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Grafting siloxane-containing methacrylates from surfaces

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Polymer brushes- densely packed polymer chains tethered by one end to an interface- are a useful tool to control the interfacial properties of a substrate. These properties can be fine-tuned by control of the chemistry of the constituent monomer, as well as the thickness and grafting density of the brush. One such example are brushes composed of poly(dimethyl siloxane) (PDMS). Owing to its siloxane (Si-O) backbone, PDMS exhibits various desirable properties, including high hydrophobicity and 'liquid-like' mobility. Surface-tethered PDMS chains have therefore demonstrated potential in a plethora of applications ranging from lubricating surfaces[1] to liquid-repellent coatings.[2]
Most existing techniques for the preparation of PDMS brushes do not control structural attributes such as the grafting density, film thickness and uniformity- properties which have been shown to have a large influence on the interfacial characteristics of the coating.[3]
To address this shortcoming, this study aims to synthesise and characterise polymer brushes based on structurally similar silicon methacrylate monomers including 3-[tris(trimethylsiloxy)silyl]propyl methacrylate (SiMA) and the bespoke 3-(3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propoxy)-2-hydroxypropyl methacrylate (SIGMA, provided by GEO Specialty Chemicals). These hydrophobic monomers resemble the structure of PDMS due to their pendant siloxane moieties and are amenable to synthesis via controlled radical polymerisation techniques. This allows brushes to be synthesised via a controlled "grafting-from" polymerisation, whereby polymer chains are grown directly from the surface, affording fine control over the grafting density, film thickness and polydispersity of the chains.
Initial characterisation experiments will probe the effect of solvent quality on the behaviour of the brushes via in situ ellipsometry, sliding contact angle measurements, quartz crystal microbalance with dissipation monitoring (QCM-D) and neutron reflectometry (NR). Subsequent investigations will explore potential applications of the novel polymer brushes as lubricating surfaces via atomic force microscopy friction measurements and combined rheometry-NR (rheo-NR). Initial synthetic results and in-situ swelling experiments will be presented.

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[2] L. Wang, T. J. McCarthy, *Angew. Chemie Int. Ed.* **2016**, 55, 244–248.
[3] I. J. Gresham, S. G. Lilley, A. R. J. Nelson, K. Koynov, C. Neto, *Angew. Chemie - Int. Ed.* **2023**, 62, e202308008.

Topics

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