AFM studies on microtribology of concentrated polymer brushes in solvents

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Abstract. In concentrated polymer brushes (CPBs) prepared by surface-initiated living radical polymerization, graft chains in a good solvent are highly stretched, nearly to their full length, giving properties quite different and unpredictable from those of semi-dilute polymer brushes (SDPBs) previously studied. This paper reviews our recent studies on the microtribology of confronted CPBs in solvents. Atomic force microscopy revealed that the CPBs of poly(methyl methacrylate) and poly(styrene) showed dramatically low frictional coefficients in good solvents compared with those of the corresponding SDPBs. This was reasonably ascribed to confronted CPBs hardly mixing with each other due to their huge osmotic and elastic interactions. The lubrication mechanism of CPBs was discussed according to the sliding-speed dependency of frictional coefficient, and two different mechanisms, boundary and hydrodynamic lubrications, were suggested. Thermo-responsive lubrication was also demonstrated for the CPB of poly(N-isopropyl acrylamide). We believe that these studies will open up a new route to precision surface modification for “super” lubrication.

1. Introduction
Polymers densely end-grafted on a solid surface are obliged to stretch away from the surface, forming a so-called “polymer brush”, which can dramatically change various surface properties including optical, electrical, chemical, thermodynamic, mechanical, rheological, and tribological ones.1-3 Because of their important role in many areas of science and technology, polymer brushes have been extensively studied theoretically and experimentally. These polymer brushes were mostly categorized into the “semi-dilute” polymer brush (SDPB), in which polymer chains swollen in a solvent overlap with each other but their volume fraction is still so low that the free energy of interaction can be approximated by a binary interaction, and the elastic free energy, by that of a Gaussian chain.6-8

Figure 1. Conceptual illustration from SDPB to CPB.
Successful application of living radical polymerization (LRP) made it possible to graft various low-polydispersity polymers including simple homopolymers, end-functionalized polymers, block/random/gradient copolymers, and functional polymers. At the same time, this technique brought about a striking increase of graft density: its maximum value for e.g., poly(methyl methacrylate) (PMMA) grafted on a silicon wafer reached 0.6 chains/nm$^2$. This density was more than 1 order of magnitude higher than those of typical SDPBs, going deep into the regime of concentrated polymer brushes (CPBs) which had been little explored systematically because of the unavailability of such brush samples. The CPBs of PMMA swollen in a good solvent exhibited an equilibrium film thickness as large as 80-90 % of the full (contour) length of the graft chains, indicating that the chains are extended to a similarly high degree. Such CPBs have been found to show properties quite different and even unpredictable from those of SDPBs. In this paper, we review our recent studies focusing on the tribological properties of CPBs in solvents.

2. Experimental section
The CPB samples were synthesized by surface-initiated atom transfer radical polymerization (ATRP), as described previously. The number- and weight-average molecular weights ($M_n$ and $M_w$) are the values, as determined by gel permeation chromatography (GPC), for the free polymers which were simultaneously produced from the free (unbound) initiator added to the polymerization solution for controlling graft polymerization. There are reasons to believe that the molecular characteristics of the free polymers closely approximate those of the graft polymers. Table 1 lists the molecular characteristics of the CPB samples used in this study. The SDPB samples were prepared by the so-called “grafting-to” method, for which a polymer with a triethoxysilyl group at the chain end was synthesized by the ATRP using (2-bromo-2-methyl)propionyloxypropyltrioethoxysilane (BPE) as a free initiator. The layer thickness $L_d$ in a dry state, of the brushes on a silicon wafer was determined by spectroscopic ellipsometry (M-2000U, J. A. Woolam, USA), and the graft density $\sigma$ was evaluated from $L_d$ and $M_n$ values. It was reasonably assumed that nearly the same brushes were also formed on the silica probe particle.

The structure and compressibility of swollen brushes on a silicon wafer were measured by atomic force microscopy (AFM; NanoWizard, JPK Instruments AG, Germany or SPA-400+SP13800N, SII NanoTechnology Inc., Japan) using an unmodified silica probe particle which was glued on a rectangular cantilever (see Figure 2). The force curves were obtained by measuring the normal force $F_N = k_N \Delta z$, where $k_N$ is the normal spring constant and $\Delta z$ is the normal displacement of the

| Sample  | $M_n$ a) | $M_w/M_n$ a) | $\sigma$ / chains nm$^2$ | $\sigma^*$ b) |
|---------|---------|--------------|-----------------|-------------|
| PMMA    | 122,000 | 1.39         | 0.51            | 0.37        |
|         | 88,000  | 1.17         | 0.53            | 0.38        |
| PS      | 37,000  | 1.27         | 0.49            | 0.37        |
| PNIPAM  | 50,000  | 1.15         | 0.70            | 0.53        |

a) the values for the free polymers.
b) the reduced graft density (per cross-sectional area of chain, which is estimated from the bulk density of monomer in this case); the maximum value of $\sigma^*$ is unity, corresponding to the close packing of graft chain with all-trans conformation.
cantilever) as a function of separation. The measured force $F_N$ can be reduced to the free energy $G_f$ of interactions between two parallel plates according to the Derjaguin approximation, $F_N/R = 2\pi G_f$, where $R$ is the radius of the probe particle.

The frictional properties between swollen brushes were also measured by AFM in the same configuration except that the silica probe particle was also modified with polymer brushes (see Figure 2). The lateral (frictional) force $F_l$ was evaluated according to the equation, $F_l = k_l \theta_l/2R$, where $k_l$ is the torsional spring constant and $\theta_l$ is the angular (torsional) displacement of the cantilever. $\theta_l$ was monitored as a function of $F_N$, while the sample substrate was loaded with the silica probe particle and slid back and forth along the direction normal to the cantilever at differing sliding speeds $v$.

3. Results and discussion

3.1. Tribological properties of CPB in good solvent

Figure 3 shows the normal force curves (without lateral modulation) for the CPB and SDPB of PMMA compressed by the (unmodified) silica probe particle in toluene (TOL). Upon compression, the $F_N$ between the swollen brushes was completely repulsive. The data for the SDPB was nearly consistent to the scaling theory derived by de Gennes using the scaling approach. The CPB ($\sigma = 0.51$ chains/nm$^2$, $M_n = 122,000$, $M_w/M_n = 1.39$), however, gave much steeper force profile, meaning that the brush layer is more resistant to compression: with $F_N/R > 1$ mN/m, the CPB layer was compressible only to $D/L_e \approx 0.7$, in contrast to $D/L_e < 0.2$ for the SDPB. This strong resistance against compression must be characteristic of CPB due to an extremely high osmotic pressure, being one of important properties for the development of tribomaterials.

The strong resistance against compression and dense anchoring of graft chains in CPBs are expected to drastically improve tribological properties such as friction, wear, and lubrication as compared with those of SDPBs. Figure 4 plots the frictional coefficient $\mu = F_l/F_N$ vs. normal force $F_N$ (load) between confronted brushes at a sliding speed of $v = 20$ $\mu$m/s, which is in a regime of the boundary lubrication discussed below. The SDPB ($\sigma = 0.024$ chains/nm$^2$, $M_n = 90,000$, $M_w/M_n = 1.27$) had two different regime of friction: at low applied loads, the $F_l$ and hence the $\mu$ value is very low (<0.001), and then at an onset of the threshold, the $F_l$ steeply increases with increasing $F_N$, approaching a constant $\mu$ value of about 0.1 (for higher loads). Such a transition from low to high-frictional stages was already reported by Klein et. al., who measured the frictional properties between the SDPB of poly(styrene) (PS) in TOL using the

![Figure 2. AFM setup for microtribology measurements](image)

![Figure 3. Plot of $F_N/R$ vs normalized separation $D/L_e$ for (a) CPB and (b) SDPB of PMMA in TOL.](image)
surface force apparatus. This transition was ascribed to the interpenetration (mixing) of the brushes at high loads. More interestingly, the $F_L$ between the CPBs of PMMA ($\sigma = 0.53$ chains/nm$^2$, $M_n = 88,000$, $M_w/M_n = 1.17$) showed no such transition, staying at low values, lower than $5 \times 10^{-4}$ in the whole range of loads studied. This $\mu$ value is believed to be one of the lowest of all materials and comparable to that achieved for the SDPBs of polyelectrolyte with the help of a charge effect. This extremely low-friction property was reasonably ascribed to the fact that swollen CPBs hardly interpenetrate each other due to the large osmotic pressure and highly stretched chain conformation (entropic interactions).

This mechanism of “super lubrication” of CPBs should be effective not only in a microscopic scale as verified by AFM but also in a macroscopic scale. Kobayashi et al. studied the tribological property of the CPBs by sliding the stainless or glass probe with $R = 5$ mm on the brush surface in the air as well as in solvents. Although the $\mu$ did not reach the low value obtained in a microscopic scale, the CPBs of PMMA were found to have better frictional property and better wear resistance than the corresponding spin-coated PMMA film. These properties may be improved by increasing the brush thickness and/or decreasing the surface roughness of substrates.

3.2. Lubrication in mixtures of good and poor solvents

In order to discuss the mechanism of lubrication in detail, we measured the $\mu$ value as a function of sliding speed $v$ for the CPB of PS ($\sigma = 0.49$ chains/nm$^2$, $M_n = 37,000$, $M_w/M_n = 1.27$) in mixtures of TOL and isopropanol (IPA) (as good and poor solvents, respectively). Figure 5 shows the results at $F_N = 20$ nN, corresponding to the high-load regime as mentioned above. It should be noted that the SDPB gave a nearly constant and high $\mu$ value independent of $v$ (the data are not shown in the figure). First of all, we discuss the $v$ dependency of $\mu$ in pure TOL. The data suggest the two regions in the $v$ dependency; at a high $v$ region, the $\mu$ value increases with increasing $v$. We ascribed the high $v$ region to the hydrodynamic lubrication, in which the frictional property must be related to the viscosity of solvent (in the swollen brush). The slope of the line in this regime was estimated to be ca. 0.7. It should be unity for Newtonian fluids. The lower $v$ region in which $\mu$ is nearly constant is ascribed to the boundary lubrication, where the interaction between brushes is important. The CPB of PMMA also gave similar $v$ dependency of $\mu$, and the data at $v = 20$ $\mu$m/s discussed in the previous section were in a regime of boundary lubrication.

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Figure 4. Plot of frictional coefficient $\mu$ vs normal load $F_N$ for (a) CPB and (b) SDPB of PMMA in TOL.

Figure 5. Plot of frictional coefficient $\mu$ vs sliding speed $v$ for the CPB of PS in IPA/TOL mixtures; the figures indicate the IPA content.
Figure 5 suggests that with increasing IPA content up to at least 0.6, the \( v \) dependency line corresponding to the hydrodynamic lubrication shifted to a higher value with nearly the same slope. We determined the equilibrium thickness \( L_e \) of swollen brush in these mixed solvents, and interestingly, we found that these data in the hydrodynamic lubrication could be scaled by the degree of swelling, giving \( \mu \sim v^\alpha \left( \frac{L_e}{L_d} \right)^\beta \), where \( \alpha = 0.7 \) and \( \beta = -4 \). This would give good information to discuss the details about the hydrodynamic lubrication, which is going on by simulational and theoretical studies. Further increase in IPA content resulted in almost constant \( \mu \) value independent of \( v \). Under such poor-solvent condition, the CPB was in a non-swollen state and hence no more worked as a hydrodynamic lubricant. This might be similar to the solid-solid friction with direct contact of surfaces.

3.3. Thermoresponsive lubrication

Controlled synthesis of well-defined CPBs of PNIPAM still remained challenging. For achieving this, the condition of surface-initiated ATRP was optimized; the catalytic system of CuCl/CuCl\(_2\)/tris[2-(dimethylamino)ethyl]amine along with a surface-initiator, (2-chloropropionyloxy)hexyltriethoxy-silane enabled a controlled growth of PNIPAM brushes in DMSO at 25 °C. The brush thickness in dry state \( (L_d) \) increased proportionally with the \( M_n \) of the (low-polydispersity) free polymer (as a good measure of the graft polymer), giving a graft density of ca. 0.7 chains/nm\(^2\) which was expected to be deep in the CPB regime.\(^{16}\) We confirmed that this CPB had a large swollen thickness comparable to the full length of graft chains and a \( \mu \) value as low as \( 10^{-4} \) in ethanol, which is a good solvent for PNIPAM. Figure 6 shows (a) the degree of stretching \( L_e/L_{c,w} \) of the CPB and the frictional coefficient \( (\mu) \) between the CPBs in water as a function of temperature, where \( L_{c,w} \) is the weight-average full length of the graft chain (in all-trans conformation). The CPB of PNIPAM \((\sigma = 0.7 \text{ chains/nm}^2, M_n = 50,000, M_w/M_n = 1.15)\) was highly swollen, nearly to their full lengths \( L_{c,w} \), in water at 5 °C, gradually shrinking with increasing temperature down to an almost non-swollen state above 30 °C. This is reasonably understood in terms of the decreasing solvent quality of water for PNIPAM and hence the decreasing osmotic pressure; the CPB is more difficult to be swollen than the SDPB because of the much larger penalty of conformational entropy in the former. Interestingly, a dramatic change in \( \mu \) between brushes (more than 3 orders of magnitudes) was observed at around 30 °C, below which it stayed at very low values (\( < 10^{-3} \)). This is ascribed to a dramatic change in structure/properties of the outermost surface.

![Figure 6](image)

**Figure 6.** Plots of (a) degree of stretching \( L_e/L_{c,w} \) and (b) frictional coefficient \( \mu \) as a function of temperature for the CPB of PNIPAM in water.
4. Conclusion
Recent successful application of living radical polymerizations has made it possible to modify solid surfaces with various end-grafted polymers of exceptionally high graft density, allowing us to investigate deeply into the CPB regime of graft density. Among other fascinating features of CPBs, their solvent-induced super lubrication was described in this paper. In contrast to SDPBs which gave a transition in frictional coefficient with increasing applied load, CPBs gave no such transition. This unique feature of CPBs was discussed to originate in entropic interactions in common for all kinds of CPBs in good solvents. In this regard, surface-initiated LRP and the CPBs thereby obtained are opening up a versatile route to the creation of new tribomaterials that have never been realized by the conventional techniques of surface modifications. Hopefully, this progress will lead to a wealth of applications.

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