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Investigation of molecular diffusivity of photoresist membrane using coarse-grained molecular dynamics simulation

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Abstract

Biocompatible permeable membranes integrated with a microfluidic system, which allow the diffusion of biological molecules with certain molecular weight, are desirable in biomedical applications. This paper reports on a molecular level study of the molecules permeability of epoxy-based chemically-amplified photoresists in MEMS by employing a coarse-grained molecular dynamics simulation. For analyzing diffusion coefficient of molecular in photoresists, Kremer-Grest model (bead-spring model) with an extended angle bending potential was employed. The simulation results show that, with increasing the cross-linked ratio of photoresists, the diffusion coefficient of small molecules in photoresist have larger diffusion coefficient, and which suggests photoresist membrane can be used as permeable membranes with controllable permeability by varying photolithography parameters.

Keywords: Photoresist; Molecules permeability; Molecular dynamics simulation; Membrane

1. Introduction

There is an on-going trend towards applying 3-dimensional (3D) photolithography to polymer-based microfluidic systems since they can offer many new opportunities for fundamental biophysical studies and applications. For example, epoxy-based chemically-amplified negative photoresists in MEMS (commercially available SU-8[TM] and TMMR[®], hereafter photoresist) are usually adopted in microfluidic devices for many biomedical applications [1]. Recently, the fabrication of nano-porous membrane structure by photoresist serving as a permeable membrane in microfluidics has been proposed by authors [2]. Although the fabricated permeable membrane exhibits a sufficient mechanical strength [3], its molecular diffusivity for biological applications has been under the investigations. This paper reports on a

molecular level study of the molecules permeability of photoresists by employing a coarse-grained molecular dynamics (CGMD) simulation and its experimental verification.

2. Coarse-Grained Molecular Dynamics Simulation

2.1. Simulation model for photoresist

Figure 1(a) shows the chemical structure of the photoresist monomer before the UV exposure. Due to expensive computational costs, a full-atomistic MD simulation cannot be performed for photoresists. To overcome this problem, CGMD simulation using the Kremer-Grest model, a bead of chain was treated as several monomer units, was performed. Although this simulation cannot account for the chemical effects of chain linkage, the chain dynamics over a long time scale can be simulated by employing an appropriate potential energy between the beads, e.g., FENE, Lennard-Jones, and Theta angle bending potentials for the modeling of photoresists [4].

In the present simulation, the photoresist monomer was divided into three groups: (1) an epoxy group, (2) a phenyl group connected to methylene, (3) an isopropylidene groups and phenyl group, which were denoted by BS1, BS2, and BS3 beads, respectively (see Fig. 1(b) and Table 1). In the MD simulation step, cross-linked photoresist structures connected between BS1 beads, which corresponds to the cross-linking reaction of photoresist during the UV exposure and the heating process of post-exposure-bake (PEB), are created.
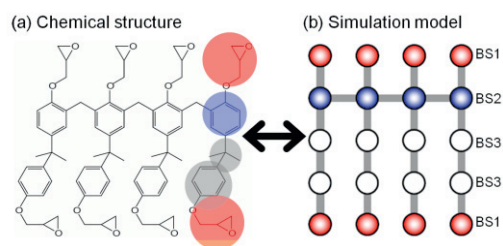

Fig. 1. (a) chemical structure of the photoresist monomer; (b) bead-spring model in the simulation

Table 1. Type of the beads employed in the CGMD simulation

Color	Functions in the model
Red	Epoxy group, to be reacted with catalyst
Blue	Phenyl group connected to methylene
White	Isopropylidene groups, phenyl groups
Green	Activated epoxy group with 2 reactive bond
Yellow	Virtual liquid
Purple	Permeable molecules

2.2. Analysis of molecular diffusivity

The cross-linked photoresist model was firstly obtained in the author-proposed CGMD simulation with NVT ensemble [4], and the calculated model was then employed for simulating the molecular diffusion. Figure 2 shows the starting configuration of coarse-grained photoresist model for the molecular diffusion analysis which consists of virtual liquid bead (VL), permeable beads (P), and photoresist beads (see also Table 1). This model can calculate a single mutual diffusion coefficient which follows the classical temperature-pressure formulation for normal diffusion. The value of the single mutual diffusion coefficient can be comparable to an experimentally measured diffusion coefficient.

The simulation detail is as follow: The glassy cross-linked photoresist model with 2000 beads was first obtained in CGMD simulation with NVT ensemble. Another cells filled with 500 VL beads. The two cells were connected to both sides of the photoresist model, and the 100 P beads were introduced into the random position of left side cell. The CGMD calculation under the condition of NVT ensemble was started, and the P beads are transported from the upstream cell (left) to the downstream cell (right) in the simulation model. When the P beads reached the downstream, they reproduced in the upstream. Thus the concentration of the P bead is always kept higher in the upstream. The single mutual diffusion coefficient

was determined by time lag method [5] which is measuring an elapsed time and number of beads representing molecule transported.
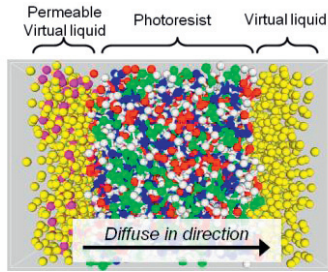

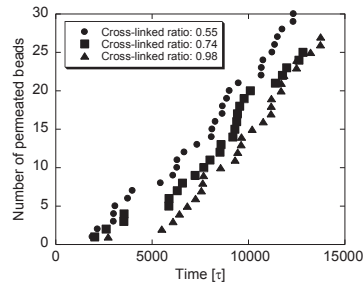Fig. 2. Coarse-grained photoresist model for the diffusivity analysis

Fig. 3. Cumulative amounts of the permeated beads plotted with the elapsed time

3. Result and Discussion

3.1. Simulation result

In order to confirm the dependency of the permeability on the cross-linked ratio, three models with different cross-linked ratio (0.55, 0.74, and 0.98) were simulated. Figure 3 shows cumulative amounts of the permeated beads dependency on the elapsed time for different cross-linked ratios, and a single mutual diffusion coefficient D can be determined by the following equation:

$$D = L^2/6t \tag{1}$$

where L is the photoresist thickness in the simulation model and t is the time lag; x-intercept derived from straight-line approximation of the plots in Fig 3. As summarized in Table 2, the calculated single mutual diffusion coefficient depends on the cross-linked ratio of the model, and decreased with increasing the cross-linking ratio.

3.2. Discussion

As a validation, the simulation results were compared with an experimentally measured single mutual diffusivity of photoresist membrane. The molecular permeability of photoresist membrane was evaluated in the microfluidic systems (Fig. 4) by measuring the diffusivity of Rhodamine-6G. In the present experiments, commercially available TMMR® (Tokyo Ohka Kogyo Company, Ltd.) was employed. The methodology for deriving the diffusivity is as follows. (1) the microfluidic systems was prepared by connecting one open end to a syringe pumps to drive Rhodamine-6G, a low molecular weight fluorescent dye, (2) the Rhodamine-6G diffused across the membrane to the upper PDMS (Polydimethylsiloxane) chamber, (3) the solution was sampled for analysis from the chamber, (4) the fluorescence spectrometer (NanoDrop 3300) was used for off-chip fluorescence measurements, and (5) diffusion coefficients were determined.

Table 3 summarizes a measured diffusivity, and which indicate the same tendency that of simulations; the permeable membrane with lower UV exposure dose has larger diffusivity due to the lower polymerization (i.e., low cross-linked ratio). These results suggest that the photoresist membrane can be used as molecular permeable membranes with controllable permeability.
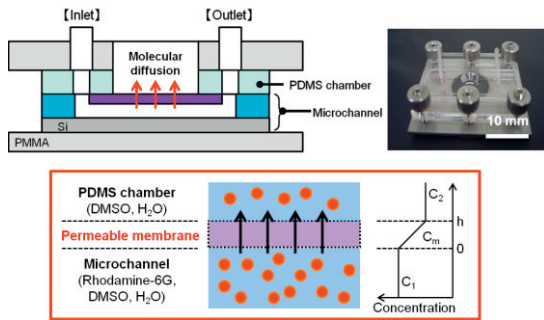
Fig. 4. Schematic of diffusivity measurement in the microfluidics

Table 2. Dependency of dimensionless diffusion coefficient on the cross-linked ratio of the CGMD simulation model. Here, σ and τ are used as units of length and time, respectively

Cross-linked ratio	0.55	0.74	0.98
Diffusion coefficient $[\sigma^2/\tau \times 10^{-2}]$	1.510	1.119	0.640

Table 3. Summary of the UV exposure dose for membrane region, thickness, and experimentally measured diffusivity of Rhodamine-6G

Exposure dose [mJ/cm^2]	10	12	14
Thickness [µm]	5.53	8.72	9.81
Diffusivity [mm/s]	0.150	0.136	0.034

4. Conclusion

A porous molecular network of photoresist for permeating biologically-relevant molecule has been successfully demonstrated by the CGMD simulation and the measuring diffusivity of Rhodamine-6G. The result confirmed that photoresist membranes in microfluidics can be used as permeable membranes with controllable permeability by the photolithography parameters such as UV exposure dose and PEB temperature. The future research should be directed to evaluate and analyze pore sizes and a molecular weight cut-off range of membranes depending on the cross-linked ratio, using a several low molecular weight fluorescent dyes.

Acknowledgements

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