Nucleation Stage in the Ti(OPr^i)$_4$ Sol−Gel Process

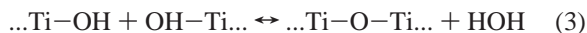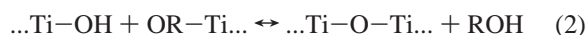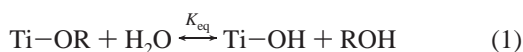**A. Soloviev,‡ R. Tufeu, C. Sanchez,† and A. V. Kanaev***

Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, CNRS, Institut Galilée, Univerité Paris-Nord, 93430 Villetaneuse, France, and Laboratoire de Chimie de la Matière Condensée, CNRS, Université Pierre et Marie Curie, 75252 Paris, France

A spectroscopic study of the initial stage of the Ti(OPr^i)$_4$ sol−gel process has been carried out. We have observed that the primary hydrolysis/condensation reaction is complete at low water concentration. At times shorter that the induction time, the reaction results in creation of nanosize nuclei. The most important finding is that the total nuclei mass, which appears almost instantaneously during the stage of mixing, is conserved throughout the process: the particles grow by nucleus agglomeration. The hydrolysis ratio $H \leq 1$ is sufficient for nucleus creation; $H > 1$ is needed for particle growth. The initial reagent mixing seems to be the key stage of the process.

Introduction

Hydrolysis (eq 1) and condensation (eqs 2, 3) reactions are the basis of the sol−gel process:[1]

$$\text{Ti−OR} + \text{H}_2\text{O} \xrightarrow{K_{eq}} \text{Ti−OH} + \text{ROH} \qquad (1)$$

$$...\text{Ti−OH} + \text{OR−Ti}... \leftrightarrow ...\text{Ti−O−Ti}... + \text{ROH} \qquad (2)$$

$$...\text{Ti−OH} + \text{OH−Ti}... \leftrightarrow ...\text{Ti−O−Ti}... + \text{HOH} \qquad (3)$$

Reactions 2 and 3 are called alcolation and oxolation reactions, respectively. The complete transformation of the Ti(OR)$_4$ metalorganic precursor into titanium oxide needs the theoretical hydrolysis ratio of $H = [\text{H}_2\text{O}]/[\text{TTIP}] = 2$. Nevertheless, Blanchard at al.[2,3] have shown that hydrolysis is not complete even if a large excess of water ($H \gg 2$) is used, which results in creation of TiO$_a$(OH)$_b$(OR)$_{4−2a−b}$ polymer structures. This has been explained (i) by the reaction partial reversibility and/or (ii) by the activation energy increase with a number of hydrolyzed OR groups: once clusters are formed, OR groups in large clusters should possess lower reactivity compared to that of monomers.

Less attention has been paid to the sol−gel reaction kinetics. It is known that a relatively long induction period separates the stage of the solid formation from the beginning of the process. During this no visual changes in the solution are observed. For this reason this period has often been considered as the hydrolyzed monomer accumulation stage. Precipitation of solids at $t = t_{ind}$ is induced in this model by the monomer concentration increase over a critical value. On the other hand, it has been shown in refs 2−4 using the ^{17}O NMR method that the reaction kinetics is considerably more complicated. The rate of water consummation exhibits substantial changes: it is strong at the very beginning and slow during the rest of the process. Moreover, different kinds of oxopolymers are observed in solution.[2,5] Our recent results[6−8] have shown that the hypothesis
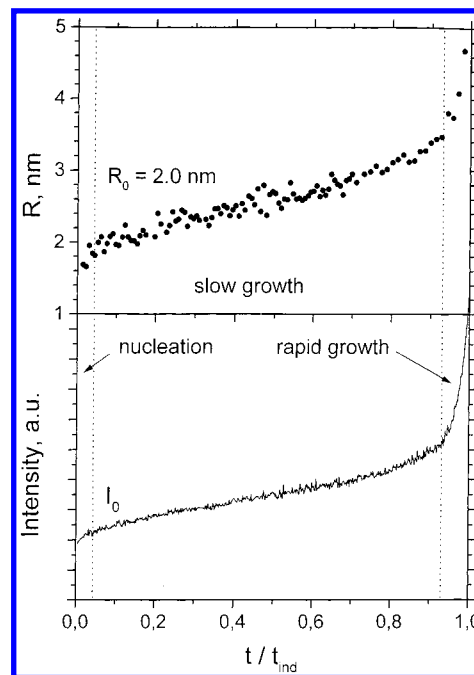

Figure 1. Typical evolution of the particle radius and scattering light intensity in the sol−gel TTIP process (experimental data taken from ref 7).

of the monomer accumulation oversimplifies the real picture. The LS (light scattering) measurements indicate at $H \geq 1.45$ the presence of slowly growing nanometric nuclei immediately after the start of the process. During the induction period these nuclei grow from 4.0 to ∼7.0 nm in size ($2R$) and then explosively precipitate (this is shown in Figure 1). It is not yet clear if nuclei continue to appear over the entire induction period. The mode of particle growth is not yet understood either: it might proceed by hydrolyzed monomer addition or by nuclei association.

In this work we will attempt to answer these issues using the example of Ti(OPr^i)$_4$ (titanium tetraisopropoxide, TTIP) as the oxide phase precursor. The study has been carried ut using UV absorption and LS techniques.

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Experimental Section

The sol−gel process has been carried out using TTIP/water/2-propanol solutions. The hydrolysis ratio H is varied between 0.1 and 3, and the TTIP molar concentration (T) is of the order of ~0.1 M. Two samples A and B were prepared. Sample A contains a solution of water in 2-propanol, and sample B contains a solution of TTIP in 2-propanol. Consequently sample B was added to A under stirring. After 1 min a spectroscopic cell was filled with a mixed solution and absorption spectra were measured at different times. Spectra were accumulated typically during 8 s. We have used TTIP of 98% purity and 2-propanol provided by Interchim and distillated water. The traces of residual water in the most pure 2-propanol were as low as $\leq 10^{-4}$ volume parts. Care has been taken for environmental humidity. It is known that the induction time t_{ind} is a strong power function of the water content (W) in the solution or of the hydrolysis ratio. The induction time measured for H = 2.7 is $t_{ind} \sim 10^2$ min and varies as $t_{ind} = 0.15T^{-1.5}(W - 1.45T)^{-4.7}$.[7] A substantial decrease in the t_{ind} value has been generally observed in colloids prepared some days after the first use of a new alcohol bottle, if no precautions were taken. This decrease is related to the progressive contamination of the 2-propanol by atmospheric water during the short time that the bottle is open. In most of the experiments this effect has been used to estimate the alcohol purity. Generally, all solutions were prepared and kept under an inert gas atmosphere (Ar, N_2).

The absorption spectra of prepared sol−gel samples have been measured using quartz cells of 20-, 10-, 2-, and 1-mm lengths. Variation of the cell length is important for the determination of the true shape of the absorption spectra without dilution of the colloid, which could induce changes in the nature or the size of produced species (e.g. clusters). An optical fiber was used to transmit the UV light continuum from the D_2-lamp to the quartz cell. The light transmitted by the quartz cell was sent by means of another optical fiber to the monochromator coupled CCD detector (Princeton). The detection system is sensitive in the spectral range between 230 and 900 nm. The linearity of the absorption measurements has been calibrated by using a solution of naphthalene in alcohol, which exhibits an absorption spectrum in the spectral domain of interest (4 ± 1 eV). It has been found that the absorbance α follows the Lambert−Beer law for values $\alpha \leq 5$ and it saturates at $\alpha \approx 7$. 2-Propanol and water do not absorb light in the UV−visible range of the spectrum. Nevertheless, changes in the solvent refractive index can influence the baseline of the measured spectra. This has been taken into account by the following simple method. In the absorbance formula $\alpha = \ln(I_0/I_{tr})$, instead of the incident D_2-lamp intensity, we used the transmitted light intensity through the optical cell filled with a net solvent (I_0); I_{tr} was the transmitted light intensity through the same cell filled with an experimental solution, prepared on the base of the same solvent.

The particle size and scattering light intensity from the sol−gel samples have been measured by the dynamic and the static LS methods using a He−Ne laser. These measurements were made in the homodyne technique of photon-correlation spectroscopy by using a 16-bit, 255-channel PC board plugged digital correlator (PhotoCor Instruments) developed by Yudin et al.[9] Depending on the colloid concentration we were able to see particles as small as $2R \sim 2$ nm.

Results and Discussion

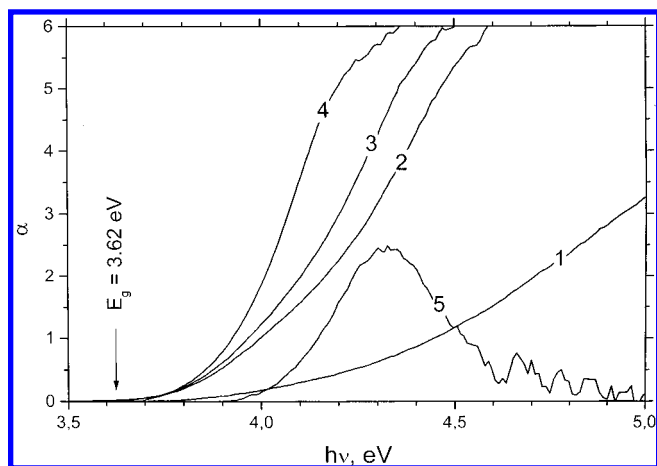Below we discuss the series of absorption measurements conducted in diluted stable and dynamically evolved solutions

Figure 2. Absorption spectra of TTIP/2-propanol solutions (water traces: $\delta \leq 10^{-4}$): 4 μL (1), 40 μL (2), 125 μL (3), and 620 μL (4) of TTIP were diluted in 5 mL of 2-propanol. The difference spectrum identified with the TTIP absorption is given by curve 5.

TTIP/H_2O in 2-propanol, where the hydrolysis ratio H varies largely around 1.

TTIP/Water/2-Propanol Stable Solutions. The stable TTIP/water/2-propanol solutions need a low water concentration. For this purpose, 2-propanol with the residual volume water content of $\delta \leq 10^{-4}$ has been used. Our estimate shows that the traces of water in 2-propanol are responsible for the hydrolysis ratio ranging from $H \sim 0.1$ in the most concentrated up to $H \sim 3$ in the most diluted TTIP/2-propanol solutions. Additionally, we have paid attention to the surrounded humidity, performing experiments under a nitrogen gas flow. We expect that TTIP molecules are only partially hydrolyzed in the concentrated solutions (as $T \gg W$) and almost totally hydrolyzed in the diluted ones ($T \ll W$). Reactions 1−3 co-proceed, and it was not possible to say a priori which are the relative populations of hydrolyzed monomers and condensed polymers in the solution. Therefore, we use the term "reacted" species (hydrolyzed or condensed), and we assume that they dominate the absorption spectra of highly diluted solutions. In the opposite limit of highly concentrated solutions, the concentration of the reacted species is limited by the residual water concentration, and the net TTIP molecules dominate the absorption spectra. Below we compare the line shape of the absorption spectra of these stable sol−gel solutions, which could clarify aspects of the reaction kinetics.

Experiments have been performed using different quantities of TTIP between 700 and 4 μL diluted in 5 mL of 2-propanol. An example of spectra evolution is shown in Figure 2. The shape of these spectra changes at about $V_{TTIP} = 125$ μL, and the shoulder appears in more concentrated samples starting at $h\nu \geq 3.95$ eV. For higher dilutions ($V_{TTIP} < 125$ μL), the spectral line shape is almost stable and we assume that the observed spectra belong to the reacted species produced in the solution after hydrolysis. Ti(OR)$_4$ contributes largely to the absorption spectra for $V_{TTIP} \geq 125$ μL. The normalized spectra show that the absorption of the diluted solutions is red-shifted with respect to the absorption of the concentrated ones by ~0.3 eV. This shift may be due to the size effect of growing clusters, but its value does not seem to be of sufficient significance to merit a detailed discussion. In our assignment, the low-energy tail in the absorption spectra between 3.6 and 3.95 eV belongs uniquely to the hydrolyzed Ti(OR)$_{4-i}$(OH)$_i$ (where R = C_3H_7 and i = 1−4) or condensed clusters (polymer or "oxo" phase). The TTIP precursor does not contribute to the absorption below 3.95 eV. The difference spectrum, which belongs to the net liquid Ti(OPr^i)$_4$, is also shown in Figure 2. One should remark that in

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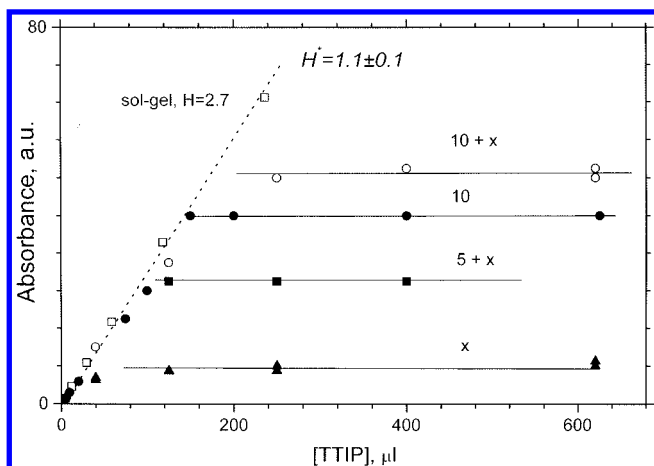*J. Phys. Chem. B, Vol. 105, No. 19, 2001* **4177**

Figure 3. Absorbance in the 3.6−3.9 eV spectral range in the TTIP/H$_2$O/2-propanol solutions versus initial TTIP concentration (l_{cell} mm). Volume of water added to 5 mL of 2-propanol is indicated in the figure in μL. The unknown water content in 2-propanol is labeled by "x". Absorbance in the sol−gel experiment with $H = 2.7$ is given by "□".

spite of the detector calibration, the line shape of the difference spectrum in the range $h\nu \geq 4.4$ eV (where the sample absorption is close to saturation) is of lower significance.

It has been found that the absorbance $\alpha = \ln(I_0/I_{tr})$ in the spectral range between 3.6 and 3.95 nm does not follow the dilution $\gamma = V_i/V_d \leq 1$ (initial-to-diluted volume ratio). A variation of γ by a factor of 15.5 results in a change of α by only a factor of ~3. We assign this saturation effect to the lack of water: the precursor TTIP molecules are efficiently hydrolyzed by traces of water in the 2-propanol, and if there is no more free water reactions 1−3 terminate. The reactions can be reversible as it is often supposed. The absorbance in our case could be a measure of the concentration of the reacted species. This last point will be discussed below to analyze the observed effect of UV absorbance.

To proceed with this issue we have carried out measurements of the absorption strength of TTIP/water/2-propanol solutions under dilution in 2-propanol. For a quantitative analysis we have measured the spectrum of the most diluted solution (40 μL TTIP/50 mL 2-propanol, in which TTIP is totally reacted) and kept it as the reference solution $\alpha^*(h\nu)$. We have fitted the low-energy tail of all measured spectra of TTIP/water/2-propanol solutions $\alpha(h\nu)$ by a function $k\alpha^*(h\nu)$, where k is a constant. According to our assignment, the fit factor k (which is equal to the absorption ratio α/α^*) is proportional to a relative concentration of the reacted species in the solution. In this way all spectral intensities were quantitatively treated on the same scale. The intensity ratio data corresponding to four experimental series are plotted in Figure 3 versus the initial TTIP concentration in the solution. Because the actual water content in the 2-propanol is unknown, we labeled the series with no water addition, 5 μL and 10 μL of water respectively with "x", "$5+x$" and "$10+x$". One more measurement is done using another bottle of freshly open high purity 2-propanol, which did not seem to contain any trace of water. We added to this solution 10 μL of water and labeled this series as "10".

We continue this discussion first using the hypothesis of the hydrolyzed species dominant contribution in the absorption. The hydrolysis reaction 1 is considered to be reversible. We apply now a simplified model describing the equilibrium between the neutral and hydrolyzed species. For the moment we do not specify how many OR groups can be hydrolyzed from four available in each TTIP molecule. The equilibrium constant is given by $K_{eq} = $ [Ti−OH][ROH]/[Ti−OR][H$_2$O]. Using defini-

tions [H$_2$O] = [H$_2$O]$_0$ − [Ti−OH] $\equiv W - t$, [Ti−OR] = [Ti−OR]$_0$ − [Ti − OH] $\equiv T - t$, and [ROH] = const $\equiv A$, we easily obtain:

$$t = K_{eq} \frac{(T - t)(W - t)}{A} \tag{4}$$

The relevant solution of the eq 4 is:

$$t = (T + W + A/K_{eq})/2 - \sqrt{(T + W + A/K_{eq})^2/4 - TW} \tag{5}$$

In the framework of this model, the absorbance α is proportional to t and one can apply eq 5 to treat the experimental data presented in Figure 3. $\alpha(T,W)$ is a linear function of T in the limit of $T \to 0$ and it is saturated in the limit of $T \to \infty$ ($W = $ const), which is due to a total water consumption in the solution. The curve behavior in the transition region between these two limits depends on the number of hydrolyzed Ti−OR groups in the TTIP molecule and is a sensitive function of the reaction reversibility and, more precisely, of K_{eq}: the higher this value the sharper and narrower is the transient region. Our analysis shows that (i) all curves start with the same linear slope, (ii) the transient region is almost absent (the saturation begins at the point where the linear slope finishes), and (iii) the change of the slope of the curve appears when $H = H^* \approx 1.0$. These findings indicate that the chemical reaction under observation is complete in the range of $H \in [0.1...1]$: $K_{eq} \gg A/W$. Most probably, it is not the hydrolysis reaction 1 but the condensation reaction 2 that is responsible for the observed effect, and the absorbing species are nuclei.

As we have just seen, the measured absorption saturates at a high TTIP concentration and it is proportional to the initial water concentration in solution: $\alpha/\alpha^* = cW$. The experimentally known values of W allow us to calibrate the y-axis in Figure 3: $c = 4.0 \mu L^{-1}$. These measurements are very sensitive and could provide a useful method for the precise determination of the water traces in alcohol.

Sol−Gel Solutions. This series of measurements has been carried out to see if nuclei are dissoluble, or in other words, if the condensation reaction 2 is reversible. Initially, the sol−gel solution of 1.5 mL TTIP with water at the hydrolysis ratio $H = 2.7$ in 30 mL 2-propanol has been prepared under stirring. The absorption spectrum has been measured during the period of the solution transparency $t \ll t_{ind}$ ($t_{ind} \approx 10^2$ min). Additionally, the transparent solution has been diluted $\gamma = $ 1:2, 1:4, 1:8, and 1:20. The dilution 1:20 completely stops any precipitation, and this solution was stable for at least 1 week. Absorption spectra were also measured in all four cases. For this series of absorption measurements a spectroscopic cell of 1-mm length was used. Additionally, the absorption spectrum of the "1:20" solution was measured in the 20-mm length spectroscopic cell. This sample should have the same optical thickness as the initial solution ($\gamma = $ 1:1) in the 1-mm cell, if no chemical changes take place. The resulting spectra are shown in Figure 4. A very good linearity between the dilution factor γ and the solution absorbance α (3.6−3.95 eV) has been found. This is shown by the dotted line in Figure 3. Moreover, the spectra with $\gamma = $ 1:1 ($l = 1$ mm) and $\gamma = $ 1:20 ($l = 20$ mm) coincide. This shows that the spectral line shape and the optical thickness $\alpha = \sigma(\lambda)Nl$ of both samples are the same (here $\sigma(\lambda)$ is the absorption cross section of species with concentration N) and proves that even a 1:20 dilution does not change the nature of the absorbing species:

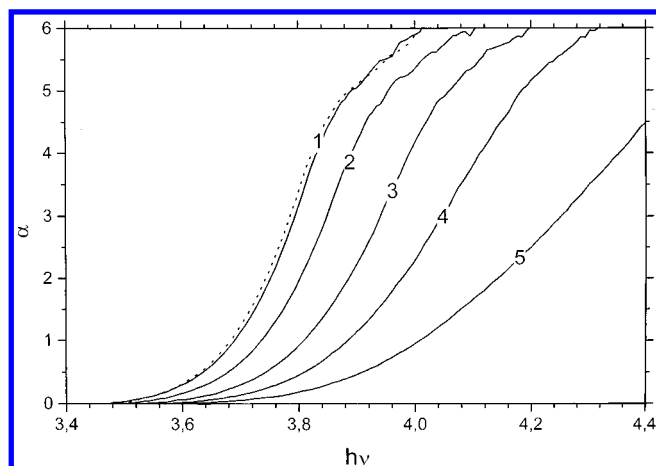$$N/\gamma = \text{const} \tag{6}$$

Figure 4. Sol−gel ($H = 2.7$) absorption spectra with dilution: 1:1 (1), 1:2 (2), 1:4 (3), 1:8 (4), and 1:20 (5) in the 1-mm optical cell. The absorption spectrum with the 1:20 dilution in the 20-mm optical cell is shown by the dotted line.
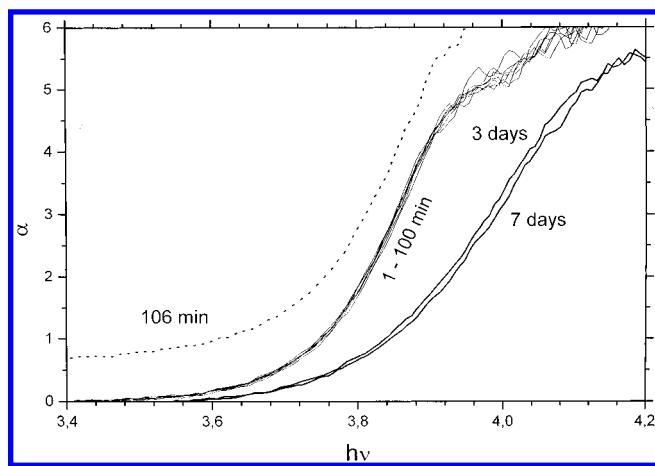

Figure 5. Absorption spectra recorded during the sol−gel process (TTIP/H_2O/2-propanol = 1.5/0.24/30 mL; $H = 2.7$; $t_{ind} \approx 10^2$ min): 1−100 min ($t < t_{ind}$), 106 min ($t > t_{ind}$), 3 and 7 days later.

Our earlier experiments showed that the scattered light intensity I_{scat} strongly increases in the very beginning of the sol−gel process indicating the creation of the 4.0 nm nuclei (see Figure 1).[6−8] However, the solutions are still highly transparent at times shorter than the induction time ($t_{ind} \sim 10^2$ min in presented experiments). As we will see, the hypothesis of nucleus stability can be verified by measurements of the scattered light intensity in the sol−gel solutions under dilution. Generally, the dilution decreases the concentration of the light-scattering particles in the zone of observation. But if the condensation reactions 2−3 are reversible, the dilution shifts those in equilibrium resulting in the nuclei dissolution. This would in addition strongly influence I_{scat}.

The performed LS measurements have shown a proportionality between the scattering light intensity and the dilution factor:

$$I_{scat} \propto \gamma \qquad (7)$$

Taking into account that $I_{scat} \propto a_0^6 N$ (where a_0 represents the nanoparticle size and N is the concentration) and that N/γ does not change (as follows from eq 6), we obtain from eq 7 $a_0^6 N/\gamma$ = const and with a high accuracy

$$\alpha_0 = \text{const} \qquad (8)$$

These measurements show that the nucleus size does not change under dilution in 2-propanol. One can conclude that: (1) hydrolysis reaction efficiently proceeds during water addition; (2) hydrolyzed Ti(OR)$_3$(OH) molecules immediately react after appearance: neither accumulation nor secondary hydrolysis of these molecules is necessary for the start of the condensation reaction; and (3) 4.0-nm nuclei are stable.

It is important to emphasize that we see no changes in either the AO or the line shape of the absorption spectra in the wide range of $H \in [0.1...3]$. In relation with this result we assume that the nature of the absorbing species is conserved. Do we conclude from this result that no chemical changes occur in the solution?

A discussion of this point is related to the assignment of the observed absorption to a certain structural unit (molecule, cluster or nucleus). The LS measurements in the Ti(OPr^i)$_4$ sol−gel process at high hydrolysis ratios ($H \geq 1.45$) have shown that under constant precursor concentration the initial scattered light intensity I_0 exhibits a small dependence on H and that H influences mostly the process kinetics: d/dt(I_{scat})[7] (see an

example in Figure 1). This fact allows us to firmly assign the absorbing species to the nuclei in the range of $H \geq 1.45$.

On the other hand, it is not certain if this assignment can be used in the range of low $H \leq 1$. Recently, by using ^{17}O NMR and small-angle X-ray scattering methods, Blanchard et al.[5] have reported the structural characterization of titanium oxo polymers. In solutions with the Ti(OPr^i)$_4$ precursor and at low hydrolysis ratio there exist two stable forms: Ti$_3$(μ_3O)(OPr^i)$_{10}$ and Ti$_{11}$O$_{13}$-(OPr^i)$_{18}$. The first oxo cluster dominates at $H = 0.05$ and the second appears at $H = 0.2$. Upon increasing H, a decrease of intensity of the line assigned to Ti$_3$(μ_3O)(OPr^i)$_{10}$ and an increase of the resonances corresponding to Ti$_{11}$O$_{13}$(OPr^i)$_{10}$ is observed. The condensation ratio $k = n(O)/n(Ti)$ of these structures increases from 0.33 for the first one to 1.18 for the second, indicating that an increase in H results in the formation of more condensed species through furthers hydrolysis accompanied by reorganization of the low condensed clusters. It may be that the solution absorbance at $H < 1$ is related to the oxo clusters. In this case the energetic structures of these oxo clusters and that of the heavier oxo polymers are similar, and the size effect on the AO does not exist in the range of larger clusters. In other words, these clusters constitute the building blocks of nuclei. More experiments are required to clarify the issue of cluster kinetics.

Polymer Mass Conservation in the Sol−Gel Process. The temporal evolution of the absorption spectrum during the sol−gel process at $H = 2.7$ is shown in Figure 5. In contrast to the earlier reported results by Hartel[10] no changes have been found at $t < t_{ind}$. Both the absorption onset and the line shape are stable. At times longer than the induction time $t \geq t_{ind}$ the background level grows. This background shows little dependence on wavelength and apparently originates from the light-scattering component related to an increase of the solution opacity. Subtraction of $\Delta\alpha = 0.08$ from the spectrum at $t = 106$ min (precipitated solution) shows almost perfect agreement with the spectra of transparent colloids ($t \leq 100$ min). This means that the wavelength specific absorption component, which is clearly manifested at earlier process times, does not change even at $t \geq t_{ind}$ and that neither the nature (the general formula of the structural unit being TiO$_{2-x}$(OR)$_{2x}$) nor the concentration of the absorbing species are changed. Two more curves measured 3 and 7 days after precipitation are also presented in Figure 5. The absorbance continuously decreases with time due to the solid deposition: only the smallest nanosized particles can be still suspended in the solutions over a week.
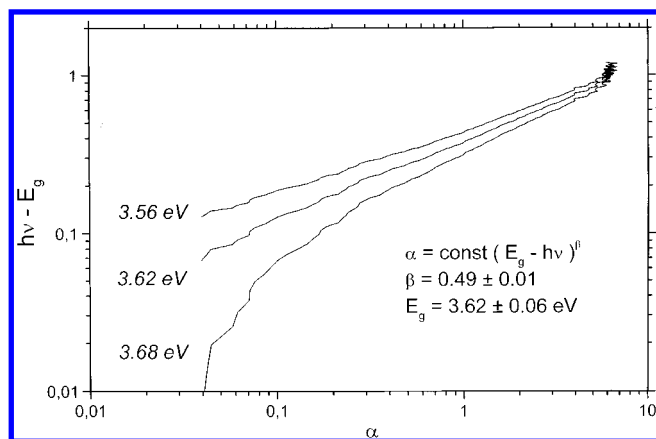
Figure 6. Determination of the AO value of the solid in the "oxo" or polymer phase.

We have found that the sol−gel absorption is due to the condensed nanometric nuclei. As we have already discussed, the measured absorption spectra do not shift during the oxo polymer solid growth, at least for particle sizes above 4.0 nm. One can therefore neglect the size effect and consider these particles as obeying the band gap of the infinite solid. To obtain the absorption onset (AO) of this solid phase, we have plotted the rising part of the absorption curve $\alpha(h\nu)$ in axes $\ln(\text{AO} - h\nu)$ and $\ln(\alpha^\beta)$. Two free parameters (AO and β) could be found from of the linear fit through the experimental data. First, by minimizing χ^2 of the least-squares fit the value of AO has been obtained. Second, keeping the obtained value of AO, the β-factor can be extracted from the fitted slope. The best fit shows AO = 3.62 ± 0.06 eV and the power factor $\beta = 0.49 \pm 0.1$, which indicate the indirect character of the interband transitions with $E_g = 3.62$ eV. This procedure is presented in Figure 6. The obtained value of E_g is in agreement with the earlier published value in ref 11. AO of this solid phase is situated 0.42 and 0.62 eV higher than that of the anatase and rutile phases of TiO$_2$. Moreover, the spectrum exhibits a long exponential tail below 3.6 eV indicating intense subband transitions. We assign the nuclei and precipitated powders to the solid in the polymer or "oxo" phase, which serves as a precursor of the anatase crystalline phase of TiO$_2$ and which can be transformed to the last by thermal treatment at 400 °C.[11]

From our measurements we know that the UV absorption between 3.6 and 3.95 eV is due exclusively to the condensed polymers, initially presented in the form of nanosized nuclei. We have carried out absorption measurements that show solid mass conservation during particle growth:

$$M_S = \text{const} \qquad (9)$$

Particle Growth Mode. As we have discussed earlier[6−8,11] the polymer or "oxo" phase appears in the form of 4.0 nm ($2R$) nuclei in the beginning of the sol−gel process. This value is close to the gyration radius $R_g = 25$ Å determined by SAXS measurements on titanium oxopolyleric sols and gels.[5] These nuclei slowly grow in size and precipitate, being ∼7−8 nm in diameter.[7,8] The mass conservation (eq 9) is a very important result, which allows us to understand the particle growth mode.

First, the total solid mass conservation imposes the condition that this mass is created at the very early stage of the sol−gel process − during the reagents TTIP/2-propanol and H$_2$O/2-propanol mixing. The dominant hydrolysis−condensation reactions seem to be eqs 1 and 2 (not eq 3) as they occur at the first TTIP + H$_2$O contact. This can be illustrated by the following.

We have seen in Figure 3 that the absorbance in the range 3.6−3.95 eV does not change with H for $H \leq 1$ if [H$_2$O] = const and for $H > 1$ if [TTIP] = const. This means that the lower of two reagent concentrations, min([TTIP],[H$_2$O]), defines the absorbance and hence the created mass of the solid.

As we have seen, the secondary hydrolysis does not contribute (or contributes weakly) to the absorption: the stable and irreversible absorption spectra of the condensed nuclei appear at a very low hydrolysis ratio of $H \leq 0.1$. It is instructive to note that there is practically no difference between the curve slopes $\alpha(V_{\text{TTIP}})$ at low TTIP concentrations corresponding to [H$_2$O] = const and $H = 2.7$ (see Figure 3). Using the above-described calibration of the α-axis, we have easily obtained that the quantity of water used for the total solid mass created in the sol−gel experiment with $H = 2.7$ corresponds to the hydrolysis ratio $H_{\text{sol}} = 1.1−1.2$. This value is in good agreement with an earlier obtained value $H^* \approx 1.0$, at which the slope of the $\alpha(T)$ curve changes (Figure 3). We conclude that even a higher water concentration does not change considerably the solid composition, and we attribute $H^* = 1.1 \pm 0.1$ to the critical hydrolysis ratio, which separates two domains of the sol−gel kinetics. It is interesting to note that this value is close to the condensation ratio of the Ti$_{11}$O$_{13}$(OPr^i)$_{10}$ oxo cluster ($k = 1.18$). This cluster or species with a close chemical composition could be responsible for the observed absorption below 3.95 eV.

Second, the particles could not grow by Ostwald repining, because nuclei are stable as show by our LS measurements. Moreover, the hydrolyzed monomers do not dominantly contribute to the absorption. If now the absorption was due to nuclei growing by these monomers addition, the total mass of the solid M_S would increase, which should have a consequence on absorbance as $\alpha \propto M_S$. This is not our case. We believe that the driving force for the particle slow growth during the induction period of the sol−gel process is the secondary hydrolysis of the surface OR groups, which results in the agglomeration of primary particles. In contrast to the primary hydrolysis, which exclusively results in the solid-phase nucleation and which proceeds at $H \leq 1$, the secondary hydrolysis needs the hydrolysis ratio $H > 1$ to appear. It triggers the powder growth process.

No change in the initial solution absorbance has been observed in the latter stages during the sol−gel induction time.[6,7] Because of this we believe that nuclei do not undergo any structural changes during the stage of growth, they conserve the nature of the smallest building blocks of the final powders. From this point of view the process of reagents mixing in which the nuclei population appears may be a determinant factor for the powder quality.

Conclusion

We have carried out absorption measurements during the initial stage of the Ti(OPr^i)$_4$ sol−gel process. The experimental results show that the hydrolysis/condensation reaction takes place during the mixing of the reagents and that it is complete at low $H \leq 1$. A critical hydrolysis ratio $H^* = 1.1 \pm 0.1$ separates the two domains "nucleation/growth" of the sol−gel kinetics: the absorbance between 3.6 and 3.95 eV increases with H when $H \leq H^*$ and it is independent of H when $H > H^*$. We believe that the first hydrolysis of TTIP begins a fast nucleation process resulting in nanosized titanium-oxo alkoxo clusters: neither a second hydrolysis of TTIP nor an accumulation of hydrolyzed molecules are needed. The total polymer mass appears at this stage in the form of these clusters (size reaches 4.0 nm at $H \geq 1.45$) and is conserved during the process.

The subsequent powder particle growth proceeds by the aggregation of nucleus. The second hydrolysis of the particle surface OR group seems to be responsible for this growth and needs a hydrolysis ratio higher than $H*$ to appear. The mixing of the initial reagent seems to be the key stage of the TTIP sol−gel process.

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