

## Water Lubrication System Supported by High-density Hydrophilic Polymer Brush

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### Introduction

High-density and well-defined surface-grafted polymer, so-called "polymer brush",<sup>1</sup> is a promising method for improving the lubrication properties of solid surfaces.<sup>2</sup> Especially, the water lubrication systems using hydrophilic polymer or polyelectrolyte brush have also been well-studied by Klein,<sup>3</sup> Osada,<sup>4</sup> and Sheth et al.<sup>5</sup> because of its applications to medical implant devices<sup>6</sup> such as artificial joints<sup>7</sup> as well as environmentally friendly technologies. The authors have also reported that hydrophilic polymer brush with hydroxy groups on the side chains exhibit a low friction coefficient in water.<sup>8</sup> In the human body, phospholipid and hyaluronic acid act as a boundary lubricant, and play important role in lowering friction and in the protection of articular cartilage. In this work, the authors focused on specially-designed methacrylate containing a phosphorylcholine unit in the side chain, 2-methacryloyloxyethyl phosphorylcholine (MPC). Poly(MPC) is well known as a super-hydrophilic and biocompatible polymer. The high-density poly(MPC) brush is expected to have improved the water-lubrication properties.

### Experimental

The preparation procedure for the silicon wafer immobilized with the radical initiator was described previously.<sup>8</sup> A typical surface-initiated ATRP of MPC was performed as follows: the initiator-immobilized silicon wafer, CuBr (0.025 mmol), 4,4'-dimethyl-2,2'-bipyridyl (0.050 mmol), ethyl 2-bromoisobutylate (EB, 0.025 mmol), and methanol solution of MPC (6.5 mmol) were introduced into a glass tube under argon atmosphere. The polymerization reaction was carried out at 303 K for 12 h under argon to simultaneously generate poly(MPC) brush from the substrate and free poly(MPC) from EB. The reaction mixture was poured into THF to precipitate the free polymer, and the wafer was washed with methanol using a Soxhlet apparatus for 12 h.

The frictional coefficient of the polymer brushes was recorded on a Tribostation Type32 (Shinto Scientific Co. Ltd.) by sliding a glass ball ( $\phi 10$  mm) on the substrates over a distance of 20 mm at a sliding velocity of 90 mm/min under loading of 0.49 N at 298 K. Humidity was controlled by a blowing ratio of dry N<sub>2</sub> gas and humid air. The theoretical contact area between a glass ball probe and a silicon wafer under these conditions can be calculated to be  $3.51 \times 10^{-9}$  m<sup>2</sup> by Hertz's contact theory, and the average pressure on the contact area was estimated to be 139 MPa.

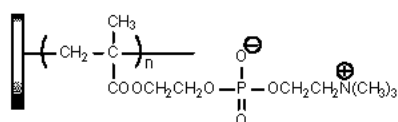


Figure 1. Chemical structure of poly(MPC) brush

### Results and discussion

The number-average molecular weights ( $M_n$ ) of obtained poly(MPC) brushes on silicon wafer were estimated to be approximately 30,000 ~ 90,000 by size-exclusion chromatography of the corresponding free polymer using water as a eluent. The AFM observation revealed that a homogeneous polymer layer was formed on the substrate, and the surface roughness was 0.8 ~ 1.5 nm in a dry state in a  $5 \times 5 \mu\text{m}^2$  scanning area. The thickness of the polymer brush was determined to be ca. 10~30 nm by ellipsometer. The graft density was estimated to be ca. 0.20 chain/nm<sup>2</sup> based on the linear relationship between  $M_n$  and the thickness. Advancing and receding contact angles of poly(MPC) brush against water were 11° and 5 ~ 7°, respectively,

indicating a stable super hydrophilicity of poly(MPC) brush.

Figure 2(a) shows the friction coefficient of poly(MPC) brush surface measured by sliding a glass ball in air, water, and toluene at 298 K. Under the dry N<sub>2</sub> atmosphere, a high friction coefficient was observed probably due to the strong adhesive interaction between poly(MPC) brush and the glass probe. In contrast, the brush surface afforded a lower friction coefficient with increasing humidity. It is supposed that water molecules adsorb on the surface of highly hydrophilic poly(MPC) brush and work as a lubricant to moderate the interaction between brush and probe. In addition, water-swollen poly(MPC) brush compressed by a probe sphere would generate a repulsive force against a high normal load due to the osmotic pressure originating from steric interactions between the high-density brushes and probes.<sup>10</sup> These water-lubrication systems restrict the direct contact of a probe with the substrate to reduce the friction force. Contrary to our expectations, the friction coefficient in water was higher than that in humid air condition. These results suggest that in water, hydrodynamic lubrication would take place by the drainage of viscous water from the polymer brush layer as it is squeezed by two solid surfaces with a narrow gap,<sup>11</sup> although additional experimental evidence is needed to confirm this hypothesis. Furthermore, swollen and extended poly(MPC) brush chains in water should have increased actual contact area between brush and probe to result in a higher friction coefficient, compared with in the case of humid air. In toluene, which is a poor solvent for poly(MPC), a higher friction coefficient was observed, probably because the interaction between polymer and glass probe increased.

As similar lubrication tendency was observed when a brush-immobilized glass ball was used as a sliding probe, as shown in Figure 2(b). The friction coefficient under the highly humidified air condition was significantly reduced to 0.02, which is lower than that under aqueous conditions. It is supposed that hydrophilic MPC units covered with water molecules effectively reduce the friction force, creating a good water lubrication system.

In conclusion, the authors found that effective water lubrication takes place on the surface of high-density hydrophilic poly(MPC) brush, even in humid air, resulting in extremely low friction and excellent wear resistance.

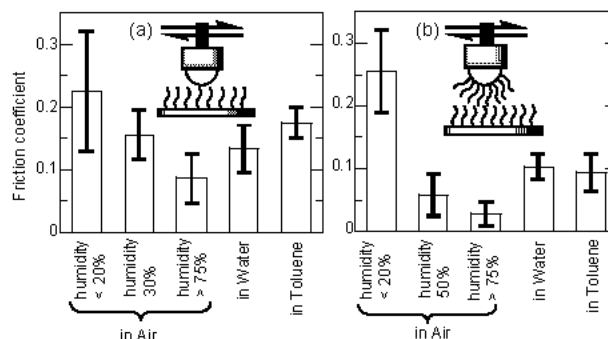


Figure 2. Friction coefficient of poly(MPC) brush under sliding a glass ball (a) and brush-grafted-glass ball (b) in air, water and toluene.

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