Polymerizations

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Nanocomposites Prepared by Twin Polymerization of a Single-Source Monomer**

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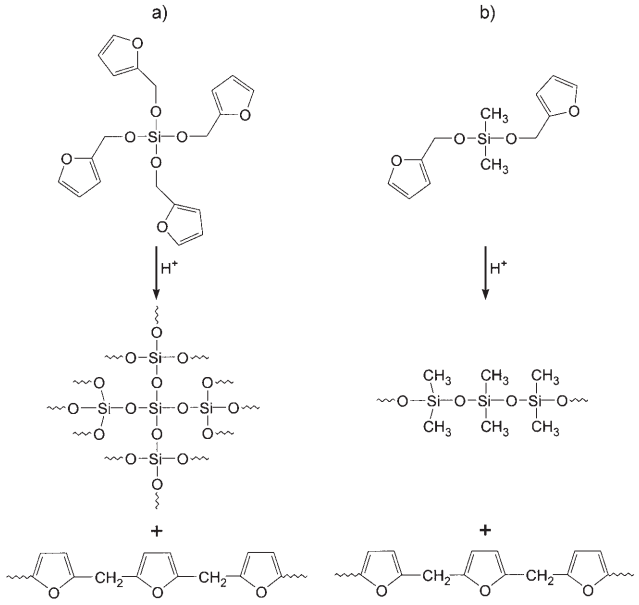
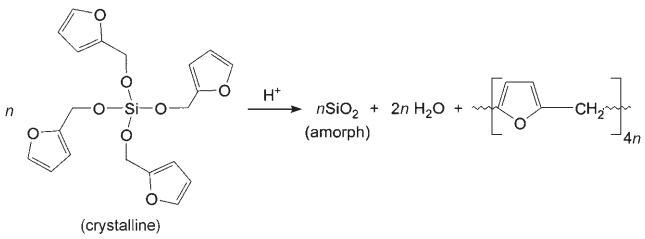
We describe herein a new type of polymerization for the synthesis of nanocomposites in which one monomer undergoes two different polymerization reactions simultaneously and on the same timescale. The monomer must be constructed in such a way that two structurally different homopolymers are generated by a single polymerization mechanism. The functionalities of the covalently combined monomers determine whether a monomer unit undergoes cross-linking or linear chain propagation. Because two structurally different polymers are generated from one "mother" monomer, the process should be designated as twin polymerization.

We have demonstrated the principle of the method with the cationic polymerizations of tetrafurfuryloxysilane (TFOS) and difurfuryloxydimethylsilane (DFOS; Scheme 1). The functionality of the silane moiety of TFOS for cross-linking is four since all four furfuryloxy substituents can be cleaved hydrolytically; in contrast, DFOS has a functionality of only two since the two Si–C bonds are stable under the reaction conditions. The functionality of the furfuryl component is always greater than two but is difficult to determine because cross-linking and branching reactions take place in cationic processes.

Since the formation of the SiO_2 network and the polymerization of furfuryl alcohol (FA) are mechanistically coupled, interpenetrating networks are formed as a polymer blend. As a result of this coupling, the two polymerization processes are synchronized. As shown in Scheme 2, the step-growth polymerization is initiated by cleavage of the Si–O–C bond. Depending on the point of view, poly(furfuryl alcohol) (PFA) is the condensation by-product of SiO_2 production or SiO_2 is the by-product of PFA production. Both processes are closely associated on the basis of the cationic growth



Scheme 1. Cationic polymerization of a) TFOS with formation of a SiO_2 network and PFA and b) DFOS with formation of poly(dimethylsilane) and PFA.



Scheme 2. Cationic polymerization of TFOS. The scheme represents the brutto conversion and does not give information on the mechanism of the partial reaction. Detailed mechanistic studies will be undertaken in future work.

mechanism, as SiO_2 can form only as rapidly as the furfuryloxy unit is cleaved. The energy balance of the polymerization of TFOS outlined in Scheme 2 can be calculated by using the increment method [Eq. (1)–(3); D = bond dissociation energy].[1] The driving force of this reaction is the significant gain in bond energy on going from amorphous Si–O to crystalline Si–O and the strength of the H–O bonds in the water molecule formed as a by-product in the condensation of the silanol group.

$$\Delta H^\circ = 4\,D(\mathrm{O{-}C}) + 4\,D(\mathrm{Si{-}O}) - 2\,D(\mathrm{Si{-}O}) - 4\,D(\mathrm{H{-}O}) - 4\,D(\mathrm{C{-}C}) \quad (1)$$

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

$$\Delta H^\circ = (4 \times 420 + 4 \times 480 - 2 \times 942 - 4 \times 480 - 4 \times 315)\ [\mathrm{kJ\,mol^{-1}}] \quad (2)$$

$$\Delta H^\circ = -1464\ \mathrm{kJ\,mol^{-1}} \quad (3)$$

Our method differs fundamentally from known processes in which functionalized tetraalkoxysilanes are polymerized and then subsequently introduced into a sol–gel process with water.[2] For instance, Novak and co-workers used silicon alkoxides possessing polymerizable vinyl or ester groups to produce nanocomposites.[3–6] However, in their approach fluoride ions serve as the catalyst in the sol–gel process, and a ruthenium catalyst is used for the ring-opening metathesis polymerization of the alkoxy groups. The chain polymerization of the organic groups and the SiO_2 formation are not associated in the same mechanism, and the polymerizations, each with its own initiator, proceed independently of each other. Therefore, it is extremely difficult to synchronize the timescales of the two processes.

We tested different cationic initiators and experimental conditions for the synthesis of a nanostructured PFA/SiO_2 composite by cationic polymerization. Experimental data are summarized in Table 1. The polymerizations were carried out

Table 1: Experimental conditions for the polymerization of TFOS.

Sample/initiator	TFOS/initiator[a]	Conditions	C content [%][b]
C1/HCl(aq)	1	60 °C, melt	57
C2/HCl(aq)	10	60 °C, melt	59
C3/HCl(aq)	50	60 °C, melt	55
C4/HCl(aq)	100	60 °C, melt	53
C5/CF_3COOH	10	60 °C, melt	58
C6/CF_3COOH	50	60 °C, melt	45
C7/CF_3COOH	10	25 °C, CH_2Cl_2[c]	57
C8/CF_3COOH	50	25 °C, CH_2Cl_2[c]	53

[a] Molar ratio. [b] Carbon content of the resulting composites after purification by extraction with acetone and drying. [c] $c = 1.534\ \mathrm{mol\,L^{-1}}$.

in the melt (neat TFOS) or in CH_2Cl_2 solution. In the melt, the acid-catalyzed reaction proceeds very rapidly and is complete in a few minutes to a few hours, depending on the catalyst concentration; in solution the reaction requires up to five days. The polymerization process is strongly exothermic after initiation and yields a hard black insoluble material. The black color of cationically produced PFA is typical.[7–9] The carbon content of the product does not differ significantly from that of the monomer. The PFA/silica composite is not porous ($\mathrm{BET} < 1\ \mathrm{m^2\,g^{-1}}$). It is completely amorphous as indicated by the one broad signal in the X-ray diffraction (XRD) spectrum observed at $2\theta = 20°$; small-angle X-ray scattering (SAXS) measurements at short and long detector distances also did not show any sharp peaks. The complete conversion of the crystalline monomer is confirmed (see the Supporting Information). Melting points and/or a glass transition temperature could not be found by differential scanning calorimetry (DSC; see the Supporting Information).

Thermogravimetric (TG) plots and differential thermoanalysis of the PFA/silica composite are depicted in the Supporting Information. Weight loss starts at about 320 °C, and the T_{50} value (the temperature at which half of the carbon had been burned) is 425 °C. The weight loss of pure PFA starts at about 300 °C and its T_{50} is 400 °C (see the Supporting Information), but significant weight loss for this sample was observed already at 100 °C. This result demonstrates the increased thermal stability of the PFA/SiO_2 composite.

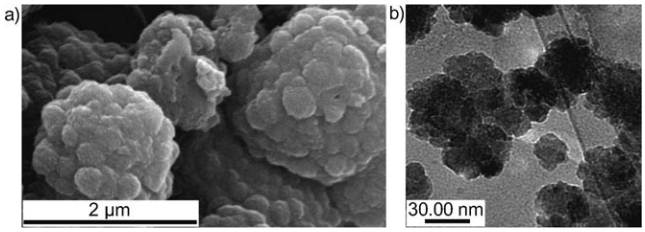

Figure 1. a) SEM and b) TEM images of the PFA/SiO_2 composite **C1**.

The composite exhibits a very uniform morphology. Investigations using electron microscopy showed cauliflower-like fractal microstructures with features down to the nanometer range (Figure 1). Energy-dispersive X-ray (EDX) analyses of the composite confirm the regular distribution and the ideal alternation of carbon, oxygen, and silicon (Figure 2).

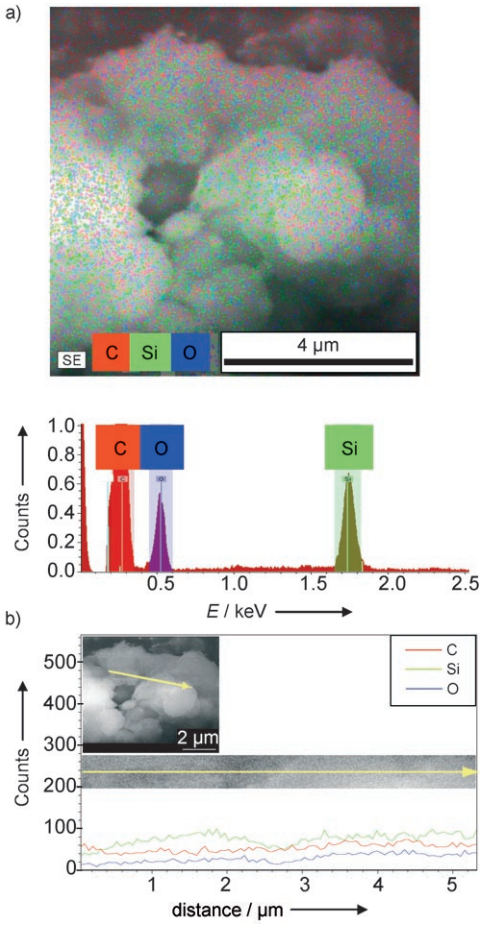

Figure 2. a) EDX spectrum of the resulting PFA/SiO_2 composite **C1** and b) an EDX linescan analysis.

The complete cleavage of the Si–O–C bond is confirmed by the disappearance of the monomer peak of TFOS at $\delta = -82$ ppm in the ^{29}Si cross-polarization magic-angle spinning (CP-MAS) NMR spectrum. The clean formation of the SiO_2 phase is supported by the characteristic Q^2, Q^3, and Q^4 signals in the solid-state ^{29}Si CP-MAS NMR spectrum (Figure 3). The

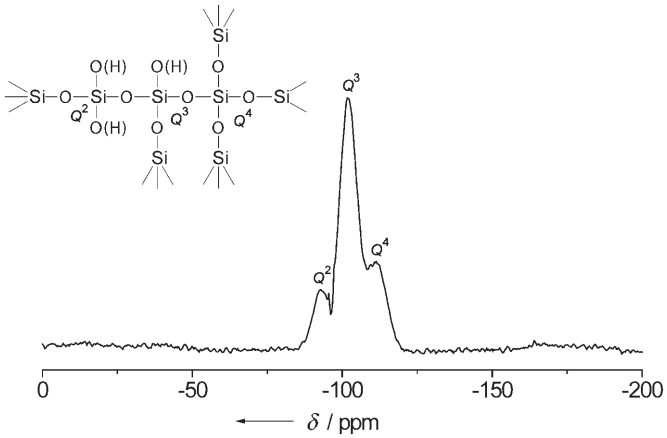

Figure 3. Solid-state ^{29}Si{^{1}H} CP-MAS NMR spectrum of the PFA/SiO_2 composite **C2** recorded at a spinning frequency of 5 kHz.

solid-state ^{13}C{^{1}H} CP-MAS NMR spectrum of the composite shows all the expected signals of PFA. The PFA contains a high proportion of conjugated sequences as can be seen from the presence of signals at $\delta = 95$, 130, and 155 ppm.[10,11] The broad signal at $\delta = 40$ ppm indicates cross-linked structures in the polymer.[8] The signal at $\delta = 58$ ppm due to the methylene group of the monomer has completely disappeared (Figure 4).

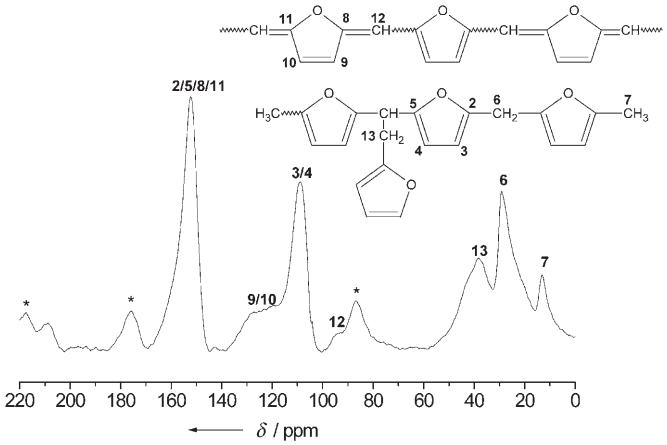

Figure 4. Solid-state ^{13}C{^{1}H} CP-MAS NMR spectrum of the PFA/SiO_2 composite recorded at a spinning frequency of 7 kHz. Spinning side bands are marked with *.

Besides the cross-linking reactions, acid-induced cleavage of the furan ring also occurs. The signal of the carbonyl group at about $\delta = 200$ ppm is attributed to formed levulinic acid.[9] This assumption is supported by the DRIFT spectrum (see the Supporting Information).

Our results show that tetrafurfuryloxysilane undergoes cationic polymerization to give two separate, structurally different, cross-linked polymers. The functionality of the silane component can be changed deliberately to three and two by using trifurfuryloxymethylsilane and difurfuryloxydimethylsilane, respectively. Accordingly, the concept can be extended to various monomer structures and mixtures, showing a wide field for future studies.

We found that the twin polymerization of DFOS catalyzed by $(CF_3SO_2)_2O$ proceeds with phase separation. Black, porous PFA particles form (Figure 5a and the Supporting Information) along with colorless, liquid cyclooligodimethylsilane. The solid-state ^{13}C CP-MAS NMR spectrum of the PFA component is almost identical to that of composite C2 shown in Figure 4. The SEM image of the PFA component (Figure 5a) shows particles agglomerated to a size of about 600 nm; the specific surface area is about 25 $m^2 g^{-1}$. The absence of silicon in this organic polymer was proved by EDX analysis (Figure 5b). The soluble phase was identified as cyclooligodimethylsilane on the basis of its mass spectrum (Supporting Information) and its ^{1}H NMR spectrum.

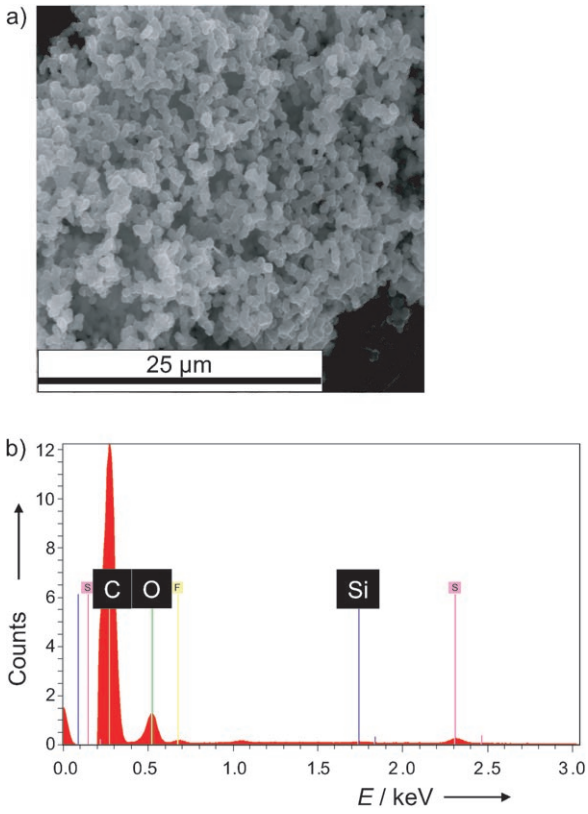

Figure 5. a) SEM image and b) EDX spectrum of the PFA particles resulting from the cationic polymerization of DFOS. (DFOS/$(CF_3SO_2)_2O$ 10:1) in CH_2Cl_2 ($c = 0.73$ mol L^{-1}) at 25 °C.

The novel PFA/SiO_2 nanocomposites can be used for preparing mesoporous silica by thermal oxidation with air (Figure 6). The white SiO_2 obtained after oxidation shows a uniform pore structure (Supporting Information) and a very

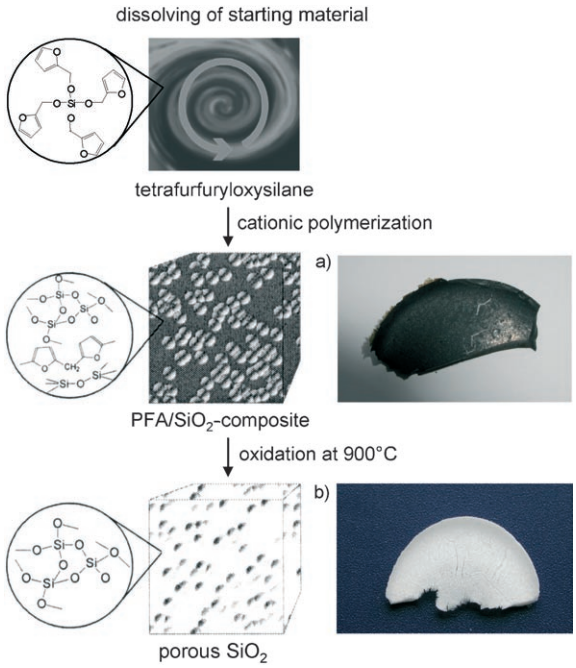

Figure 6. Schematic representation of the cationic polymerization of TFOS and subsequent oxidation at 900 °C of the PFA/SiO_2 composite: a) monolithic PFA/SiO_2 composite **C2**; b) monolithic silica sample **C2-ox** after oxidation.

narrow pore size distribution in the nanometer range (Supporting Information).

By varying the central atom (metal instead of silicon) and the monomer component (Scheme 2), a new strategy for the synthesis of porous metal oxides (TiO_2, B_2O_3, mixed oxides, etc.) with high pore volumes and very narrow pore radius distribution (even for monoliths) is available for future study. It is also possible to use the novel PFA/silica composites as precursors for SiC as well as for the preparation of nanostructured carbon-containing micropores. Such materials have potential applications in hydrogen storage and as porous solid catalysts.[12–24] We expect that a variety of composite materials may be accessible by the twin polymerization method described herein.

Experimental Section

For IR measurements, a Bio-Rad FTIR spectrometer FTS 165 was used. Liquid samples were measured as thin films between KBr windows, and solid samples were measured as KBr pellets. The solid-state $^{13}C\{^1H\}$ CP-MAS (100.6 MHz) and the $^{29}Si\{^1H\}$ CP-MAS (79.5 MHz) NMR spectra were recorded at 9.4 T on a Bruker Digital Avance 400 spectrometer equipped with 4- and 7-mm double-tuned probes capable of MAS at 12 and 5 kHz, respectively. Contact times of 5.5 ms for ^{13}C and 3 ms for ^{29}Si for cross-polarization from ^1H to ^{13}C and ^{29}Si were used. Data acquisition was performed with proton decoupling (TPPM). NMR spectra were referenced to adamantane (^{13}C, $\delta = 38.5$ ppm) and kaolin (^{29}Si, $\delta = -92.5$ ppm).

The following measurements were carried out: SEM and EDX analyses (Philips SEM 515), TEM (Philips CM 20 FEG; 200 kV), TG analyses (Perkin Elmer TGA 7), DSC (Mettler DSC 30), elemental analyses (Vario EL, Elementar Analysensysteme, Hanau), specific surface area (Sorptomatic 1990 and Ströhlein AREA-meter II; for samples with very small surface areas), XRD (Seifert FPM XRD 7), SAXS (threefold pinhole system with a detector distance of 336–1643 mm).

Chemicals: KOH, TEOS, dimethoxydimethylsilane, and FA are commercially available products. FA was distilled immediately before use, TEOS (Acros) was used without further purification.

Preparation of TFOS:[25] Tetraethoxysilane (90 mL, 0.4 mol) and FA (141 mL, 1.6 mol) were mixed, and 0.3 wt % of KOH was added. The mixture was stirred for 3 h at 80 °C and 65 mbar. Then the pressure was reduced over 1 h to 3 mbar and the by-products were distilled off. The product was obtained at 240 °C and 0.4 mbar. Light-yellow crystals precipitated at 0 °C and could be recrystallized from diethyl ether (m.p. 58 °C). Polymerization of TFOS in the melt: TFOS (2 g, 4.81 mmol) was melted and 41 μL of conc. HCl was added dropwise at 25 °C. Polymerization of TFOS in solution: TFOS (2 g, 4.81 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and 35.7 μL of CF_3COOH or 41 μL of conc. HCl was added (TFOS/initiator 10:1). In both cases the solution was stirred for 2 h and left to stand for polymerization at 25 °C. After 3 h of polymerization in the melt or after 2 days of reaction in solution a hard, black product was obtained. The samples were extracted with CH_2Cl_2 for 24 h and then dried under vacuum at 40 °C until the sample weight was constant. Oxidation: The sample was heated to 900 °C in air (2.3 K min^{-1}) and kept there for 1 h. PFA: The PFA/silica composites were treated with aqueous HF solution and were stirred at room temperature for 24 h.

Preparation of DFOS: Dimethoxydimethylsilane (37 g, 0.25 mol) and FA (49 g, 0.5 mol) were mixed, and 0.1 wt % of KOH was added. The mixture was stirred for 6 h at 60 °C. Then the pressure was reduced over 6 h to 100 mbar and the by-products were distilled off. The product, a light-yellow liquid, was obtained at 120 °C and 0.3 mbar. Yield: 72 %. Polymerization of DFOS in solution: DFOS (1.1 g, 4.4 mmol) was dissolved in 5 mL of CH_2Cl_2, and 73 μL of $(CF_3SO_2)_2O$ dissolved in 5 mL of CH_2Cl_2 was added (DFOS/initiator 10:1). The solution was stirred for 2 h and left to stand for polymerization at 25 °C. After 2 days a black product was obtained. The samples were extracted with CH_2Cl_2 and dried under vacuum at 40 °C.

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