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The preparation of HfC/C ceramics *via* molecular design†

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Polymer derived ceramics have received lots of attention throughout the last few decades. Unfortunately, only a few precursor systems have been developed, focusing on silicon based polymers and ceramics, respectively. Herein, the synthesis of novel hafnium containing organometallic polymers by two different approaches is reported. Dialkenyl substituted hafnocene monomers were synthesized and subsequently polymerized *via* a free radical mechanism. Salt metathesis reactions of hafnocene dichloride with bifunctional linkers led to the formation of polymeric materials. NMR spectroscopic methods – in solution as well as in the solid state – were used to characterize the organometallic polymers. Ceramics were finally obtained after cross-linking and thermal treatment under argon (T_{max} = 1800 °C). SEM investigations, elemental analyses, Raman spectroscopy and XRD investigations identified the pyrolyzed products as partially crystalline HfC/C mixed phases.

I. Introduction

Due to its extraordinary properties in regard of hardness and temperature resistance, hafnium carbide (HfC) is of great interest for many technical applications that demand tough materials. The availability of literature on the fabrication of monolithic hafnium carbide or composites based thereon is limited.[1,2] There are some reports dealing with hot-pressed HfC compounds, leading to products of a mean grain size between 40 and 60 μm.[3,4] Usually, HfC powders are prepared by high-temperature reactions of powder mixtures of carbon and hafnium (Hf), hafnium hydride (HfH$_2$) or hafnium oxide (HfO$_2$).[5–9] These methods are not only time and energy consuming but they also yield mostly low density materials of relatively small particle size. In cases where HfC coatings are desired, CVD processes starting from hafnium chloride (HfCl$_4$), methane and hydrogen are used.[10–13] Thin films of carbon-rich hafnia are synthesized by pulsed laser deposition.[14] Recently, the preparation of polymer-derived SiOC/HfO$_2$ nanocomposites has been reported.[15,16] The application of a polymer to ceramic conversion approach to the fabrication of HfC powders and coatings promises to be more efficient than the procedures cited above. However, only a few attempts to synthesize HfC following alternative pathways have been published so far, either starting from oxygen containing hafnium organic compounds or hafnocene dichloride.[17–23] Although introduced oxygen might be removed during processing, experimental procedures avoiding oxidic intermediates would be preferable. Following that thought,

our research group occupied itself with the synthesis of non-oxide polymeric precursors containing hafnium–carbon bonds and their subsequent pyrolytic conversion into hafnium carbide.

Organometallic compounds of group IV metals have been studied in numerous ways throughout the last decades. However, in most cases, titanium and zirconium species were examined while hafnium did not get much attention.[24–28] Thus, experimental data on hafnium compounds containing Hf-C σ-bonds is limited. Fortunately, the reactivities of zirconium and hafnium are very similar. As a result, experimental procedures – known from zirconium – can easily be transferred to hafnium. Still, there are some peculiarities that make working in the field of organometallic hafnium chemistry an interesting task.

The results reported herein focus on two different synthetic routes that have been followed: the radical polymerization of alkenyl substituted hafnocene derivatives on the one hand and polymer synthesis by salt-metathesis reactions of hafnocene dichloride with dilithioalkynyl compounds on the other hand. Both approaches led to the desired polymers, which could be converted into HfC materials.

II. Experimental procedures

General remarks

All reactions were carried out in dry glassware in an argon atmosphere. Solvents were dried according to standard methods and stored under argon. If not noted otherwise, reagents were used as received from the suppliers.

Analytical methods

NMR spectra of soluble compounds were obtained at ambient temperature (Varian INOVA 300 (¹H: 299.8 MHz; ¹³C: 75.4 MHz;

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^{29}Si: 59.6 MHz), Varian INOVA 400 (^{1}H: 399.8 MHz; ^{13}C: 100.5 MHz; ^{29}Si: 79.4 MHz)). Chemical shifts δ were referenced to tetramethylsilane (TMS).

IR spectra were obtained from KBr-pellets on a Bruker Tensor 27 spectrometer. Pyrolyzed samples were characterized using SEM/EDS (Jeol JSM 6400), XRD (Seifert, XRD 3000P), and Raman spectroscopy (Horiba Jobin Yvon, LabRAM). ^{13}C MAS spectra were recorded at room temperature on an Avance II 300 spectrometer (Bruker) in an external magnetic field of 7.05 T. The measurements were performed with 2.5 mm standard double-resonance MAS probes (Bruker) which were operated with zirconia rotors. A rotation frequency of 12 kHz was set for all experiments and the spectra were referenced with respect to trimethylsilane (TMS). Contact times t_H were set to 3 ms and the recycle delay was chosen between 3 and 20 s. For all experiments broadband proton decoupling *via* a SPINAL64 sequence[29] was applied. The ^{13}C nuclei were excited *via* the proton bath by employing a ramped cross-polarization sequence where the ^{1}H pulse amplitude was decreased linearly by 50%.[30] Elemental analyses were performed at "Mikroanalytisches Labor Pascher, An der Pulvermühle 1, 53424 Remagen-Bandorf, Germany".

Synthesis of Polymer I

The synthesis of Polymer I (Scheme 1) required three steps: preparation of a suitable Grignard compound, alkylation of hafnocene dichloride and radical polymerization of the dialkenyl hafnocene derivative.
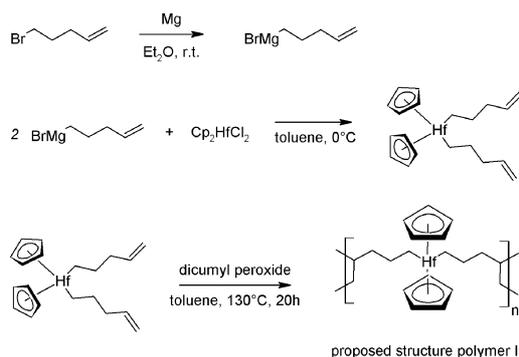
Scheme 1 Synthesis of Polymer I.

5-Bromo-1-pentene was added slowly to a suspension of magnesium turnings in diethyl ether. When the reaction was completed, its product – ω-pentenyl magnesium bromide – was added to a cold solution of hafnocene dichloride in toluene and stirred overnight. Solids were filtered off and the remaining solution dried under vacuum. After extraction with pentane, Cp$_2$Hf(ω-pentenyl)$_2$ was isolated in 76% yield and characterized by NMR spectroscopy.

(^{1}H NMR (C$_6$D$_6$): δ 0.05 (Hf-CH_2-CH$_2$-), 1.50 (-CH$_2$-CH_2-CH$_2$-), 2.03 (-CH$_2$-CH_2-CH =), 5.91 (-CH$_2$-CH = CH$_2$), 5.08 (-CH=CH_2), 5.61 (Cp).

^{13}C NMR (C$_6$D$_6$): δ 58.1 (Hf-CH_2-CH$_2$-), 32.1 (-CH$_2$-CH_2-CH$_2$-), 42.4 (-CH$_2$-CH_2-CH =), 140.0 (-CH$_2$-CH=CH$_2$), 114.2 (-CH = CH_2), 109.8 (Cp)).

Polymerization was initiated by admixing of 3 wt% dicumyl peroxide to a solution of Cp$_2$Hf(ω-pentenyl)$_2$ in toluene and refluxing overnight. Evaporation of volatiles afforded Polymer I as a waxy orange solid.
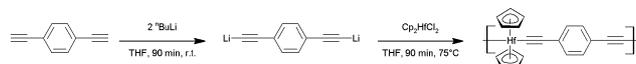
Synthesis of Polymer II

Polymer II was prepared *via* a salt metathesis reaction of hafnocene dichloride with 1,4-dilithio-1,3-butadiyne which was obtained by reacting hexachlorobutadiene with four equivalents of *n*-butyllithium in tetrahydrofuran/hexane (Scheme 2).[31] As the reaction proceeds very quickly at ambient temperature, the solution of 1,4-dilithio-1,3-butadiyne was cooled to –78 °C before the addition of hafnocene dichloride. After complete addition of hafnocene solution, the cold bath was removed and the mixture was stirred for several minutes before quenching with trimethylchlorosilane. Filtration gave a black insoluble solid, which was washed with tetrahydrofuran, dried *in vacuo* and identified as polymer II by solid state NMR spectroscopy.
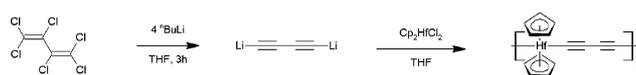
Scheme 2 Synthesis of Polymer II.

Synthesis of Polymer III

Polymer III was synthesized in a similar manner to polymer II by coupling hafnocene dichloride with 1,4-bis(lithioethynyl)benzene (Scheme 3). After purification, polymer III was obtained as an insoluble, yellow powder and characterized by solid state NMR spectroscopy.


Scheme 3 Synthesis of Polymer III.

Thermolysis

Pyrolytic conversion of polymers I to III was carried out in an argon atmosphere with a heating rate of 3 K min^{-1} until a maximum temperature of T_{max} = 1800 °C was reached. Samples were held at T_{max} for two hours and then cooled to room temperature.

III. Results and discussion

Attempts to synthesize Cp$_2$Hf(ω-butenyl)$_2$ by reaction of hafnocene dichloride with ω-butenyl magnesium bromide under various conditions led to the formation of a mixture containing mono- and disubstituted hafnocene. Similar reactions using ω-pentenyl magnesium bromide as an alkylation agent gave exclusively the disubstituted product Cp$_2$Hf(ω-pentenyl)$_2$ in moderate yields. For NMR spectroscopic measurements, solutions of Cp$_2$Hf(ω-pentenyl)$_2$ in C$_6$D$_6$ were prepared. The NMR dataset reported on hafnium alkyl compounds is rather limited.[25,28,32] Therefore, complete characterization and assignment of NMR signals of Cp$_2$Hf(pentenyl)$_2$ was achieved by 1D ^{1}H and ^{13}C

NMR spectra (Fig. 1) in combination with 2D NMR experiments (COSY, HSQC, HMBC; ESI†).
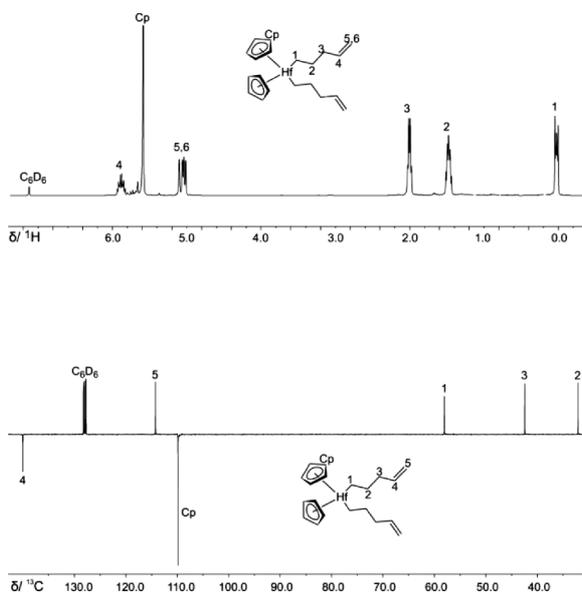
Fig. 1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of $Cp_2Hf(\omega\text{-pentenyl})_2$, C_6D_6.

$Cp_2Hf(\omega\text{-pentenyl})_2$ was dissolved in toluene, admixed with dicumyl peroxide and heated to reflux in order to perform radical polymerization. The resulting substance was examined by NMR spectroscopy. ^{1}H- as well as ^{13}C NMR spectra contained a variety of signals corresponding to alkyl chains. Furthermore, the signals assigned to Hf-CH$_2$ units at typical high frequencies, were found in the NMR spectra of $Cp_2Hf(\omega\text{-pentenyl})_2$ and had been preserved in the high-molecular product. Considering these findings, a possible molecular structure for polymer I has been proposed (Scheme 1).

A second approach to the synthesis of hafnium organic polymers is the above mentioned coupling reaction between hafnocene dichloride and difunctional lithio compounds. Salt metathesis reaction of hafnocene dichloride with 1,4-dilithio-1,3-butadiyne under elimination of lithium chloride led to an insoluble powder which was characterized by solid state ^{13}C MAS NMR spectroscopy (Fig. 2). Polymer II shows an intense sharp signal corresponding to the cyclopentadienyl ligands (111.8 ppm) as well as two broad signals corresponding to C_α (133.8 ppm) and C_β (69.7 ppm). The signal assigned to C_α is remarkably shifted towards lower field, while the one corresponding to C_β can still be detected in the region which is typical for an alkyne carbon. Based on
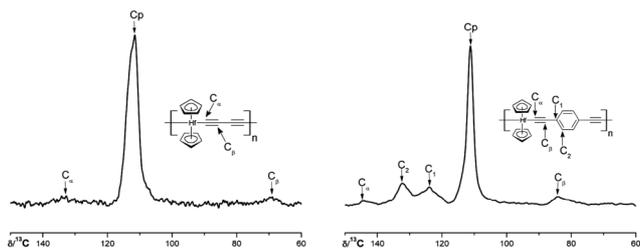
Fig. 2 ^{13}C MAS NMR spectra of polymer II (left) and polymer III (right).

Table 1 Results of elemental analysis

|	C [wt.%]	Hf [wt.%]	Carbide C [mol%]	Graphite C [mol%]
HfC[34]	4.5–6,7	93.2–95.5	100	0
I	14.7	81.3	~62	~38
II	23.9	70.9	~80	~20
III	9.9	85.6	~42	~58

these data, a molecular structure for polymer II (Scheme 2) was proposed.

The salt metathesis reaction of hafnocene dichloride with 1,4-bis(lithioethynyl)benzene was conducted in order to produce polymer III, which was recovered as an insoluble powder after purification. Characterization of a sample by solid state ^{13}C MAS NMR spectroscopy (Fig. 2) allowed the assignment of signals to specific atom positions in the polymer chain as follows: Cp 112.0 ppm, C_α 145 ppm, C_β 83.9 ppm, C_1 123.9, C_2 132.2 ppm. Signals for C_β and $C_{1,2}$ are in good agreement with the data obtained from 1,4-diethynylbenzene[33] as expected. Due to the influence of hafnium, the signal corresponding to C_α is strongly shifted towards lower field.

As the goal of our investigations was the preparation of hafnium carbide ceramic materials, thermogravimetric analyses of the three polymers were accomplished in order to estimate pyrolysis behaviour and ceramic yields. Experimental data show that heat treatment of samples of polymers I to III (1200 °C, 3 K min^{-1}, Ar) is accompanied by a weight loss of 38–46%. Calculations on the basis of polymer structures gave theoretical ceramic yields of 42.6 wt% (57.6% weight loss) for polymer I, 53.4 wt% (46.6% weight loss) for polymer II and 44.0 wt% (56.0% weight loss) for polymer III. These values correspond to the formation of pure HfC during pyrolysis. Elemental analyses of the samples pyrolyzed at 1800 °C in an Ar atmosphere led to different HfC/C compositions depending on the molecular structure of the polymer (Table 1). Polymer III contains two Cp-ligands as well as a bridging phenylene-group in the repeating unit. These groups tend to evaporate during pyrolysis which leads to the lowest carbon content of the investigated ceramic residues. In contrast, the pyrolysis product of polymer II shows the highest carbon content. This polymer is mainly composed of the carbon forming, hydrogen poor ethynyl groups.

During pyrolysis hafnium reacted quantitatively with excess carbon to form HfC. According to the phase diagram for the system hafnium–carbon,[34,35] these findings correspond to a mixed phase consisting of HfC on the one hand and free carbon on the other hand and explain the disagreement between theoretically and experimentally found ceramic yields. The proof for the occurrence of free carbon was found by means of Raman spectroscopy. Two strong Raman bands at 1310 cm^{-1} (D-band) and 1598 cm^{-1} (G-band) were detected (Fig. 3). Due to peak positions and the ratio of peak heights, $I(D)/I(G)$, the carbon phase could be identified as nanocrystalline graphite.[36]

The presence of crystalline HfC in the samples pyrolyzed at 1800 °C was confirmed by XRD measurements. The XRD patterns were fully consistent with hafnium carbide (cubic, NaCl-type) in all cases as indicated by the Hf-C phase diagram.[35] Additionally, SEM investigations indicated the presence of crystalline particles within the ceramic residues of polymers I, II and III after pyrolysis at $T_{max} = 1800$ °C (Ar atmosphere). In the case of polymer I, small crystallites of approximately 1 µm in size were detected
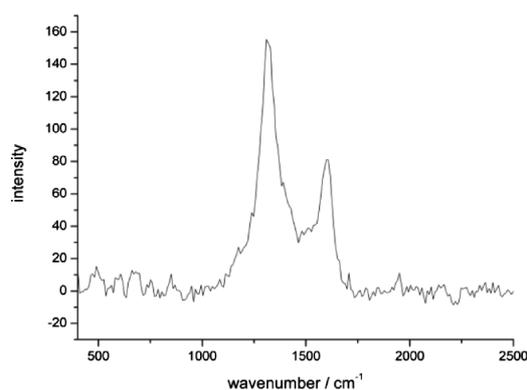
Fig. 3 Raman spectrum of pyrolyzed polymer II (1800 °C, Ar, 3 K min⁻¹), λ = 623 nm.
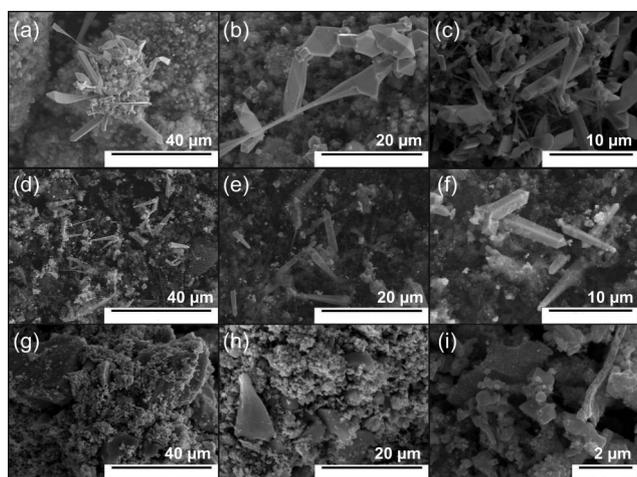
Fig. 4 Scanning electron micrographs of pyrolyzed samples of polymer I (a)–(c), polymer II (d)–(f), polymer III (g)–(i). At higher magnification distinct crystallites of HfC (detected by XRD) are noticeable. (Heating rate 3 K min⁻¹, 1800 °C, argon).

at high magnification (Fig. 4a–c). Crystallite size was estimated to range from 2 to 5 μm for a sample of II (Fig. 4d–f) and from 5 to 20 μm for sample III (Fig. 4g–i).

IV. Conclusions

Hafnium organic polymers were successfully prepared starting from hafnocene dichloride following two different synthetic pathways. An organometallic monomer was synthesized, isolated and polymerized *via* a free radical mechanism. Alternatively, salt metathesis reactions between bi-functionalized starting compounds were conducted, yielding polymeric products.

After preparation, organometallic compounds were characterized by means of ¹H- and ¹³C NMR spectroscopic methods. Pyrolysis behavior of the polymers was investigated *via* TGA measurements in an argon atmosphere, indicating ceramic yields within a range of 54–62 wt% after heat treatment up to 1000 °C.

Cross-linking of our preceramic polymers – either by radical or thermal initiation– was followed by heat treatment up to a maximum temperature of 1800 °C. The resulting ceramic residues were examined by various analytical methods such as SEM, XRD, Raman spectroscopy and elemental analysis. The results

of these studies prove that the preparation of HfC starting from organometallic polymers at relatively low temperatures is possible, giving partial crystalline hafnium carbide/carbon mixed phase systems as final products. Thus, the preceramic polymers described within this article are interesting candidates for processing of HfC based coatings or as matrix materials in ceramic matrix composites.

Acknowledgements

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