DOI: 10.1002/ejic.200701348

The Polymerization of Tetrahydrofuran Initiated by Niobium(V) and Tantalum(V) Halides

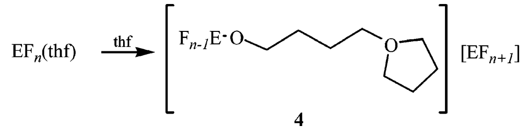
Fabio Marchetti,[a][‡] Guido Pampaloni,*[a] and Timo Repo[b]

Keywords: Niobium / Tantalum / Halides / Poly(tetrahydrofuran) / Polymerization

The halides MX_5 (M = Nb, Ta, X = F, Cl, Br) (**1**) are effective in promoting the polymerization of tetrahydrofuran (thf). The polymerization reactions promoted by MCl_5 and MBr_5 proceed via the ionic species **3**, which forms from MX_5(thf) (**2**) by attack of the incoming monomer to the metal-bonded thf. The metal-bonded thf of **3** is not involved in the immediately successive steps of the reaction. The $[TaF_6]^-$ anion is not formed when the polymerization is initiated by TaF_5. The activities of the promoters increase according to the series $TaBr_5 < NbCl_5 < TaCl_5 < TaF_5$. The latter possesses high activity and produces high molar mass poly(tetrahydrofuran) (67100 g/mol).

Introduction

The ring-opening polymerization of various oxygenated heterocycles may be induced by Lewis acids, for which the chain-propagation mechanism via trialkyloxonium ion intermediates has been suggested.[1] As far as the polymerization of tetrahydrofuran (thf) is concerned, halides such as the chlorides of aluminum, tin(IV), antimony(V), and iron(III), as well as BF_3 and PF_5 have been tested as catalytic precursors.[2] From the series of Lewis acids only PF_5 activates thf in the absence of promoters such as alkylene oxides, α-halo ethers, or acyl chlorides.[3] As it has been accepted that the intermediates in the initial stages of the thf polymerization catalyzed by halides of main-group elements are ionic compounds such as **4** (see Scheme 1),[3] the high stability of the $[PF_6]^-$ anion is considered as the driving force of the initiation of the polymerization.

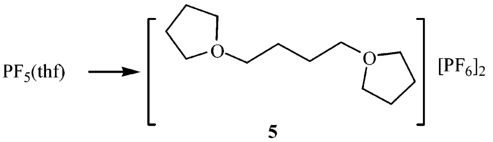


4

E = B, n = 3; E = P, n = 5

Scheme 1. Formation of ionic intermediates in the polymerization of thf induced by BF_3 or PF_5.

As a confirmation of the existence of ionic intermediates, compound **5** was isolated from the reaction of PF_5 with thf in 1,2-dichloroethane[3] [Equation (1)].



5 (1)

Noteworthy is the fact that the halides of the transition metals have received only little attention: short communications on the activities of $NbCl_5$, $TaCl_5$, and WCl_6 as catalysts of thf polymerization appeared some decades ago, but the mechanism was not discussed.[4]

In the framework of our studies on the reactivity of the metal pentahalides MX_5,[5] with oxygen donor ligands,[6] we recently reported the adducts MX_5(thf) [M = Nb, X = Cl; M = Ta, X = F, Cl, Br (**2a**–**e**) and M = Nb, X = Cl, Br; M = Ta, X = Cl, Br, I (**3a**–**f**)], obtained by reactions of MX_5 with limited amounts of thf.

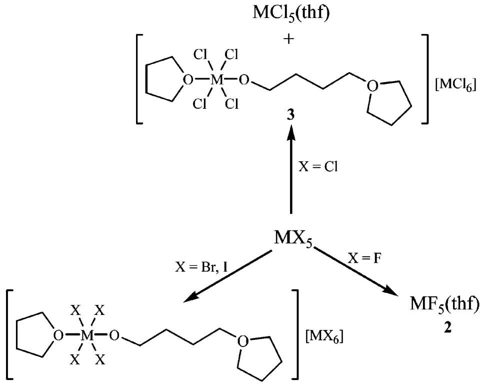
The outcomes of the reactions summarized in Scheme 2 depend strongly on the nature of the halide: the tendency for the formation of the ionic adducts of type **3** increases clearly along the series F << Cl < Br, I. This trend has been correlated to the metal–halide bond energy,[6b] which decreases on increasing the atomic weight of the halide.[7] Since the formation of compounds **3** requires halide migration from one metal centre to another, this step is kinetically favoured for the heaviest halides.

On the basis of the reactivity of **2** and **3** towards additional thf, the hypothesis was formulated[6b] that complexes **2** and **3** are intermediates during the course of the thf polymerization initiated by the respective parent halides **1**, and that the formation of **2** and **3** takes place stepwise at

---

[a] Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35, 56126 Pisa, Italy
Fax: +39-050-2219-246
E-mail: pampa@dcci.unipi.it
[b] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki
P. O. Box 55, 00014 Helsinki, Finland

[‡] Born in Bologna (Italy) in 1974



M	X	M/thf ratio		M/thf ratio	
Nb	Cl	2:1	**2a**	2:3	**3a**
Nb	Br	–		2:3	**3b**
Ta	F	1:1	**2c**		
Ta	Cl	2:1	**2d**	2:3	**3d**
Ta	Br	4:1	**2e**	2:3	**3e**
Ta	I	–		2:3	**3f**

Scheme 2. Reactivity of MX_5 (**1**) with limited amounts of thf.

the early stages of the process. The fact that a fluorinated species of type **3** was not isolated suggests that the polymerization of thf induced by TaF_5 may proceed by alternative pathways. In order to investigate this point, an NMR study of the polymerization reaction initiated by TaF_5 was undertaken.

On the other hand, the isolation of **3** opens a new theme of discussion about the initial steps of the polymerization promoted by MX_5 (X = Cl, Br, I), because compound **3** contains an intact, metal-bonded, thf molecule. Therefore, two potential routes may be outlined for the formation of **3** from **2**:

(1) The incoming thf attacks the thf ligand of **2** resulting in C–O bond formation.

(2) The incoming thf coordinates the metal centre of **2** and is not involved in the formation of the new C–O bond.

A possible mechanism regarding the formation of **3** has been based on NMR investigations and will be presented herein.

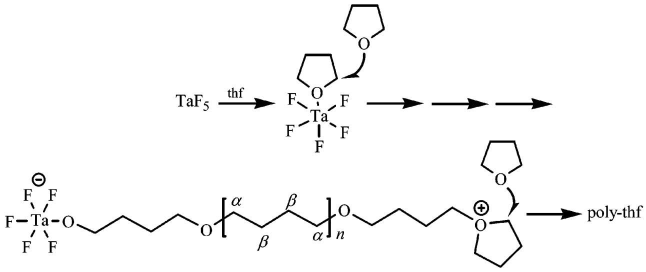
Finally, the possibility that the polymerization of tetrahydrofuran promoted by MX_5 proceeds according to different pathways depending on the halide, and that the nature of the initiator itself may influence the properties of the polymer, prompted us to carry out the polymerization reactions in the presence of TaF_5, $TaCl_5$, $NbCl_5$, or $TaBr_5$.

Results and Discussion

1. NMR Studies on the Reaction of TaF_5 with Large Amounts of thf

In order to understand whether the polymerization of tetrahydrofuran promoted by TaF_5 takes place through the formation of ionic species or not, we monitored the reaction of TaF_5 with a large excess (ca. 18 equiv.) of thf, in CD_2Cl_2 solution by NMR spectroscopy (^1H, ^{13}C, and ^{19}F; see Experimental Section).

The ^1H NMR spectrum after 20 min presents two broad multiplets centred at δ = 3.65 and 1.73 ppm, beside signals of some unreacted thf, and minor resonances at δ = 4.64, 2.26, and 2.04 ppm. The major peaks (δ = 3.65, 1.73 ppm) are attributable to the α-CH_2 and β-CH_2 protons, respectively, within the central portion of the polymeric chain (vide infra) (α- and β-positions with respect to the oxygen atoms; see Scheme 3). These ^1H NMR signals find correspondence in the ^{13}C NMR resonances observed at δ = 70.7 (α-C) and 27.3 (β-C) ppm.



Scheme 3. Possible mechanism for the polymerization of thf initiated by TaF_5.

The ^{19}F NMR spectrum recorded 1 min after mixing the reagents shows the resonances due to **2c**.[6b] After 20 min, the solution had darkened, and the ^{19}F NMR spectrum exhibits two broad resonances at δ = 81.0 and 39.7 ppm, typical[6c] of $TaF_5(O)$ species (*O* = oxygen donor ligand), together with minor signals at δ = 72.1, 58.9, 51.8, 45.3, and 42.4 ppm (Figure 1). Similar features are displayed in the ^{19}F NMR spectrum (in [D8]thf solution) recorded 20 min after the addition of TaF_5.

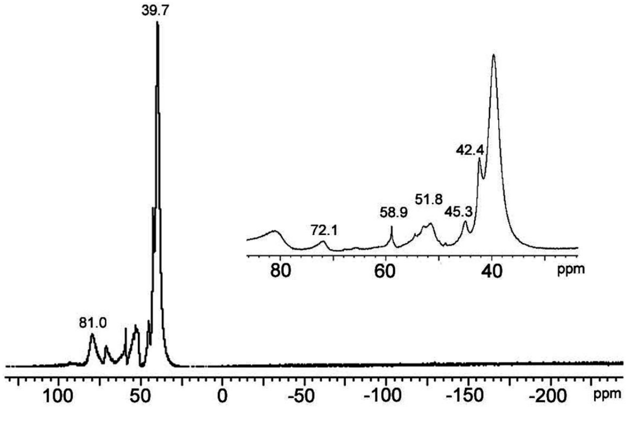


Figure 1. Reaction of TaF_5 and thf in CD_2Cl_2. ^{19}F NMR spectrum of the reaction mixture 20 min after mixing of the reagents.

The complete absence of peaks occurring at negative chemical shifts in the ^{19}F NMR spectra is particularly meaningful; it indicates that no $[TaF_6]^-$ anion[6c] is present in the reaction medium at any stage. In other words, the polymerization reaction mediated by TaF_5 seems to take place without the occurrence of halide migration and formation of ionic species in contrast to what was found for the other tantalum (niobium) halides.

2. NMR Studies on the Transformation of 2 → 3

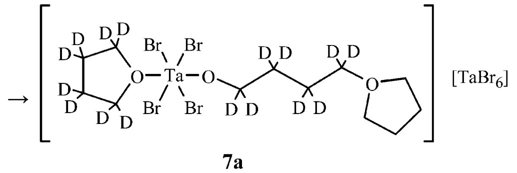
The NMR characterization[6b] of the ionic complex **3e** was supported by gs-HSQC and gs-HMBC experiments,[8] and the NMR characterizations of the analogous compounds were established by means of the experiments carried out on **3e**. We reported that the ^{1}H NMR spectrum of **3e** (in CD_2Cl_2 solution) exhibits a series of multiplet resonances which were attributed to 12 α-methylene protons (multiplets centred at δ = 5.51, 4.93, 3.50 ppm) and to 12 β-methylene protons (δ = 2.20, 1.93, 1.69 ppm), respectively.[6b] A more detailed reading of the gs-HMBC spectrum has established that the resonance at δ = 5.51 ppm is related to the intact thf ring coordinated to the tantalum centre (see Scheme 2). Actually, only one HMBC correlation for the α-CH_2 protons of this thf ligand may be predicted on the basis of the molecular structure. Indeed, the only correlation found for the ^{1}H NMR resonance at δ = 5.51 ppm is with a ^{13}C peak at δ = 31.4 ppm, ascribed to the β-methylene units of the same ring. The broad ^{1}H resonance at δ = 4.93 ppm correlates with three high-field ^{13}C signals at δ = 29.3, 28.6, and 26.4 ppm and has been assigned to the two CH_2 units placed in α-position with respect to the oxonium moiety. This latter attribution is in accordance with NMR spectroscopic data available in the literature and regarding oxonium units of living poly-thf species.[9]

In order to determine the sequence according to which three thf molecules combine to give **3e**, we first decided to prepare the complex $TaBr_5$(tdf) (tdf = [D_8]thf) (**6b**), which is the analogous deuterated form of **2e** [see Equation (2)].

$TaBr_5$ + tdf → $TaBr_5$(tdf)
6b (2)

When complex **6b** is treated with 0.5 equiv. of thf, **7a**, the analogous partially deuterated form of **3e**, is obtained [Equation (3)].

2 $TaBr_5$(tdf) + thf →



7a

(3)

The structure of compound **7a** was established by ^{1}H NMR spectroscopy and confirmed by elemental analysis for Ta and Br. The ^{1}H NMR spectrum displays resonances centred at δ = 4.90 and 2.20 ppm. The absence of the multiplet attributable to a thf ligand (δ = 5.51 ppm; see above and Figure 2) is in fact consistent with hypothesis (1) noted in the Introduction. The fact that such a multiplet is not seen even in the presence of a large excess of thf in solution (see Figure 2) suggests that no exchange occurs between free and coordinated thf, at least during the first stages of the reaction.

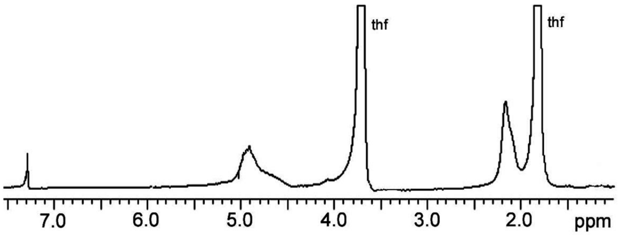
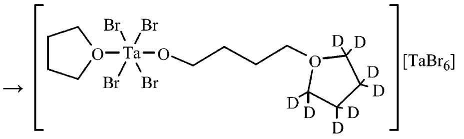


Figure 2. Reaction of $TaBr_5$(tdf) and thf. ^{1}H NMR spectrum of the reaction mixture 10 min after mixing of the reagents.

Afterwards, from the reaction of $TaBr_5$(thf) (**2e**) with 0.5 equiv. of tdf [Equation (4)], compound **7b** was isolated and characterized by ^{1}H NMR spectroscopy and elemental analyses. The ^{1}H NMR spectrum consists of large multiplets centred at δ = 5.50, 4.88, 3.50, 2.20, 1.90, and 1.69 ppm (Figure 3). The ^{1}H NMR features related to **7b**, combined with those of **7a**, show that the formation of the ionic compound occurs by attack of external thf on the metal-coordinated form.

2 $TaBr_5$(thf) + tdf →



7b

(4)

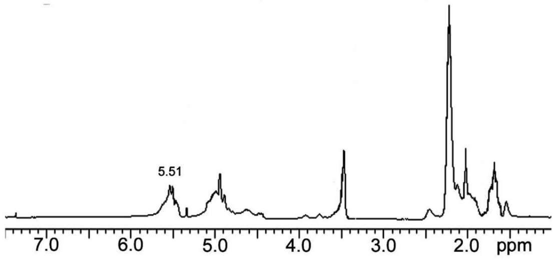
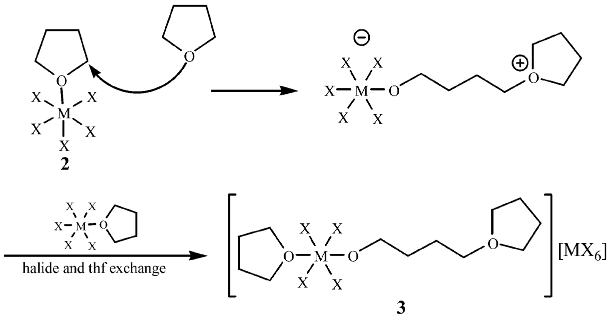


Figure 3. Reaction of $TaBr_5$(thf) and tdf. ^{1}H NMR spectrum of the reaction mixture 10 min after mixing of the reagents.

Similar investigations were carried out on the chloride derivative $TaCl_5$(tdf) (**6a**), but the resulting products could not be characterized unequivocally, due to the fact that complex **3d** is always formed in the presence of significant amounts of **2d**.[6b] However, it is noteworthy that the NMR spectrum recorded for the mixture obtained by treating **6a** with thf did not present signals in the region at $\delta \approx$ 5.45 ppm.[6b] On the other hand, a broad resonance at δ = 5.45 ppm was detected in the mixture derived from the reaction of $TaCl_5$(thf) (**2d**) with tdf. In other words, although the NMR investigations performed on the chlorinated adduct **2d** and on its deuterated counterpart **6a** were not exhaustive, they pointed to the same conclusions as the NMR studies on the brominated analogues.

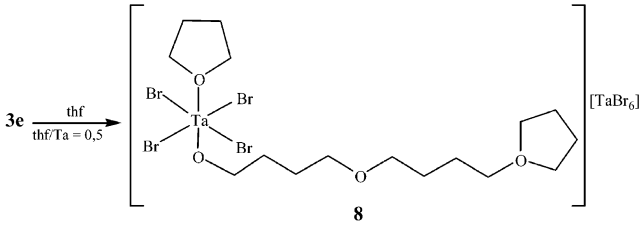
According to the NMR evidence, the formation of complexes of type **3** should occur by attack of uncoordinated thf on the metal-coordinated thf ring of **2**, followed by ligand exchange involving a halide and the thf of a second MX_5(thf) unit, in agreement with hypothesis (1) of the Introduction (see Scheme 4).



M = Nb, X = Cl; M = Ta, X = Cl, Br

Scheme 4. Possible mechanism for the formation of **3** from **2** and thf.

The possibility that adducts of type $[MX_4(thf)_2][MX_6]$ form before the addition of further thf should be excluded on the basis of the fact that heating of solutions of complexes TaX_5(thf) [X = Cl (**2d**), Br (**2e**)] in $CDCl_3$ at reflux temperature for 30 min did not result in any change of the IR and ^1H NMR spectra of the compounds (a low-field shift of the signal of the α-CH_2 protons of coordinated thf due to the formation of a cationic species would be expected). This point indicates that the halide migration process requires the addition of further thf to take place. Hence, in order to obtain information on the mechanism of the following steps of the polymerization process, we treated compounds **3** with further amounts of thf. However, the reactions of **3a**,**d** with thf afforded complicated mixtures of products, for which NMR characterization was made difficult by their low solubility. On the other hand, we were able to isolate and characterize a product from the reaction of the bromo species **3e** with thf, with a thf/Ta molar ratio of 1:2. This product was identified as compound **8** by means of IR and NMR spectroscopy and elemental analyses (see Scheme 5).



Scheme 5. Synthesis of compound **8**.

A major spectroscopic feature related to **8** is given by the ^1H NMR resonance at δ = 5.58 ppm, attributed to the thf ligand. Further resonances due to α-CH_2 protons appear as broad multiplets at δ = 5.00 and 3.59 ppm, whereas the signals awarded to the β-CH_2 protons are seen at δ = 2.23, 1.95, and 1.76 ppm. On the basis of the isolation of **8**, it is reasonable to assume that the polymerization steps, immediately following the formation of **3**, proceed by sequential attacks of the incoming monomer to the oxonium unit. In other words, the thf ligand, as it is present in **3**, seems not to be involved in the formation of a polymer chain.

As ring-opening polymerizations of thf promoted by both TaF_5 and MX_5 (M = Nb, Ta, X = Cl, Br) proceed via oxonium ions, the metal halides can be considered here as initiators rather than true catalytic centres.

3. Polymerization of thf

The polymerization of thf by $TaCl_5$ and $NbCl_5$ was presented over 40 years ago,[4a] and data concerning yields and reduced viscosities were reported and compared with those obtained by using WCl_6 as the catalyst.[4b] In agreement with these data, both the yields and the viscosities associated with the polymers decreased depending on the catalyst used, according to the series $WCl_6 > TaCl_5 > NbCl_5$. We performed the polymerization of thf by using TaF_5, $TaCl_5$, $NbCl_5$, or $TaBr_5$. In every case, the metal halides were used in a 0.25% molar ratio with respect to thf, in agreement with the experiments reported in the literature.[4a] The reactions were carried out at ambient temperature and prolonged for 15 d, in order to let the processes reach the respective equilibria (Table 1). The resulting polymeric materials were identified as poly(tetrahydrofuran) by IR[2b] and NMR[9] analyses.

Table 1. Selected results for the polymerization of thf, promoted by niobium and tantalum halides.[a]

Initiator	Time	Conversion [%]	M_n [g/mol]	M_w [g/mol]	M_w/M_n
TaF_5	15 d	66	2370	32500	13.68
$TaCl_5$	15 d	54	2380	4350	1.83
$NbCl_5$	15 d	40	5190	12700	2.44
$TaBr_5$	15 d	25	470	780	1.65
TaF_5	1 h	16	40100	67100	1.67
TaF_5	3 h	36	35300	64500	1.83

[a] Reaction conditions: Bulk polymerization, MX_5/thf molar ratio 0.0025, T = 298 K.

According to the polymerization results, the activity of the tantalum halides increases in the order $TaBr_5 < TaCl_5 < TaF_5$, with $NbCl_5$ having a somewhat lower activity than its tantalum analogue. In addition to the polymerization activity, the nature of the halide also has a marked influence on the mean degree of polymerization; whereas $TaBr_5$ and $TaCl_5$ produce only oligomeric products, TaF_5 yields polymers with significantly higher molar mass (M_w = 32500 g/mol). It is also worth noting that $NbCl_5$ provides polymers with a three-times higher molar mass than $TaCl_5$.

The data reported in Table 1 indicate that, although the reactions initiated by $TaBr_5$ and $TaCl_5$ proceed via cationic adducts (see Scheme 4), these latter have minor activities in polymerization, with respect to the zwitterionic F-containing compounds (see Scheme 3). In addition, in spite of the fact that the polymerization processes operated by $TaBr_5$ and $TaCl_5$ require halide migration at a very early stage, and that this migration seems to be kinetically favoured by a decrease of the metal–halide bond energy, $TaCl_5$ exhibits greater activity than $TaBr_5$. The conclusion can be drawn that the polarization of the M–X bond, rather than the neat charge of the propagating species or the M–X bond energy, plays a key role in determining the nature of the polymeric material.

In the case of TaF_5, the ring-opening polymerization of thf appeared to be very fast indeed, the thf conversion being 16% and 36% after 1 and 3 h, respectively. In both cases similar polymers with high molar mass are obtained, thus excluding the possibility for living polymerization.

The high reactivity of TaF_5 is also reflected in the polydispersity values (PDI). While $TaBr_5$ and $TaCl_5$ provide oligomer/polymer with a small PDI value (<2) even after extended reaction time, TaF_5 is susceptible to initiation of side reactions, and thus under similar reaction conditions polymers with significantly larger PDI values (13.68) are obtained. Further comparison of TaF_5-initiated polymerizations supported the presence of side reactions leading to the chain scission, and thus broadening of the PDI values. The short polymerization times provide poly(tetrahydrofuran) with a narrow PDI and a molar mass almost twice as high as those received after prolonged polymerization times.

Conclusions

In this paper the polymerization of thf promoted by group 5 metal halides MX_5 has been studied. NMR experiments have outlined that the polymerization initiated by TaF_5 involves zwitterionic species in which the growing chain holding the oxonium moiety is bonded to a $\{TaF_5\}$ unit. In contrast, the polymerization initiated by $NbCl_5$, $TaCl_5$, and $TaBr_5$ proceeds with halide migration and formation of the ionic species **3**. The latter results from attack of a thf molecule on the metal-bonded thf of MX_5(thf), causing ring opening and formation of a C–O bond. The isolation and characterization of the longer-chain intermediate **8** suggests that the thf ligand of **3** is not involved in the polymerization, at least in the first stages of the process.

Polymerization experiments under similar experimental conditions revealed that the activities of the metal halides increase according to the series Br < Cl < F and Nb < Ta. Furthermore, the molecular weights of the resulting polymers increase along the series Br < Cl < F, and with TaF_5 a high molar mass poly(tetrahydrofuran) (67100 g/mol) can be prepared. These evidences point out that the polarization of the M–X bond, rather than other factors, determine the properties of the polymer.

Experimental Section

General Considerations: All manipulations of air- and/or moisture-sensitive compounds were performed under pre-purified argon using standard Schlenk techniques. The reaction vessels were oven-dried at 150 °C prior to use, evacuated (10^{-2} Torr) and then filled with argon. $TaCl_5$ was purchased from Fluka, while $TaBr_5$,[10] $TaCl_5$(thf),[6a] and $TaBr_5$(thf)[6a] were prepared according to published procedures. Solvents and liquid reagents were distilled before use under argon from appropriate drying agents: CH_2Cl_2, CD_2Cl_2, and $CDCl_3$ from P_4O_{10}, thf and [D_8]thf (tdf) from Na/benzophenone. Infrared spectra were recorded at 298 K with an FT IR-Perkin–Elmer spectrometer equipped with a UATR sampling accessory (solid samples). NMR measurements were performed at 298 K with a Varian Gemini 200BB spectrometer. The chemical shifts for ^1H and ^{13}C NMR spectroscopy were referenced to internal TMS. The chemical shifts for ^{19}F NMR spectroscopy were referenced to $CFCl_3$. Carbon and hydrogen analyses were performed at the Dipartimento di Chimica Farmaceutica of the University of Pisa with a Carlo Erba model 1106 instrument, paying particular attention to the more sensitive compounds which were weighed and directly introduced into the analyzer. The halide content was determined by the Volhardt method[11] after exhaustive hydrolysis of the sample. Tantalum was analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The halide and the metal analyses were repeated twice to their reproducibility. Gel permeation chromatography (GPC) was performed with a Waters instrument equipped with a Styragel guard column, 7.8 × 300 mm, Styragel capillary columns, and Viskotek 270 Dual Detector, connected with Waters 2487 UV and Waters 2410 RI detectors; thf was used as an eluent with a flow rate of 0.8 mL/min. The calibrations were performed with polystyrene standards from Polymer Standards Service GmbH.

Reactions of TaF_5 with Large Amounts of thf: (a) TaF_5 (75 mg, 0.27 mmol) was introduced into an NMR tube as a suspension in CD_2Cl_2 (0.5 mL), then thf (0.40 mL, 4.9 mmol) was added. Dissolution of TaF_5 occurred rapidly, and the ^{19}F NMR spectrum recorded after 1 min displayed two peaks at δ = 80.5 and 39.1 ppm, attributed to TaF_5(thf) (**2c**).[6b] NMR spectra of the darkened solution after 20 min: ^1H NMR (200 MHz, CD_2Cl_2): δ = 4.64, 3.65 (br. m, major, α-CH_2), 2.26, 2.04, 1.73 (br. m, major, β-CH_2) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2): δ = 74.4, 73.0, 72.3, 70.7 (major, α-CH_2), 69.1, 66.9, 55.8, 55.3, 54.8, 54.0, 30.0, 27.3 (major, β-CH_2), 24.9 ppm. ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ = 81.0 (br., major, *trans*-F), 72.1, 58.9, 51.8, 45.3, 42.4, 39.7 (br., major, *cis*-F) ppm. **(b)** TaF_5 (75 mg, 0.27 mol) was completely dissolved in [D_8]thf (0.7 mL) in an NMR tube. ^{19}F NMR spectrum of the solution after 20 min: δ = 81.6 (br., major, *trans*-F), 74.3, 54.3, 46.8, 43.3, 41.1 (br., major, *cis*-F) ppm. 10 min after the recording of this spectrum, the content of the NMR tube was too viscous to run further NMR experiments.

Preparation of TaX_5(tdf) [X = Cl (6a), Br (6b)]: [D_8]thf (0.025 mL, 0.28 mmol) was added to a suspension of $TaCl_5$ (0.190 g, 0.530 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 h, then it was filtered to remove unreacted $TaCl_5$. Removal of the solvent gave a colourless microcrystalline solid corresponding to $TaCl_5$(tdf) (**6a**). Yield: 0.106 g, 86%. $C_4Cl_5D_8OTa$ (438.4): calcd. Cl 40.4, Ta 41.3; found Cl 39.8, Ta 41.0. $TaBr_5$(tdf) (**6b**), yellow microcrystalline solid, from [D_8]thf (0.040 mL, 0.44 mmol) and $TaBr_5$ (1.50 g, 2.58 mmol). Yield: 0.256 g, 88%. $C_4Br_5D_8OTa$ (660.6): calcd. Br 60.5, Ta 27.4; found Br 60.0, Ta 27.1.

Reactions of TaX_5(tdf) with thf: Compound **6b** (0.190 mg, 0.288 mmol) was dissolved in CH_2Cl_2 and treated with thf

(0.012 mL, 0.15 mmol). The resulting solution was stirred for 30 min, then the solvent was removed to afford **7a** as a yellow microcrystalline solid. Yield: 0.173 mg, 86%. $C_{12}H_8Br_{10}D_{16}O_3Ta_2$ (1393.3): calcd. Br 57.3, Ta 26.0; found Br 56.9, Ta 25.6. ^1H NMR (200 MHz, $CDCl_3$): δ = 4.90 (m, 4 H, α-CH_2), 2.20 (m, 4 H, β-CH_2) ppm. The reaction of **6a** with thf was performed according to a procedure analogous to that described for **6b**. Clear characterization of the resulting product was not possible; however, the ^1H NMR spectrum (in $CDCl_3$ solution) did not show signals in the range δ = 5.20–5.70 ppm.

Reactions of TaX_5(thf) with tdf: Compound **2e** (0.220 g, 0.337 mmol) was dissolved in CH_2Cl_2 and treated with [D_8]thf (0.015 mL, 0.16 mmol). The resulting solution was stirred for 30 min, then the solvent was removed to afford **7b** as a yellow microcrystalline solid. Yield: 0.198 g, 89%. $C_{12}H_{16}Br_{10}D_8O_3Ta_2$ (1385.3): calcd. Br 57.7, Ta 26.1; found Br 57.2, Ta 25.9. ^1H NMR (200 MHz, $CDCl_3$): δ = 5.50 (m, 4 H, α-CH_2), 4.88 (m, 2 H, α-CH_2), 3.50 (m, 2 H, α-CH_2), 2.20, 1.90, 1.69 (m, 8 H, β-CH_2) ppm. The reaction of **2d** with tdf was performed according to a procedure analogous to that described for the preparation of **7b**. Clear characterization of the resulting product was not possible; however, the ^1H NMR spectrum ($CDCl_3$ solution) revealed a broad resonance centred at δ = 5.45 ppm.

Preparation of Compound 8: A solution of **3e** (0.420 g, 0.305 mmol) in dichloromethane (25 mL) was treated with thf (0.013 mL, 0.160 mmol), and the resulting mixture was stirred for 30 min. Then, the solvent was removed, and complex **8** was obtained as a yellow solid. Yield: 0.354 g, 80%. $C_{16}H_{32}Br_{10}O_4Ta_2$ (1449.3): calcd. C 13.3, H 2.2, Br 55.1, Ta 25.0; found C 13.0, H 2.0, Br 54.3, Ta 24.7. IR (solid): $\tilde{\nu}$ = 2955 (m), 2875 (w), 1592 (m), 1446 (wm), 1345 (w), 1259 (m), 1085 (s), 1042 (m), 994 (ms), 953 (m), 797 (vs) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ = 5.58 (m, 4 H, α-CH_2-thf ring), 5.00, 3.59 (m, 12 H, α-CH_2), 2.23 (m, 8 H, β-CH_2), 1.95, 1.76 (br. m, 8 H, β-CH_2, thf and oxonium rings) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 82.0, 81.2, 80.2, 79.8, 79.4, 70.5 (α-CH_2), 33.2, 30.0, 29.4, 28.5, 27.5, 26.3 (β-CH_2) ppm.

Synthesis of Poly(tetrahydrofuran) – General Procedure: MX_5 was added to thf (MX_5/thf molar ratio 0.0025), and the resulting mixture was stirred for a variable time, during which a progressive increase of the viscosity was noticed. The residual solvent was removed, and the crude polymer was dissolved in thf/water (10:1). A colourless material was obtained upon removal of the solvent in vacuo. IR (solid): $\tilde{\nu}$ = 2941 (m), 2862 (s), 2802 (wm), 1491 (w), 1474 (w), 1459 (w), 1372 (m), 1251 (w), 1209 (w), 1111 (vs), 996 (s), 806 (w), 745 (w) cm^{-1}. ^1H NMR (200 MHz, [D_8]thf): δ = 3.53 (m, $C_\alpha H_2$), 1.73 (m, $C_\beta H_2$) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_8]thf): δ = 71.3 (C_α), 27.2 (C_β) ppm. **(a) TaF_5 as Initiator:** (1) thf (21.2 mL) added to TaF_5 (0.180 g, 0.652 mmol), time 15 d, yield 66%. (2) thf (5.3 mL) added to TaF_5 (0.045 g, 0.163 mmol), time 1 h, yield 16%. (3) thf (7.6 mL) added to TaF_5 (0.065 g, 0.236 mmol), time 3 h, yield 36%. **(b) $TaCl_5$ as Initiator:** thf (20.8 mL) added to $TaCl_5$ (0.230 g, 0.642 mmol), time 15 d, yield 10.0 g, 54%. **(c) $NbCl_5$ as Initiator:** thf (15.6 mL) added to $NbCl_5$ (0.130 g, 0.481 mmol), time 15 d, yield 5.5 g, 40%. **(d) $TaBr_5$ as Initiator:** thf (9.2 mL) added to $TaBr_5$ (0.165 g, 0.284 mmol), time 15 d, yield: 2.0 g, 25%.

Acknowledgments

The authors wish to thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Roma), Programma di Ricerca Scientifica di Notevole Interesse Nazionale 2004-5, and the Academy of Finland (project no: 77317) for financial support. Ms. Eeva Kaija is acknowledged for the GPC measurements.

---

[1] S. Penczek, P. Kubisa, K. Matyjaszewski, *Adv. Polym. Sci.* **1980**, *37*, 1–141.

[2] a) H. Meerwein, D. Delfs, H. Morschel, *Angew. Chem.* **1960**, *72*, 927–1006; b) P. Dreyfuss, M. P. Dreyfuss, *Adv. Polym. Sci.* **1967**, *4*, 528–590, and references therein.

[3] R. Hoene, K.-H. W. Reichert, *Makromol. Chem.* **1976**, *177*, 3545–3570, and reference therein.

[4] a) Y. Takegami, T. Ueno, R. Hirai, *J. Polym. Sci. A1, Polym. Chem.* **1966**, *4*, 973–974; b) Y. Takegami, T. Ueno, R. Hirai, *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1222.

[5] The fluorides of niobium(V) and tantalum(V) have tetranuclear structures in the solid state, while the corresponding heavier halides are dinuclear in the solid state and mononuclear in the vapour phase: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Clarendon Press, Oxford, **1993**. For the sake of simplicity, in this paper the general formula MX_5, when dealing with the niobium(V) and tantalum(V) halides, will be used.

[6] a) F. Marchetti, G. Pampaloni, S. Zacchini, *Dalton Trans.* **2007**, 4343–4351; b) F. Marchetti, G. Pampaloni, S. Zacchini, *Inorg. Chem.* **2008**, *47*, 365–372; c) F. Marchetti, G. Pampaloni, S. Zacchini, *Eur. J. Inorg. Chem.* **2008**, 453–462.

[7] *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, USA, **1996**, pp. 9–51; D. Belli Dell'Amico, F. Calderazzo, G. Pampaloni, *Inorg. Chim. Acta*; DOI 10.106/j.ica.2008.01.015.

[8] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* **1993**, *31*, 287–292.

[9] S. Kobayashi, H. Danda, T. Saegusa, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3214–3220; K. Matyjaszewski, S. Penczek, *J. Polym. Sci., Polym. Chem.* **1974**, *12*, 1905–1912; J. Hrkach, K. Matyjaszevski, *Macromolecules* **1990**, *23*, 4042–4046.

[10] F. Calderazzo, P. Pallavicini, G. Pampaloni, P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.* **1990**, 2743–2746.

[11] D. A. Skoog, D. M. West, *Fundamentals of Analytical Chemistry*, 2nd ed., Holt, Rinehart and Winston, Chatham, UK, **1974**, p. 233.

Received: December 18, 2007