a Preparative Macromolecular Chemistry, Institute for Chemical Technology and Polymer Chemistry, Engesserstraße 18, 76128 Karlsruhe, Germany,
b Institute for Applied Materials (IAM-ESS) & Karlsruhe Nano Micro Facility (KNMF), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany,
c Zoological Institute, Cell- and Neurobiology and Centre for Functional Nanostructures (CFN), 76131 Karlsruhe, Germany,
d Soft Matter Synthesis Laboratory, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany,
e Polymer Standards Service GmbH, In der Dalheimer Wiese 5, 55120 Mainz, Germany.

* Corresponding author: vanessa.trouillet@kit.edu

XPS-Characterization of Surface Modified Epoxide Microspheres

Andrew P. Vogt[a], Michael Kaupp[a], Vanessa Trouillet[b], Alexandra M. Greiner[c], Udo Geckle[b], Leonie Barner[d], Thorsten Hofe[e], Christopher Barner-Kowollik[a, d]

Introduction

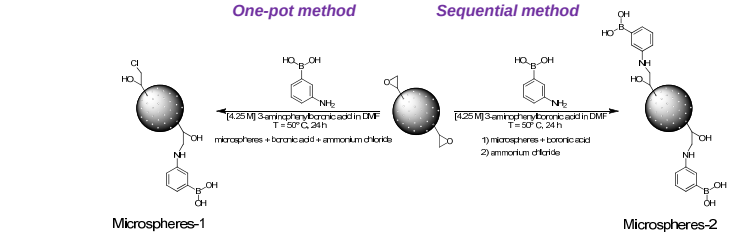
Microspheres made of cross-linked polymers play an important role in a variety of applications such as medicine, chromatography and organic synthesis. One important parameter for the performance of microspheres in these applications is the availability of functional (polymeric) groups on the particle's surface.

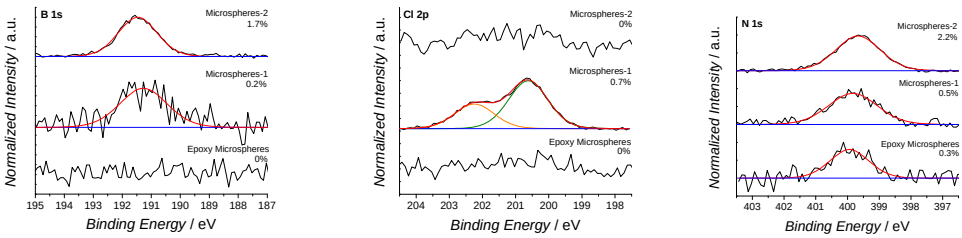
Experimental

X-ray Photoelectron Spectroscopy (XPS): ThermoFisher Scientific **K-Alpha** Spectrometer

Scanning Electron Microscopy (SEM): Zeiss **Supra 55** FE-SEM

A Facile Route to Boronic Acid Functional Polymeric Microspheres via Epoxide Ring Opening

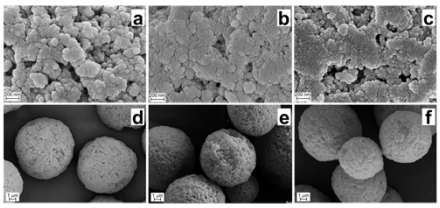




B 1s XP spectra:
The microspheres-1 show a very weak boron signal, whereas a successful functionalization with boronic acid can be observed in the case of the microspheres-2. The boron concentration increased by a factor of 8.

Cl 2p XP spectra:
The microspheres-1 clearly show chlorine at the surface. Due to the nucleophilic attack of chloride, provided by the ammonium chloride, at the epoxide, a functionalization employing boronic acid is hindered. On the contrary, the microspheres-2 are free of chlorine, as desired.

N 1s XP spectra:
The signal intensity clearly increases in the case of the sequential method in comparison to the one-pot method.



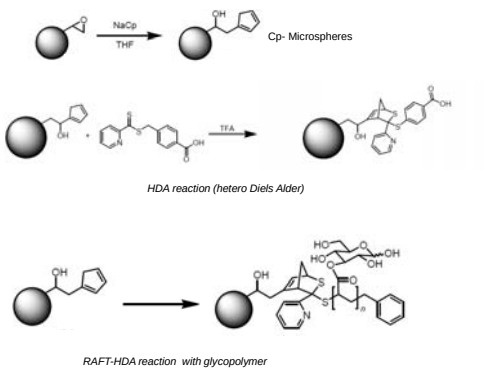
SEM images of epoxide (a, d), microspheres-1 (b, e), and microspheres-2 (c, f) evidencing that the particle shape is maintained after the nucleophilic ring opening reactions. The top row (a-c) exhibits the porous nature of the microspheres with an average pore size of 1000 Å.

The importance of the synthetic procedure for the preparation of the boronic acid functionalized microspheres is demonstrated:

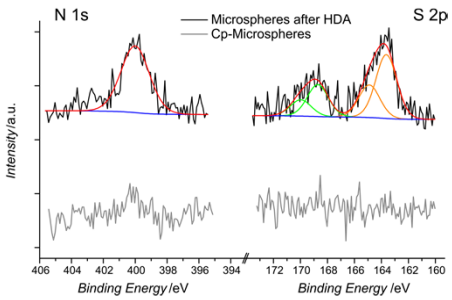
In comparison with the one-pot method, the sequential synthetic strategy promotes the functionalization in case of nucleophilic ring opening of an epoxide.

The microspheres-1 show very few boronic acid (0.2 %) whereas the microspheres-2 contain about 8 times more boronic acid (1.7 %).

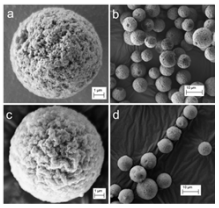
Modular Design of Glyco-Microspheres via Mild Pericyclic Reactions



Grafting Characterization



XP Spectra of Cp-functional microspheres before and after HDA reaction. The presence of nitrogen and sulfur after the grafting reaction is clearly shown.
The S $2p_{3/2}$ at 168.7 eV is assigned to sulfur in the oxidation state +6.



SEM images of the non-modified pGMA microspheres with an average pore size of 1000 Å (a and b), and the same spheres after Cp-functionalization and RAFT-HDA reaction with glycopolymer (c and d).

Acknowledgement
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References
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[2] Kaupp, M.; Vogt, A. P.; Natterodt, J. C.; Trouillet, V.; Gruendling, T.; Hofe, T.; Barner L.; Barner-Kowollik, C.; Polym. Chem. 2012, 3, 2605–2614.

Conclusion

The characterization of functionalized microspheres was successfully demonstrated with XPS. This surface analysis technique revealed detailed information about the chemical composition of modified surfaces and contributed significantly to the successful verification of the grafting.