Investigation of the complexation and hydrolysis–condensation of titanium(IV) n-butoxide [Ti(OBu^n)$_4$] with some unsaturated mono and dicarboxylic acids

Birsen S. Buyuktas*
Department of Chemistry, Akdeniz University, 07058 Antalya, Turkey

Abstract

Titanium tetra-n-butoxide, [Ti(OCH$_2$CH$_2$CH$_2$CH$_3$)$_4$; Ti(OBu^n)$_4$] was reacted with some unsaturated mono- and di-carboxylic acids such as t-cinnamic acid (TCA; C$_6$H$_6$CH=CHCOOH), maleic acid (MA; HOOCCH=CHCOOH) and itaconic acid [ITA; HOOCCH$_2$C(=CH$_2$)COOH]. Complexation ratios of the complexes (mol of the acid per Ti atom in the complexes) were determined by FTIR spectroscopy. The structure of the complexes was supported by the ^{13}C-n.m.r., ^{1}H-n.m.r. and FTIR spectra. It was observed that MA, ITA and TCA behave as bidendate ligands. MA and ITA are dicarboxylic acids that complexed with Ti(OBu^n)$_4$ in a 2:1 mol ratio (Ti:MA and Ti:ITA). TCA is a monocarboxylic acid which was complexed with Ti(OBu^n)$_4$ with a mol ratio of 1:1 (Ti:TCA). Hydrolysis reactions of these complexes were performed by Karl–Fischer titration. The hydrolysis reaction rate of the modified Ti(O-Bu^n)$_4$ was reduced with complexation by these carboxylic acids.

Introduction

Metal alkoxides, M(OR)$_4$ are generally very reactive and react vigorously with water [1–3]. Because of their high reactivity towards water, some organic ligands can be used in order to slow down the rate of the hydrolysis. Generally, these ligands are carboxylic acids, alcohols, alkanolamines, β-diketones and β-ketoesters, Schiff bases, oximes, hydroxylamines and glycols. They may react with metal alkoxides to afford homo- and heteroleptic derivatives involving metals in novel coordination states and geometries [4–12].

Detailed chemistry of the metal alkoxide precursors was investigated by Mehrotra [5] and Sanchez et al. [6]. They implied that molecular complexity of metal alkoxides depends on the nature of the metal, alkoxy group and type of the solvent. The molecular complexity increases with the atomic size of the metal within a given group M(OR)$_4$ (M = Ti, Zr, Hf, Th) and decreases with increasing bulkiness of the OR group because of steric hindrance effects [2, 8].

Structures of the titanium alkoxides [Ti(OR)$_4$] were determined by Sanchez et al. and Babonneau et al. [7, 8]. Structural data of titanium alkoxides were provided by X-ray absorption experiments. Titanium alkoxides including primary alkoxy groups (such as OEt, OPr^n, OBu^n) are trimeric species with a pentacoordinated metal atom and monomers with secondary or tertiary alkoxy groups (such as OAm^t, OBu^t) in a tetrahedral environment of Ti [6].

The high reactivity of metal alkoxides towards water leads to complex hydrolysis and polymerization chemistry. During hydrolysis, the alkoxo (–OR) groups are replaced, either by hydroxo (OH$^-$) or oxo (O^{2-}) ligands. This reaction is influenced by a number of factors such as nature of the alkyl (R) group, the nature of the solvent, the concentration of the species present in solution, the water to alkoxide molar ratio and the temperature. Following equation represents the initial stage of a continued hydrolysis process [2]:

Hydrolysis

The hydroxy-metal alkoxides (A) tend to react further in two ways (dealcoholation and dehydration) and to form the metal oxo-alkoxide derivatives.
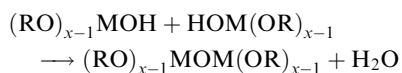

Dealcoholation

$$(RO)_{x-1}MOH + ROM(OR)_{x-1}$$
$$\longrightarrow (RO)_{x-1}MOM(OR)_{x-1} + ROH$$

---
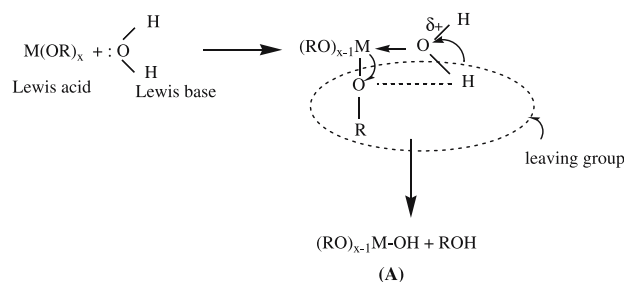
* Author for correspondence: E-mail: bbirsen@akdeniz.edu.tr

Dehydration

$$(RO)_{x-1}MOH + HOM(OR)_{x-1}$$
$$\longrightarrow (RO)_{x-1}MOM(OR)_{x-1} + H_2O$$

The hydrolysis of titanium alkoxide and the effects of hydrolytic polycondensation parameters were studied by Yoldas [13]. He reported that, titanium alkoxides hydrolyze vigorously with water producing polycondensates whose equivalent oxide content varies from *ca.* 70% to over 90%. This variation reflects the average molecular size and the nature of the terminal bonds. Golubko *et al.* studied the hydrolysis of $Ti(OR)_4$ (R = Et, ^iPr, ^nBu) at various concentrations of titanium alkoxides and ratios $h = [H_2O]/[Ti(OR)_4]$ in alcoholic media. They concluded that hydrolysis of $Ti(OBu^n)_4$ is approximately 150 times slower than that of $Ti(OEt)_4$ [14].

Carboxylic acids are often used in sol-gel chemistry of titanium and zirconium alkoxides to moderate their high reactivity. An exothermic reaction occurs and a clear solution can be obtained when acetic acid is added to $Ti(OBu^n)_4$. ^{13}C and ^1H-n.m.r. of the modified metal alkoxides show that acetate groups are bonded to titanium and IR spectra indicate that CH_3COO^- (AcO^-) behaves as a bidendate ligand [15]. The reaction between $Ti(OBu^n)_4$ and acetic acid (AcOH) is as follows:

$$Ti(OBu^n)_4 + AcOH \rightarrow Ti(OBu^n)_3(OAc) + BuOH$$
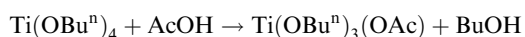
Recently, unsaturated carboxylic acids, such as acrylic and methacrylic acids, were used to modify some titanium alkoxides for the preparation of new inorganic–organic copolymers [16, 17].

In this study, we report the modification of $Ti(OBu^n)_4$ with two dicarboxylic acids (MA and ITA) and a monocarboxylic acid (TCA) and the hydrolysis behavior of the resultant modified $Ti(OBu^n)_4$. The differences of the complexation ratio of $Ti(OBu^n)_4$ between dicarboxylic acids (MA and ITA) and monocarboxylic acid (TCA) was also investigated. The rate of the hydrolysis reactions of the modified $Ti(OBu^n)_4$ with the di- and mono-carboxylic acids was considerable slower than unmodified $Ti(OBu^n)_4$.

Experimental

MA, ITA, TCA and $Ti(OBu^n)_4$ were purchased from Aldrich. *n*-Butanol was supplied by Merck, dried over anhydrous $MgSO_4$ for 24 h, and freshly distilled before using as the reaction solvent. DMSO and $CDCl_3$ were also supplied from Merck and were used to record n.m.r. spectra of the pure ligands and the complexes, respectively. Deionized water was used in hydrolysis reactions.

^1H-n.m.r. and ^{13}C-n.m.r. spectra of the ligands and the complexes were recorded with a 200 MHz Gemini Varian Spectrometer. The complexation ratio of the complexes was determined with a MIDAC Spectrofile 240 plus FTIR spectrometer. Hydrolysis reactions of the complexes were investigated with a METTLER DL 18 Karl–Fischer titrator.

Preparation of the complexes

To determine the maximum complexation ratio, MA and ITA were reacted with $Ti(OBu^n)_4$ in a mol ratio of 1.0, 0.7 and 0.5 mol acids per mol Ti atom. TCA was reacted with $Ti(OBu^n)_4$ in a mol ratio of 1.0, 1.5 and 2.0 mol acids per mol of Ti.

A solution of the carboxylic acid (1 mmol, 1.160 g for MA, 1.311 g for ITA and 1.480 g for TCA) in 5 ml of *n*-BuOH was added dropwise to a solution of $Ti(OBu^n)_4$ (1 mmol, 0.3403 g) in 5 ml of *n*-BuOH at room temperature. The reaction solution was stirred in a closed vessel. There was no rise in temperature and no precipitation was observed during the reaction. A clear solution was obtained and used for FTIR characterization. FTIR spectra of the each complex were recorded 1, 24, 72 and 120 h after addition of the carboxylic acid.

The same reaction was repeated with a mol ratio of 0.7, 0.5 mol of MA and ITA, 1.5 and 2.0 mol TCA per mol $Ti(OBu^n)_4$.

According to the FTIR results, $Ti(OBu^n)_4$ is complexed with MA and ITA in a mol ratio of 0.5 mol carboxylic acid per mol Ti, signed as C1 and C2 respectively, and with TCA in a mol ratio of 1 mol carboxylic acid per mol Ti, signed as C3. After describing the maximum complexation ratio, the structures of the complexes were supported by ^1H-n.m.r. and ^{13}C-n.m.r. spectra and hydrolysis reactions of the complexes were performed by Karl–Fischer titrator.

Hydrolysis of the complexes

1, 2, 3 and 4 mmol of water in 5 ml of *n*-BuOH was separately added to 1 mmol of the solutions of C1 in 5 ml of *n*-BuOH. Each hydrolysis solution of C1 was stirred at room temperature and simultaneously, the percentage of unreacted water was measured 5 times with 1 h periods by the Karl–Fischer coulometric titration. The same hydrolysis reaction was repeated with C2 and C3. The hydrolysis graphs of the complexes were obtained by plotting the mol of consumed water *versus* 1 mol of added water to the complex. Hydrolysis reaction graphs of C1, C2 and C3 were shown in Figures 1, 2 and 3, respectively.

Results and discussion

Bis-titanium (IV) tri-butoxide maleate
[[Ti(OBu^n)$_3$]$_2$(MAn)] (C1)

Table 1 shows FTIR spectral data of the pure ligands (MA, ITA and TCA) and the complexes (C1, C2 and
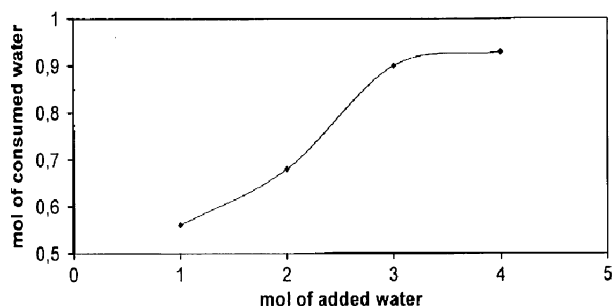
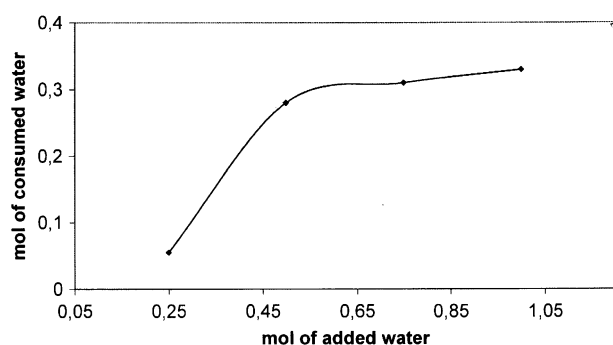*Fig. 1.* The hydrolysis graphic of C1 (mol of consumed water *versus* added water).

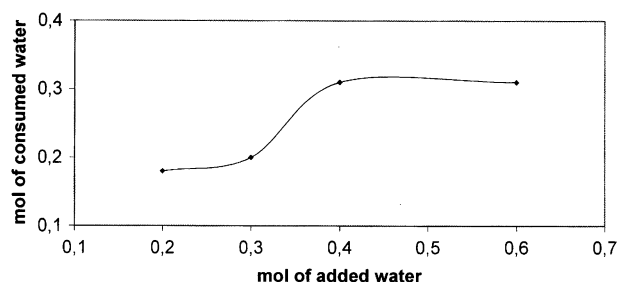*Fig. 2.* The hydrolysis graphic of C2 (mol of consumed water *versus* added water).

Fig. 3. The hydrolysis graphic of C3 (mol of consumed water *versus* added water).

C3) in the 1950–1450 cm^{-1} spectral range. Maximum complexation ratio of C1 was determined by FTIR spectroscopy. In the IR spectrum of pure MA, the –C=O peak belonging to the carboxylic group was observed at 1713 cm^{-1}. This band has been reduced in the complexes of 1.0 and 0.7 mol of MA per mol Ti atom and is not shown in Table 1. The peak of the –C=O disappeared in the complex of 0.5 mol of MA

*Table 1.* FTIR spectrum of the pure ligands and the complexes

Compound	υ(C=O)	υ(C=C)	$(COO^-)_{asym}$	$(COO^-)_{sym}$
MA	1713	1625	–	–
C1	–	–	1543	1452
ITA	1705	1643	–	–
C2	–	–	1562	1456
TCA	1689	1637	–	–
C3	–	–	1540	1462

per mol Ti atom. It indicates that 0.5 mol of MA completely reacted with 1 mol of $Ti(OBu^n)_4$. The molar Ti:MA ratio of the C1 was reported as 2:1. The stretching vibration peaks of C=C group in MA was observed at 1625 cm^{-1}. The C=C stretching band is missing in complex C1 because of the symmetrical structure of C1. In the IR spectrum, stretching of a C=C bond is often weak and sometimes is not observed at all in symmetrical molecules. Weak absorption due to overtones or combinations may occur in this region and could be mistaken for a C=C stretching mode [22]. In the complex C1, the stretching vibration of the asymmetric and the symmetric COO^- groups were observed at 1543 and 1452 cm^{-1}, respectively. The frequency separation ($\Delta\upsilon$) that is the difference between υ(COO) sym and υ(COO) asym is calculated as 91 cm^{-1}. According to Theiele and Panse [16], if the frequency separation (Δv) value ranges between 75 and 130 cm^{-1} then a carboxylic group bonds to the metal as a bidentate ligand.

The ^{1}H-n.m.r. spectral data of the C1 is given in Table 2. The chemical shift located at 3.48–3.69 ppm indicates the protons in –CH_2 of the *n*-butoxy group (–$OCH_2CH_2CH_2CH_3$) bonded to the Ti atom. The symmetric double chemical shifts at 5.8 and 6.4 ppm that has formed a roof on the spectrum assigned the protons of CH=CH group of the MA [22]. Carboxylic acid protons resonance was not observed on ^{1}H-n.m.r. It indicates that acetate groups are bonded to the titanium atom while two mols of butanol were released in to the reaction solution. In the ^{13}C-n.m.r. spectrum (Table 3), carboxylic group resonances of the pure MA and C1 were observed at 169 and 171 ppm, respectively.

A probable structure of the complex is as follows.
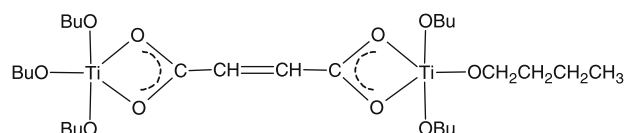
The reaction between MA and Ti $(OBu^n)_4$ can be written as:

$$2Ti(OBu^n)_4 + MA \rightarrow [Ti(OBu^n)_3]_2(MAn) + 2BuOH$$
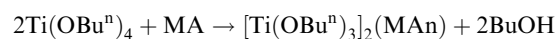
MAn: maleate anion

Bis-titanium (IV) tri-butoxide itaconate
[[Ti(OBu^n)$_3$]$_2$(ITAn)] (C2)

The FTIR spectral data of the pure ITA and C2 are shown in Table 1. The broad bond at 1705 cm^{-1} is attributed to the stretching vibration of C=O group of ITA. Although this band has been reduced in the complexes of 1.0 and 0.7 mol of ITA per mol Ti atom, it has not completely disappeared. It indicates that the complexes of both mol ratios have unreacted carboxylic acids in their reaction solutions. The stretching vibration of the C=O group completely disappeared in

Table 2. ^{1}H-n.m.r. of C1 and MA in CDCl$_3$ (δ ppm)

Compound	–COOH	–CH=CH–	^{a}CH$_3^b$CH$_2^c$CH$_2^d$CH$_2$O– (OBu^n)	
MA	12.20	6.30	–	
C1	–	5.80–6.40	3.48–3.69^d	1.48–1.65^c
			1.14–1.45^b	0.73–0.98^a

Table 3. ^{13}C-n.m.r. of C1 and MA in CDCl$_3$ (δ ppm)

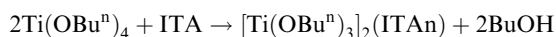| Compound	–COOH	–CH=CH–	^{a}CH$_3^b$CH$_2^c$CH$_2^d$CH$_2$O– (OBu^n)	
MA	169	132	–	
C1	171	130	64.6^d	36.7^c
			21.2^b	16.9^a

the spectrum of the complex of 0.5 mol ITA per mol Ti atom. It confirms that the carboxylic group of ITA was completely bonded to Ti atom and the maximum complexation ratio is 2:1 Ti:ITA. Furthermore the peak at 1643 cm^{-1} indicates the stretching vibration of C=C group of ITA. Asymmetric and symmetric ν(COO$^-$) group vibrations of the C2 were observed at 1562 and 1456 cm^{-1}, respectively. The calculated frequency separation ($\Delta\nu$) of C2 is 106 cm^{-1}. It was concluded that ITA was bonded to Ti as a bidentate chelating ligand [16, 17, 20].

The ^{1}H-n.m.r. spectral data of pure ITA and C2 are shown in Table 4 and the ^{13}C-n.m.r. spectral data of them are shown in Table 5. The carboxylic group proton resonance was not observed in the ^{1}H-n.m.r. spectrum, and the carboxylic carbon atoms resonances were observed at 178 ppm in the ^{13}C-n.m.r. of the C2. These results support bonding of the carboxylic group to the Ti(OBu^n)$_4$ as a bidentate ligand.

According to the spectroscopic data, the structure of C2 can be given as follows:
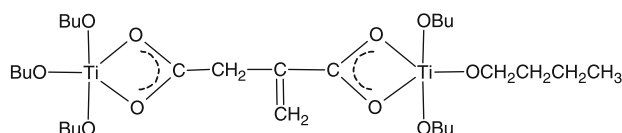
The reaction between ITA and Ti (OBu^n)$_4$ can be written as:

$$2Ti(OBu^n)_4 + ITA \rightarrow [Ti(OBu^n)_3]_2(ITAn) + 2BuOH$$

Table 4. ^{1}H-n.m.r. of C2 and ITA in CDCl$_3$ (δ ppm)

Compound	–COOH	–C=CH$_2$–	–OOCCH$_2$–	^{a}CH$_3^b$CH$_2^c$CH$_2^d$CH$_2$O– (OBu^n)	
ITA	12.30	5.70–6.10	3.20	–	
C2	–	5.80–6.30	2.84–3.12	3.77–4.46^d	1.44–1.81^c
				1.09–1.40^b	0.75–0.97^a

ITAn: itaconate anion

Titanium(IV) tri-butoxide cinnamate [[Ti(OBu^n)$_3$] (TCAn)] (C3)

The FTIR spectral data of the pure TCA and C3 are shown in Table 1. The strong band at 1689 cm^{-1} indicates the stretching vibration of C=O group of pure TCA. This band has been reduced in the complexes to 1.5 and 2.0 mol of the TCA per mol Ti atom. The vibration of the carbonyl group disappeared in the complex of 1.0 mol of TCA per mol Ti atom. According to the FTIR spectral data, the maximum complexation ratio of Ti(OBu)$_4$ with TCA is 1:1. The peak at 1637 cm^{-1} is assigned to the aliphatic C=C group in TCA. Asymmetric COO$^-$ and symmetric COO$^-$ group vibrations of C3 were observed at 1540 and 1462 cm^{-1}, respectively. The frequency separation ($\Delta\nu$) value is 78 cm^{-1}. It indicates that the COO$^-$ group of TCA was bonded to the Ti atom as a bidentate ligand to C3.

The chemical shifts of the TCA and C3 on the ^{1}H-n.m.r. and the ^{13}C-n.m.r. are summarized in Tables 6 and 7, respectively.

The carboxylic acid proton resonance of TCA was not observed in the ^{1}H-n.m.r. spectrum and the carbon atom resonance of carboxylic acid group was observed at 175 ppm on ^{13}C-n.m.r. spectrum of C3. These results show that the acetate group of the TCA is bonded to Ti atom in the complex C3.

FTIR, ^{1}H-n.m.r. and ^{13}C-n.m.r. results support the following structure for C3.

The reaction between TCA and Ti(OBu^n)$_4$ can be written as:

$$Ti(OBu^n)_4 + TCA \rightarrow [Ti(OBu^n)_3(TCAn)] + BuOH$$
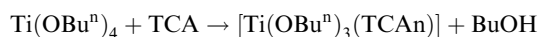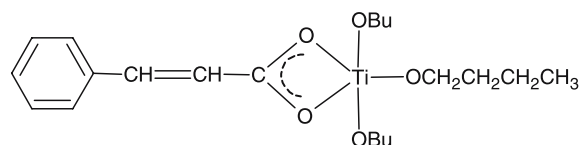
TCAn: *trans*-cinnamate anion

In the Karl–Fischer titration 0.93, 0.33 and 0.31 mol water were consumed to the extent of per mol of C1, C2 and C3, respectively. No precipitation was observed during the hydrolysis reactions of the complexes. The carboxylic groups of the ligands allow to obtain strong M–OOC chelating complexes and they became more stable towards the hydrolysis. Both MA and ITA have two carboxylic groups and they react in Ti(OBu^n)$_4$ with 2:1 molar ratio as Ti:MA and Ti:ITA. It was expected that water required by C1 and C2 should be similar and close to 0.93 mol of water. Unexpectedly, C2 required 0.33 mol of water for complete hydrolysis. The reason for this is the π-overlap between COO$^-$ and C=C groups of the itaconic acid in C3 [19]. Simply it can be shown as follows:

Table 5. ^{13}C-n.m.r. of C2 and ITA in CDCl$_3$ (δ ppm)

Compound	–CCOO–	–OOCCH$_2$–	–C=CH$_2$–	–C=CH$_2$–	–OOCCH$_2$–	^{a}CH$_3^b$CH$_2^c$CH$_2$ ^{d}CH$_2$O– (OBu^n)	
ITA	173	169	137	129	39.2	–	
C2	178	170	137	130	36.7	64.5^d	37.1^c
						20.9^b	15.6^a

Table 6. ^{1}H-n.m.r. of C3 and TCA in CDCl$_3$ (δ ppm)

Compound	–COOH	^{e}–CH=CH-ph	^{f}–CH=CH-ph	^{a}CH$_3^b$CH$_2^c$CH$_2^d$CH$_2$O– (OBu^n)	
TCA	12.00	7.32–7.76	6.45–6.59	-	
C3	-	7.26–784	6.47–6.63	3.37–3.89^d	1.47–1.71^c
				1.17–1.46^b	0.74–0.98^a

^{e}Aromatic proton.
^{f}Aliphatic proton.
-ph: phenyl.

Table 7. ^{13}C-n.m.r. of C3 and TCA in CDCl$_3$ (δ ppm)

Compound	–COO–	^{e}–CH=CH-ph	^{f}–CH=CH-ph	^{e}–CH=CH–	^{a}CH$_3^b$CH$_2^c$CH$_2^d$CH$_2$O– (OBu^n)	
TCA	169	146	136	120–132	–	
C3	175	145	137	129–132	64.5^d	36.6^c
					21.1^b	15.5^a

^{e}Aromatic carbon.
^{f}Aliphatic carbon.
-ph: phenyl.
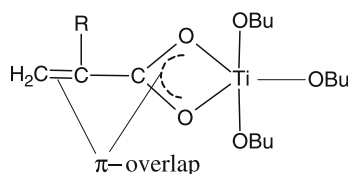
Conclusions

As a result, it was concluded that Ti(OBu^n)$_4$ can be modified by unsaturated di- and mono-carboxylic acids such as maleic, itaconic and *t*-cinnamic acids. The complexation ratio of the dicarboxylic acids with Ti(OBu^n)$_4$ is 1:2 as carboxylic acid:Ti, while monocarboxylic acid reacts to Ti(OBu^n)$_4$ with a mol ratio of 1:1 as carboxylic acid:Ti. The hydrolysis reaction rate of the modified Ti(OBu^n)$_4$ has been reduced with complexation by these carboxylic acids. Furthermore, hydrolysis reactions of formed complexes can provide structurally and chemically different building blocks for new ceramic and coating materials. All of the carboxylic acids that we have used as chelating ligands for Ti(OBu^n)$_4$ have C=C bond in their molecular structure so that the subsequent polymerization reactions are usually possible.

Acknowledgments

References

1. R.C. Mehrotra, *J. Non-Cryst. Sol.*, **100**, 1 (1988).
2. (a) D.C. Bradley, R.C. Mehrotra and D.P. Gaur, *Metal Alkoxides*, Academic Press, New York, 1978; (b) D.C. Bradley, R.C. Mehrotra, I.P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London, 2001.
3. B.E. Yoldas, *J. Mater. Sci.*, **12**, 1203 (1977).
4. H. Schmidt, *J. Non-Cryst. Sol.*, **100**, 51 (1988).
5. R.C. Mehrotra, *J. Non-Cryst. Sol.*, **121**, 1 (1990).
6. C. Sanchez and J. Livage, *New J. Chem.*, **14**, 513 (1990).
7. J. Wen and G.L. Wilkes, *Chem. Mater.*, **8**, 1677 (1996).
8. M. Navabi, S. Doeuff, C. Sanchez and J. Livage, *J. Non-Cryst. Sol.*, **121**, 31 (1990).
9. C. Sanchez, F. Babonneau, S. Doeuff and A. Leaustic, in *Ultra-structure Processing of Advanced Ceramics*, J.D. Mackenzie and D.R. Ulrich (Eds.), Pergamon Press, 1987, Vol. 2, p. 335.
10. F. Babonneau, S. Doeuff, A. Leaustic, C. Sanchez, C. Cartier and M. Verdaguer, *Inorg. Chem.*, **27**, 3166 (1988).
11. J. Zhang, S. Luo and L. Gui, *J. Mater. Sci.*, **32**, 1469 (1997).
12. B.S. Buyuktas and O. Aktas, *Transit. Met. Chem.*, **31**, 56 (2006).
13. B.E. Yoldas, *J. Mater. Sci.*, **21**, 1087 (1986).

14. N.V. Golubko, M.I. Yanovskaya, I.P. Romm and A.N. Ozerın, *J. Sol-Gel Sci. Techn.*, **20**, 245 (2001).
15. C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. Non-Cryst. Sol.*, **100**, 65 (1988).
16. U. Schubert, *J. Chem. Soc., Dalton Trans.*, **16**, 3343 (1996).
17. U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich and C. Chau, *Chem. Mater.*, **4**, 291 (1992).
18. A. Lorenz, G. Kickelbick and U. Schubert, *Chem. Mater.*, **9**, 2551 (1997).
19. V.K.H. Theiele and M.Z. Panse, *Z. Anorg. All. Chem.*, **144**, 23 (1978).
20. H. Sayılkan, E. Arpaç and Tr. Doğa, *J. Chem.*, **17**, 92 (1993).
21. S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Cryst. Sol.*, **89**, 206 (1987).
22. J.B. Lambert, H.F. Shurvell, D.A. Lightner and R.G. Cooks, *Organic Structural Spectroscopy*, Prentice-Hall, Inc., New Jersey, 1998.

TMCH 6558