

Development Of Polymer Brushes For The Lubrication Of Silicon Nitride-Steel Contacts

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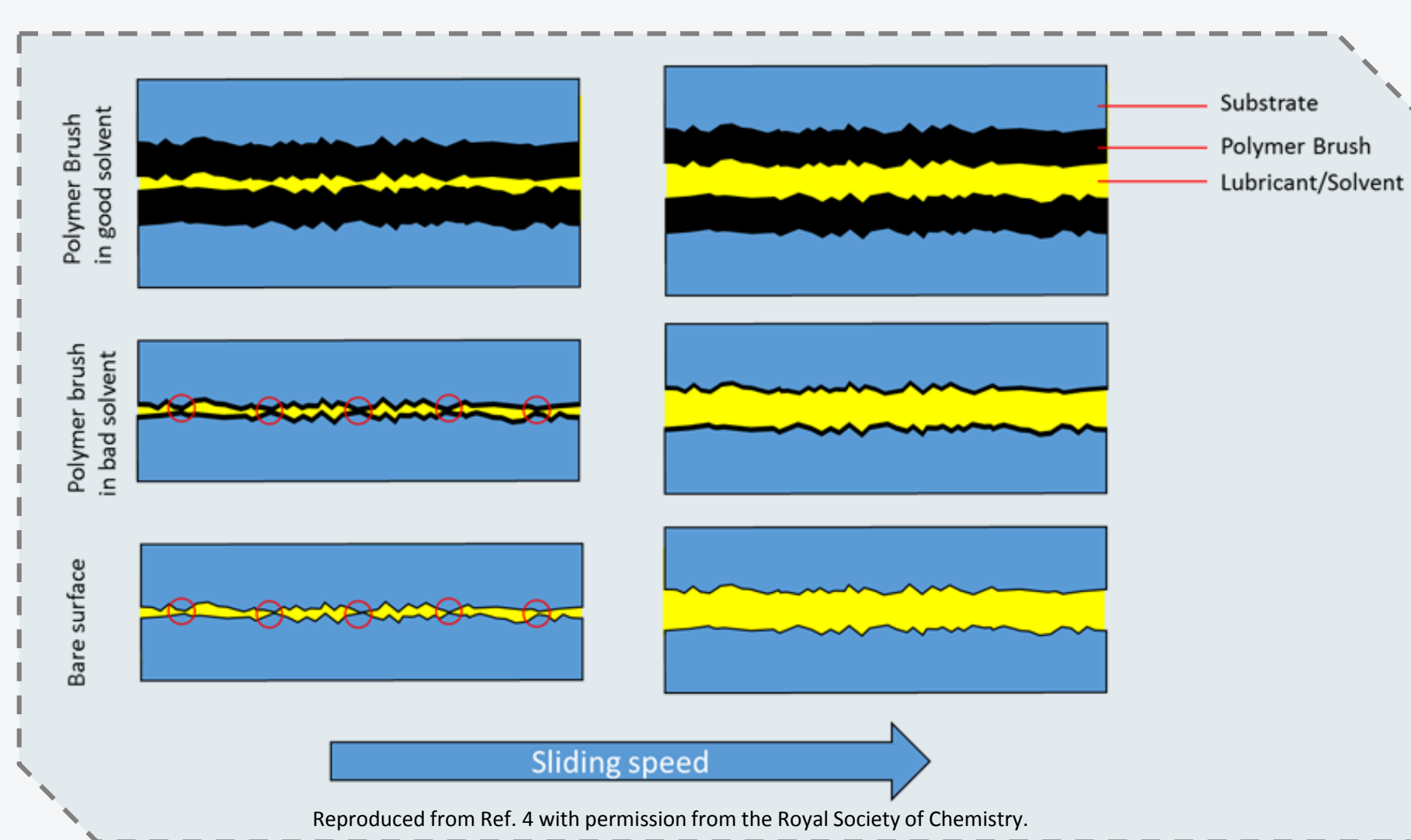
1. Introduction

Silicon nitride rolling element bearings have seen great success as hybrid bearing systems in applications including automotive, aerospace, renewables and the railway industry. The main sought after property is the relative low density of the ball bearing, with a 60% reduction in weight resulting in an 80% reduction in friction compared to classic steel bearings [1]. Compared to steel on steel contacts the coefficient of friction (COF) of hybrid systems is reduced to approximately 0.04-0.09 under oil lubricated sliding conditions and between 0.1-1.0 for dry sliding conditions [2, 3]. Current lubrication and protection solutions are focussed on lubricating metal surfaces thus are not optimised for hybrid contacts. This study aims to develop polymer brush based lubrication solutions that are optimised for silicon nitride-steel contacts through self-assembling initiators and subsequent polymerisation techniques.

Polymer brushes can be attached to surfaces either by "grafting from" or "grafting to" method using prefabricated polymers that can be attached to a surface using physisorption or chemisorption much like self-assembled monolayers (SAMs) are produced [4]. The film thicknesses and brush density of polymers produced through the "grafting to" method are limited by the molecular weights of the preformed polymer in solution which can limit the tribological properties [5]. Atom Transfer Radical Polymerisation (ATRP) is the most popular type of polymerisation for producing "grafting from" brushes due to the relative robustness of the technique [6]. For example, unlike the other techniques, rigorously dry working conditions are not needed and reactions are very tolerant of a variety of monomers, ligands and catalysts [4].

The mechanism in which solvated polymer brushes lubricate is thought to be as follows [4, 7, 8].

1. The resistance to rearrangement of the grafted chains with the repulsive nature of the brushes;
2. Lubricant entrapment in the polymer brushes;
3. High concentrations of lubricant in the outer polymer brush creates a low shear area protecting the brush system.



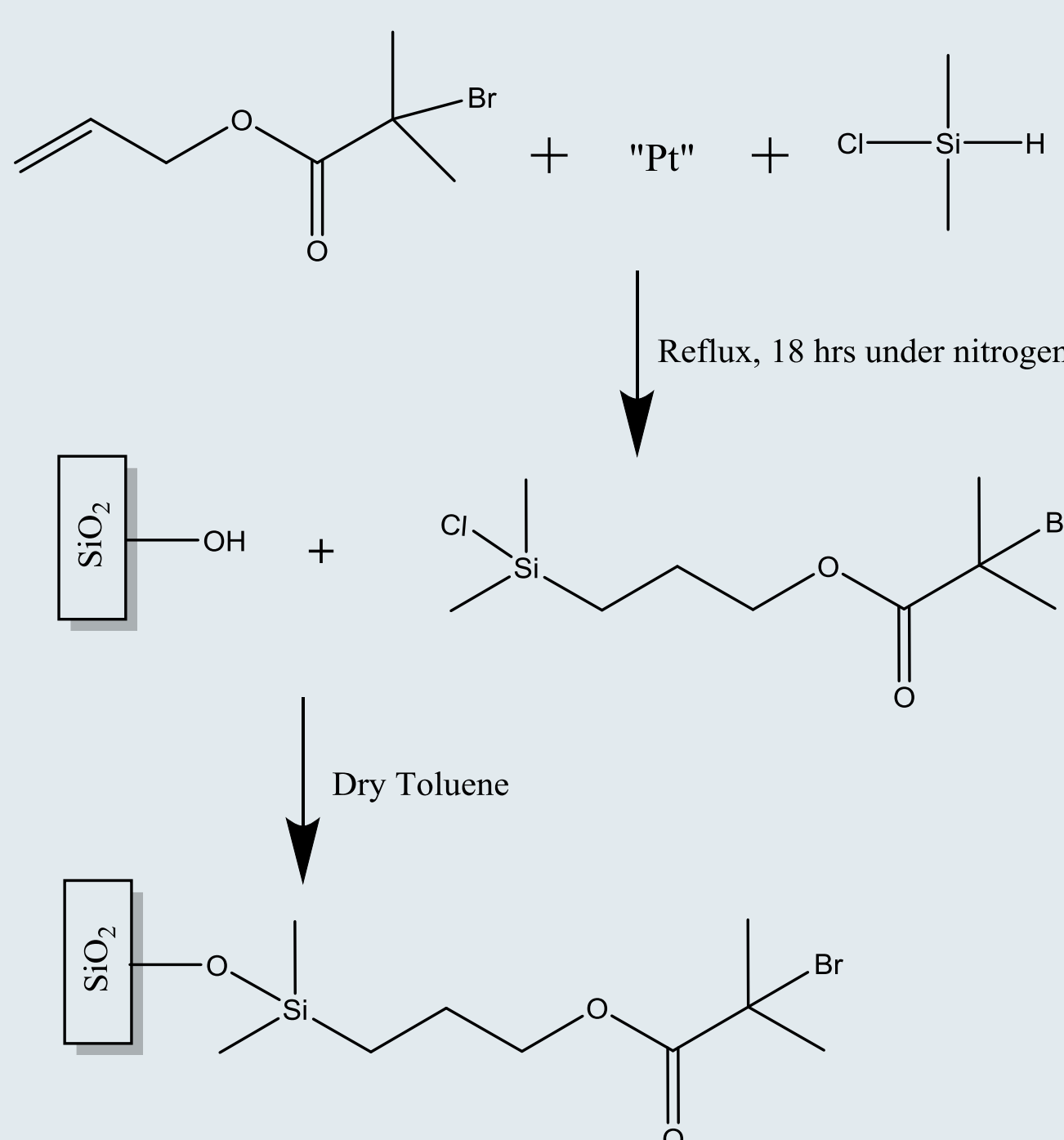
2. Synthesis of Polymer Brushes

2.1 ATRP initiator Synthesis

Method

Allyl 2-bromo-2-methylpropionate (1.6 mL), dimethylchlorosilane (10 mL) and platinum on carbon (10 mg) were added to a 25 mL round bottom flask attached to a microscale rig. The system was purged with nitrogen and then the mixture was refluxed under nitrogen for 18 hrs. The excess silane was then distilled off. The resultant solution was quickly filtered over anhydrous sodium sulphate to produce a colourless oil which was confirmed by ¹H and ¹³C NMR. The attachment of the ATRP initiator was completed in toluene as well as in a poly-alpha-olefin (PAO) synthetic oil at concentrations of 1, 2.5 and 5 mM solutions for both 2 and 18 h. A PAO 4 from ExxonMobil was selected due to its similarities with military defence standards, there are a few lubricating oils that are used, namely OMD-55, OMD-90 and OX-90 [9].

Synthesis Steps

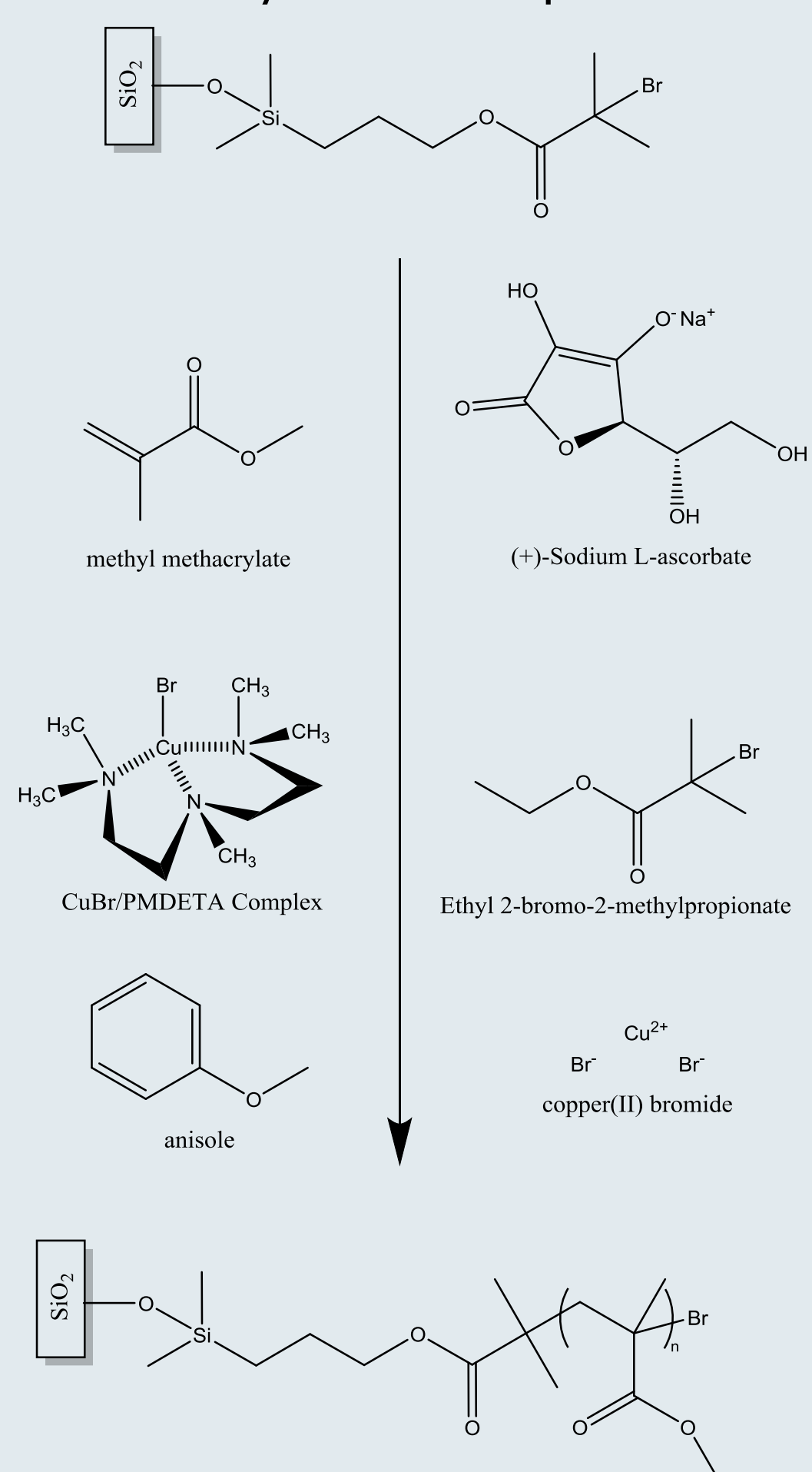


2.2 Polymer Synthesis

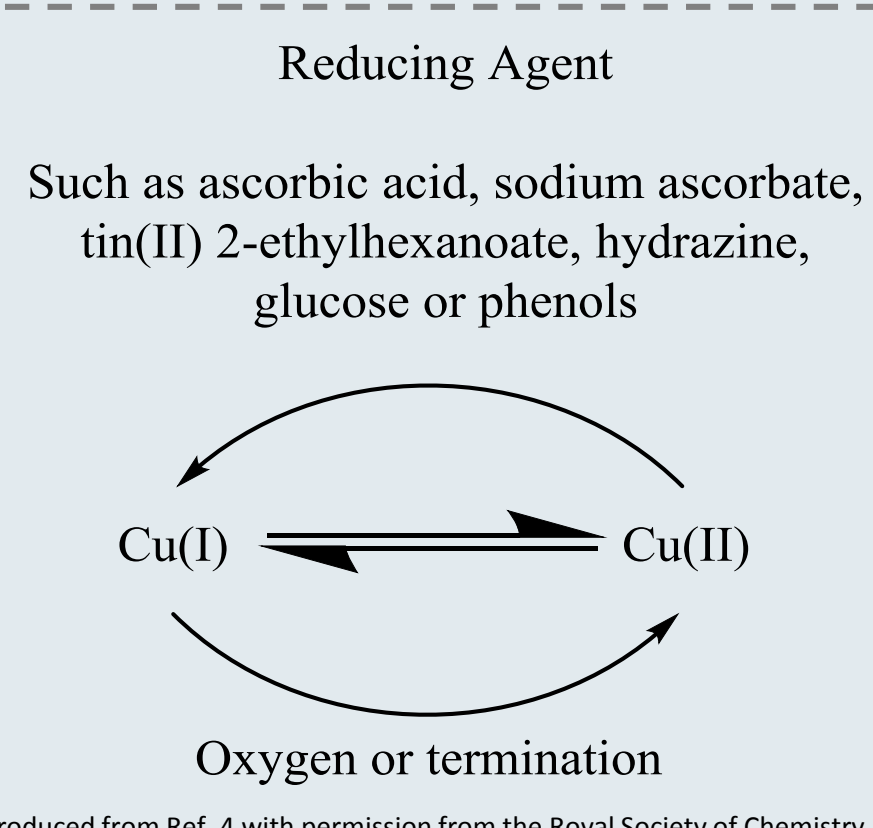
Method

To conduct the surface initiated polymerisation a 22 mL vial containing a silicon wafer with pre attached initiator was charged with: methyl methacrylate (MMA, 15 mL, 150 mmol), CuBr₂ (0.00558 g, 0.025 mmol) and PMDETA (0.043 g, 0.25 mmol) in anisole (2 mL) in addition to EBIB (0.048 g, 0.25 mmol). The vial was then bubbled with nitrogen for 5 mins then sealed. A solution of sodium L-ascorbate (0.0495 g, 0.25 mmol) in anisole (2 mL) was then syringed through the septum and the vial was placed in a thermostatic water bath at 70°C. The polymerisation was stopped when the vial was unscrewed and therefore exposing the catalyst to air. The modified wafer was removed and sonicated in tetrahydrofuran (THF) and dried in nitrogen.

Synthesis Steps



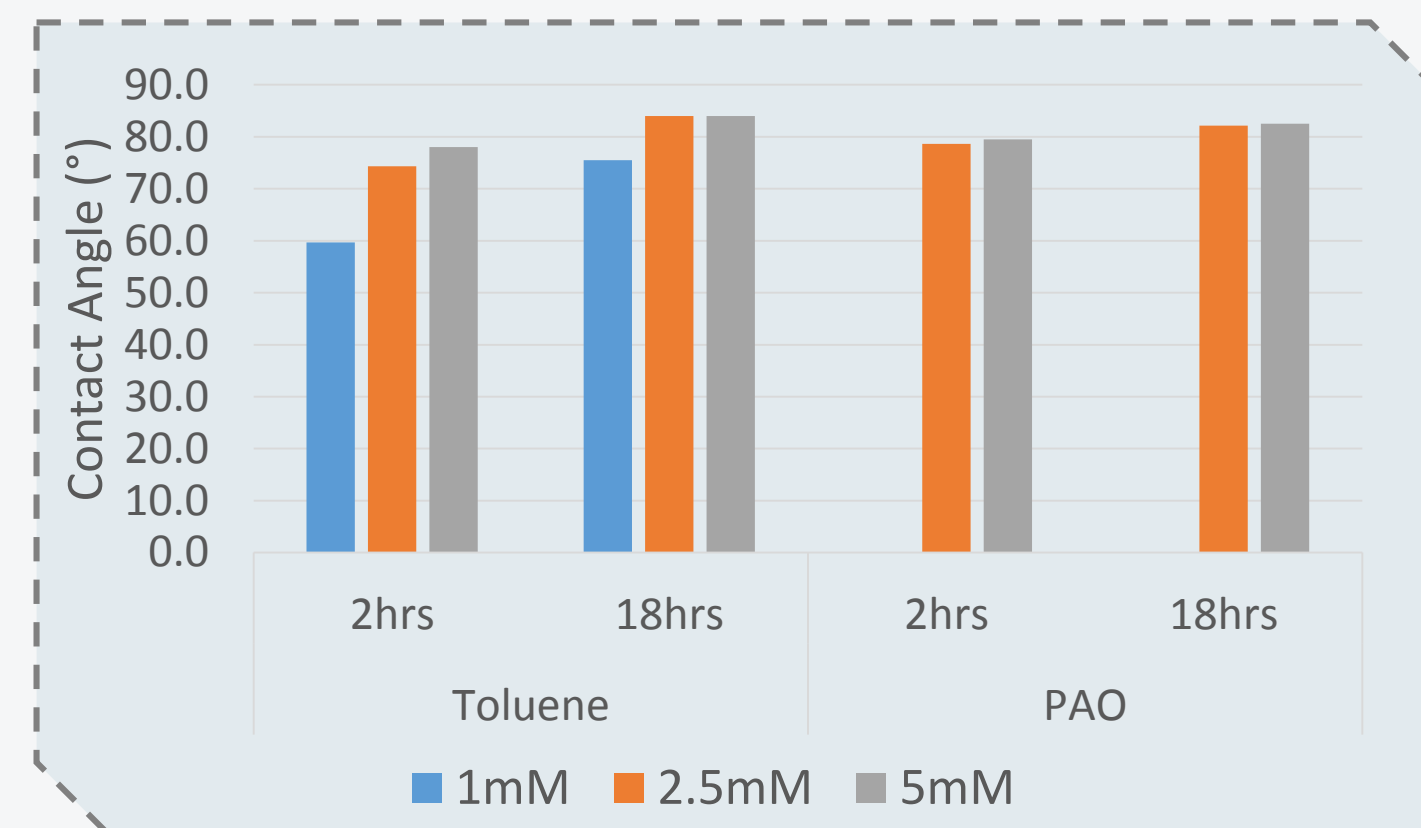
Activators Re-Generated by Electron Transfer (ARGET) is a development of ATRP and has been used to reduce the concentration of metal catalysts up to 1000 times to ppm levels [10].



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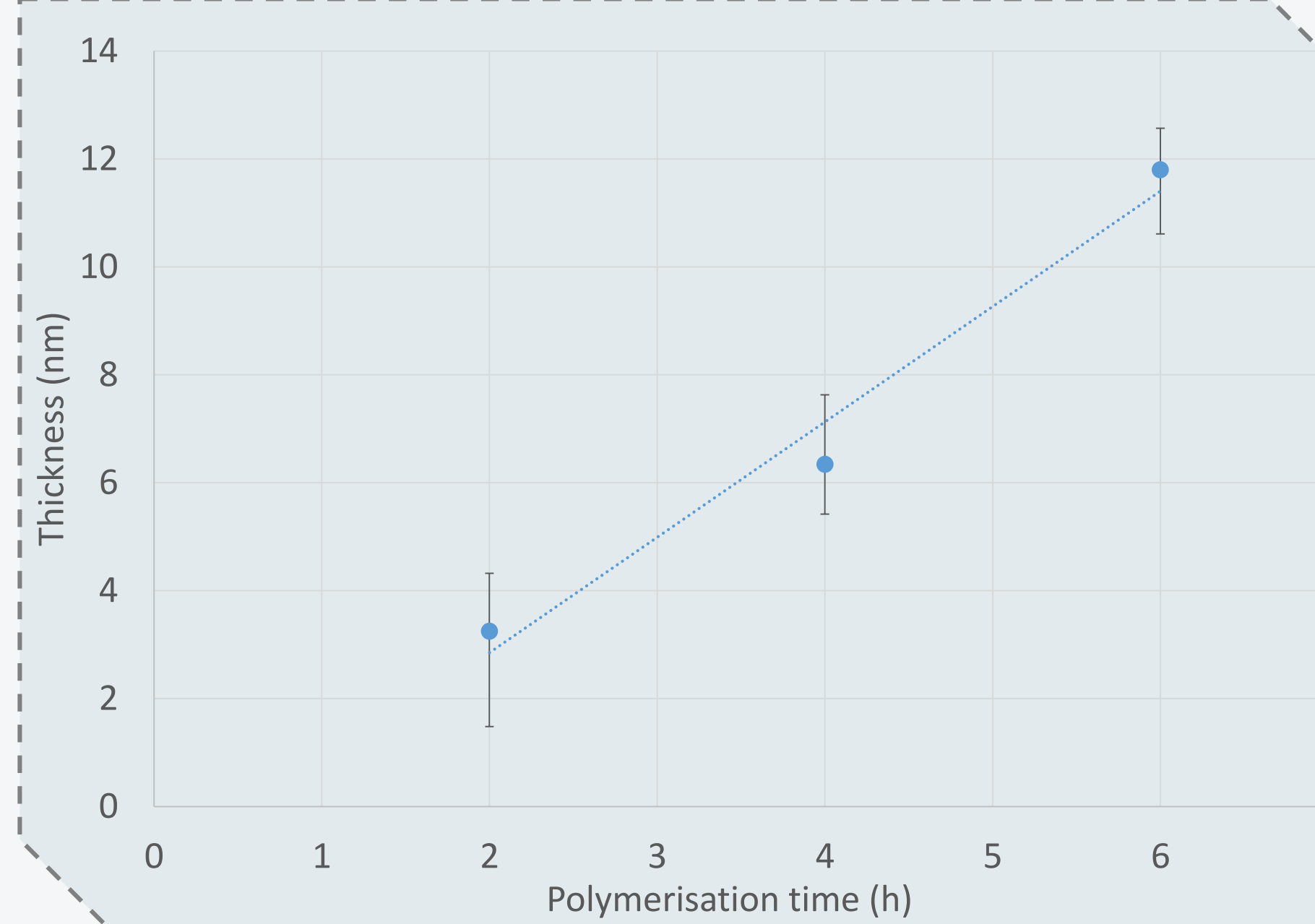
3. ATRP Initiator Self-Assembly

The contact angle data show that in all cases a monolayer of the initiator was formed on silica wafer to some degree. Self-assembled deposition of the initiating monolayer was expected to take a similar amount of time to that of octadecyltrichlorosilane, ≈2 h [1]. However, it was observed that the maximum contact angle was achieved over a longer duration of ca. 18 h at the initiator concentration 2.5 mM in toluene. It is likely this is due to steric hindrance of the two methyl groups on the silane. A monolayer was also successfully formed in PAO, but the same contact angle was not achieved as in toluene. On the other hand, it is noteworthy that a maximum contact angle (85°) was unlikely to be achieved as the PAO is an imperfect solvent [11]. In comparison to the tests in toluene, the difference of the measured contact angles between 2.5 mM and 5 mM in PAO is insignificant, and slightly higher contact angles were achieved for 2 h tests in PAO than in toluene. This may be due to the fact that an overall lower quality monolayers were formed, i.e., multilayers or agglomerations due to a higher water content in the PAO.



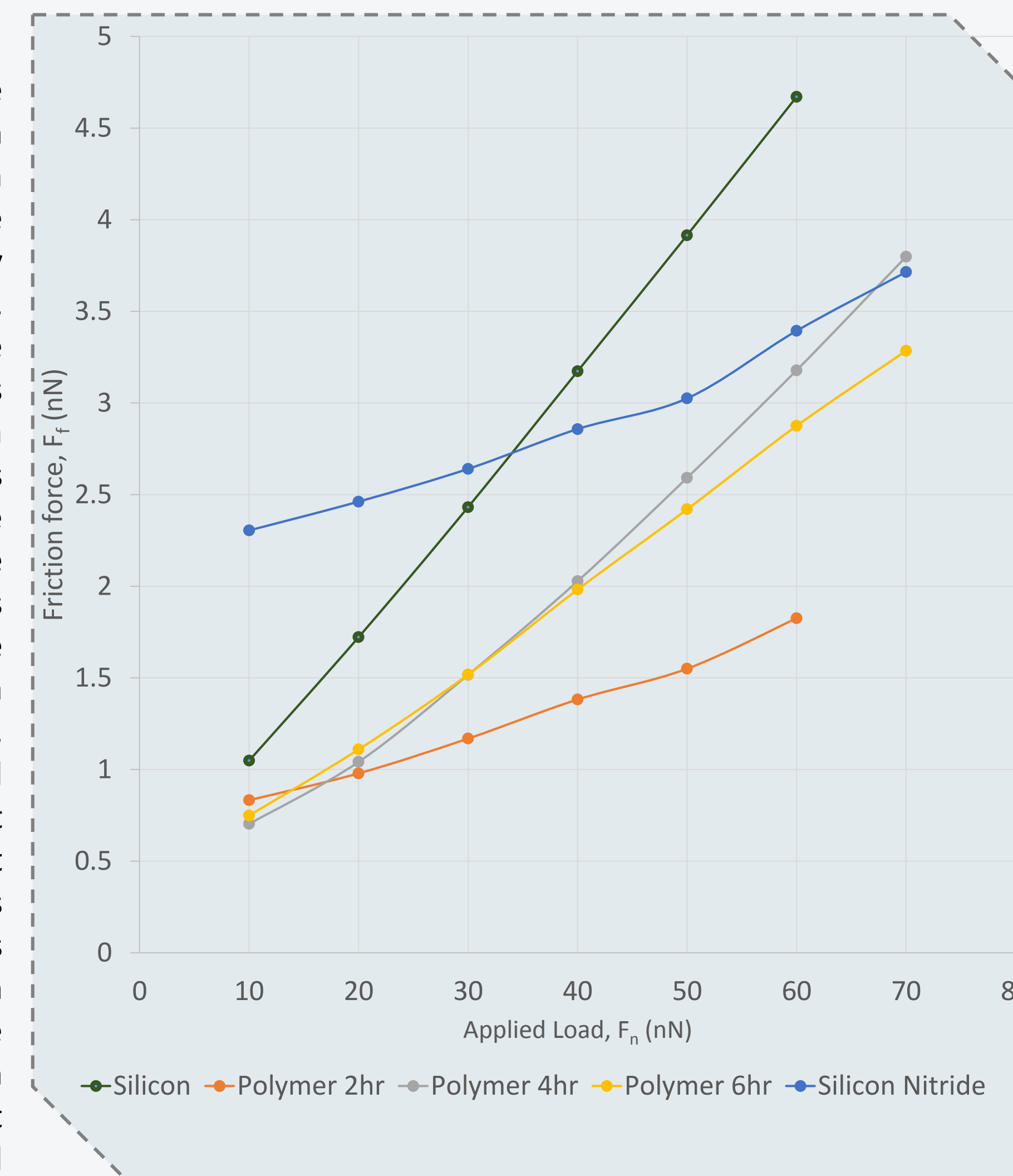
4. Polymer Growth

The graph to the right shows poly methyl methacrylate (PMMA) growth with respect to time. The dry thickness of the polymer brushes was measured by a Woolham M-2000 spectroscopic ellipsometer at three intervals, 2h, 4h, and 6h. The data was modelled with the corresponding CompleteEASE software using a three component model consisting of Si/SiO₂/Cauchy [12, 13]. It can be seen that the thickness of the polymer film grew linearly with immersion time from 3 nm to 11.5 nm over 6 h.



5. Nanotribology

Nanotribology experiments were conducted on the polymer brush modified silicon wafers using an atomic force microscope (MAC Mode III, 5500 Scanning Probe Microscopy Agilent Technologies, USA). Nanotribological tests were performed under ambient conditions in air. The results show that a reduction in friction force was achieved by all polymer brushes, see figure on the right. However, the influence of the polymer thickness is not obvious or unidirectional, i.e. the thicker polymer may not provide a lower friction force. However, comparing those with the silicon and silicon nitride surfaces without polymer brush layers, a significant reduction in friction force was achieved. Hence, the polymer has provided a protection to the silicon surface. It is interesting that the polymers formed in 4 and 6 h behaved in a similar way but different from that of the thinner layer and this will be further investigated.



6. Conclusions

In the current work it has been shown that polymer brushes have been synthesized on silicon via ARGET ATRP in a controlled manner and have the potential to form silicon nitride. The grafted structures have the promising characteristic in that they are covalently attached to the surface in question providing a stable coating for tribological contacts. It is likely that the polymer will synergize well with oil lubricated contacts and the solvated polymer brushes would trap lubricant therefore decreasing COF. Tribological properties of the PMMA brushes were analysed at the nanoscale and compared to bare substrates. The polymers formed have shown to reduce the frictional force in all thicknesses tested. However, there were two distinct behaviours to the increased normal load, with a thinner polymer surprisingly performing better. This may be due to longer chains repeated interaction with the probe. Nevertheless the reduction in friction force is promising for future applications. In addition, it is a good indicator that in an appropriate solvent or oil, it may be possible to exploit the lubricating properties of polymer brushes to a higher degree.

7. References and Acknowledgements

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