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Synthesis and molecular structure of [Ti$_4$(OPr^i)$_8$(μ,η^2-OCH$_2$CH=CHCH$_2$O)$_2$(μ$_3$,η^2-OCH$_2$CH=CHCH$_2$O)$_2$]. Application to the elaboration of low density, microcellular, doped organic materials

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The reaction between Ti(OPr^i)$_4$ and *cis*-but-2-ene-1,4-diol [HOCH$_2$CH=CHCH$_2$OH] in 1 : 1 stoichiometry at room temperature gave [Ti$_4$(OPr^i)$_8$(μ,η^2-OCH$_2$CH=CHCH$_2$O)$_2$(μ$_3$,η^2-OCH$_2$CH=CHCH$_2$O)$_2$] **1** which was characterized by single crystal X-ray diffraction. Its molecular structure consists of an open-shell tetranuclear polyhedron with terminal isopropoxide ligands while the unsaturated diolates act as bridging-chelating ligands assembling five- and six-coordinated metals. The Ti–O bond lengths are in the range 1.77(1)–2.12(1) Å with Ti–OPr^i < Ti–η^2-OC$_6$H$_4$O < Ti–μ-OC$_6$H$_4$O. Compound **1** was used for doping polystyrene foams elaborated by a emulsion/polymerization (w/o) process with traces of titania. Microcellular polystyrene foams with a low density (0.048–0.055 g cm^{-3}) doped with titania (0.72–1.5 Ti wt%) have been obtained. The influence of a number of parameters such as the nature of the radical initiator, of the precursor, of an electrolyte and of the amount of surfactant, on the properties of the foams has been evaluated. The influence of various polymerizable ligands, but-2-ene-1,4-diolate, 2-(methacryloyloxy)ethyl acetoacetate and 3-allyloxy-1,2-propanediolate, has been investigated. The results indicate the first of these to give the best results. The precursors were characterized by FTIR, ^{1}H NMR, elemental analysis and the foams by IR, elemental analysis, SEM/EDX and compressibility measurements.

Introduction

Hybrid organic–inorganic materials synthesized by sol–gel processing are increasingly derived from modified alkoxides.[1] When the metal coordination sphere involves a polymerizable ligand, materials displaying an organic as well as an inorganic network can be obtained and combine the properties of inorganic and organic materials. Transition metal derivatives bearing polymerizable ligands can be used to extend the network to form hybrid organic–inorganic polymers.[2] A number of polymerizable ligands such as diols[3] (*e.g. cis*-but-2-ene-1,4-diol), β-diketoesters[4] [*e.g.* 2-(methacryloyloxy)ethyl acetoacetate] or acids[5] (*e.g.* acrylic, methacrylic, ...) can be used. Highly porous materials possess a unique set of properties including high stiffness, high surface area, low thermal conductivity and low relative permittivity.[6] The specific properties of microporous materials open up medical, biomedical, optical, thermal, catalytic and acoustic applications[7] and are required for studies of radiative wave propagation. Low density microcellular materials (LDMM) have been mostly investigated for study of laser–material interactions.[8] We report here the synthesis of [Ti$_4$(OPr^i)$_8$(μ,η^2-OCH$_2$CH=CHCH$_2$O)$_2$(μ$_3$,η^2-OCH$_2$CH=CHCH$_2$O$_2$] **1** and its characterization by single crystal X-ray diffraction, FTIR and ^{1}H NMR spectroscopy. Low density and microcellular materials, *i.e.* polystyrene foams, have been elaborated by a water/oil emulsion polymerization process. Titanium alkoxides with polymerizable ligands such as **1**, [Ti(OPr^i)$_2$(AAEMA)$_2$] **2** [HAAEMA = 2-(methacryloyloxy)ethyl acetoacetate] or [Ti(APO$_2$)$_2$] **3** (APO$_2$H$_2$ = 3-allyloxypropane-1,2-diol) were used for incorporation of traces of titania in the polystyrene foams.

Experimental

Reactions were performed under inert atmosphere using Schlenck tubes and vacuum line techniques. Solvents were dried and purified by standard procedures. *cis*-But-2-ene-1,4-diol, 2-(methacryloyloxy)ethyl acetoacetate and 3-allyloxypropane-1,2-diol were stored over molecular sieves. ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer. FTIR spectra were obtained on a Perkin-Elmer FTIR Paragon 500 spectrometer as Nujol mulls between KBr plates. Microanalyses were obtained from the Centre de Microanalyses du CNRS for the molecular species as well as for the foams.

Scanning electron micrographs were recorded on a SEM 505 Philips microscope equipped with an EDX analysing system. Compressibility measurements were performed on an Adamel-Lhomargy traction–compression machine. Densities were determined by the ratio of weight to the volume of cylindrical samples.

Synthesis of [Ti$_4$(OPr^i)$_8$(OCH$_2$CH=CHCH$_2$O)$_4$] 1

cis-But-2-ene-1,4-diol (0.56 ml, 6.80 mmol) was added to Ti(OPr^i)$_4$ (1.94 g, 6.83 mmol) in toluene (12 ml) and the reaction medium was stirred at room temperature for 1 h. Crystallization at −10 °C led to 1.42 g (83%) of white crystals of **1**, soluble in toluene and hexane but insoluble in THF, isopropyl alcohol and diethyl ether. Anal. Calc. for C$_{40}$H$_{80}$O$_{16}$Ti$_4$: C, 47.63; H, 7.99. Found: C, 46.52; H, 7.35%. FTIR (cm^{-1}): 1658w, 1615w [ν(C=C)]; 1324m, 1260w, 1244w, 1170s, 1163s, 1123s, 1080m, 1042m, 988s, 946m, 849s, 803w [ν(C–O) + ν(C–C)]; 761w, 719m, 665w, 633s, 610m, 593m, 520s, 465m, 437m [ν(M–O)]. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.2, 1.3 (d, J = 6.0 Hz, 48H, CH*Me*$_2$), 4.5 (sept, J = 6.0 Hz, 2H, C*H*Me$_2$), 4.70, 4.72 (sept, 6H, C*H*Me$_2$); 4.95, 5.0 (br, 16H, CH_2O); 5.8, 5.9 (m, 8H, CH).

Synthesis of [Ti(OPr^i)$_2$(AAEMA)$_2$] 2

HAAEMA (4 ml, 20.95 mmol) was added to a solution of Ti(OPr^i)$_4$ (2.98 g, 10.48 mmol) in 15 ml of toluene. Evaporation to dryness after 20 h left a yellow oil (5.69 g, 90%) which was miscible in most organic solvents. FTIR (cm^{-1}): 1723s [ν(C=O)] 1638s, 1615s, 1575s, 1530s [ν(C=O) + ν(C=C)], 1410m, 1325m, 1279vs, 1160vs, 1126m, 1075m, 1046m, 995s, 949m, 881m, 853m, 812m, 790m [ν(C–O) + ν(C–C)]; 744m, 620m, 602m, 591m, 528m, 455m, [ν(M–O)]. ^{1}H NMR ($CDCl_3$, 20 °C): δ 1.0–1.3 (overlapping d, 12H, CH*Me*$_2$), 1.9 (m, 12H, MeCO and *Me*C=CH_2), 4.2 (m, 8H, CH_2), 4.7 (sept, J = 6.1 Hz, 2H, C*H*Me$_2$), 5.0 (s, 2H, OCHCO), 5.5 and 6.1 (s, 2H, CH=CH).

Synthesis of [Ti(APO$_2$)$_2$] 3

3-Allyloxypropane-1,2-diol (1.4 ml, 11.32 mmol) was added to Ti(OPr^i)$_4$ (1.64 g, 5.77 mmol) in 20 ml of toluene and after 60 h, the solvent was removed *in vacuo*. The yellow solid was washed twice with 10 ml of hexane and dried (1.69 g, 95%). Compound **3** was soluble in toluene, isopropyl alcohol, diethyl ether and THF but insoluble in hexane. Anal. Calc. for $C_{12}H_{20}O_6Ti$: C, 46.79; H, 6.49. Found: C, 46.03; H, 6.40%. FTIR (cm^{-1}): 1644m [ν(C=C)]; 1263w; 1151s, 1084s, 1021s, 920m, 861m, 804w [ν(C–O) + ν(C–C)]; 638m; 559w, 526w [ν(M–O)]. ^{1}H NMR ($CDCl_3$, 20 °C): δ 3.0–5.0 (overlapping m, 14H, CHO and CH_2O), 5.3 (m, 4H, H_2C=C), 5.9 (m, 2H, C=CH).

Synthesis of titanium doped polystyrene foams

Compound **1** was added to a solution consisting of styrene, divinylbenzene, Span 80 and trigonox 21S. The solution was slowly introduced in a cylindrical glass container containing 40 ml of a Na_2SO_4 aqueous solution (deionized water, resistivity 18.2 MΩ cm^{-1}). The composition of the organic and aqueous phases used for the elaboration of polystyrene foams doped with titanium derived from **1** are summarized in Table 1. The emulsion was obtained by stirring the mixture in a double barrelled syringe pump device. The polymerization was carried out at 60 °C in an oven for 12 h. The foams were soaked for one day in water to eliminate salts and two days in ethanol to remove residual surfactant, and then dried at 80 °C.

Crystallography of 1

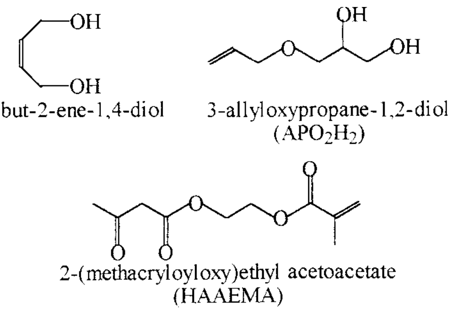
Crystals of **1** suitable for X-ray studies were obtained directly from the reaction medium. The selected crystal was mounted into a Lindemann capillary. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. A decay of 30% was observed in the intensities of two checked reflections during data collection and the usual linear correction was applied. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[9] Scattering factors and corrections for anomalous dispersion were taken from ref. 10. The structure was solved by using SHEXLS-86[11] and refined by full-matrix least squares with anisotropic thermal parameters for Ti, O and C atoms. The model reached convergence for the values of R and R_w listed in Table 2 with other crystallographic information.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/188. See http://www.rsc.org/suppdata/jm/1999/3027/ for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization of modified titanium alkoxides

Titanium isopropoxide was modified with the polymerizable potentially bidentate O-donor ligands shown below



cis-but-2-ene-1,4-diol
3-allyloxypropane-1,2-diol (APO_2H_2)
2-(methacryloyloxy)ethyl acetoacetate (HAAEMA)

Ti(OPr^i)$_4$ was allowed to react with *cis*-but-2-ene-1,4-diol (1 : 1 stoichiometry) in toluene at room temperature. A compound analysing as [Ti(OPr^i)$_2$(OCH_2CH=$CHCH_2O$)] **1** was obtained in 83% yield from the reaction medium by crystallization at −10 °C. Its IR spectrum indicates the presence of absorption bands at 1648 and 1615 cm^{-1} assigned to ν(C=C) vibrations. The absence of ν(OH) absorption bands suggests complete deprotonation of the diol [ν(CH) at 3341 cm^{-1} for the free diol]. The ^{1}H NMR spectra of compound **1** displays signals of the isopropoxide ligands and of the CH=CH moiety in a 2 : 1 integration ratio. The isopropoxides appear magnetically non-equivalent and occur as two doublets at δ 1.2 and 1.3 for the CH_3 groups whereas three septuplets are observed for the CH groups at δ 4.5, 4.7 and 4.72. The signals of the unsaturated ligands are rather broad, and are observed at δ 4.95 and 5.0 (CH_2 groups) and at δ 5.8 and 5.9 (CH groups). The overall spectroscopic and analytical data indicate that the diolate ligands are linked to the metals without loss of the unsaturated moiety.

The reaction between Ti(OPr^i)$_4$ and HAAEMA (1 : 1 stoichiometry) in toluene at room temperature yields a yellow oily product **2** in 90% yield. Its IR spectrum shows absorption bands at 1638, 1615, 1575 and 1530 cm^{-1} assigned to ν(CO) (by comparison with a band at 1748 cm^{-1} for free HAAEMA) and to ν(C=C) vibrations. The ^{1}H NMR spectrum presents a septuplet at δ 4.7 characteristic of CH of isopropoxide groups and a singlet at δ 5 characteristic of CH of the ketoesterate ligands, with an integration ratio of 1 : 1.

Table 1 Formulation of the emulsions TiPS1 (x = 0.1), TiPS2 (x = 0.2), TiPS3 (x' = 0.1) and TiPS4 (x' = 0.2)

Organic phase	2.2 g Span 80 (20%) 4.0 g St 4.8 g DVB 0.23 g trigonox 21S	1.65 g Span 80 (15%) 4.6 g St 5.7 g DVB 0.23 g trigonox 21S
Aqueous phase	x g precursor 250 ml H_2O 0.23 g Na_2SO_4	x' g precursor 250 ml H_2O 0.23 g Na_2SO_4
Emulsion	2.8 g of organic solution in aqueous solution made up to 40 ml	

Table 2 Crystallographic data for **1**

Chemical formula	$C_{40}H_{80}O_{16}Ti_4$
Formula weight	1008.6
Crystal system	Monoclinic
Space group	$P2_1/c$
Linear absorption coefficient, μ/cm^{-1}	6.05
R	0.0840
R_w ^{a}	0.0777
a/Å	14.061(4)
b/Å	10.546(3)
c/Å	18.890(6)
V/Å^3	2765(10)
T/K	298
Z	2
Number of data collected	3816
Number of unique data collected	3372
R_{int}	0.089

$^a w = w'[1-[(\|F_o\|-\|F_c\|)/6\sigma(F_o)]^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with three coefficients 6.18, −2.21 and 3.97 for a Chebyshev series, for which X is F_c/F_c(max.)

Table 3 Selected bond distances (Å) and angles (°) for $[Ti(OPr^i)_2(OCH_2CH{=}CHCH_2O)]_4$ ^{a}

Ti(1)···Ti(1′)	3.252(4)	Ti(1)···Ti(2)	3.307(3)
Ti(1)–O(1)	2.121(6)	Ti(1)–O(2)	1.822(7)
Ti(1)–O(3)	1.958(7)	Ti(1)–O(4)	2.070(6)
Ti(1)–O(4′)	1.968(6)	Ti(1)–O(5)	1.779(7)
Ti(2)–O(1)	1.949(7)	Ti(2)–O(3)	2.087(7)
Ti(2)–O(6)	1.77(1)	Ti(2)–O(7)	1.78(1)
Ti(2)–O(8)	1.767(9)		
O(1)–Ti(1)–O(2)	84.6(3)	O(1)–Ti(1)–O(3)	69.6(3)
O(2)–Ti(1)–O(3)	102.6(3)	O(1)–Ti(1)–O(4)	89.8(3)
O(2)–Ti(1)–O(4)	167.5(3)	O(3)–Ti(1)–O(4)	85.8(3)
O(1)–Ti(1)–O(4′)	92.2(3)	O(2)–Ti(1)–O(4′)	96.3(3)
O(3)–Ti(1)–O(4′)	152.1(3)	O(1)–Ti(1)–O(5)	165.3(3)
O(2)–Ti(1)–O(5)	93.4(3)	O(3)–Ti(1)–O(5)	96.8(3)
O(4)–Ti(1)–O(4′)	72.7(3)	O(4)–Ti(1)–O(5)	94.8(3)
O(4′)–Ti(1)–O(5)	102.4(3)	O(1)–Ti(2)–O(3)	70.5(3)
O(1)–Ti(2)–O(6)	125.5(4)	O(3)–Ti(2)–O(6)	90.9(4)
O(1)–Ti(2)–O(7)	91.9(4)	O(3)–Ti(2)–O(7)	162.4(4)
O(6)–Ti(2)–O(7)	98.7(5)	O(1)–Ti(2)–O(8)	119.1(4)
O(3)–Ti(2)–O(8)	90.6(4)	O(6)–Ti(2)–O(8)	111.5(5)
O(7)–Ti(2)–O(8)	99.5(5)	Ti(1)–O(1)–Ti(2)	108.6(3)
Ti(1)–O(3)–Ti(2)	109.7(3)	Ti(1)–O(4)–Ti(1)	107.3(3)
Ti(1)–O(1)–C(1)	122.3(6)	Ti(2)–O(1)–C(1)	127.8(6)
Ti(1)–O(2)–C(4)	140.5(7)	Ti(1)–O(4)–C(8)	125.2(6)
Ti(1)–O(3)–C(5)	126.2(7)	Ti(2)–O(3)–C(5)	124.1(7)
Ti(1′)–O(4)–C(8)	124.9(6)	Ti(1)–O(5)–C(9)	139.7(7)
Ti(2)–O(6)–C(12)	172.9(13)	Ti(2)–O(7)–C(15)	167.6(21)
Ti(2)–O(8)–C(18)	144.6(11)		

^{a}Primed atoms are related to unprimed equivalent by the symmetry operation $1-x$, $-y$, $2-z$.

The presence of a $C{=}CH_2$ functionality is evidenced by singlets at δ 5.0 and 5.5. The spectroscopic and analytical data are in agreement with the formula $Ti(OPr^i)_2(AAEMA)_2$, analogous to $Ti(OPr^i)_2(thd)_2$ (Hthd = 2,2′,6,6′-tetramethylhepta-3,5-dione) with six-coordinated titanium.

A similar ligand exchange procedure but with two equivalents of 3-allyloxypropane-1,2-diol (APO_2H_2) and one equivalent of $Ti(OPr^i)_4$ was used to obtain compound **3** in 95% yield. Its IR spectrum indicates the presence of an absorption band at 1644 cm^{-1} assigned to a ν(C=C) vibration. The absence of ν(OH) absorption bands suggests complete deprotonaton of the diol [ν(OH) at 3399 cm^{-1} for the free diol]. The ^1H NMR spectrum of compound **3** shows multiplets at δ 5.3 and 5.9 characteristic of the $CH{=}CH_2$ moiety. The formula $Ti(APO_2)_2$ is in accord with the spectroscopic and analytical data.

The identity of compound **1** was established by single crystal X-ray diffraction. Suitable crystals were grown directly from the reaction medium. Its molecular structure consists of an open-shell tetranuclear polyhedron of formula $[Ti_4(OPr^i)_8(\mu,\eta^2\text{-}OC_2HCH{=}CHCH_2O)_2(\mu_3,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2]$ (Fig. 1). Relevant interatomic distances and angles are collected in Table 3. Two types of surroundings for the metals are observed, Ti(1) and Ti(1′) are six-coordinate whereas Ti(2) and Ti(2′) are only five-coordinate with a distorted bipyramidal trigonal stereochemistry. The isopropoxide ligands are all in terminal positions. The dianionic ligands derived from *cis*-but-2-ene-1,4-diol are chelating-bridging, two being chelating doubly bridging (μ,η^2) [O(2)–O(1) and O(2′)–O(1′)] and the two others assembling the metals in a triply bridging manner (μ_3,η^2) [O(3)–O(4) and O(3′)–O(4′)]. The Ti–O bond lengths are in the range 1.767(9)–2.121(6) Å with the ordering $Ti{-}OPr^i < Ti{-}\eta^2\text{-}OC_4H_6O < Ti{-}\mu\text{-}OC_4H_6O$. A similar variation has been observed for the titanium ethyleneglycolate isopropoxide $[Ti_5(OPr^i)_9(\mu\text{-}OPr^i)(\mu,\eta^2\text{-}OC_2H_4O)(\mu_3,\eta^2\text{-}OC_2H_4O)_3(\mu_4,\eta^2\text{-}OC_2H_4O)]$.[12] The values of the terminal $Ti{-}OPr^i$ bond lengths [1.767(9)–1.779(7) Å] are similar to those reported in the literature.[13] The diolate $Ti{-}OC_4H_6$ bond lengths are significantly longer than those observed for $[Ti(OC_2H_4O)_3]^{2-}$ in which the glycolate ligands are all chelating.[14] The Ti···Ti distances, 3.252(4) Å for Ti(1)···Ti(1′) and 3.307(3) Å for Ti(2)···Ti(2′), are comparable to those observed for other titanium tetranuclear alkoxides.[13] The bite angles of the seven-membered diolate rings are quite large, with values of 84.6(3) and 85.8(3)° for the μ- and μ_3-types respectively. A variety of frameworks have been reported for

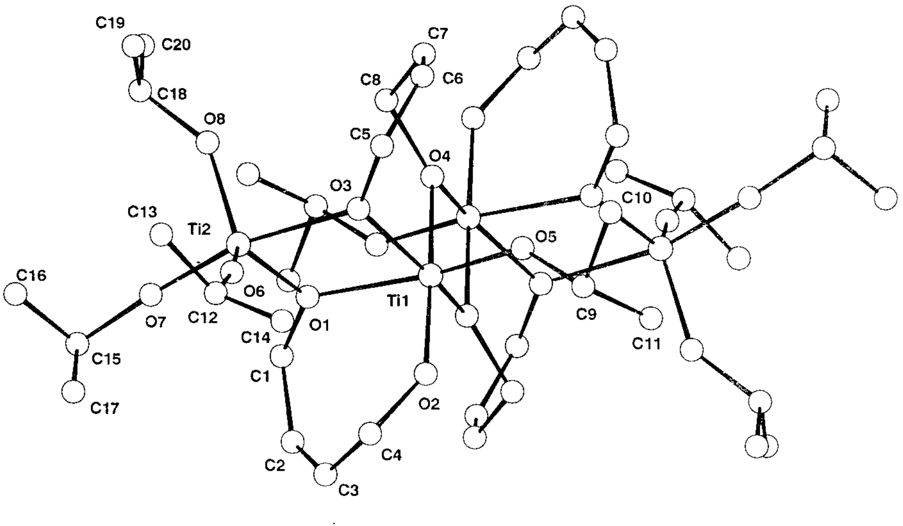
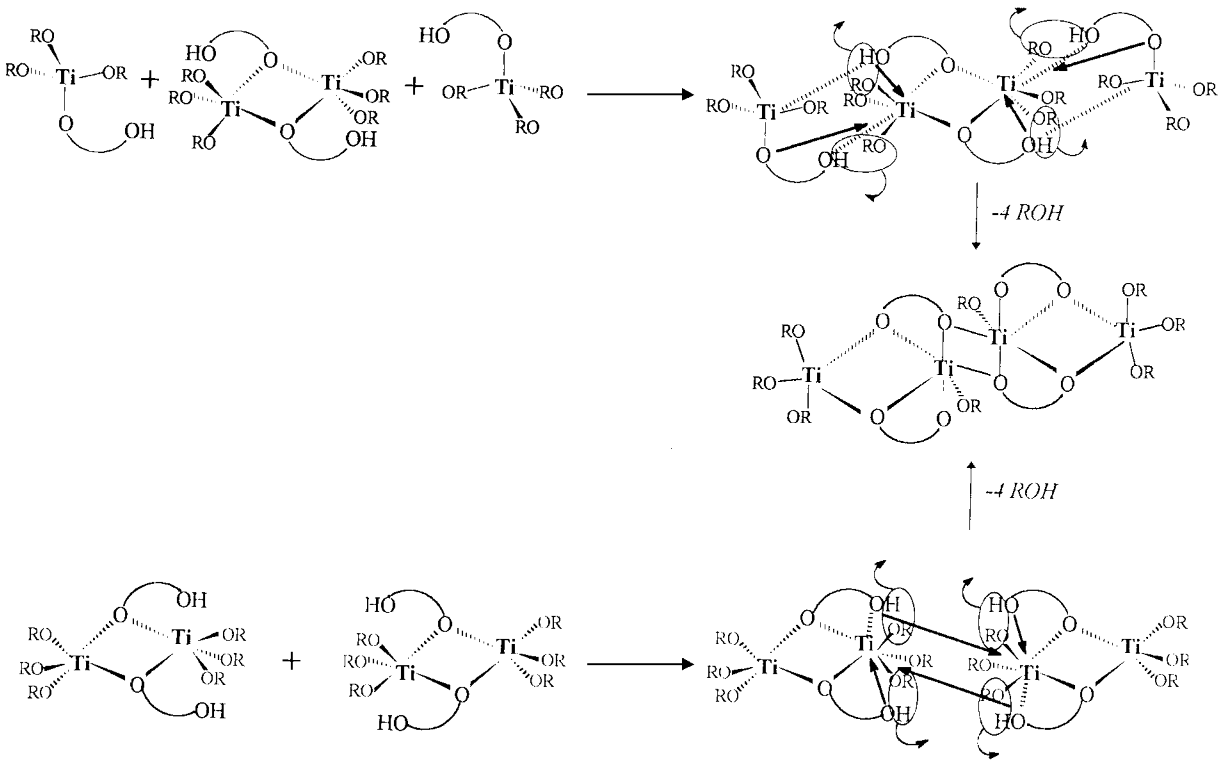


Fig. 1 Molecular structure of $[Ti_4(OPr^i)_8(OCH_2CH{=}CHCH_2O)_4]$ showing the atom numbering scheme.



Scheme 1 Possible mechanism of formation of the [Ti$_4$(OPr^i)$_8$(OCH$_2$CH=CHCH$_2$O)$_4$] molecule.

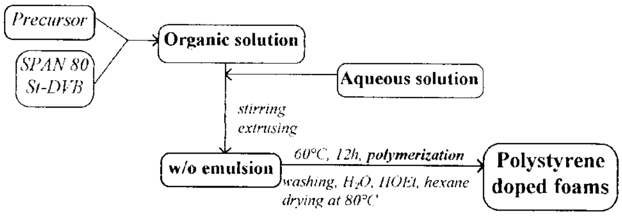
Ti$_4$ species, *e.g.* rhombohedral such as for Ti$_4$(OMe)$_{16}$ or derivatives with tridentate ligands [(TME)$_2$Ti$_4$(OPr^i)$_{10}$][14] [TMEH$_3$ = tris(hydroxymethyl)ethane], tetrahedral such as for oxocyclopentadienyls Ti$_4$O$_6$(C$_5$Me$_5$)$_4$,[15] or a ladder type core as for [Ti$_4$(μ_3-O)$_2$(μ-OPr^i)$_2$(OPr^i)$_8$L$_2$] (L = acac[16] or 5,5′,6,6′,7,7′,8,8′-octahydrobinaphtholate[17]). Compound **1** has a non-linear Ti$_4$O$_6$ chain arrangement (Ti···Ti···Ti angle 112.4(1)°] in which the distribution of isopropoxide ligands differ for the titanium atoms. The assembly of [Ti$_4$(O-Pr^i)$_8$(OCH$_2$CH=CHCH$_2$O)$_4$] might be achieved by condensation of several species *e.g.* [Ti$_2$(OPr^i)$_6$(OCH$_2$CH=CHCH$_2$O)$_2$] and [Ti(OPr^i)$_3$(OCH$_2$CH=CHCH$_2$OH)] with elimination of alcohol molecules (Scheme 1). Compound **1** is obtained in reproducible and high yields and is a well characterized non-oxo titanium alkoxide with polymerizable ligands. Its structure is related to that of [Nb$_4$(OPr^i)$_{10}$(OC$_2$H$_4$O)$_5$] which was obtained by reacting niobium isopropoxide and 2-hydroxyethylmethacrylate.[18]

Synthesis and characterization of polystyrene doped foams

Low density microcellular materials (LDMM) are a particular class of porous materials and are used as deuterium and tritium sponges in direct-drive target designs (Internal Confinement Fusion, ICF experiments).[19] These materials are based on low-atomic weight atoms, usually carbon and hydrogen. The study of the interactions between laser light and matter requires doping of LDMM materials by elements which can provide spectroscopic probes. Titanium is such a candidate since it gives rise to a relatively simple K-shell spectroscopic signal in the plasma. A small and uniform cell size with a tailored cell structure (*i.e.* cell wall thickness and cell opening) are required for useful LDMMs. Compound **1** was used as a source of titanium for access to polystyrene foams doped with titania by an emulsion–polymerization process. Styrene and divinylbenzene form a copolymer which is modified by the introduction of a polymerizable alkoxide. The introduction of a molecular precursor was observed to destabilize the emulsion. Therefore the morphology of the foams will change whereas their chemical properties are essentially identical to those of the non-doped polymer.

Elaboration of the foams. Various fabrication processes of low density microcellular materials have been reported. Except for aerogels, these are based on the separation of polymer solution phases and of inverse emulsions.[20] The polystyrene foams doped with titania were elaborated in two steps: formation of an inverse concentrated emulsion and subsequent polymerization of the organic phase. The introduction of soluble titanium alkoxides in a solvent (toluene) or directly into the organic solution allowed doping of the foams and the process is summarized in Scheme 2. The organic monomers used for the polymerization are styrene (St) and divinylbenzene (DVB) in 1 : 1 stoichiometry, the latter allowing cross-linking reactions which lead to good mechanical properties for the foams.[21,22] Two types of radical initiators were evaluated for the polymerization process, inorganic sodium persulfate Na$_2$S$_2$O$_8$ and organic *tert*-butyl-2-ethyl hexanoate peroxide (trigonox 21S). A stable emulsion was obtained by adding a non-ionic surfactant monooleate sorbitol, Span 80, which has an HLB (hydrophilic–lypophilic balance) value of $\approx$4.5. The different compositions used are listed in Table 1.

The influence of a number of parameters, such as dissolution of the precursor in an additional solvent, toluene or directly into the organic phase, the amount of surfactant, of precursor, nature of the radical initiator, of the precursor and presence of an electrolyte (AlCl$_3$·6H$_2$O or Na$_2$SO$_4$) in the aqueous phase, was evaluated. As a general feature, the formation of a stable



Scheme 2 Preparation of the porous PS doped foams.

emulsion was a prerequisite for obtaining foams with acceptable mechanical properties. The presence of a metallic precursor in the organic phase tends to destabilize the emulsion and, as a result, an increase of the speed and duration of agitation *via* a double barrelled syringed pump device in comparison to elaboration of non-doped foams was required.

The process used is the reverse of the 'standard' process of emulsion–polymerization which has ben used for the fabrication of polymer lattices.[23] In the standard route, the dispersed oil phase is polymerized to yield a collection of polymeric spheres; with an inverse emulsion, the continuous phase is polymerized yielding a rigid matrix.[23] The water droplets act actually as templates for the formation of cells. Holes are formed in the thin films separating water droplets and an open microstructure is formed. The foams were purified by washing. The samples were soaked for one day in water and two days in ethanol and then dried at 80 °C.

The morphology of these materials will depend mostly on the characteristics of the emulsion. Aronson and Petko have shown that the introduction of electrolytes into the aqueous phase stabilizes an inverse concentrated emulsion[24] and the influence of two electrolytes (Na_2SO_4 and $AlCl_3{\cdot}6H_2O$) was studied. The most regular structures were obtained when the emulsion was stabilized by Na_2SO_4 in association with Span 80 as surfactant. Polymerization was initiated by radicals, either organic or inorganic. The mineral initiator (dissolved in the aqueous phase) allowed the production of polystyrene doped foams which were more resistant mechanically and with smaller cells than were obtained with the organic initiator.[25] The presence of a water soluble initiator favours the polymerization at the oil/water interface and fixes the structure before coalescence. Ions can also increase the stability of the emulsion. Polystyrene doped foams were also elaborated from titanium alkoxides dissolved in toluene prior to addition to the solution containing the organic monomers. However, the presence of toluene destabilized the emulsion and the resulting foam structures were irregular.

Properties of the doped foams. The foams were characterized by elemental analyses for the determination of the amount of metal and by scanning electron microscopy to monitor the homogeneity of the sample, the microstructure, the morphology and the cell size. Dispersion of the metal was investigated by EDX. Topography (analysis on a length of 2 mm) and cartography studies (on an area of 4 mm^2) were also made for each foam as well as density measurements. Table 4 summarizes the characteristics of various samples denoted TiPS1, 2, 3, 4.

The morphology is described by the cell size, its geometry and by the thickness of the film between cells. Emulsion-derived foam structures generally display spherical cells surrounded by a thin film. When regular interconnections (pores) between cells are observed, the porosity of the material is increased. The morphology of the material is dictated by the initial emulsification parameters. The influence of the amount of surfactant, for instance, may be seen with samples TiPS1 and TiPS3 obtained using 20 and 15% of Span 80, respectively. The foams elaborated with 15% Span 80 and 0.88% Ti were less homogeneous and showed larger cells than those prepared with 20% of surfactant. Indeed, a low amount of surfactant will not stabilize an emulsion with small droplets, as division of the aqueous phase is less effective and, as a result, the cells are larger. In addition, some monomer is available to form thick walls and the interconnection between the cells (pores) is low as illustrated in Fig. 2. An increase in surfactant from 15 to 20% increases the interface area between the two phases, and the number of smaller cells increase. No emulsion is formed when the organic phase contains 25% of Span 80 and the optimal proportion of surfactant for the elaboration of doped polystyrene foams was found to be 20% when **1** was used as the source of titania. The polystyrene foams derived from $[Ti_4(OPr^i)_8(OCH_2CH{=}CHCH_2O)_4]$ have a regular structure with spherical, open cells and pores. The SEM micrographs in Fig. 3 show the microstructure of foams doped with 0.70% Ti.

The percentage of titanium (as titania) in the polystyrene foams (TiPS1, 2, 3, 4) was in the range 0.72–1.5 wt%. Microanalyses have shown that the amount of titania is, for the majority of samples, *ca.* 10–45% lower than the amount of metallic precursor used in the process (Table 2). These results were observed for samples elaborated with 20% of Span 80 in

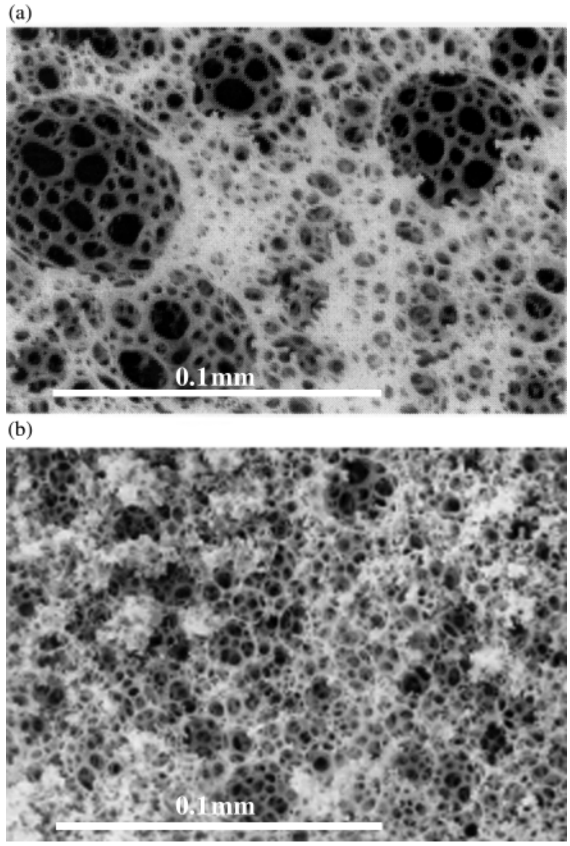


Fig. 2 SEM micrographs of (a) TiPS1 (15% Span 80, 0.88% Ti) and (b) TiPS3 (20% Span 80, 0.72% Ti).

Table 4 Properties of the doped foams

			Cell size/μm		Aspect	
Sample	M(%)	Density/g cm^{-1}	Average	Dispersion	Homogeneity[a]	Opening pores[b]
TiPS1	0.72	0.049	14	6–20	+ +	+ +
TiPS2	1.05	0.051	40	30–45	+ +	+
TiPS3	0.88	0.055	26	17–56	−	+ +
TiPS4	1.5	0.048	—	14–170	− −	+ +

[a]Homogeneity: + +: very homogenous, −: a number of small inhomogeneities, − −: large inhomogeneities. [b]Opening pores: + +: open pores and numerous cells, +: open pores and few cells.

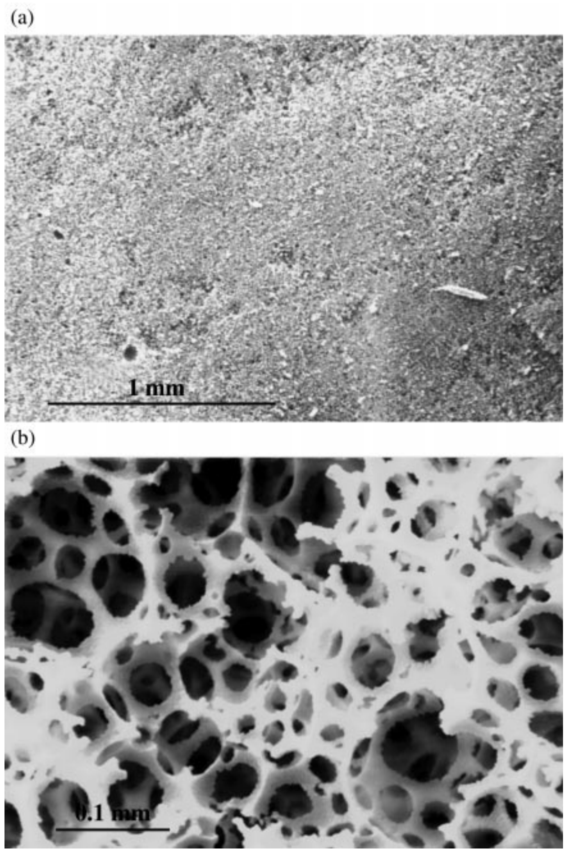


Fig. 3 SEM micrographs of TiPS1 at (a) low and (b) high magnification.

the organic phase. An increase of the amount of titania in the foams with respect to the amount of precursor used was observed with 15% Span 80 (90–100%), whereas an increase of the surfactant (48%) induces less incorporation of titania. The amount of metal introduced as titania thus depends on the amount of surfactant in the organic phase. Therefore, the stability of the emulsion also influences the incorporation of titania. FTIR spectra of the foams often display an absorption band at 1743 cm^{-1} attributed to the ν(C=O) vibration of Span 80 despite careful washing. Part of surfactant is not eliminated by the washing procedure even with longer soaking times and by extraction with hexane or isopropyl alcohol using a Soxhlet extractor. It is difficult to determine the amount of residual Span 80 in the foams. Span 80 consists essentially of sorbitan monooleate and it was suggested prevously that Span 80 can be hydrolysed to form oleic acid and sorbitol at 50 °C during the polymerization process.[25] However the ν(C=O) absorption band of oleic acid at 1711 cm^{-1} was not observed in the IR spectra of the foams. Another alternative might be participation of Span 80 in the polymerization process and thus its introduction into the organic network. The percentage of titania in the foam will thus be smaller than expected on the basis of the amount of precursor used. Hydrolysis of the bond between the metal and the polymerizable ligand might be another reason for a reduced incorporation of titania in the organic network.[26]

The dispersion of the metal, as investigated by topography and cartography, appears to be homogeneous to a depth of 2 mm and over an area of 4 mm^2. The amount of metal influences the morphology; the diameter of the pores increases with an increased percentage of titania but the overall microstructure remains essentially the same. The foam obtained with 0.72% Ti (TiPS1) displays a structure with cell sizes ranging from 6 to 20 μm while that doped with 1.05% titanium (TiPS2) affords cells with larger size, in the range 30–45 μm. As mentioned previously, the metallic species destabilize the inverse emulsion, leading to the division of the disperse phase being less effective, with larger droplets and resulting cells. The density of the polystyrene doped foams has been determined by the ratio of the weight to the volume of cylindrical samples and are of low density (0.048–0.055 g cm^{-3}).

Compressibility measurements were undertaken at 20 °C for TiPS1 (0.72% Ti) and TiPS2 (1.05% Ti) (Table 5). The mechanical characteristics [Young's modulus (E) and elastic strength (R_e)] of foams doped with titania vary with the density, the size of cells and the amount of metal. The values of E and R_e of the two samples are similar and are comparable to those obtained for non-doped polystyrene foams.

Other polymerizable titanium alkoxides, *i.e.* $Ti(APO_2)_2$ **3** and $Ti(OPr^i)_2(AAEMA)_2$ **2** were also used for introduction of traces of titania in polystyrene foams. Foams elaborated with these titanium alkoxides and with compound **1** were compared with the metallic precursors being dissolved in toluene (0.1–0.3 M) prior to use. The quality of the foams obtained with **2** and **3** was lower than for $[Ti_4(OPr^i)_8(\mu,\eta^2\text{-}OCH_2CH{=}CH\text{-}CH_2O)_2(\mu_3,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2]$ **1**. The foams obtained with **2** and **3** have poor mechanical properties and display irregular porous structure with ill defined cells despite adjustment of the parameters to obtain stable emulsions. As shown by the X-ray structure the diolate ligands of **1** are all in bridging positions. In the case of **2** and **3** the ligands are likely to display chelating coordination modes[3] and while their unsaturated functionality is thus more accessible for homo- and co-polymerization reactions, in comparison to the μ-OC_4H_6O ligands, a drawback is their higher flexibility. Alkoxides for which the ligands bear pendant polymerizable functions such as AAEMA or APO_2 are less favourable for the elaboration of foams than those with the unsaturated moiety in a more rigid surrounding as observed for **1**. This flexibility added to a higher lability toward hydrolysis might be responsible for the poor quality of the resulting foams.[26]

Conclusion

Polystyrene foams doped with titania could be elaborated by a water/oil emulsion polymerisation process using titanium alkoxides bearing unsatured ligands, but-2-ene-1,4-diolate and 2-(methacryloyloxy)ethyl acetoacetate. These foams are low density microcellular materials and were characterized by SEM, FTIR and compressibility measurements. The formation of stable emulsions was found to be a prerequisite for obtaining foams with acceptable mechanical properties. The presence of a titanium precursor in the organic phase was shown to destabilize the emulsion and required optimization of the experimental conditions by use of the correct amount of surfactant (SPAN 80), the presence or otherwise of an additional solvent such as toluene, mineralizer, dilution, *etc.*,

Table 5 Mechanical characteristics of polystyrene foams doped with 0.72% (TiPS1) and 1.05% (TiPS2) titania

Sample	E^a/MPa	$R_e{}^b$/MPa	$R_{max}{}^c$/MPa	ε^d (%)	$R_{5\%}{}^e$/MPa	$R_{20\%}{}^e$/MPa	D^f/mm	h^f/mm
TiPS1	5.39	0.08	0.16	4.89	0.15	0.15	14.95	30.76
TiPS2	6.00	0.05	0.14	19.04	0.11	0.14	18.82	26.91

[a] E = Young's modulus. [b] R_e = Elastic strength. [c] R_{max} = Ultimate stress. [d] ε = Normal strain. [e] $R_{5\%}$ and $R_{20\%}$ = 5 and 20% strain stresses. [f] D and h, diameter and height of cylindrical sample, respectively.

for each titanium precursor. The use of an inorganic mineralizer $Na_2S_2O_8$ as well as of Na_2SO_4 as electrolyte was observed to produce more mechanically resistent foams with smaller cells than those obtained by use of an organic mineralizer. The best foams (cell size, thickness of the film, homogeneity of the sample, dispersion of the metal) were obtained with $[Ti_4(OPr^i)_8(OCH_2CH{=}CHCH_2O)_4]$ **1** as the source of titania, probably as a result of the rigidity and limited lability of the bridging diolate ligand.

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