Support Information

Biointerface effect on the self-assembly of ribonucleic acids: A possible mechanism of RNA polymerization in the self-replication cycle

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S1. Validity of simulation model

In this study, we adopted ribonucleic acid model to eliminate the complex effects including a chemical reaction and a chirality. To confirm the validity of the model, the cohesive energy, solubility, the Flory-Huggins parameter (χ), and the equilibrium structure of uridine monophosphate are calculated using all atomistic molecular dynamics simulation. Figure S1 shows the self-assembly structures of RNA nucleotide and the mean square displacement using new parameters. As a result, it was almost similar to the structure and the diffusion behavior reproduced using the original parameters.

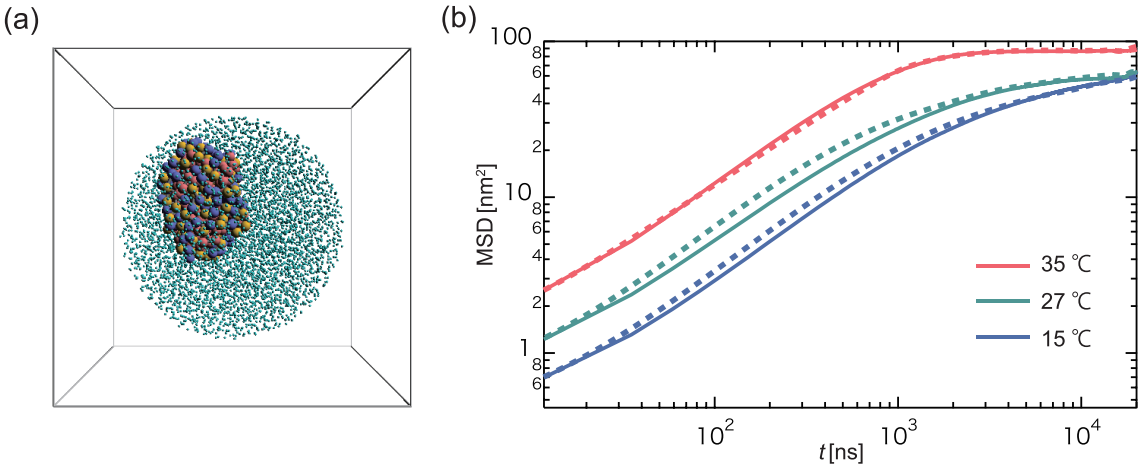

Fig. S1 (a) Equilibrium snapshot using new parameter at low temperature. (b) Mean square displacement depending on the temperature. Solid and dashed curves represent original and new parameters, respectively.

S2. Chemical structures of RNA nucleotide model

We carried out additional simulations to investigate the effect of the chemical structure of RNA nucleotides on the self-assembly behaviour. With regard to number of cytosines, four and six models were constructed. Figure S2 shows cluster size distributions in vesicle and bulk systems, and time variations of mean aggregation number depending on the number of cytosines. In both systems, larger size clusters formed as the number of cytosines increased. On the other hand, confinement by the biointerface promotes the growth of aggregates as same as Fig. 3.

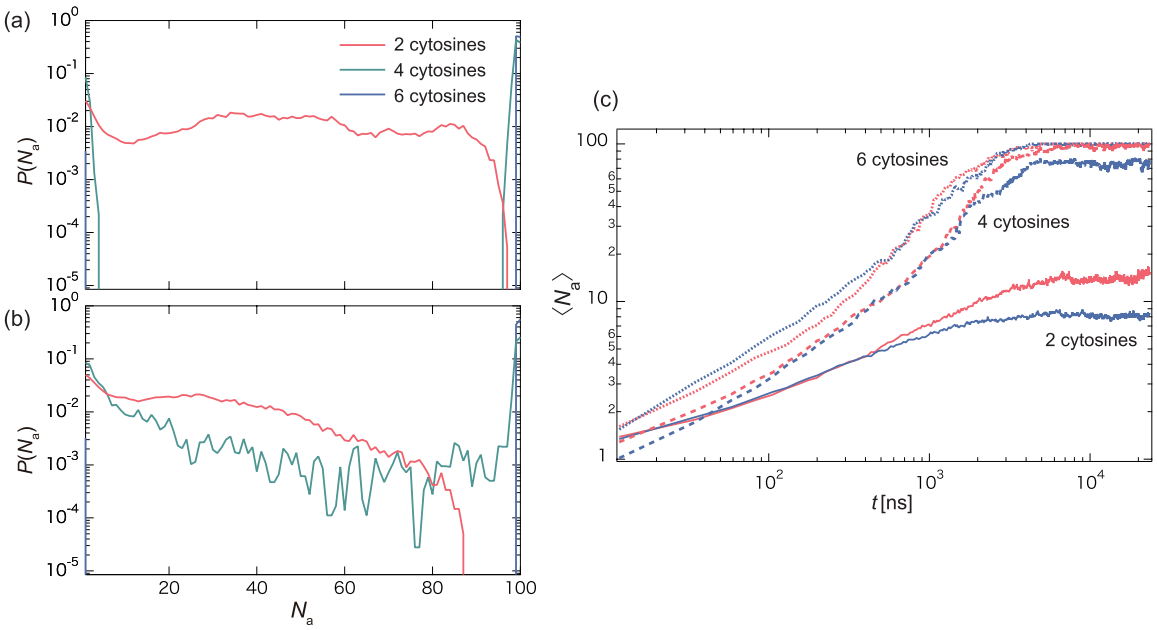

Fig. S2 Cluster size distribution in (a) vesicle and (b) bulk systems, and (c) time variation of mean aggregation number depending on the number of cytosines. Blue and red curves represent high and low temperatures, respectively.

S3. Concentration of RNA nucleotide model

The proper concentration at which the self-replication cycle begins on the primitive Earth is unknown. Therefore, we investigated the effect of the initial concentration of RNA nucleotides on the self-assembly behaviour. Figure S3 shows cluster size distributions in vesicle and bulk systems, and time variations of mean aggregation number depending on the nucleotides concentrations. It was confirmed that larger clusters were formed in vesicles than in bulk at any concentration.

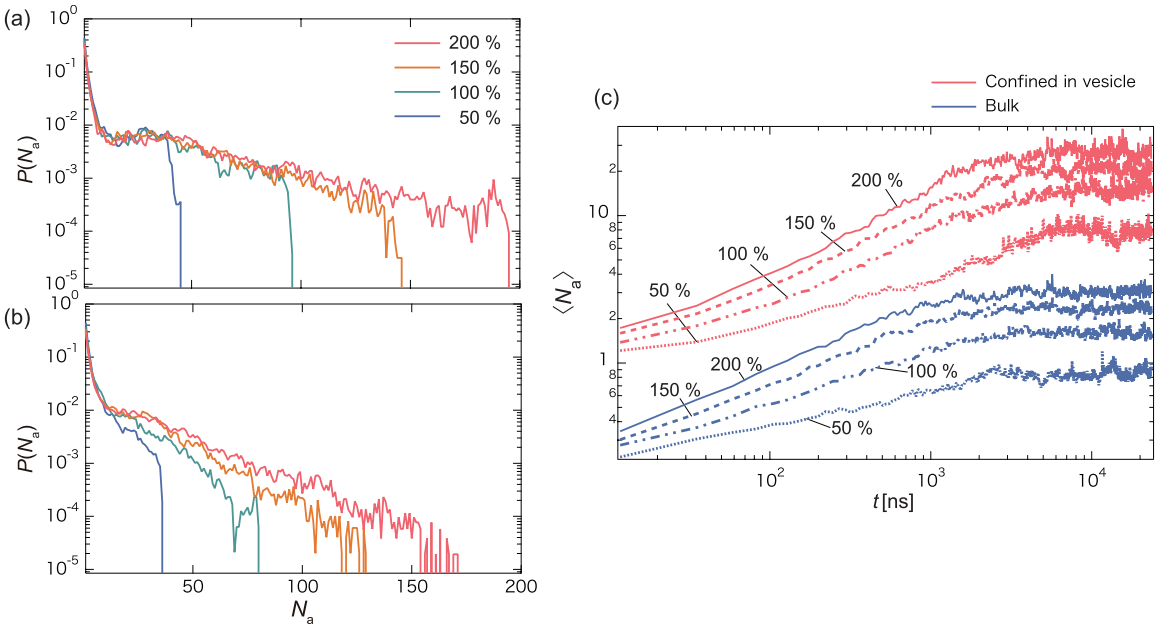

Fig. S3 Cluster size distribution in (a) vesicle and (b) bulk systems, and (c) time variation of mean aggregation number depending on the concentration of RNA nucleotides. Blue and red curves represent vesicle and bulk systems, respectively.

S4. Chemical Interaction parameters

It is known that the Flory-Huggins interaction parameter (χ parameter) depends on temperature. In DPD simulation, the interaction parameter a_{ij} is estimated based on the χ parameter. As the temperature decreases, the phase separation becomes more pronounced, which corresponds to a larger χ parameter. Here, we investigated the effect of a_{ij} at the lowest temperature (15˚C) in this study. The interaction parameters between water and lipid tail (a_{WT}) and lipid head and lipid tail (a_{HT}) are changed from 80 to 120 and 160 k_BT/r_c.

We calculated the density profile in the radial direction as shown in Fig. S4. As a_{ij} increases, the density peaks become sharper. It corresponds to forming a more ordered structure rather than a disordered liquid phase. However, similar results for the cluster size distribution and mean aggregation number growth were obtained as when a_{ij} is 80 k_BT/r_c as shown in Fig. S5. There was no significant difference in the behaviour of the self-assembly inside.

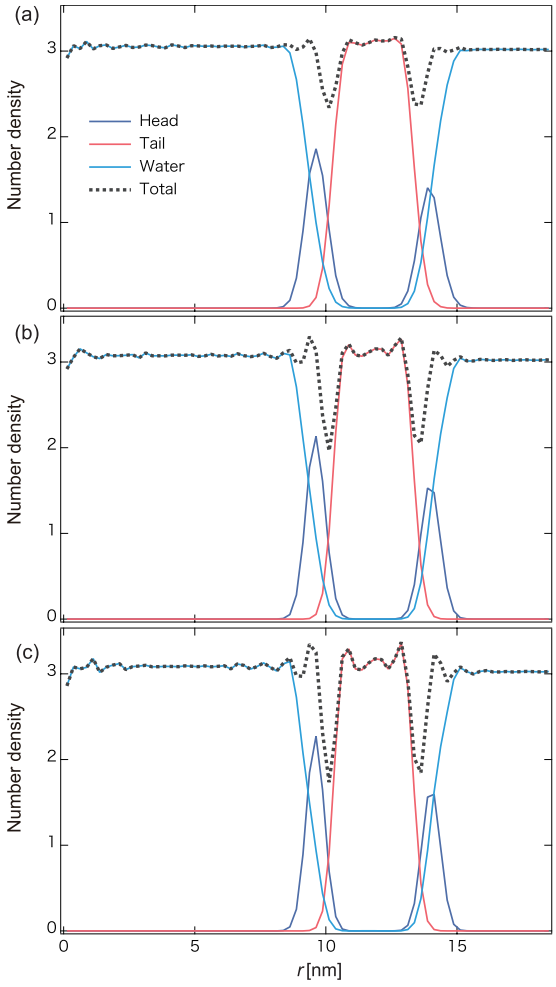

Fig. S4 Number density profiles in the radial direction for a_{ij} = (a) 80, (b) 120, and (c) 160 k_BT/r_c. The zero in the horizontal axis refers to the center of mass of the vesicle.

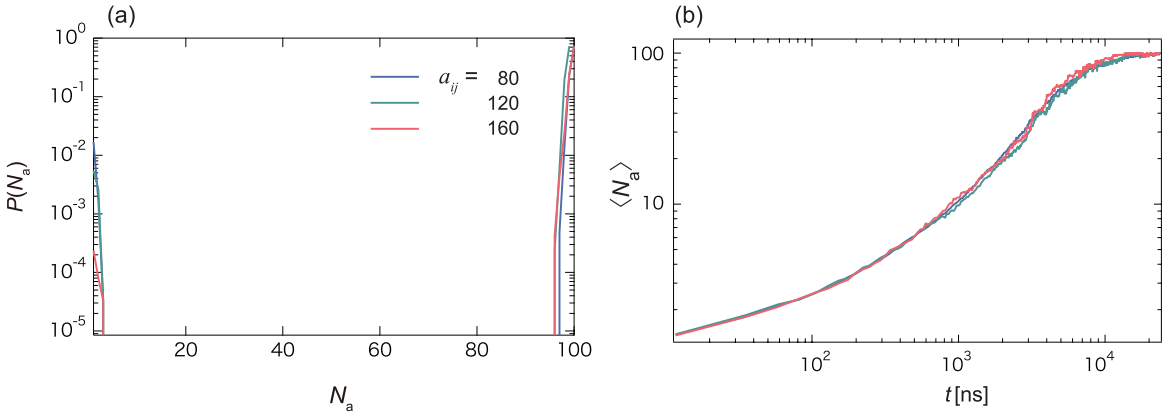

Fig. S5 (a) Cluster size distribution and (b) time variation of mean aggregation number depending on the interaction parameter. Blue, green and red curves represent a_{ij} = 80, 120, and 160 k_BT/r_c, respectively.

S5. Softness of the biointerface

In order to investigate the effect of the softness of the biointerface (the surface of the vesicle), we performed simulations by exerting a wall potential [S1,S2] and compared it with the vesicle system. Initial configurations and the equilibrium structures are shown in Fig. S6. Figure S7 shows cluster size distributions and time variation of mean aggregation number for vesicle and smoothed wall systems. The maximum cluster size and the mean aggregation number growth curve at each temperature agree well in the two systems. It suggests that the superiority of self-assembly is important to be confined in nanospace, and that the softness of interface (thermal fluctuation) is not dominant in this case.

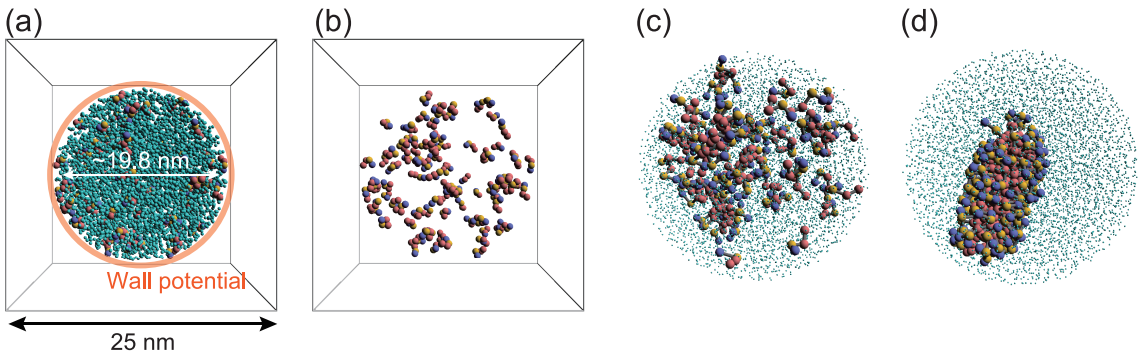

Fig. S6 (a) Initial configuration of smoothed wall system. (b) Snapshot of (a) without showing the water molecules. Equilibrium snapshots at high temperature (c) and low temperature (d).

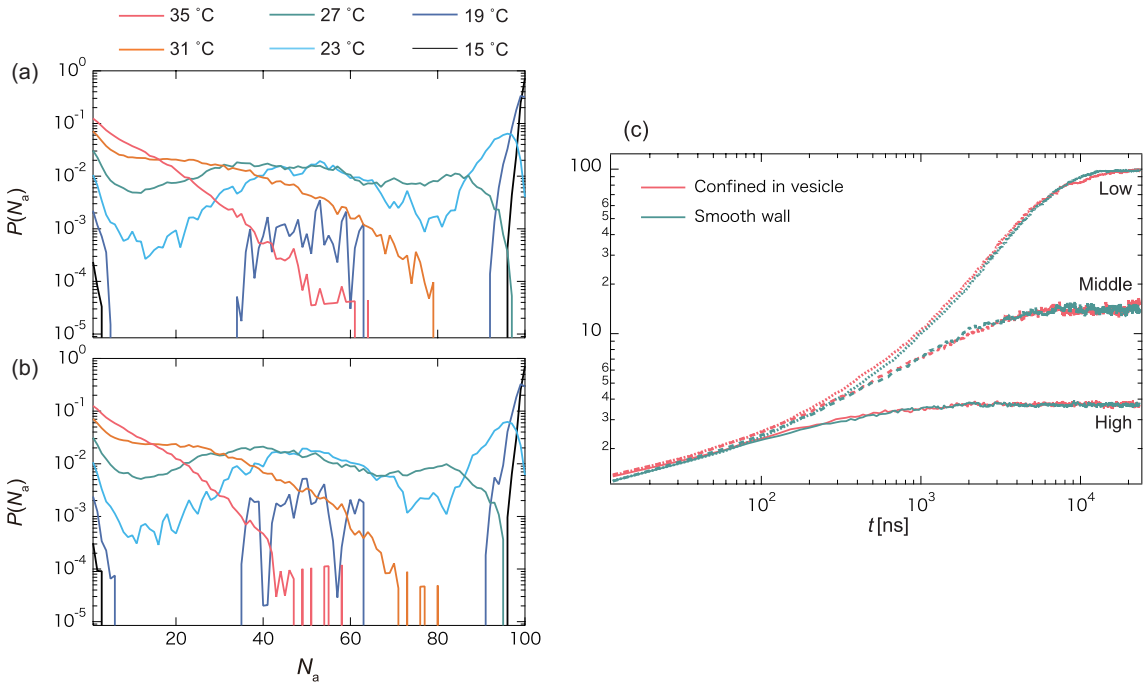

Fig. S7 Cluster size distribution depending on the temperature in the (a) soft boundary

vesicle and (b) smooth wall boundary systems. (c) Time variation of mean aggregation number in the two systems. Solid, dashed, and doted curves represent high, middle, and low temperatures, respectively.

S6. Thermal fluctuations of RNA nucleotides

We calculated the probability distribution of the mean-square radius of gyration in vesicle and bulk systems. As a result, we confirmed that the width of fluctuation increased with increasing temperature.

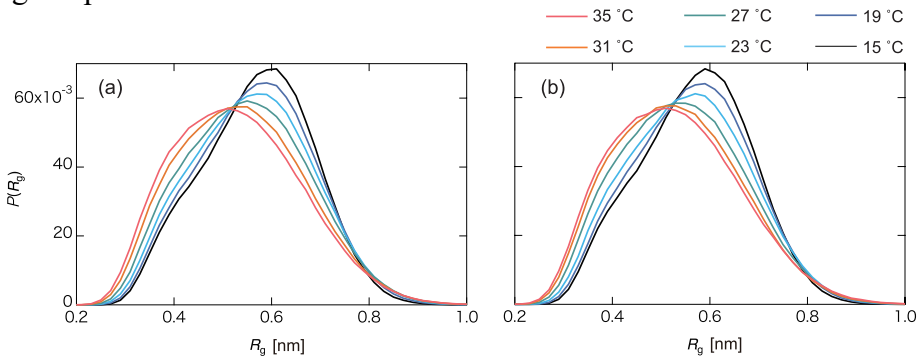

Fig. S8 Probability distribution of the mean-square radius of gyration in (a) vesicle and (b) bulk systems.

References

[S1] N. Arai, K. Yasuoka, and X. C. Zeng, *J. Am. Chem. Soc.*, **2008**, 130, 7916-7920.
[S2] N. Arai, K. Yasuoka, and X. C. Zeng, *J. Chem. Theory Comput.*, **2013**, 9, 179-187.