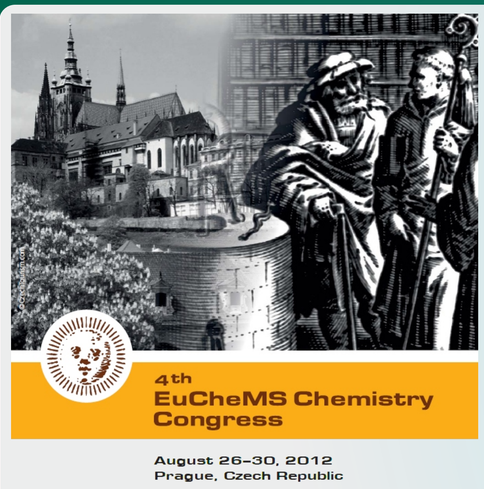


Tin oxide nanoparticles via Twin Polymerization from novel tin(IV) alkoxides

CHEMNITZ UNIVERSITY OF TECHNOLOGY

S. Brumm,[a] C. Leonhardt,[a] A. Seifert,[a] G. Cox,[b] A. Lange,[b] M. Mehring*,[a]

a) Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany

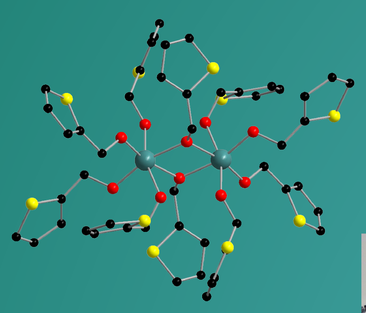
b) BASF SE, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany

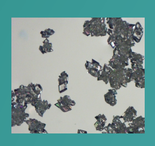
e-mail: christian.leonhardt@chemie.tu-chemnitz.de

Introduction

The development of synthetic strategies for nanostructured hybrid materials is currently a very active research area.[1] Twin Polymerization is a novel synthetic approach for nanostructured organic-inorganic hybrid materials and metal oxide nanoparticles.[2] The special character of this concept is the formation of an organic and an inorganic framework on the same timescale starting from one monomer only. Interpenetrating networks are generated and produce the nanostructure of the material. Here we present novel well-defined tin precursors for Twin Polymerization such as $Sn(OCH_2C_4H_3O)_4$, $[Sn(OCH_2C_4H_3S)_4 \cdot HOCH_2C_4H_3S]_2$, $[Sn(OCH_2\text{-}2\text{-}OCH_3C_6H_4)_4 \cdot HOCH_2\text{-}2\text{-}OCH_3C_6H_4]_2$ and $[Sn(OCH_2\text{-}2,4\text{-}OCH_3C_6H_3)_4 \cdot HOCH_2\text{-}2,4\text{-}OCH_3C_6H_3]_2$. By the use of such tin precursors in polymerization reactions in melt and in solution we were able to prepare cross-linked nanocomposites from the type polymer/SnO_2. These materials are characterized by ^{13}C and ^{119}Sn NMR in the solid state and in solution, IR, elemental analysis, BET, TEM and oxidized to give tin oxid nanoparticles.

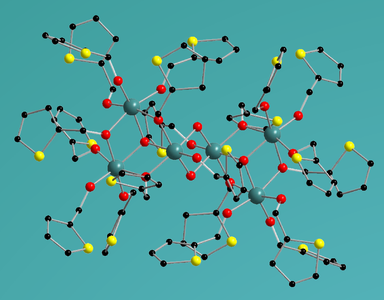
The sensitive character of the novel synthesized tin(IV)alkoxides were demonstrated by the isolation of the tin-oxocluster (**2a**), a hydrolysis product of compound **2**



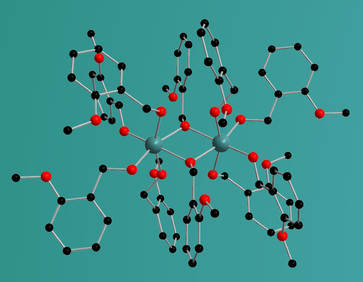


compound **2**
$[Sn(OCH_2C_4H_3S)_4 \cdot HOCH_2C_4H_3S]_2$

hydrolysis



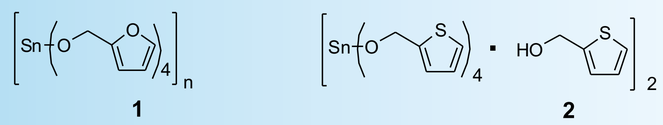
hydrolysis product of compound **2**
$[Sn_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OR)_3(OR)_6(HOR)]_2$ (R = $CH_2C_4H_3S$) **2a**



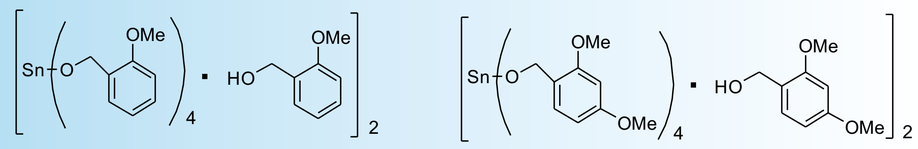
compound **3**
$[Sn(OCH_2\text{-}2\text{-}OCH_3C_6H_4)_4 \cdot HOCH_2\text{-}2\text{-}OCH_3C_6H_4]_2$

Concept

we have isolated the following novel “twin-monomers“:



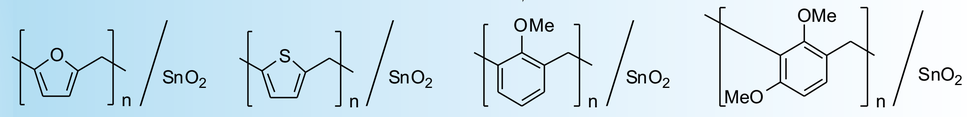
1 **2**



3 **4**

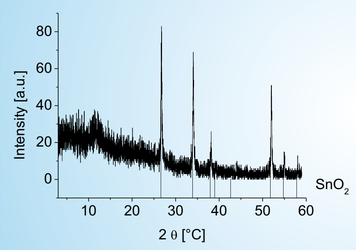
next step:
polymerisation reaction of the twin-monomers to get polymer / SnO_2 hybrid materials

$[H^+]$



A **B** **C** **D**

hybrid materials



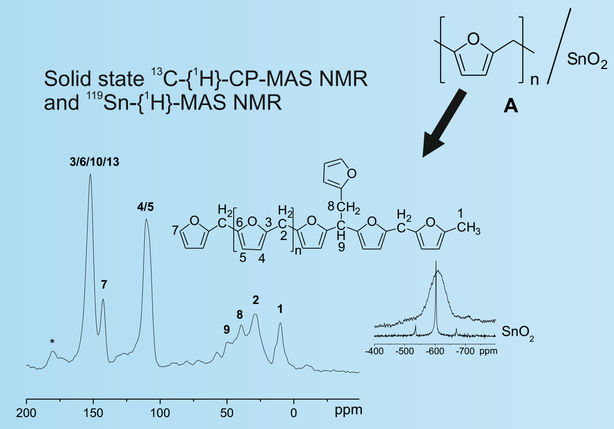
SnO_2 ← oxidation

finally:
oxidation reaction of the hybrid material to form tin oxide nanoparticles

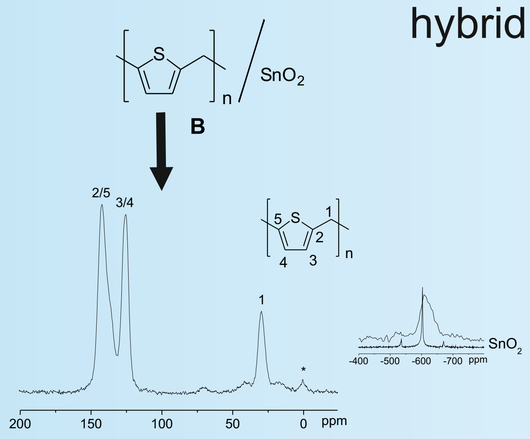
Analysis

hybrid materials

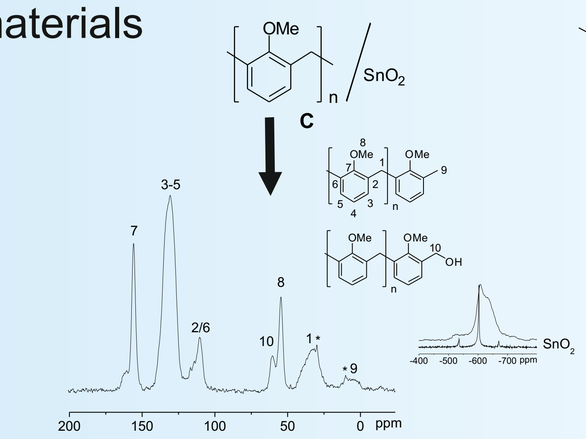
Solid state ^{13}C-{^1H}-CP-MAS NMR and ^{119}Sn-{^1H}-MAS NMR



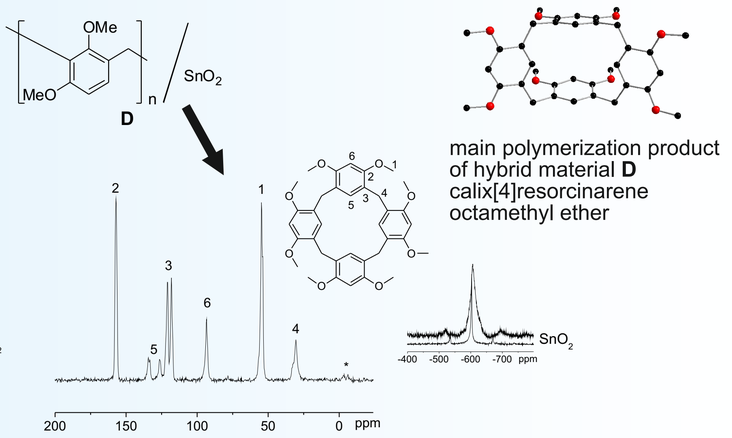
hybrid material **A**



hybrid material **B**



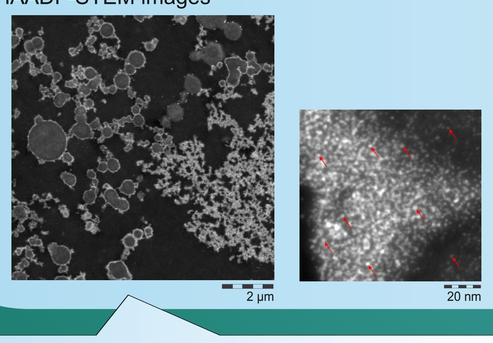
hybrid material **C**



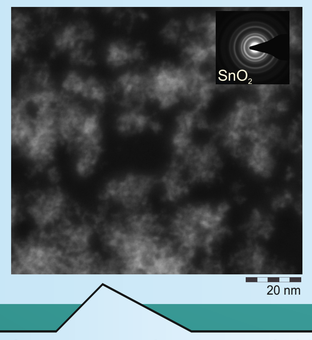
hybrid material **D**

main polymerization product of hybrid material **D** calix[4]resorcinarene octamethyl ether

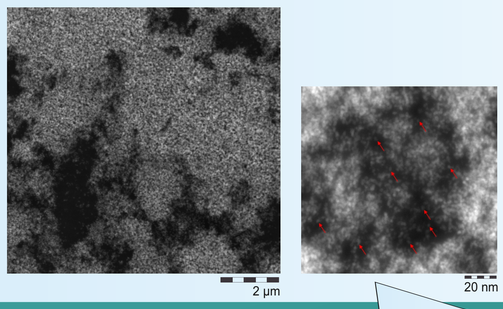
HAADF-STEM images



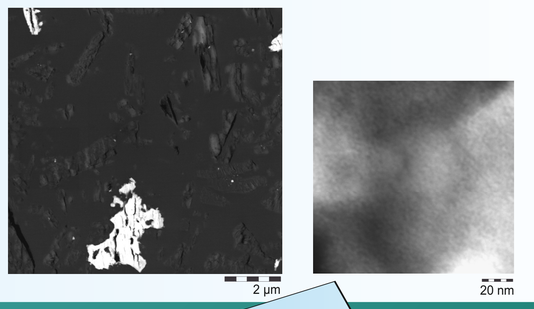
formation of oligomers and agglomerization of SnO_2 paticles on the polyfurfuryl alcohol surface



complete conversion into poly(thiophene-2-methanol) and 2-3 nm sized primary particles consisting of crystalline SnO_2 mixed up in the polymer matrix



creation of soluble oligomers and microcrystalline tin(IV)oxide primary particles (size: 2 nm) which build agglomerates distributed in the polymer matrix



complete conversion to calix[4]resorcinearene octamethyl ether and micrometer sized agglomerates of SnO_2 particles with inhomogeneous distribution

Conclusion

- We were able to synthesize novel tin-alkoxides as precursors for the twin-polymerization.
- The polymerization reactions of compound **1** in the melt and of compound **2** and **3** in solution, respectively, gave polymer / SnO_2 hybrid materials with nano-sized SnO_2-particles.
- Cyclooligomerization reaction was observed, in the case of compound **4** and calix[4]resorcinarene octamethyl ether / SnO_2 hybrid material was obtained as the main-product.
- The oxidation reaction of the created hybrid material gave according to the reaction conditions nanometer sized SnO_2 particles with different BET surfaces (in the range from 7 to 107 m^2/g) and primary particles sizes from 3 nm to 45 nm.

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[2] a) T. Löschner, A. Mehner, S. Grund, A. Seifert, A. Pohlers, A. Lange, G. Cox, H.-J. Hähnle, S. Spange, *Angew. Chem.* **2012**, 124, 3312; b) F. Böttger-Hiller, R. Lungwitz, A. Seifert, M. Hietschold, M. Schlesinger, M. Mehring, S. Spange, *Angew. Chem. Int. Ed.* **2009**, 48, 8878

Acknowledgements

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