Controlled Radical Polymerization to Design Molecularly Imprinted Polymers: Thin Films and Nanoparticles

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Free radical polymerization (FRP) still is the most popular way when synthesizing molecularly imprinted polymers [1]. Though rather straightforward in principle, it has its limitations especially regarding batch-to-batch reproducibility [2]. If electropolymerization is not an option, one aims at replacing the free radical process with controlled radical polymerization, for instance reversible-addition-fragmentation chain-transfer (RAFT) polymerization, where adding a so-called RAFT agent slows down the overall polymerization process and, in turn, yields more homogeneous chain length distributions. This has already led to some MIP applications of the process [3]. For chemical sensing, the approach leads to very apprciable results both when aiming at MIP thin films and synthesizing MIP nanoparticles through solid phase synthesis.

In contrast to FRP, RAFT polymerization easily allows for generating polymer thin films directly in situ on the surfaces of sensor devices. When immobilizing a raft agent on the gold electrodes of a quartz crystal microbalance (QCM) and choosing the proper linker for that purpose, it is possible to control the layer height of acrylate-based films by controlling the polymerization time (see Figure 1). We could demonstrate that one can use metal and oxide nanoparticles as templates to generate sensor layers that selectively re-incorporate their respective target particle. The mass-sensitive QCM signal in such cases depends on all three fundamental particle properties: diameter, density (i.e.: composition of the core), and stabilizer shell. The latter plays the largest role for in determining the interactions between the sensor layer and the respective analyte particle. Size exclusion, also works very well (include data). Of course, when assessing the absolute sensor responses, one needs to consider the different masses of different particle types.

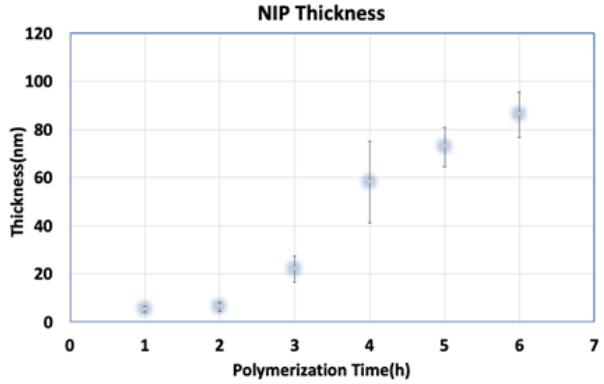

Figure 1: RAFT polymer layer height as a function of polymerization time

RAFT also improves MIP nanoparticles (nanoMIPs) that result from solid phase synthesis [4] and represent antibody mimics, e.g. targeting insulin. Combining solid-phase imprinting with RAFT leads to very homogenous nanoparticle distributions: The resulting nanoMIPs are on average 30±0.07 nm in diameter, whereas FRP leads to 44±14 nm. Particles are not only smaller, but also lead to larger sensor effects: compared to FRP, the specific response of RAFT-based nanoMIP towards insulin is about 1.5 times higher, whcih further corroborates how feasible the approach is.

References

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