Hybrid Materials

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A Modular Approach for the Synthesis of Nanostructured Hybrid Materials with Tailored Properties: The Simultaneous Twin Polymerization**

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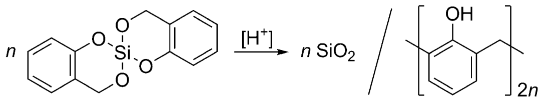
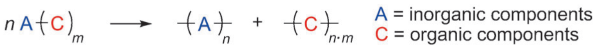
Twin polymerization (TP) has been shown to be an elegant method for the template-free synthesis of nanostructured hybrid materials and nanoscale porous inorganic oxides.[1] In TP two different polymers are formed in a single step from the so-called twin monomer (TM). These polymers can be organic or inorganic in nature. In twin monomers, polymerizable building blocks are bonded together covalently. These covalent bonds are cleaved during the polymerization process. It is thus guaranteed that the growth of the two different polymer chains can become coupled in a reaction volume, which is limited both in terms of space, and mechanistically. TP is therefore clearly differentiated from the polymerization of hetero-bifunctional monomers in which the two polymerizable groups polymerize independently of each other or in which one of the groups initially remains completely intact during the polymerization.[2–4]

In theory in TP various different polymer strands can be situated next to each other, on the molecular length scale, immediately after their formation. Therefore, in the case of certain TP, compact nanostructured hybrid materials with a very small length scale (1–2 nm) of both homopolymer domains are formed within a defined time frame.

The TP of the twin monomer 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] (SBS), which has already been investigated, leads to nanostructured hybrid materials consisting of silicon dioxide and a phenolic resin in a single process step (Scheme 1).[1a] In general, the TP of *n* molecules of the twin monomer, A-$(C)_m$ leads, by definition, to the formation of two homopolymers, -$(A)_n$- and -$(C)_{n\cdot m}$- (Scheme 2).[1a]



Scheme 1. Acid-catalyzed TP of 2,2′-spirobi[4*H*-1,3,2-benzodioxasiline] (SBS).[1a]



Scheme 2. The TP of a monomer A-$(C)_m$ does not come under the IUPAC definition of homopolymerization.[5]

SBS should therefore be classed as an A-C_2 twin monomer. The scenario in which two homopolymers are formed from one monomer is not defined by IUPAC, and also does not correspond to a homopolymerization.[5] We have therefore introduced the new term, twin polymerization, for this scenario.[1d]

Herein, we demonstrate how certain desired complex hybrid materials of the most widely differing compositions could be synthesized with the aid of a modular concept, by polymerizing two or more different twin monomers simultaneously in a single process step. We call this new method simultaneous twin polymerization (STP). It is different to a simultaneous polymerization which is the polymerization of two different monomers at the same time to give two homopolymers in a single system.[6]

The possible scenarios of simultaneous TP must also be reclassified as the classical definitions for the polymerization processes simply cannot be used. In Scheme 3 the reaction equations of three different twin monomer combinations are given. There are different reaction possibilities and thus different products, depending on whether the twin monomers both have the same potentially polymerizable groups or not.

Considers the theoretical possibilities of the simultaneous TP of *n* molecules of A-C and A-D shows why a new classification is necessary. Paradoxically, a homopolymer -$(A)_{2n}$- can be formed, because both twin monomers have the same polymerizable structural unit A and this should be defined as a copolymer, according to the classic IUPAC definition.[5] Therefore, for the situation in which several twin monomers polymerize together, the term simultaneous TP and not copolymerization should be used in future.

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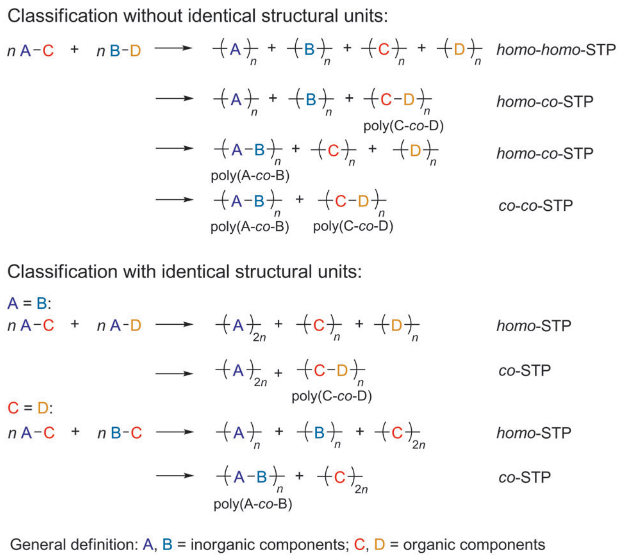
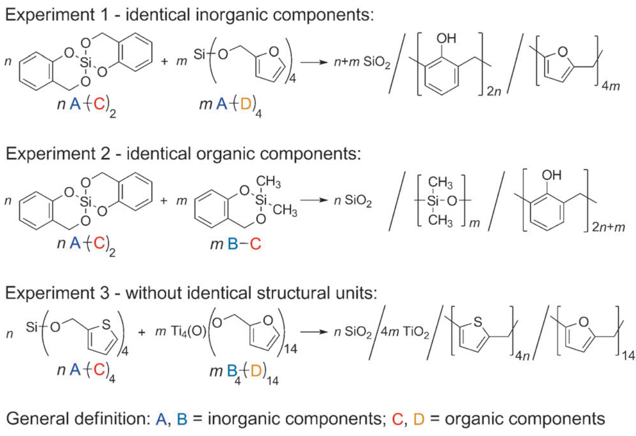


Scheme 3. Scenarios of simultaneous twin polymerization (STP) of two twin monomers, as well as the respective types of reaction, products, and classification.

It is possible, however, that in the case of two twin monomers with four different polymerizable units, the two organic units C and D can form a copolymer -(C-D)$_n$-, and the two inorganic components A and B can form homopolymers -(A)$_n$- and -(B)$_n$- (*homo-co*-STP, Scheme 3).

Using selected monomer combinations, we present herein the experimental verification of the scenarios of this new synthesis concept (Scheme 3). The experiments have been chosen so that the basic combinations of twin monomers are covered: A-(C)$_2$ and A-(D)$_4$ as combinations of twin monomers with the same inorganic component A, the combinations A-(C)$_2$ and B-C with the same organic component C, as well as monomers without the same structural units A-(C)$_4$ and B-(D)$_4$. Scheme 4 shows the simultaneous TP carried out.



Scheme 4. Three experiments on simultaneous twin polymerization (STP) of two twin monomers. In the reaction equation both the monomer type and also the theoretical hybrid materials of the homopolymers formed are presented. The formation of possible copolymers can be taken from Scheme 3.

Experiment 1 – Identical Inorganic Components

The simultaneous TP of the monomers A-(C)$_2$ and A-(D)$_4$ (Experiment 1, Scheme 4) can theoretically lead to different product combinations. The structurally different organic building blocks C and D can either form two homopolymers -(C)$_n$- and -(D)$_n$- in the reaction mixture (*homo*-STP), or can copolymerize to -(C-D)$_n$-(*co*-STP). However, for the polyfurfuryl alcohol (PFA)/phenolic resin combinations the copolymerization has not been detected to date, so *homo*-STP was expected.[7,8]

The CF_3CO_2H-catalyzed STP of SBS with tetra-furfuryloxysilane (TFOS) in CH_2Cl_2 gives, as expected, SiO_2, PFA and the phenolic resin. The simultaneous TP was investigated by examining the ^{29}Si- and ^{13}C-{^{1}H}-CP-MAS solid-state NMR spectra of the hybrid materials (for details see the Supporting Information).

The synthesis of the corresponding pure carbonized material from the SiO_2/PFA/phenolic resin hybrid materials is carried out by thermal treatment at 800 °C in an inert gas atmosphere and subsequent removal of the silica phase using 40 % HF solution. A specific surface area of the resulting carbonized material of 1290 $m^2 g^{-1}$ can be obtained in this way (for details see the Supporting Information). The specific surface area is clearly higher than that of the individual component systems (TFOS: $S_g = 160\ m^2 g^{-1}$,[1f] SBS: $S_g = 1018\ m^2 g^{-1}$).[1a] A possible explanation of this result may lie in the higher cationic reactivity of the furan compared with phenolic resin component, which leads to kinetically controlled polymerization of the organic component and thus to a smaller dimension of the SiO_2 phase, whereby a higher surface area of the carbonized material is obtained.

Experiment 2 – Identical Organic Components

If A-(C)$_2$ and B-C monomers are combined with the same organic component, the phenolic resin building block (Experiment 2, Scheme 4), two scenarios arise according to Scheme 3. The simultaneous TP of the monomers SBS and 2,2-dimethyl-4*H*-1,3,2-benzodioxasiline (DBS) was carried out in the melt with CF_3CO_2H catalysis (for experimental details see Supporting Information).

The phenolic resin units originating from the two monomers form a phenolic resin homopolymer. The reactive SiO_2 and dimethylsiloxane intermediates formed during the TP are able to form covalent bonds, as is well established from numerous publications on sol–gel processes with formation of SiO_2/dimethylsiloxane hybrid materials.[9–12] The solid-phase structure of the products was determined by using ^{29}Si- und ^{13}C-{^{1}H}-CP-MAS solid-state NMR spectroscopy (Figure 1). Extraction experiments confirm that the simultaneous TP of the monomers SBS and DBS fulfill the theoretical case of *co*-STP, as hardly any poly- or oligo-dimethylsiloxane is obtained in the soluble phase. The *co*-STP of SBS and DBS from Experiment 2 is therefore a new method for synthesizing hybrid materials from phenolic resins and SiO_2/dimethylsiloxane.

Energy-filtered transmission electron microscope images (EFTEM) show that a monolithic and nanostructured hybrid material is produced in a single process step, whereby the domain size of the nanostructures for the elements silicon

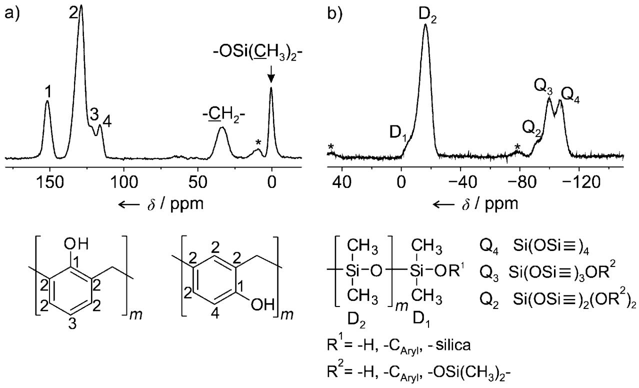


Figure 1. a) ^{13}C-{^{1}H}-CP-MAS NMR and b) ^{29}Si-{^{1}H}-CP-MAS NMR spectra of the SiO_2/dimethylsiloxane phenolic resin hybrid material from Experiment 2. The asterisk * indicates spinning side bands.

and oxygen are on the order of 2–3 nm (Figure 2). During the simultaneous TP no agglomeration or macroscopic separation of the individual components occurred.

Experiment 3 – Without Identical Structural Units

The two monomers (μ_4-oxido)hexakis(μ-furfuryloxo) octakis(furfuryloxo)tetratitanium (TiFu) and tetrathenyloxysilane (TTOS) have different inorganic and organic structural units (Experiment 3, Scheme 4). In the simultaneous TP of TiFu and TTOS four possible scenarios for product formation can result according to Scheme 3: a) mixtures of SiO_2, TiO_2, PFA, and poly(thenyl alcohol) (PTA) (*homo-homo*-STP); b) a titanosilicate and a copolymer of PFA and PTA (*co-co*-STP); c) a titanosilicate and a mixture of PFA and PTA (*homo-co*-STP); d) a mixture of SiO_2 and TiO_2, and a copolymer of PFA and PTA (*homo-co*-STP). Mixtures of products resulting from the various options could also be formed. Experimentally in the acid-catalyzed simultaneous TP of the TiFu and TTOS monomers a black solid hybrid material was obtained. The ^{13}C-{^{1}H}-CP-MAS NMR spectrum is shown in Figure 3 and the wide-angle X-ray scattering curves (WAXS) in Figure 4.

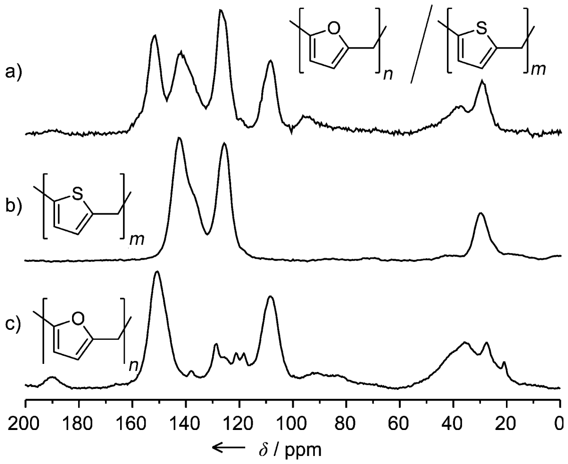


Figure 3. ^{13}C-{^{1}H}-CP-MAS NMR spectra of the hybrid materials a) from Experiment 3 with the monomer ratio TiFu:TTOS = 1:3.5 and the catalyst trifluoromethanesulfonic anhydride (Tf_2O), ([furfuryl + thenyl]: $(CF_3SO_2)_2O$ = 35:1; 16 h at room temperature), b) obtained from the TP of the twin monomer TTOS and the catalyst Tf_2O, (thenyl: $(CF_3SO_2)_2O$ = 20:1; 16 h at room temperature), c) obtained from the TP of the twin monomer TiFu and the catalyst Tf_2O, (furfuryl:-$(CF_3SO_2)_2O$ = 10:1; 16 h at room temperature).

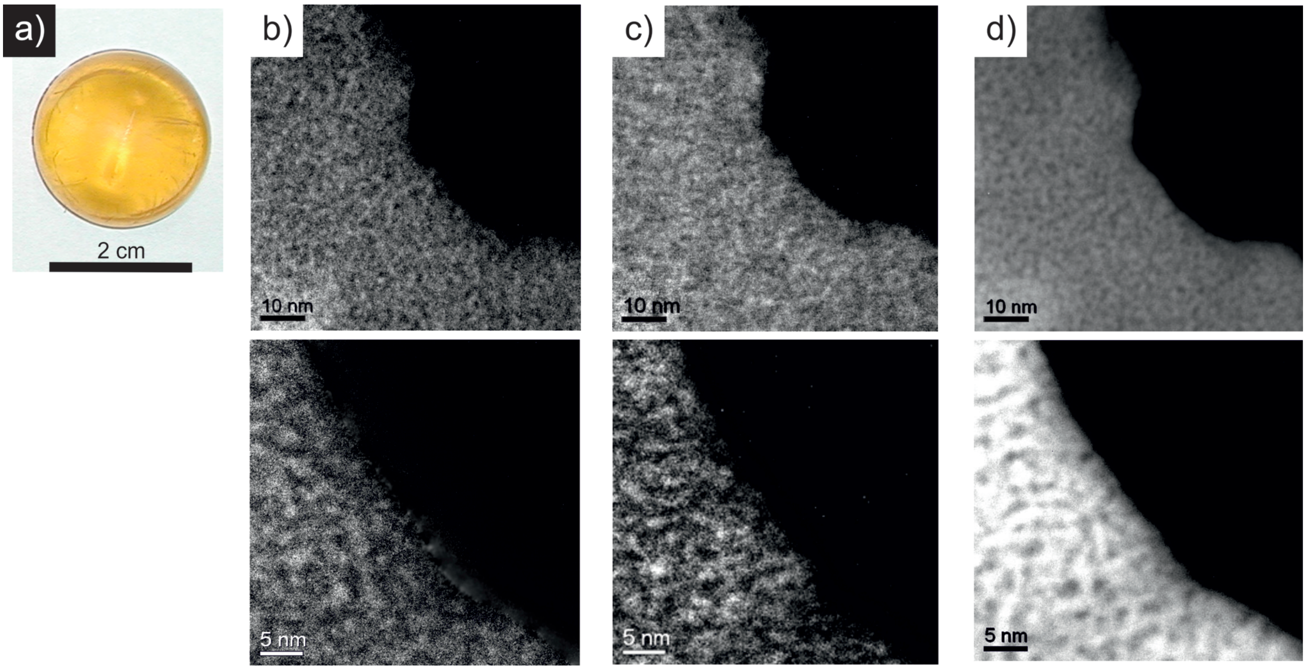


Figure 2. The transparent, monolithic SiO_2/dimethylsiloxane phenolic resin hybrid material obtained from Experiment 2 (a) and the corresponding EFTEM images showing the element distributions of oxygen (b), silicon (c), and carbon (d). The bright regions in the picture correspond to the respective element.

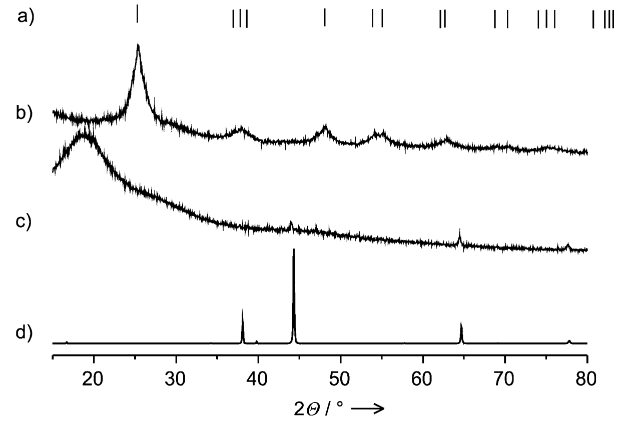


Figure 4. a) Diffraction reflections of anatase; b) oxidized hybrid material from Experiment 3 (10 h, 600 °C, air), c) hybrid material from Experiment 3, d) diffractogram of the Al sample container.

On the basis of the ^{13}C-{^{1}H}-CP-MAS NMR experiments, both the organic resins PFA and PTA can be detected next to each other. Comparison of the ^{13}C-{^{1}H}-CP-MAS NMR spectra of the hybrid material from the simultaneous TP with those of materials obtained by separate TP of TiFu or TTOS show all the NMR signals of PFA and PTA are in the spectrum of the product of simultaneous TP.

The inorganic component of the hybrid material was investigated using X-ray scattering experiments (WAXS). The diffractograms of the hybrid material and the oxidized residue are shown in Figure 4 b and c in comparison with the aluminum sample container (Figure 4 d) and the comparison reflections of anatase (Figure 4 a).

The material obtained after simultaneous TP is amorphous to X-rays. The oxidation of this material at 600 °C gives a white powder, which is partially crystalline. Anatase could be detected as a crystalline phase. The dimensions of the coherent scattering regions were determined using the Debye–Scherrer relationship and found to be 6 nm.

The result is similar to that of the TP of TiFu, in which X-ray amorphous materials are also obtained, which only give highly crystalline titanium oxides after oxidation.[1e] After oxidation, anatase (TiO_2) is present as a pure phase in a SiO_2 matrix.

The simultaneous TP of types A-$(C)_4$ und B_4-$(D)_{14}$ (Experiment 3, Scheme 4) can probably be assigned as *homo-homo*-STP. The organic phase is polymeric, PFA and PTA being mainly present as homopolymers. The inorganic phase of the oxidized material consists of a mixture of TiO_2 (anatase) and SiO_2 (X-ray amorphous), whereby X-ray amorphous SiO_2/TiO_2 mixed phases cannot be ruled out entirely. Varying the reactivity of the organic monomer components in simultaneous TP to determine whether titanosilicates can be obtained is currently being carried out.

The given examples show that the concept of simultaneous TP has enormous potential for the synthesis of nanostructured hybrid materials with the most widely differing compositions.

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