

Soft Matter exercise: Polymer brushes

1) How can one determine the molecular weight and molecular weight distribution of polymers grafted from surfaces using controlled radical polymerization ?

Molecular weights and molecular weight distributions can be measured with GPC. This will require to cleave the brush polymers from the surface using a chemical reaction that cleaves the bond between the polymer and the substrate.

Problem: Typically, brushes are grown from planar 5 x 5 mm² substrates. How much material does this give you (assume density of 1 gr/mL and film thickness of 50 nm)? This problem can be overcome by (i) using larger planar substrates or (ii) nanoparticles.

Sometimes polymers cannot be easily cleaved from the substrate, e.g. due to the presence of sensitive side chain functional groups. In that case, sometimes a sacrificial initiator is added to the polymerization solution. The molecular weight that is then measured by GPC is then taken as a measure of the molecular weight of the surface grafted polymers. This is not without controversy, as one can argue that the kinetics of chain growth in solution (with the sacrificial initiator) are different from that of the polymers that are grown via surface-initiated polymerization.

For further details see: <https://pubs.acs.org/doi/10.1021/acs.chemrev.6b00314> and <https://pubs.acs.org/doi/10.1021/cr900045a>

2) Which experiments can you propose that can be used to determine the grafting density of polymer brushes?

$$\text{Grafting density} = (h \rho \text{ NA})/(\text{Mn})$$

Planar brushes: (i) Mn is determined as discussed under question 1. (ii) The film thickness (h) can be determined using AFM (patterned brushes) or via ellipsometry.

Nanoparticles: For polymer brush modified nanoparticles, TGA can be used to determine the mass of polymer per gram of polymer modified nanoparticle. This combined with information on the particle diameter then gives the brush thickness. (ii) Mn is determined as discussed under question 1.

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