Functional Materials

MS.3.P075
Towards the 3D investigation of pore space in molecularly imprinted polymers (MIPs)

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Molecular imprinted polymers (MIPs) are polymer films or polymer particles containing selective binding sites for an analyte molecule (so-called template) within the synthetic polymer network [1]. The template molecules are mixed with functional monomers, which are able to interact with the template, forming a so-called pre-polymerization complex. These complexes are co-polymerized in the presence of crosslinker monomers. After polymerization, the template molecules are removed, resulting in a rigid polymer network with binding sites, which are complementary in size, shape and functionality to the template molecule. These binding pockets are highly selective for the template molecule, and hence many applications like specific sensing layers, imprinted membranes, selective extraction matrices for separation and chromatography and antibody mimicking can be envisaged [1].

The pore space and interconnectivity of pores are crucial for the efficiency of MIPs. Pore volume, diameter and surface area are usually investigated by Brunauer-Emett-Teller (BET) measurements [2] of bulk samples. Transmission Electron Microscopy (TEM) was used in an attempt to visualize binding pockets [3], however the structure of pores within a specific MIP and the imaging and investigation of interconnectivity has not yet been demonstrated.

In this study we present first results towards the investigation and visualization of pore space in MIP particles using focused ion beam – electron microscopy (FIB/SEM) tomography. As a model MIP the beta-blocker drug propranolol was imprinted using methacrylic acid as functional monomer and divinylbenzene (DVB) or a mixture of DVB and ethylenglycoldimethaacrylate (EGDMA) as crosslinker with azobisisobutyronitrile as radical initiator to create a bulk polymer. Adding EGDMA as a second crosslinker yields a polymer with modified structure and polarity. In addition, as a control non-imprinted polymers (NIP) were prepared in absence of the template molecule, respectively. After grinding and sieving, the MIP particles were treated with osmium tetroxide and uranyl acetate using freeze substitution and Epon embedding [4,5] to enhance contrast in secondary electron (SE) images. This procedure is usually applied for biological samples and was used here to visualize of pore space and reduce adverse effects due to local heating.

Prior to the 3D investigations using auto slice & view routine, several embedded MIP particles were examined by cross-sectioning perpendicular to the surface (Fig 1, B- F). SE images show contrast between the Epon and the polymer matrix of the MIP (cloudy dark and bright areas), with the MIP polymer blotched by bright spots. The bright spots can be attributed to the metal loading (Os and U).

Figure 2 shows a 3D model of a reconstructed section of a MIP particle. The pores seem to be elongated with a limited interconnection between the pores, which may be attributed to the embedding and preparation process. Hence, alternative sample preparation will be presented in order to enhance the contrast between polymer matrix and Epon epoxy and therefore improving the visualization of the pore space.

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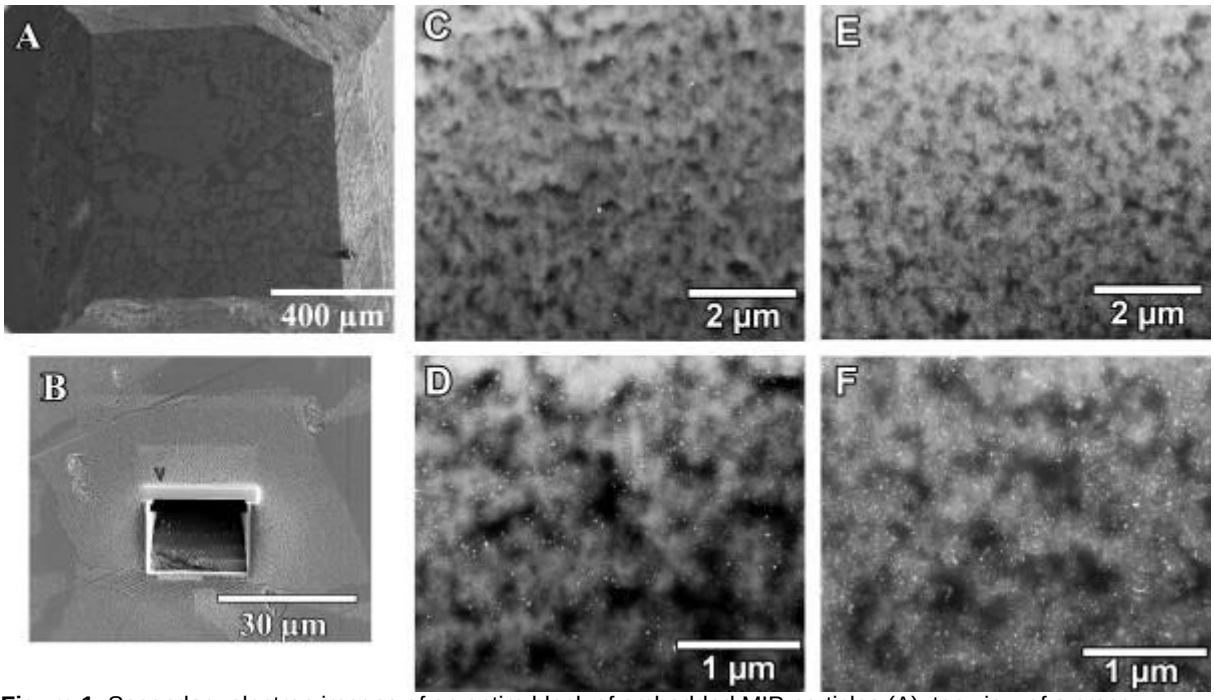

Figure 1. Secondary electron images of an entire block of embedded MIP particles (A), top view of a cross-section within a MIP particle (B), exemplary images of the front of cross-sections in different MIP particles showing pore space (dark areas) and local enrichment of Os and U: MIP polymerized by DBV only (C&D), MIP polymerized with a mixture of DBV and EGDMA (E&F).

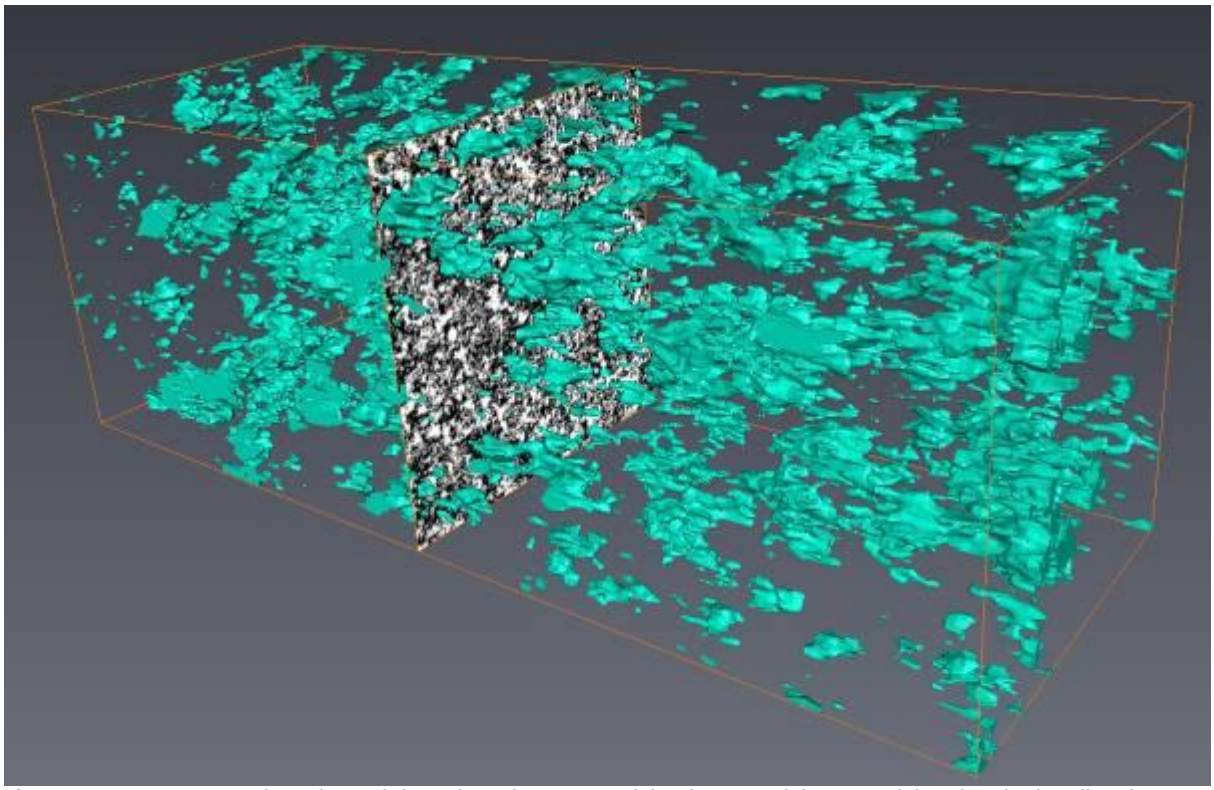

Figure 2. 3D reconstruction of a serial section of a MIP particle, the greenish parts of the sketch visualize the pores: length of the box 1.4 x 1.4 x 3.7 µm, MIP polymerized with a mixture of DBV and EGDMA.