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Refractory Metal-Containing Polymers and Nanocomposites: Preparation and Properties

Gulzhian I. Dzhardimalieva, Svetlana I. Pomogailo, Nina D. Golubeva, Anatolii D. Pomogailo*

Summary: Novel polymers containing refractory metal in the main chain or side chains can be prepared. An attractive approach is polymerization of the Hf (Ta, Nb)-monomers with (meth)acrylate, fumarate or monomethylmethacrylate ethyleneglycol groups, synthesized for the first time in this study. New types of hafnium (tantalum, niobium)-containing nanocomposites are prepared by combining polymer synthesis and controlled thermolysis. The composition and structure of the synthesized metal-containing precursors and thermolysis products are determined by elemental analysis, IR and ^{1}H-NMR spectroscopies, X-ray diffraction and TEM analysis.

Keywords: hafnium carbide; metal nanoparticles; metal-containing polymers; nanocomposites; refractory elements; thermolysis

Introduction

Hafnium (tantalum, niobium) carbides and oxides are refractory compounds with high thermal stabilities and chemical inertness. They are popular materials for hard and environmental coatings in ultra high temperature applications. Traditionally these materials have been prepared by high temperature powder techniques that are limited in their ability to generate homogeneous systems with controlled compositions and properties. We have elaborated a novel approach that employs metal-containing monomer and metallopolymer precursor routes to such materials.[1–5] It comprises; (i) thermal transformations of metal-containing monomers (MCM); i.e., compounds comprising a metal equivalent and a polymerisable group containing multiple bonds, involving solid-state (co)polymerization of the monomers (ii) thermolysis of the metallopolymers formed to generate nanoparticles stabilized with a polymer matrix. In this work we report on the study of synthesis and structure of the metallopolymer precursors and nanocomposites based on refractory elements.

Experimental Part

Hf(IV)-monomers and polymers were prepared according to a procedure described in our previous work.[3] $M(OEt)_5$ ($M = Ta$, Nb) were synthesized from metal chlorides in the presence of dry C_2H_5OH and NH_3 as reported elsewhere.[9] All experiments were carried out under anaerobic conditions, and metal-containing monomers appear unstable toward the atmosphere in solution or in the condensed state.

Synthesis of Tantalum (Niobium)-Containing Monomers $M(OC_2H_5)_4(OCH_2CH_2OCO(Me) = CH_2)$ ($M = Ta$, Nb)

To the solution of $M(OC_2H_5)_5$ in benzene stoichiometric quantity of monomethacrylic ether of ethylene glycol in benzene was added. The reaction was stirred for 1 h. An azeotrope mixture of benzene and C_2H_5OH was distilled at 75.5 °C. The yield of monomers was

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Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russia
E-mail: dzhardim@icp.ac.ru

93–95%. IR, ν/cm^{-1}: 432, 476, 592, 636, 916, 1072, 1116, 1148, 1576, 1728.

Polymerization of Metal-containing Monomers

1 g of the monomer, 0.01 g azobisisobutyronitrile, 30 mL of hexane were placed into glass ampoule. Then the ampoule was degassed and sealed under vacuum. The reaction was carried out at 70 °C for 2 h. The metallopolymer product was isolated by filtration, washed and dried in vacuum at 40 °C.

Thermal Transformations of Metal-containing Precursors

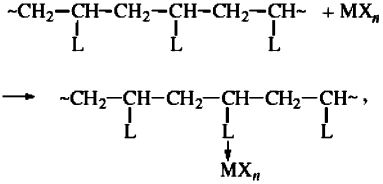
Thermolysis was performed isothermally, at 370, 600, and 1000 °C and occasionally in the range 1350–1400 °C. The tube containing the sample was placed in an isothermally heated zone, whose volume was approximately 5% of the total volume of the reactor. The process was run in a self-generated atmosphere, under dynamic vacuum, or in argon (p = 72–74 kPa). The kinetics of gas evolution were followed using a membrane manometer.

IR Absorption Spectra

FT IR spectra of both precursors and reaction products, gaseous and condensed, were measured in the range 400–4000 cm^{-1} (Specord 75 IR spectrophotometer). Gaseous reaction products were also analyzed by mass spectrometry using an MS-3702 quadrupole mass spectrometer (75 eV). Molecular-weights of insoluble polymers were evaluated by thermomechanical analysis according to procedure.[10] X-ray diffraction studies of powder samples were performed on a DRON UM-2 diffractometer with Cu $K\alpha$- radiation. In electron-microscopic examination, we used JEOL JSM-840 and JEM-100CX instruments, and HRTEM JEOL 3010. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE III instrument working at 500 MHz. Chemical shifts of proton δ are recorded in ppm with reference to internal tetramethylsilane.

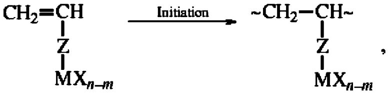
Results and Discussions

There are currently three basic approaches to the preparation of metal-containing polymers[6]: (I) reactions of metal compounds with functionalized linear polymers in which the main polymer chain remains unchanged (so-called polymer-analogous conversions); (II) polycondensation of appropriate precursors, a process in which a metal ion is incorporated into the main chain, and its removal leads to destruction of the polymer; (III) polymerization and copolymerization of metal-containing monomers (recently devised approach):



$$\sim CH_2-\underset{L}{CH}-CH_2-\underset{L}{CH}-CH_2-\underset{L}{CH}\sim + MX_n \longrightarrow \sim CH_2-\underset{L}{CH}-CH_2-\underset{\begin{subarray}{c}L\\ \downarrow\\ MX_n\end{subarray}}{CH}-CH_2-\underset{L}{CH}\sim, \quad (I)$$

$$HL{-}R{-}LH + MX_n \xrightarrow[-2HX]{} \sim L{-}R{-}L{-}MX_{n-2}\sim, \quad (II)$$



$$CH_2=\underset{\begin{subarray}{c}Z\\ |\\ MX_{n-m}\end{subarray}}{CH} \xrightarrow{\text{Initiation}} \sim CH_2-\underset{\begin{subarray}{c}Z\\ |\\ MX_{n-m}\end{subarray}}{CH}\sim, \quad (III)$$

where L, X, and Z are functional groups, and R is a bridge group.

Unfortunately, little or no data have been reported on the preparation of Hf (Ta, Nb)- containing polymers. Most effort has been concentrated on polymers containing Ti and, to a lesser extent, Zr, electronic analogs of hafnium.[6]

Hear, we describe the synthesis of Hf (Ta, Nb)-containing polymers obtained by (co)polymerization of the appropriated monomers (process III).

Synthesis of Hf (Ta, Nb)-containing Monomers and Polymers

Preparation of Hf-polymers Through Polymerization of Metal-containing Monomers

Reacting $HfCl_2$ with the sodium or potassium salt of acrylic or methacrylic acid, we obtained for the first time Hf(IV)-containing monomers. Hafnium oxoacrylates and methacrylates were synthesized according to the scheme:

$$\begin{aligned}&HfOCl_2 + 2CH_2 = C(R)COONa\\&\quad\rightarrow HfO(CH_2 = C(R)COO)_2\\&\qquad + 2NaCl \qquad (1)\end{aligned}$$

$$\begin{aligned}&HfOCO_3 + 2CH_2 = C(R)COONa\\&\quad\rightarrow HfO(CH_2 = C(R)COO)_2\\&\qquad + CO_2 + H_2O \qquad (2)\end{aligned}$$

$$R = H\,(1),\ CH_3\,(2)$$

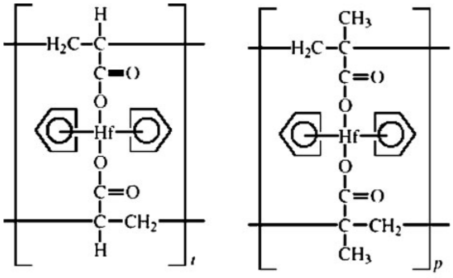
$HfOCl_2$ reacts with fumaric acid to form the coordination polymer:

$$\begin{aligned}&HfOCl_2 + HOOC{-}CH\\&\quad = CH - COOH\\&\quad\rightarrow -(Hf(O) - OCOCH\\&\quad = CH{-}COO){-}n + 2HCl \qquad (3)\end{aligned}$$

The IR spectra of these monomer and polymer precursors show absorption bands due to carboxylate groups (($\nu_s^{COO} = 1373$, 1449, 1461 cm^{-1}; $\nu_{as}^{COO} = 1544$, 1548 cm^{-1}), which indicates that the complexes have bidentate and bridge structures.

The strong absorptions in the range 800–1000 cm^{-1} are attributable to the $\delta_{OH}(H_2O)$, $\pi(-CH = CH_2)$, and $\nu_{cc}(=CH-C)$ modes.[7] At the same time, the broad bands between 700 and 900 cm^{-1}, characteristic of ...HfOHfO ... chains, are missing. Carboxylates of cyclopentadienyl derivatives of hafnium, $Cp_2Hf(CH_2{=}CHCOO)_2$ (**4**) and $Cp_2Hf(CH_2{=}C(CH_3)COO)_2$ (**5**), were obtained by reacting Cp_2HfCl_2 with the potassium salt of acrylic or methacrylic acid. The composition and structure of these compounds were determined by elemental analysis and IR spectroscopy and described in detail in our previous work.[3]

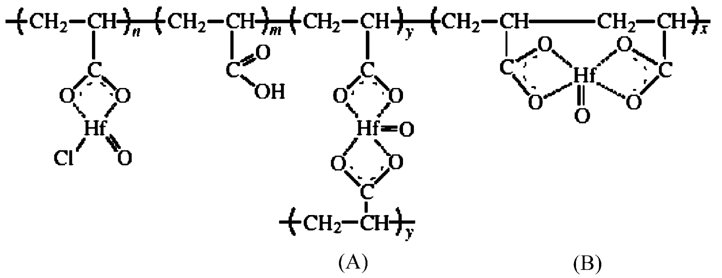
Their IR spectra show bands arising from the carboxylate group ($\nu_s^{COO} = 1373$, 1446, 1458 cm^{-1}; $\nu_{as}^{COO} = 1538$, 1549, 1567 cm^{-1}) and also (ν MO (432, 452, 492, 640, 676 cm^{-1}) and (νCC (1636, 1638 cm^{-1}). In addition, the spectra of these compounds show strong absorptions at 3004, 3005 (CH stretches), 1421, 1446 (CC stretches), 1018, 1020 (in-plane CH bends), 814, and 816 cm^{-1} (out-of-plane CH bends), which are due to vibrations of the Cp ring.[8] Most of the synthesized monomers are insoluble in organic solvents. Their thermal polymerization yields high-molecular polymers (based on $HfO(OCOCH{=}CH_2)_2 \cdot H_2O$ (**1**), $HfO(OCOC(CH_3){=}CH_2)_2\ H_2O$ (**2**), $Cp_2Hf(OCOCH{=}CH_2)_2$ (**4**), and $Cp_2Hf(OCOC(CH_3){=}CH_2)_2$ (**5**) (e.g., $\overline{M}_n = 132000$, $\overline{M}_w = 224000$ for **1**). These polymers range in Hf content from 37 to 51 wt %, just as the corresponding monomers. IR spectroscopy results confirm that the cyclopentadiene structure is retained during polymerization:



Polymer of **4** Polymer of **5**

Preparation of Hf-Containing Polymers via Polymer-Analogous Conversions (Process I)

By reacting methanolic solutions of PAA and $HfOCl_2$, up to 34 wt % Hf can be introduced into the polymer. The IR spectra of such macrocomplexes show a strong, narrow absorption band at 1720 cm^{-1}, which points to a significant concentration of unreacted carboxyl groups. At the same time, the presence of totally symmetric (1328 and 1457 cm^{-1}) and asymmetric (1751 cm^{-1}) stretching modes of COO – confirms that the hafnium ions are in bidentate and bridge coordination with carboxylate ions. Moreover, the presence of residual chlorine (up to 2.6%) in the synthesized macrocomplex indicates that the PAA–Hf(IV) polymer chain contains monosubstituted hafnium oxychloride units. The general structural scheme of the oxypolyacrylate complex has the form



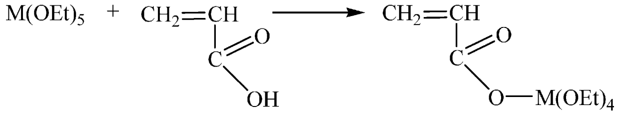
In addition to interchain coordination (A), intramolecular cyclization (B) cannot be ruled out. Moreover, the formation of cross-linked structures may also be contributed by oxobridges with the participation of hafnyl groups, as will be shown below.

Preparation of Ta(Nb)-polymers Through Polymerization of Metal-containing Monomers

Alkoxide metal derivatives with unsaturated ligands are usually synthesized by reacting an unsaturated alcohol with a metal compound via a direct interaction of the alcohol with metal halides, the interaction of alcohol with alkoxymetal halides, substitution of the saturated alkoxy groups by the unsaturated ones, etc..[9] In the first case the reliance is placed on a high reactivity of the M−Cl bond. An ammonium modification of this method consists of a reaction in the presence of NH_3 which binds the liberated HCl. This permits high yields and avoids side reactions. Tantalum (niobium)-monomers were synthesized by transesterification reactions:

$$MCl_5 \xrightarrow[NH_3]{EtOH} M(OEt)_5 + NH_4Cl \qquad (4)$$

$$\begin{aligned} &M(OEt)_5 + R'OH \\ &\quad \rightleftharpoons M(OEt)_4(OR') + EtOH \\ &M = Ta(6);\ Nb(7), \\ &R' = CH_2CH_2OCOC(CH_3) = CH_2 \end{aligned} \qquad (5)$$



$$M(OEt)_5 + CH_2{=}CH{-}C({=}O)OH \longrightarrow CH_2{=}CH{-}C({=}O){-}O{-}M(OEt)_4$$

(6)

The composition and structure of the Ta(Nb)-monomers were determined by elemental analysis and IR- and NMR-spectroscopies (Table 1, Figure 1).

Table 1.
Elemental analysis and IR-spectroscopy data for Ta(Nb)-monomers

MCM	Weight percent (found/calcd)			Frequencies of stretching vibrations in the IR absorption spectra, ν/cm^{-1}			
	M	C	H	C=C	C=O	M−O	CH_2
$Ta(OEt)_4(OCH_2CH_2O\ COC(CH_3) = CH_2)$	36.96/36.93	32.94/34.28	5.58/5.91	1640	1720	560, 652	2968
$Nb(OEt)_4(OCH_2CH_2OCOC(CH_3) = CH_2$	23.0/23.13	41.07/41.79	6.35/7.21	1637	1720	592, 636	2960

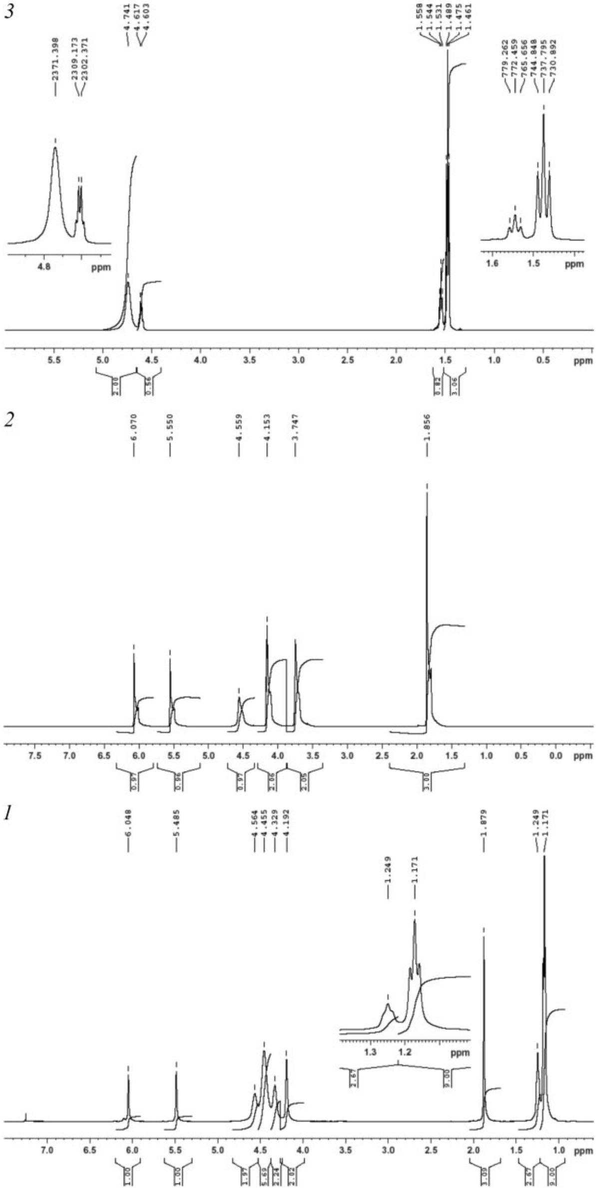


Figure 1.
^{1}H-NMR spectra for Ta(OEt)$_4$(OCH$_2$CH$_2$OCOC(CH$_3$) = CH$_2$) (1), HOCH$_2$CH$_2$OCOC(CH$_3$) = CH$_2$) (2) and Ta(OC$_2$H$_5$)$_5$.

^{1}H NMR spectra of tantalum ethoxide, monomethacrylic ether of ethylene glycol, and Ta(OEt)$_4$(OCH$_2$CH$_2$OCOC(CH$_3$)=CH$_2$) are presented in Figure 1. It is demonstrated that the one $-$OCH$_2$CH$_3$ group in tantalum ethoxide was substituted by OCH$_2$CH$_2$OCOC(CH$_3$)=CH$_2$ because there is no $-$OH signal at 1.9–2.0 ppm in ^{1}H NMR spectrum of Ta(OEt)$_4$(OCH$_2$CH$_2$OCOC(CH$_3$)=CH$_2$). But chemical shifts are appeared which is the existing evidence of =CH$_2$, $-$OCH$_2$ in the Ta-monomer.

The radical polymerization of monomers **6** and **7** in the presence of azo-bis-isobutyronitrile (AIBN) in benzene yields

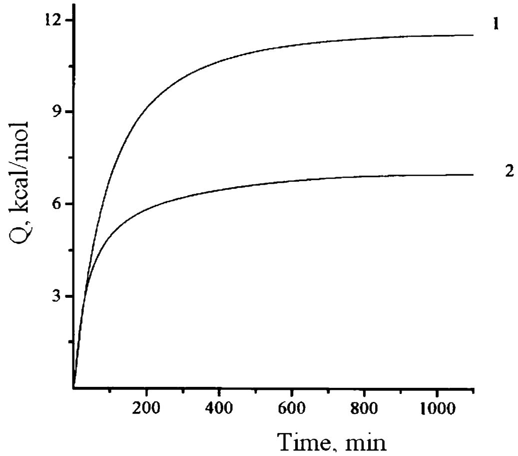
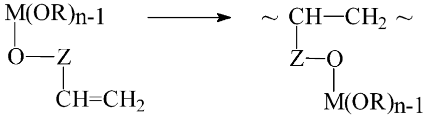


Figure 2.
Kinetics of specific heat evolution during the radical polymerization of $Nb(OEt)_4(OCH_2CH_2OCOC(CH_3) = CH_2)$ (1), $Ta(OEt)_4(OCH_2CH_2OCOC(CH_3) = CH_2)$ (2).

the appropriated metal-containing polymers:



$$\begin{array}{l} M(OR)_{n-1} \\ | \\ O{-}Z \\ \quad | \\ \quad CH{=}CH_2 \end{array} \longrightarrow \begin{array}{l} \sim CH{-}CH_2 \sim \\ \quad | \\ \quad Z{-}O \\ \qquad | \\ \qquad M(OR)_{n-1} \end{array} \tag{7}$$

The yield of polymer products is equal to 45–56 wt. %. According to elemental analysis the metal content corresponds to the calculated one and is equal to 23.0 wt. % (Nb) or 35.1 wt.% (Ta). As shown in Figure 2, the rate of the radical polymerization of Ta(V) and Nb(V) alkoxides with unsaturated ligand $-OCH_2CH_2OCOC(CH_3){=}CH_2$ depends on the metal ion nature.

The kinetic peculiarities and mechanism of the radical polymerization of these metal-containing monomers as well as the properties of polymers obtained will be studied in future.

Thermal Transformations of Metal-Containing Precursors

The solid-state thermolysis under consideration can be initiated by reactions taking place around structural inhomogeneities (point defects, dislocations, cracks, vacancies, and others) and propagating to structurally homogeneous regions. From this viewpoint, solid-state polymerization initiates thermal decomposition of the metal-containing polymer, which is a product common to these coupled processes. Polymer-mediated synthesis plays a key role in the formation of nanoparticles: impregnation processes lead to severe aggregation of metal-containing particles during thermolysis.

It should be mentioned that such kinetic behavior of gas evolution is typical for multistage successive reactions which are the first order ones with decreasing rate constants for the each subsequent stage. At a given conversion time, increasing the thermolysis temperature increases the total gas volume evolved and, accordingly, the weight loss. The slope of the gas release and weight loss curves is a nonlinear function of time, which indicates that the contribution of the pyrolysis of the volatile reaction products increases with temperature. The net weight loss is, as a rule, lower than would be expected for decomposition of the polymers to HfO_2 or HfC (%):37.4 (43.4) for **1**, 31.8 (38.3) for **3**, and 53.3 (57.7) for **4** (Figure 3).

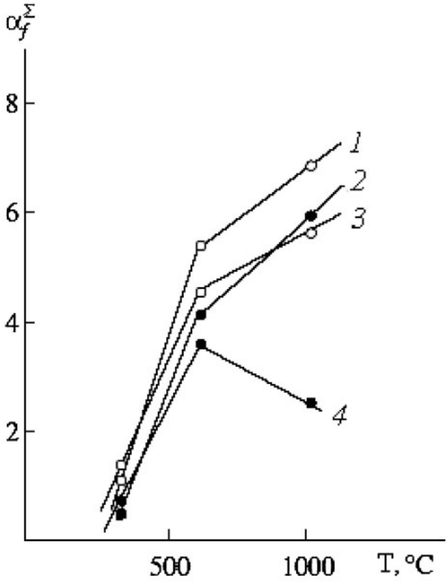


Figure 3.
Yield of thermolysis products as a function of temperature for hafnium-containing precursors: (*1*) 5, (*2*) 1, (*3*) 4, (*4*) 3.

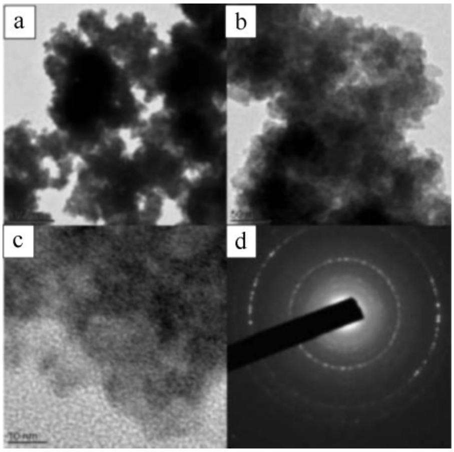


Figure 4.
Morphology and microstructure of Ta-containing nanoparticles according to the electron diffraction and TEM.

Composition of Solid Pyrolysis Products of Hf (Ta, Nb)-containing Polymers

Optical examination of 370 °C thermolysis products indicates that all of the powders are close in morphology and consist of irregularly shaped particles containing opaque inclusions. At 600 and 1000 °C we obtained opaque, coke-like substances. The solid thermolysis products were also characterized by X-ray diffraction (Table 2).

All of the 300 °C thermolysis products, except sample **3**, were amorphous. Sample **3** consisted of an amorphous phase and crystalline HfO_2. The solid product of the 600 °C thermolysis of **1** consisted of well-crystallized *m*- HfO_2 (monoclinic) and trace amounts of HfC with different degrees of crystallinity (sample **1** after thermolysis consisted of a mixture of *m*-HfO_2 and *t*-HfO_2). The product of the 600 °C thermolysis of **4** was amorphous. In the case of **3** (hafnyl fumarate), the solid phase consisted of HfC and trace levels of HfO_2.

One possible reason is the formation of ordered HfC_y phases. It should also be taken into account that the pyrolysis of organic ligands may lead to the formation of carbon (graphitization). This seems to be evidenced by the diffraction peaks close in position to those from hexagonal carbon (*h*-C): 3.36 (100), 2.03 (50), 1.67 (80), 1.16 (50), 0.99 (40), and 0.83 Å (40). For **3**, the

Table 2.
Effect of thermolysis temperature on the phase composition of solid thermolysis products.

	Phase composition		
	370 °C	600 °C	1000 °C
1	Amorphous	$m{-}HfO_2 + t{-}HfO_2 + HfC^*$	$m{-}HfO_2 + t{-}HfO_2 +$ HfC^*
3	Amorphous + $t{-}HfO_2 + HfC^*$	Amorphous + HfC + $t{-}HfO_2^*$	$m{-}HfO_2 + HfC^*$
4	Amorphous	Amorphous	$m{-}HfO_2 + t{-}HfO_2 +$ HfC^*
5	Amorphous	Amorphous	$m{-}HfO_2 + t{-}HfO_2 +$ HfC^*

Note: *m* and *t* denote monoclinic and tetragonal phases, respectively.* Heavily disordered phase.

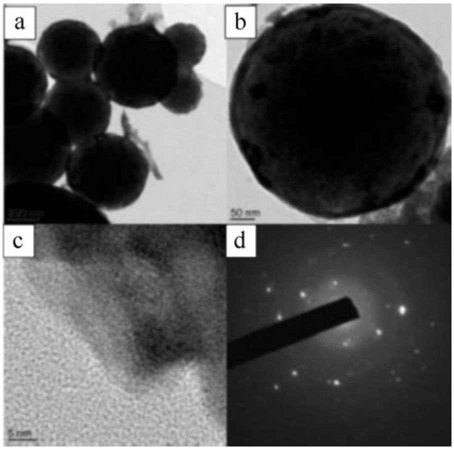


Figure 5.
Morphology and microstructure of Nb- containing nanoparticles according to the electron diffraction and TEM.

percentage of HfC decreases with increasing temperature, and the sample consists of a mixture of m HfO_2 and trace levels of HfC. According to electron-microscopic examination, the powder particles had irregular shapes and were mostly agglomerated. The structure of specimen was mostly amorphous however HRTEM studies revealed presence of nanocrystallites (Figures 4 and 5).

The size of the crystallites was about a 3–10 nm. Furthermore the presence of nanocrystallites was confirmed by electron diffraction.

Conclusion

Polymers containing Hf(Ta, Nb) can be prepared by any of the known processes for synthesis of metal-containing polymers. An attractive approach is polymerization of the Hf(Ta, Nb) monomers with (meth)acrylate and fumarate groups, synthesized for the first time in this study. We investigated the thermolysis of the synthesized organometal polymers in a self-generated atmosphere between 300 and 1000 °C and determined the compositions of the gas and solid phases that were formed in the static nonisothermal system. This analysis, in conjunction with x-ray diffraction results, indicates that pyrolysis leads to the formation of metal–polymer nanocomposites consisting of crystalline Hf(Ta, Nb)-containing nanoparticles stabilized by the polymer matrix.

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