a_{AC} = a_{BC}$ ; and the tunable interaction strength between the particles can be set to 25.0 ~ 33.0. In summary, the interaction parameter between any two particles are listed in table 1 of the main text.

### Simulation details

All simulations are performed in NVT ensemble using LAMMPS package<sup>5</sup>, and combined with NVE strategy to update position and velocity of the system. The visual molecular dynamics (VMD) software package<sup>6</sup> is employed for trajectory visualization and analysis. The total number density in the system is defined as  $\rho = N/V$ ; and the number density is set to  $\rho = 3$ . In that case, the total number of particles in the box is set to  $N = 3 \times L_x \times L_y \times L_z$ . The time integration of motion equation is done using modified velocity-Verlet algorithm, and time step  $\Delta t = 0.04$ .

### Simulation results

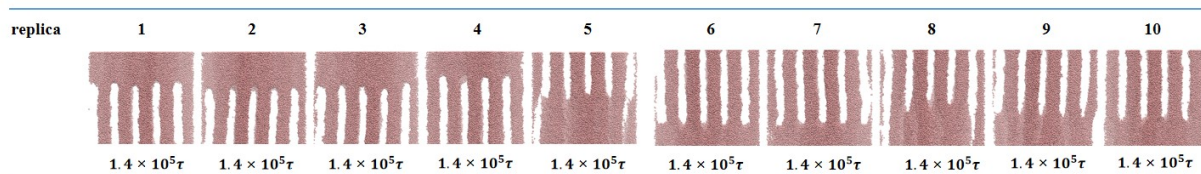
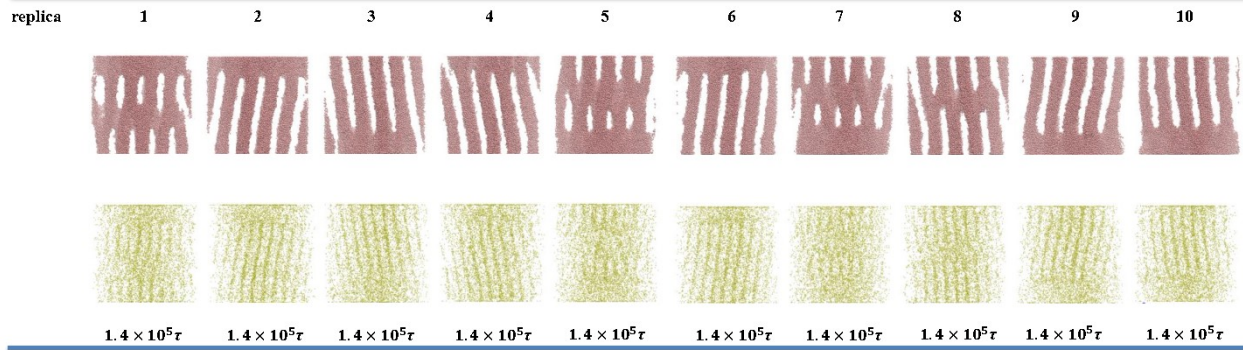
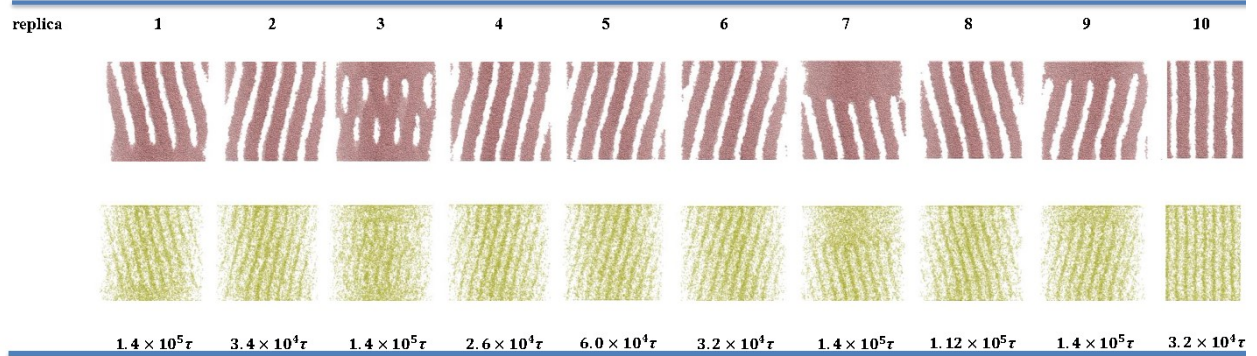


Fig. S2 Simulation results from ten separated initial homogenous states generated by different random numbers at  $t=1.4 \times 10^5 \tau$  for the AB diblock copolymer in a thin film. For the purpose of clarity, only Block A was drawn in this figure.

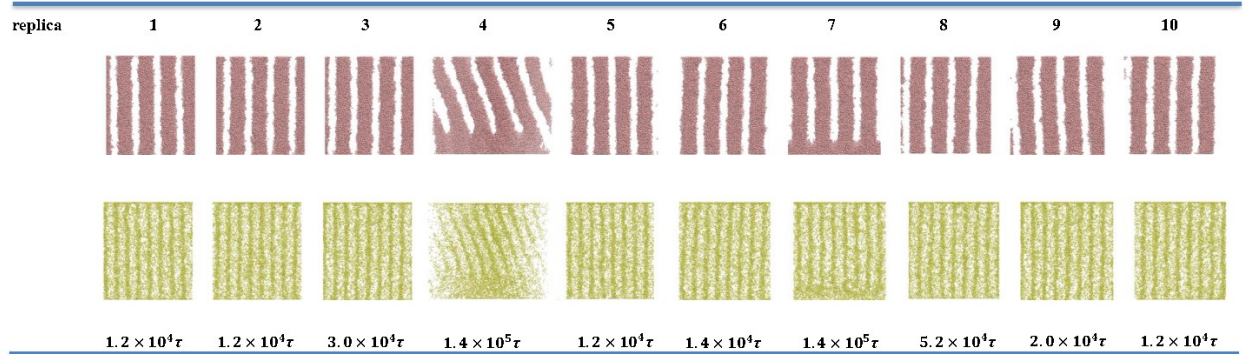
$\varphi = 5.0\%, a_{AC} = 32$



$\varphi = 7.3\%, a_{AC} = 32$



$\varphi = 9.5\%, a_{AC} = 32$



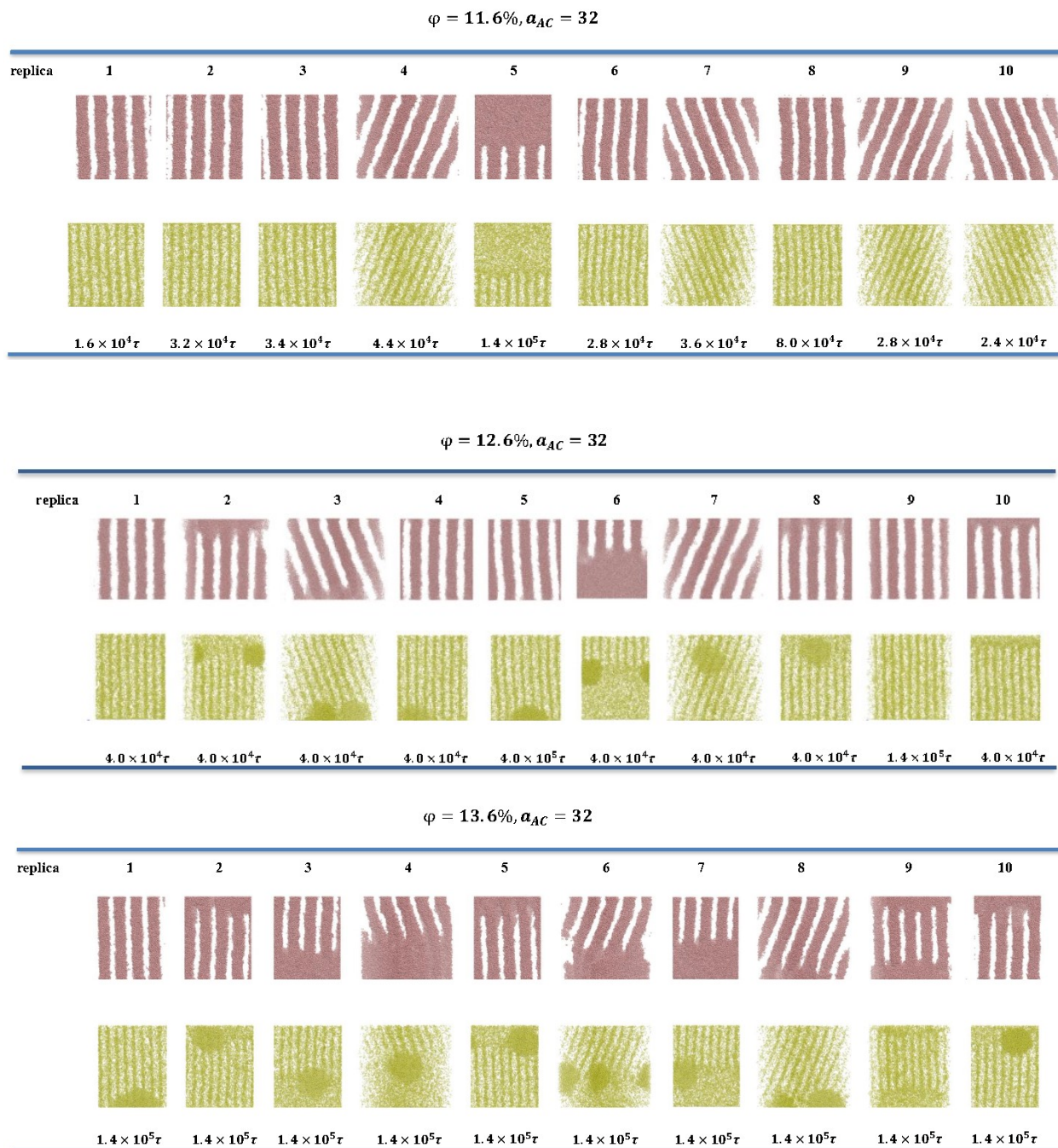
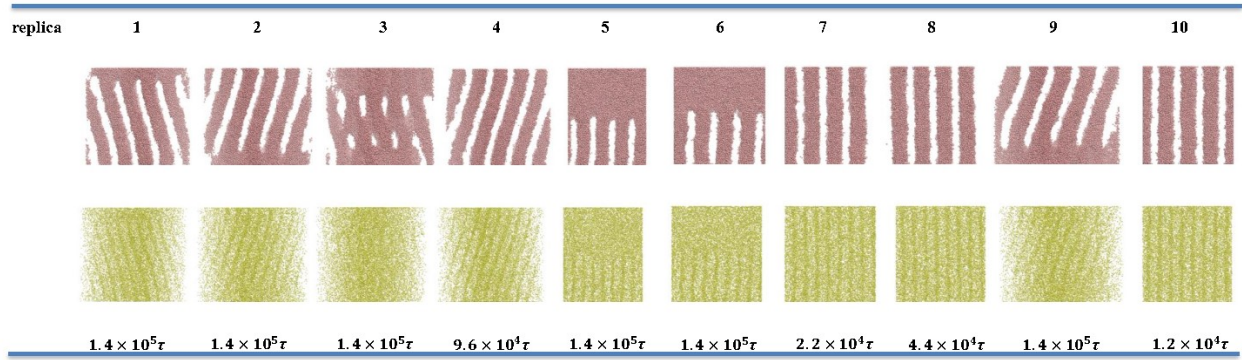
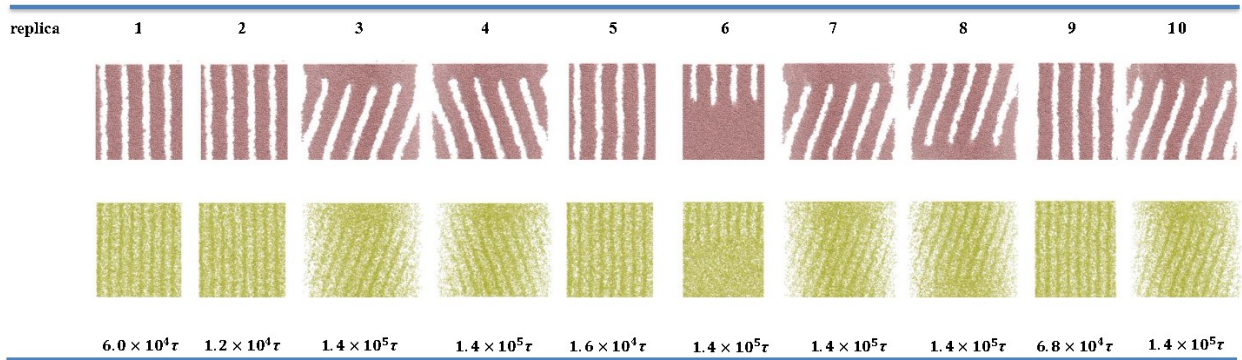


Fig. S3. Simulation results for various volume fractions of C molecule when  $\alpha_{AC} = \alpha_{BC} = 32$ , and  $\alpha_{AB} = 40$ , and corresponding distribution of C molecules (yellow color). The structure patterns are the vertical views of  $xz$  or  $yz$  planes, or the views after rotating the box horizontally with an angle (corresponding to the slanting strips).

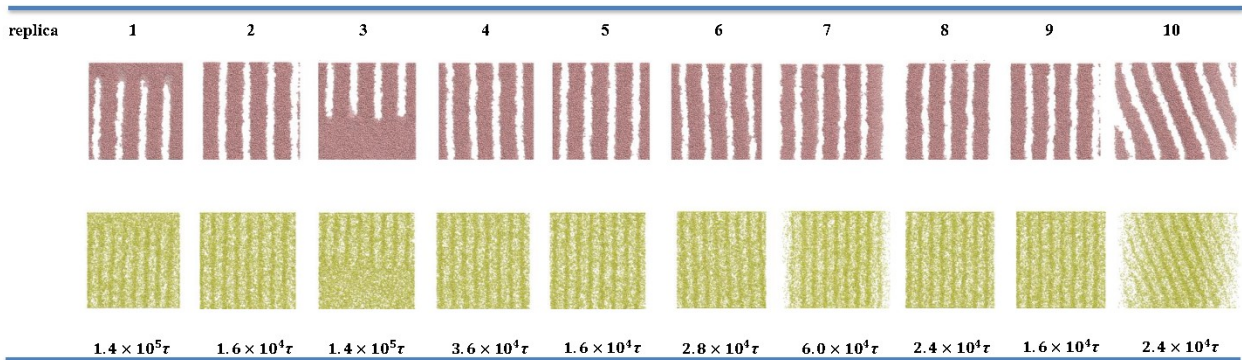
$\varphi = 11.6\%$ ,  $a_{AC} = 25$

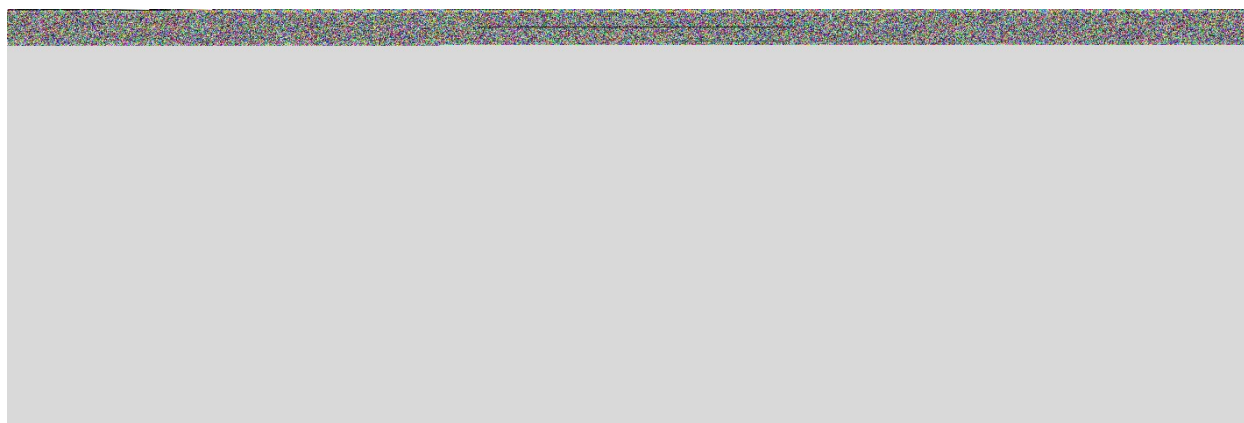


$\varphi = 11.6\%$ ,  $a_{AC} = 29$

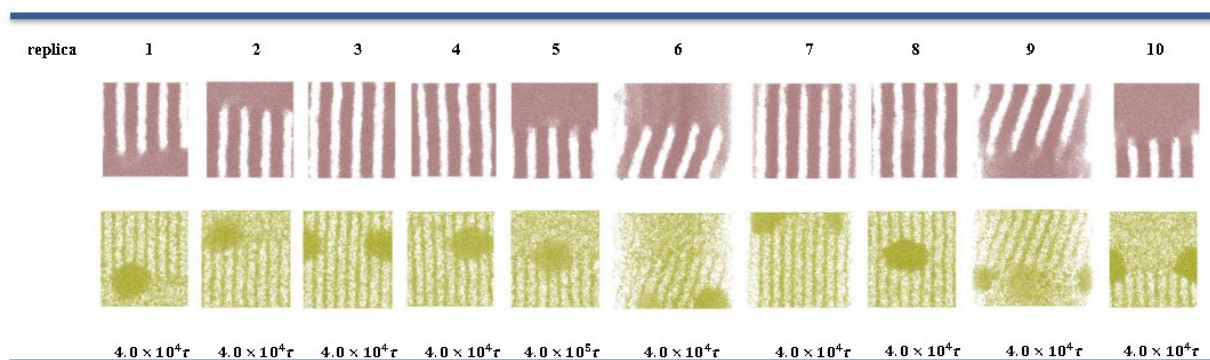


$\varphi = 11.6\%$ ,  $a_{AC} = 30$





$\varphi = 11.6\%$ ,  $a_{AC} = 32.5$



$\varphi = 11.6\%$ ,  $a_{AC} = 33$

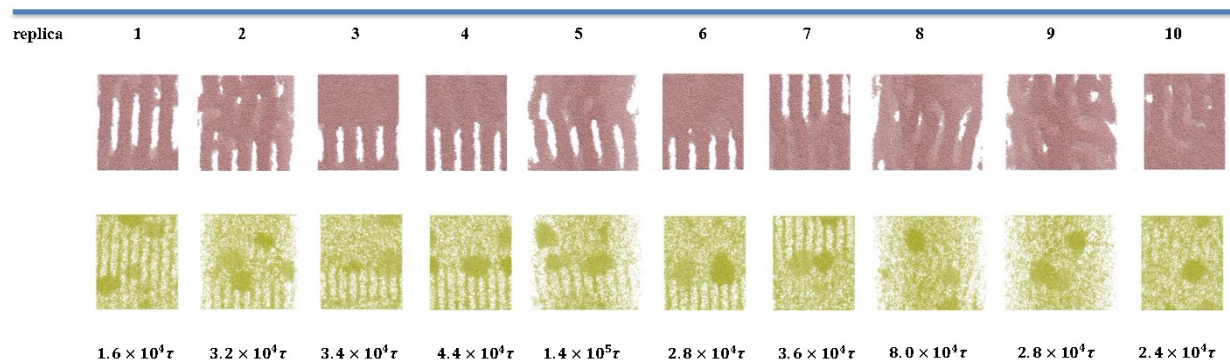


Fig. S4. Simulation results for various values of  $a_{AC}$  ( $a_{AC} = a_{BC}$ ) and  $a_{AB} = 40$  when C molecule volume fraction  $\varphi$  is 11.6%, and corresponding distribution of C molecules (yellow color). The structure patterns are the vertical views of  $xz$  or  $yz$  planes, or the views after rotating the box horizontally with an angle (corresponding to the slanting strips).



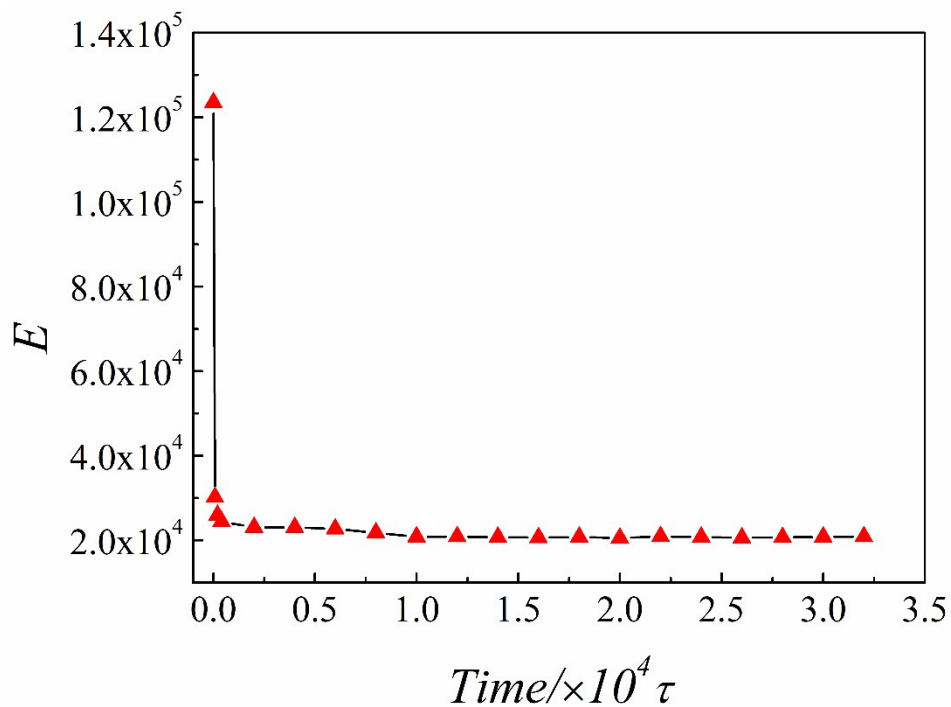


Fig. S5 Variation of the interaction energy ( $E$ ) among polymers in the system with simulation time for a sample at  $a_{AB}=40$  ( $a_{AC} = a_{BC}$ ) and  $\varphi = 0$  (i.e. without C molecule) .

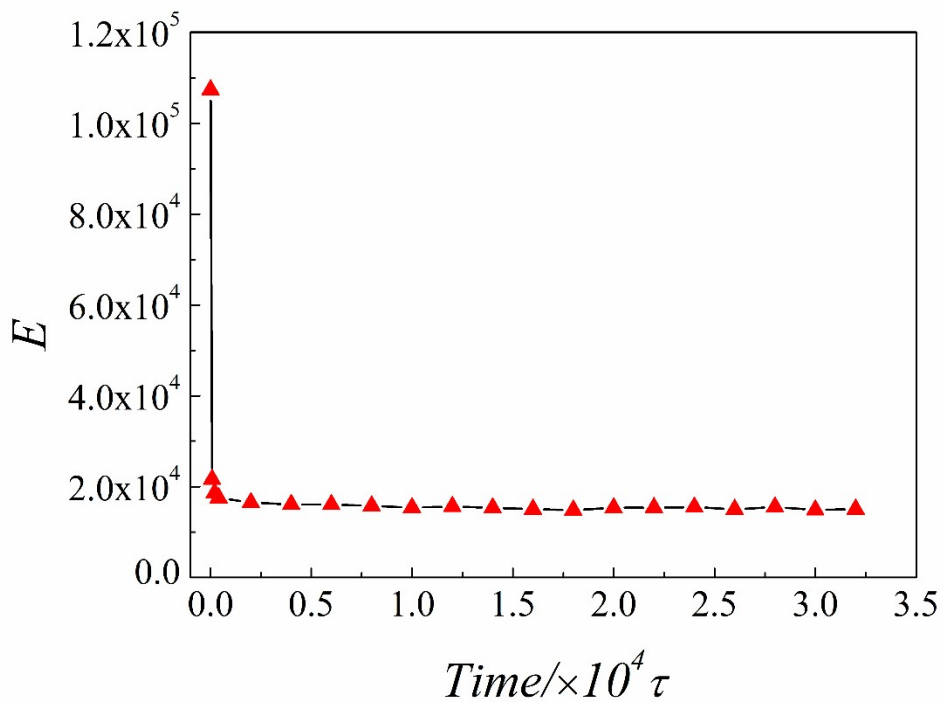


Fig. S6 Variation of the interaction energy ( $E$ ) among polymers in the system with simulation time for a sample at  $a_{AC}=32$  ( $a_{AC} = a_{BC}$ ),  $a_{AB}=40$  and  $\varphi = 11.6\%$ .

## Reference

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