

MODIFICATION OF PRECERAMIC POLYMERS AND INVESTIGATION OF THEIR POROSITY DEVELOPMENT

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INTRODUCTION

Porous ceramics are essential components in different challenging applications. Due to their unique properties such as low density, high permeability, high thermal shock resistance and high chemical stability, they are used in a wide field of applications, including filtration, absorption, membranes (e.g. for hydrogen separation) or light weight structural materials.^[1]

The production of microporous ceramics from preceramic polymers has gained increasing scientific interest in the recent past. The main reasons are that the production of polymer-derived ceramics (PDCs) can be achieved with processing techniques not accomplishable with traditional powder technology.^[2] On the other hand, significantly reduced synthesis temperatures and the lowered energy consumption make the PDC route a matter of economical and ecological interest.^[3]

The objective of this work is to get a better understanding of how the presence of different organic groups in the preceramic polymer influences the resulting micropore structure during the thermal polymer-to-ceramic conversion process. For this purpose, a preceramic polymer is modified by nucleophilic substitution using different alkyl bromides as substituents.

EXPERIMENTAL PROCEDURE

In a first step a polyvinylsilazane (Durazane 1800, durXtreme GmbH, Germany) was modified by nucleophilic substitution, bringing organic groups of different size into the structure of the polymer (Fig. 1). The addition of Hünig's base (N,N-Diisopropylethylamine) prevents side-reactions by building a quaternary ammonium salt with hydrogen bromide.

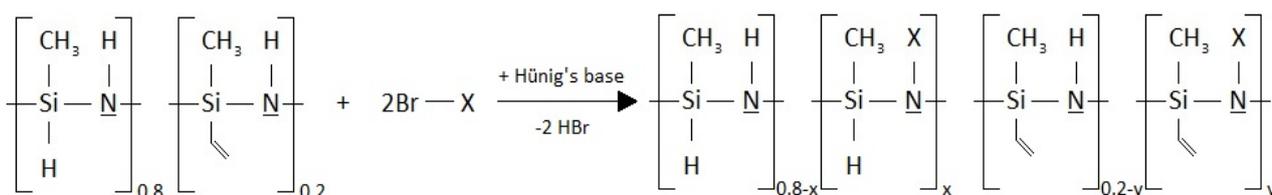


Fig. 1 Modification of a commercially available poly(vinyl)silazane by nucleophilic substitution

In a second step the modified polymer was heated under nitrogen atmosphere up to 250 °C, which results in the formation of cross-links between the polymer chains due to the presence of vinyl moieties. Cross-linking takes place without addition of further reagents, although the formation temperature can be lowered through addition of a radical initiator (e.g. dicumyl peroxide^[4]).

In a final step the cross-linked polymer was heated under nitrogen atmosphere up to 600 °C. This leads to a polymer-to-ceramic conversion process, including chemical decomposition and molecular rearrangement processes, resulting in a microporous ceramic.

Structure and composition of the educts, products and of all occurring intermediate products (e.g. the modified polymers) were characterized using a variety of analysis methods, including elemental analysis, NMR and FTIR. The pore structure and the specific surface area of the produced ceramics were analyzed using N₂-physisorption.

RESULTS AND DISCUSSION

Modification of the poly(vinyl)silazane compound by nucleophilic substitution was successful for a variety of substituents. By employing a pyrolytic conversion treatment, these materials could successfully be converted into microporous materials. N₂-physisorption measurements (Fig. 2) indicate that the pore width of the produced ceramics is around one nanometer. The pore width does not appear to correlate with the size of the attached groups, possibly due to molecular rearrangement processes. The measured BET surface areas were between 220 and 235 m²/g, significantly higher than the BET surface area of the ceramics received from the unmodified polymer. These first results are a major step towards the development of novel microporous materials, suitable e.g. for membrane applications.

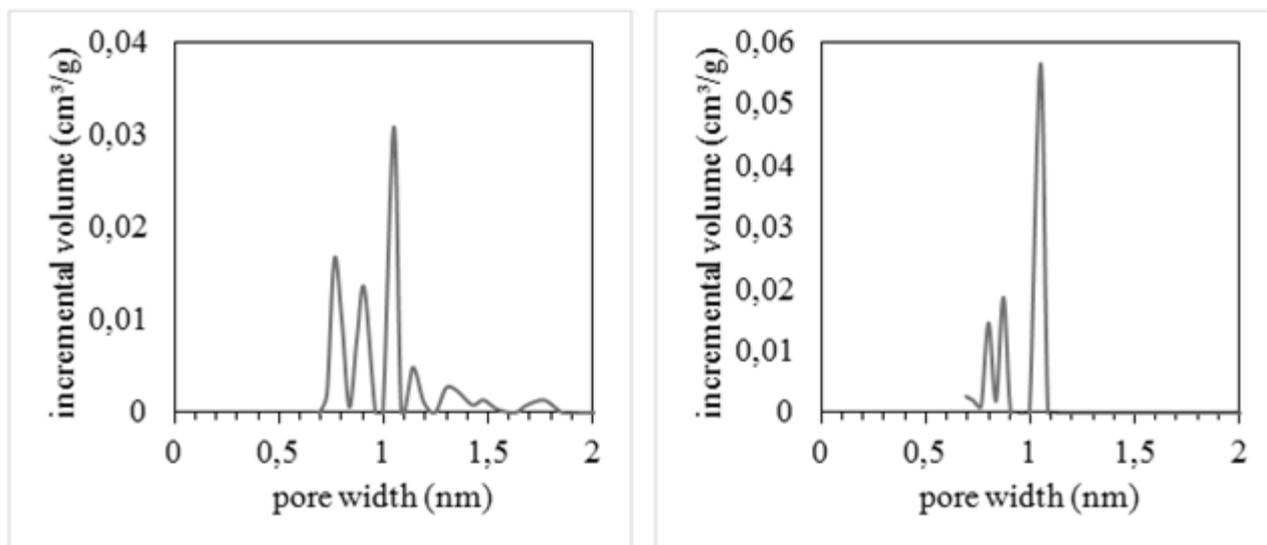


Fig. 2 Pore width distributions obtained by NLDFT analysis of N₂-physisorption data (used substituents: left: 1-Bromobutane, right: α -Bromo-p-xylene)

CONCLUSIONS

Novel nanoporous compounds could be generated by pyrolytic conversion of modified preceramic polymers based on polysilazanes. Analysis by N₂-physisorption shows that the modification of the preceramic polymer leads to pore structures in the size range of 1 nm in the final product. However, further work is required in order to understand how the resulting microporosity can be tailored.

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