Modelling polymer brush coatings in contact with gasses

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What is a polymer brush?
How to prepare such brushes?

2.1.2 Polymer brush preparation

There is a wide variety of methods that are commonly used for the grafting of polymer brushes to surfaces. This can be done via physisorption or stable chemical bonds [62]. During physisorption processes, polymer chains are adsorbed onto a substrate by one of their ends, being that the one that has a stronger affinity with the substrate. These are weak interaction processes, such as hydrogen bonding or Van der Waals interactions [63]. When polymer chains are physisorbed on substrates, it is easy to degraft them due to the weakness of the grafting point bonds. A schematic representation of how polymers are attached by physisorption is shown in Figure 2.5a.

When polymer chains are attached by stable chemical bonds, this attachment can be performed by means of two different approaches: the “grafting to-” or “grafting from-” methods. These type of grafting methods, in comparison of the physisorption ones, give more stable binding between the polymer chains and the substrate. Due to this reason, among others, covalent grafting of polymer brushes was the selected method for the brush growth of this work, and will be described in detail in the following section.

Grafting to- and grafting from- methods

During “grafting to-” methods, a pre-synthesised and end-functionalized polymer chain reacts with a suitable substrate, as represented in Figure 2.5b. This reaction only occurs under optimized conditions, so the polymer chains react covalently with the anchoring points present on the substrate. With this approach it is possible to obtain end-functionalized polymers with a narrow molecular weight distribution (MWD). Since the polymer chains are already pre-synthesised, there is choice regarding how those are grown, being living anionic, cationic or radical polymerization some of the options one can choose from. The largest drawback of this technique is that lower grafting densities are obtained in comparison to “grafting from-” methods. This is due to the steric repulsion existing between polymer chains, that would hamper their binding to the substrate when the distance between polymer chains is very small. The macromolecular chains diffuse through the already existing polymer chains and reach the reactive sites located on the substrate in order to create new chains. There is an energetic barrier that has to be overcome, which increases as the number of already anchored chains on the substrate increases. This is why grafting densities become even lower when the used polymer chains have a larger size [63, 64].

Figure 2.5: Polymer brush grafting methods, where a) shows a physisorption process, b) “grafting to-” and c) “grafting from-” methods. Initiator molecules are represented with (blue) spheres and monomer units with smaller (gray) spheres.

The “grafting from-” approach overcomes the drawbacks from the “grafting to-” techniques, being the most used method nowadays. With this technique it is possible to obtain thick polymer brushes with high grafting densities. Initiator molecules are first immobilized on the surface prior to the polymerization step (blue spheres in Figure 2.5c). Next, polymer brushes are grown from those initiators by the attachment of monomer units (gray spheres) by means of surface initiated polymerization techniques. The main drawback of this synthetic approach is the difficulty of experimental performance and characterization of the obtained brushes.

Polymer brushes for gas separations


Pizzoccaro-Zilamy et al., Industrial & Engineering Chemistry Research 2018, 57, 16027–1604
Polymer brushes for sensing

Figure 4: (a) The swelling response as measured by SE of the dense brush ($n = 0.1$ chains/nm$^2$) after exposure to acetone vapor at $t = 0$ and to dry nitrogen gas at $t = 53$ min and (b) the measured change in oscillation frequency (fundamental) upon exposure to acetone vapor for a PMA brush versus a crystal with a brush as measured by QCM.

By Catarina Esteves

Yang et al. Advanced Materials 25, 1150 (2013)
Polymer Brushes in Contact with Air / Vapors

Guido Ritsema van Eck
Lars Veldscholte

Rick Cohen, Maria Brio Perez and Rens Horst

Leon Smook
Summary Brushes in Liquid

- Good solvent: Brushes are swollen and extended.
- Poor solvent: Brushes collapse and aggregate.
Summary Brushes in Liquid

Brushes in Air are Different

At 100% relative humidity there is only 2 wt. % water in the air
Three component system
Brushes in Contact with Vapors

Ab-/adsorption in polymer brushes at varying polymer self-affinity

Solvent
Polymer
Swelling

Only adsorption
Ab- and adsorption

Polymer self-affinity
Brushes in Contact with Vapors

\[ W = -\epsilon_{ps} + \frac{1}{2}(\epsilon_{ss} + \epsilon_{pp}) \]

\[ \chi = \frac{zW}{k_B T} \]
Comparison to Theory

\[
\ln \left( \frac{P}{P_{\text{sat}}} \right) = \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 + \frac{3 P_g^2}{\phi_p}.
\]

Summary

• Polymer brush coatings behave different in air then in liquid
• The Flory Huggins theory can be employed to describe vapor absorption in brushes
• The correct brush-design can lead to collaborative effects and enhanced gas-sorption
Thank you!