Articles

Characterization of Titanium and Zirconium Valerate Sol–Gel Films

Kathryn G. Severin and Jeffrey S. Ledford*

Department of Chemistry, The Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1322

Beatrice A. Torgerson and Kris A. Berglund

Departments of Chemical Engineering and Chemistry, The Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1322

FTIR and XPS have been used to characterize titanium and zirconium valerate thin films prepared using sol–gel techniques. Films were prepared by hydrolysis of titanium(IV) isopropoxide or zirconium(IV) *n*-propoxide in excess valeric acid at room temperature. Film solution chemistry, from precursors to cast films, was followed with FTIR. The structure and chemical composition of films spin cast from fresh and day-old solutions were determined. Results of these studies suggest that all films consist of a metal–oxygen polymer backbone coordinated with bidentate valerate ligands. No evidence for the presence of alkoxide ligands has been found. A small amount of water is present in all cast films. While solution aging experiments indicate that the zirconium film structure does not change with solution reaction time, carboxylate ligand concentrations are higher in titanium films made from aged solutions. Titanium films made from aged solutions contain slightly less than 1.5 valerate ligands/titanium atom. Zirconium films are more highly carboxylated with almost two valerate groups per metal center.

Introduction

The sol–gel process is an attractive approach for the synthesis of glasses, ceramics, and organic–inorganic composite materials.[1–4] The advantages of sol–gel techniques arise from the high purity of the metal alkoxide precursors, the molecular homogeneity of the intermediate sols, and the low processing temperatures necessary to prepare materials. In addition, the rheological properties of many sols and gels make them suitable for film preparation using methods such as spin casting and dip coating.[4–7] Thus considerable effort has been devoted to the development of new thin film materials using sol–gel techniques. Understanding the chemistry involved in film synthesis will lead to better control of the sol–gel process and, ultimately, to the ability to produce films which are tailor-made for particular applications.

Hydrolysis and condensation reactions of silicon alkoxides have been extensively studied and, consequently, the relationship between sol–gel chemistry and polysilicate structure is reasonably well understood.[8–12] In comparison, the sol–gel chemistry of transition-metal alkoxides has been less completely characterized. Transition-metal sol–gel chemistry differs from that of silicon because transition metals have a variety of coordination states available and lower electronegativities than silicon.[13–16] Both the ability to increase coordination number and the electropositive nature of transition metals result in alkoxide hydrolysis and condensation rates which are usually orders of magnitude greater than that of silicon alkoxides. Therefore, unless some form of chemical control is employed, hydroxide and/or oxohydroxide species precipitate immediately upon hydrolysis of transition-metal alkoxides. Chemical control of transition-metal alkoxide hydrolysis and condensation reactions is often achieved by adding

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complexing reagents such as organic acids or β-diketones.[17-33] When these ligands react with metal alkoxides, new molecular species are produced with altered structures and reactivities. Complexation promotes decoupling between hydrolysis and condensation[34] and facilitates the preparation of uniform, transparent coatings.[35] Strong complexing ligands are more stable toward hydrolysis than alkoxide ligands due to chelate, electronic, and steric hindrance effects. Thus, the organic ligands become anchored to the transition-metal oxo–polymeric backbone and form organic–inorganic networks.

The role of acetic acid as a complexing agent in the sol–gel chemistry of titanium and zirconium alkoxides has been examined in some detail.[22-32] We have previously reported that optically transparent, porous films can be produced at ambient temperatures from mixtures of acetic acid, water, and titanium, zirconium, or hafnium alkoxides.[32] However, these films tend to be of poor quality and are soluble in water. We found that film properties could be improved by complexing with longer chain carboxylic acids. Films produced using valeric acid (n-C_4H_9COOH) are not only transparent and porous but also hydrophobic and show greater integrity and better adhesion to glass substrates than those prepared with acetic, propanoic, or butyric acid.[33] Our previous work with carboxylic acid/transition-metal alkoxide sol–gel chemistry also focused on the effect of acid and water concentration on the structure of solutions, monoliths, and films.[32,33]

A major goal of this work is to gain a more detailed understanding of the chemistry involved in the production of films from titanium(IV) isopropoxide ($Ti(OPr^i)_4$) or zirconium(IV) n-propoxide ($Zr(OPr^n)_4$) and valeric acid. It is generally acknowledged that there are three principal reaction steps in the synthesis of sol-gel materials from transition-metal alkoxides and carboxylic acids.[5,13,15,18,34,36] The first is a nucleophilic substitution of an alkoxide ligand
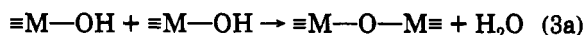
by a carboxyl ligand:

$$M(OR)_4 + xR'COOH \rightarrow M(OR)_{4-x}(OOCR')_x + xROH \quad (1)$$
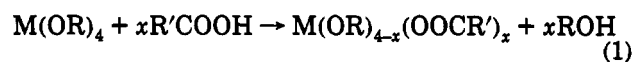
Alcohol is a byproduct of this reaction. The second is the hydrolysis of one or more of the remaining alkoxide groups:

$$\equiv M\text{—}OR + H\text{—}OH \rightarrow \equiv M\text{—}OH + ROH \quad (2)$$
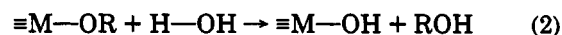
Carboxylate ligands can be hydrolyzed but this occurs less readily. Hydrolysis initiates condensation. In condensation, hydroxyl groups react with hydroxyl or alkoxide groups on other metal centers producing M–O–M bonds and water or alcohol, respectively:

$$\equiv M\text{—}OH + \equiv M\text{—}OH \rightarrow \equiv M\text{—}O\text{—}M\equiv + H_2O \quad (3a)$$

$$\equiv M\text{—}OR + \equiv M\text{—}OH \rightarrow \equiv M\text{—}O\text{—}M\equiv + ROH \quad (3b)$$

Esterification reactions also play a fundamental role in the solution chemistry of acetic acid modified alkoxides.[27-29,36] Esters can be formed by the reaction of a carboxylic acid with either an alcohol molecule or an alkoxide ligand producing water or a hydroxyl ligand, respectively.[29] The importance of esterification reactions in the chemistry of valeric acid modified alkoxides is not known.

Carboxylate ligands can adopt a variety of coordination modes and as bidentate bridging ligands, can act as network formers. The separation ($\Delta\nu$) between the asymmetric ($\nu_{as}(COO)$) and symmetric ($\nu_s(COO)$) carboxyl stretch frequencies can be used as an indicator of carboxylate coordination mode.[37] Separations much greater than that of the ionic form of the ligand tend to indicate monodentate coordination; otherwise, bidentate coordination is implied. It has also been suggested that bidentate bridging ligands typically exhibit $\Delta\nu$ values similar to ionic species, while bidentate chelating ligands show smaller splittings.[37] This reasoning has been applied to determine coordination mode of acetate ligands in sols and gels.[22,28,32] Carboxylate coordination mode can also be inferred from the frequency of the $\nu_{as}(COO)$ absorbance band in the infrared spectrum of a material. Grigor'ev found that the greater the OCO bond angle, the higher the $\nu_{as}(COO)$ frequency.[38] Since bond angle tends to decrease with coordination mode: monodentate > bidentate bridging > bidentate chelating, $\nu_{as}(COO)$ bands of considerably higher frequency than in the spectrum of the ionic form of the ligand suggest the presence of monodentate ligands.

The first half of this paper is devoted to a Fourier transform infrared spectroscopy (FTIR) study of the sol–gel solution chemistry specific to valeric acid modified $Ti(OPr^i)_4$ and $Zr(OPr^n)_4$. Information is obtained which can be related to the rate, extent, and mechanism of the sol–gel reactions in these systems. The second part of the paper involves the characterization of titanium and zirconium valerate films. The structure and chemical composition of these films, including the nature and concentration of ligands, are elucidated using a combination of FTIR and X-ray photoelectron spectroscopy (XPS).

Experimental Section

Materials. Titanium(IV) isopropoxide, zirconium(IV) n-propoxide 70% in n-propanol, isopropyl alcohol (99.5%, HPLC

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grade), and valeric acid (99+%) were obtained from Aldrich Chemical Co. and used without further purification. All syntheses used chemicals obtained from freshly opened bottles and distilled, deionized water. Sodium valerate was prepared by mixing valeric acid with sodium carbonate (Aldrich Chemical Co.).

Solution Preparation. The methods used to synthesize films were based on techniques developed in these laboratories for the preparation of transition metal carboxylate thin films.[33] Reactions were carried out at room temperature in capped vials. Molar ratios of metal alkoxide:valeric acid:water of 1:9:1.5 were used to prepare the films. Valeric acid was added to the alkoxide, immediately followed by water. A vortex mixer was used to vigorously stir solutions following the addition of each reactant. The reaction between valeric acid and both metal alkoxides was exothermic. The resulting titanium solutions were clear and colorless; zirconium solutions were clear and slightly yellow.

Two sets of titanium solutions were prepared. In the first, isopropyl alcohol was added to titanium isopropoxide before the addition of valeric acid. The alcohol concentration was the same as in the 70% Zr(OPr^n)$_4$ solution (2.3 alcohol:1 alkoxide). The second set of titanium solutions was prepared without the addition of alcohol. Results of the analysis of both sets of titanium solutions and the films prepared from these solutions were identical within experimental error. Results presented in this paper are for titanium solutions and films prepared without added isopropyl alcohol.

Film Preparation. Solutions were deposited onto the desired substrate (quartz or KBr) and spun for 5 min. Films were air-dried overnight and stored in a desiccator. All films prepared in this study were transparent and colorless and exhibited complete and uniform coverage of quartz substrates. Each solution and film was prepared in triplicate. To simplify discussion, titanium and zirconium films cast immediately after solution preparation are denoted Ti00 and Zr00, respectively. Films prepared from solutions aged for 24 h before casting are denoted Ti24 and Zr24.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were obtained using a Mattson Instruments Galaxy 3020 Fourier transform infrared spectrometer. Data acquisition and processing were performed using an Enhanced First software package. The mid-IR region (4000–400 cm^{-1}) was examined with a resolution of 2 cm^{-1}. Films were cast on KBr windows; solution spectra were obtained from a drop of solution placed between two KBr windows. To identify artifacts which could be due to reactions with KBr, several films were cast on Ge and analyzed with FTIR. Spectral features were the same for films cast on both substrates. *In situ* heating experiments were performed under nitrogen purge (99.5%, AGA Gas Co.) using a stainless steel sample holder equipped with cartridge heaters (Omega). The temperature was fixed using an Omega CN 1200 controller.

X-ray Photoelectron Spectroscopy (XPS). Films cast on quartz slides were analyzed with a Perkin-Elmer surface science instrument equipped with a Model 10-360 precision energy analyzer and an omnifocus small spot lens. All spectra were collected using a Mg anode (1253.6 eV) operated at a power of 300 W (15 kV and 20 mA) with an analyzer pass energy of 50 eV. Three regions were scanned in each film: C1s, O1s and the most intense metal core band (Ti 2p or Zr 3d). Binding energies were referenced to adventitious carbon (C1s = 284.6 eV) and were measured with a precision of ±0.1 eV. Empirically derived sensitivity factors[39] were used for quantitative XPS calculations involving the C1s and O1s. For the Ti 2p and Zr 3d, sensitivity factors were derived from the analysis of TiO$_2$ and ZrO$_2$ (Aldrich Chemical Co., 99.99+%). XPS peaks were fitted with 20% Lorentzian–Gaussian mix Voigt functions using a nonlinear least-squares curve-fitting program.[40] Each reported result is based on the analysis of at least three films. It must be noted that the use of XPS to evaluate film composition assumes that the films are homogeneous.

Figure 1. FTIR spectra of (a) valeric acid; (b) Ti(OPr^i)$_4$, (c) isopropyl alcohol, (d) Zr(OPr^n)$_4$ in *n*-propanol, and (d) *n*-propanol.

Results and Discussion

FTIR Spectra of Reactants. The FTIR spectra of reactants, as well as those of isopropyl alcohol and *n*-propanol, are shown in Figure 1. The assignment of FTIR absorption bands for valeric acid (Figure 1a) is straightforward.[41,42] Three methyl and methylene C–H stretching absorbances are observed at 2962, 2935, and 2876 cm^{-1} superimposed on an O–H absorbance centered near 3000 cm^{-1}. The strong absorbance observed at 1711 cm^{-1} is due to a dimeric carboxylic COO asymmetric stretch. Bending and stretching vibrations of C–O–H groups are observed at 1414, 1280, and 940 cm^{-1}. Skeletal vibrations are evident at 1382, 1109, and 752 cm^{-1}.

In the FTIR spectrum of Ti(OPr^i)$_4$ (Figure 1b) absorbance bands are assigned as follows: the band at 1126 cm^{-1} is due to a combination of skeletal and C–O stretches,[43] that observed at 1002 cm^{-1} is a ν(C–O)Ti vibration,[44] a skeletal vibration band is at 852 cm^{-1},[44] and a ν(Ti–O) band appears at 621 cm^{-1}.[43] Due to steric hindrance by bulky isopropoxide groups, Ti(OPr^i)$_4$ is monomeric with a coordination number of four.[30,45] Isopropyl alcohol (Figure 1c) can be most easily distinguished from the alkoxide by the sharp bands at 953 and 818 cm^{-1}.

Absorption bands in the spectrum of Zr(OPr^n)$_4$ in *n*-propanol (Figure 1d) are assigned based upon the

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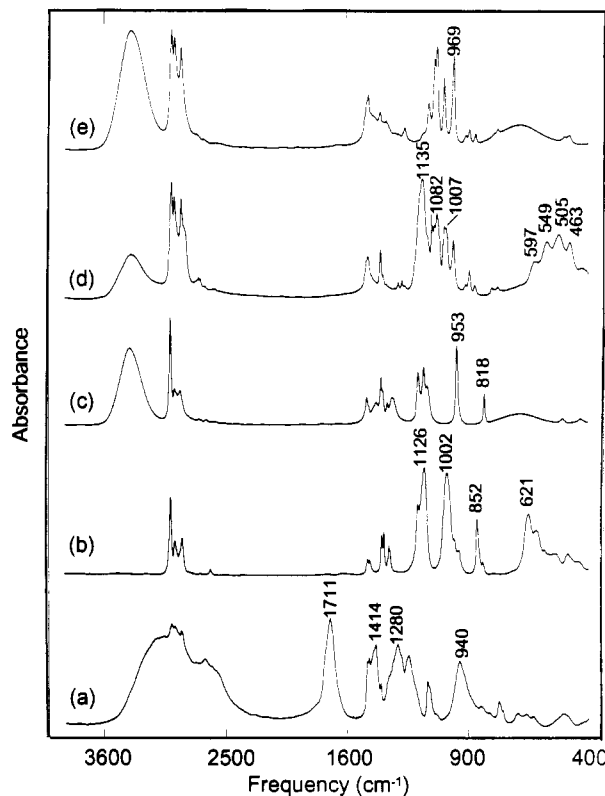(40) Software provided by Dr. Andrew Proctor, University of Pittsburgh, Pittsburgh, PA.

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analysis of similar alkoxides.[13,43] The strong band at 1135 cm^{-1} is attributed to a combination of ν(C–O)Zr and skeletal stretches, bands observed at 1082 and 1007 cm^{-1} are also associated with the alkoxide and may be due to ν(C–O)Zr vibrations, and those observed at 597, 549, 505, and 463 cm^{-1} are attributed to ν(Zr–O). Alcohol absorbances between 1100 and 900 cm^{-1} make it difficult to determine structure based upon ν(C–O)Zr bands; however, multiple bands in the low-frequency region are consistent with an oligomeric structure. Ebulliometric studies by Bradley and Carter[46] indicate that Zr(OPr^n)$_4$ is oligomeric in *n*-propanol with a molecular complexity of 2.44. The zirconium coordination sphere is also thought to be increased by solvation in *n*-propanol.[47] This limits the extent of oligomerization compared to that in nonpolar solvents. *n*-Propanol (Figure 1e) can be identified a sharp band at 969 cm^{-1}.

Solution Reactions. Solution reactions were investigated by preparing a series of alkoxide–acid mixtures with increasing valeric acid concentrations. In addition to the spectra of 1:1 (alkoxide:acid) mixtures of each alkoxide and valeric acid, spectra of reaction mixtures with the lowest detectable level of unreacted valeric acid are shown. The concentration of these solutions indicates the number of valerate ligands which can be readily coordinated to each alkoxide. To the latter solution, water was added at a molar concentration of 1.5 water/metal alkoxide. This is the concentration of water in film solutions and is sufficient water to completely hydrolyze carboxylated alkoxides provided that condensation also occurs. Analysis of these solutions avoids interference due to excess valeric acid present in the 1:9 film mixtures. It is recognized that the presence of excess valeric acid may alter the solution chemistry; however, fundamental information about the interaction of solution species can be obtained by analyzing mixtures with lower acid concentration.

To evaluate the coordination mode of valerate ligands in solutions and films, sodium valerate was prepared and analyzed with FTIR. The absorbances for sodium valerate can be assigned by analogy to those of sodium acetate reported by Spinner.[48] Absorbances at 1562 and 1421 cm^{-1} ($\Delta\nu$ = 141 cm^{-1}) are ν_{as}(COO) and ν_s(COO) bands, respectively, of the ionic valerate groups.

Titanium Solutions. Figure 2 shows the FTIR spectra of Ti(OPr^i)$_4$ (Figure 2a), 1:1 and 1:1.5 mixtures of this alkoxide and valeric acid (Figure 2b,c, respectively), and the latter mixture after the addition of water (Figure 2d). For a 1:1 mixture (Figure 2b), no free valeric acid is observed (1711 cm^{-1}) and ν_{as}(COO) bands (1575 and 1529 cm^{-1}) are present. This means that all of the valeric acid has reacted and formed valerate ligands which are bonded to titanium. The frequency of the ν_{as}(COO) bands are close to that of ionic valerate (1562 cm^{-1}) and, therefore, are assumed to be due to bidentate valerate ligands. On the basis of its frequency, the stronger, higher energy ν_{as}(COO) band (1575 cm^{-1}) is probably due to bridging valerate ligands. Whether the lower energy band is due to bridging or chelating ligands cannot be determined.

The appearance of absorption bands characteristic of isopropyl alcohol (953 and 818 cm^{-1}) indicates that valerate ligands have displaced alkoxide ligands producing alcohol. Interestingly, the alkoxide absorbance at 1002 cm^{-1} in
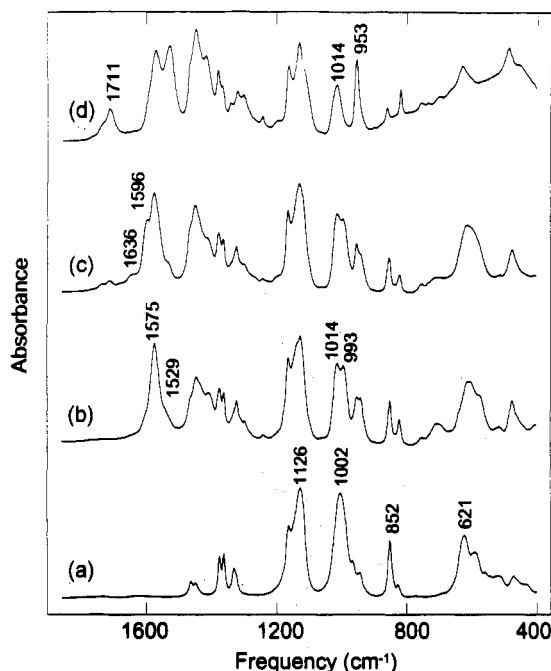

Figure 2. FTIR spectra of (a) Ti(OPr^i)$_4$, (b) 1:1 mixture, and (c) 1:1.5 mixture of Ti(OPr^i)$_4$ and valeric acid, (d) 1:1.5:1.5 mixture of Ti(OPr^i)$_4$, valeric acid, and water.

Ti(OPr^i) is now split into two distinct bands at 1014 and 993 cm^{-1}. This suggests that in the 1:1 solution, there are two types of alkoxide ligands present, probably terminal and bridging alkoxides, respectively. The assignment is based upon other alkoxides: typically terminal alkoxides have higher vibrational frequencies than bridging alkoxides.[13] The replacement of a bulky isopropyl group with a valerate ligand not only increases the coordination to five, but the decrease in steric hindrance also allows a further increase in coordination number to six with the formation of alkoxide bridges. The transformation of Ti-(OPr^i)$_4$ from a monomeric to an oligomeric structure was also reported by Sanchez et al.[49] for acetic acid modification of this alkoxide.

The spectrum of the 1:1.5 solution contains a band at 1711 cm^{-1} due to dimeric valeric acid. Apparently, titanium centers do not accommodate a second valerate ligand as readily as they accept the first. On average, there are between 1 and 1.5 valerate ligands/titanium atom in this solution. There are two new bands (1636 and 1596 cm^{-1}) due to ν_{as}(COO) absorbances. While the latter may be ascribed to bidentate bridging ligands, the band at 1636 cm^{-1} probably indicates the formation of monodentate valerate ligands. This is consistent with steric hindrance at the titanium center which would make bidentate coordination more difficult. Alcohol and alkoxide bands are very similar to those observed in the 1:1 solution spectrum. It should be noted that there is a small absorbance band at 1734 cm^{-1}. The assignment of this band will be discussed in some detail later in this paper.

Figure 2d shows the spectrum of the 1:1.5 mixture after the addition of water. There is still a substantial terminal alkoxide band at 1014 cm^{-1} but the bridging alkoxide band at 993 cm^{-1} is no longer evident. Apparently, bridging alkoxide groups are more readily hydrolyzed than terminal

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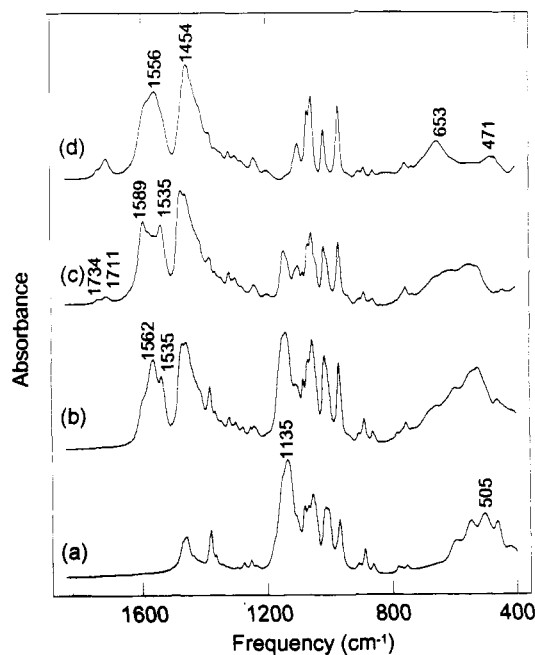
Figure 3. FTIR spectra of (a) Zr(OPr^n)$_4$ in n-propanol, (b) 1:1 mixture and (c) 1:2 mixture of Zr(OPr^n)$_4$ and valeric acid, (d) 1:2:1.5 mixture of Zr(OPr^n)$_4$, valeric acid, and water.

alkoxides. Condensation is occurring as evidenced by the presence of a rising background in the low-energy portion of the spectrum that is commonly attributed to phonon bands in a titanium oxygen network.[50] The increase in valeric acid concentration indicates that valerate ligands are also displaced by the addition of water. Sanchez *et al.*[30] also observed that free acid was formed when greater than 1 mol of water/metal alkoxide was added to acetate modified titanium alkoxides. The high-frequency ν_{as}(COO) bands present in the solution spectra before the addition of water (1636 and 1596 cm^{-1}) are no longer present. Either these carboxylates are preferentially hydrolyzed or the decrease in steric hindrance which occurs when isopropyl groups are hydrolyzed allows conversion from monodentate to bidentate coordination. Two ν_{as}(COO) bands of about equal intensity are present and of the same frequency as that in the 1:1 solution spectrum (Figure 2b). As stated previously, the higher energy band is probably due to bidentate bridging ligands and the lower may be due to either bridging or chelating ligands.

It should be noted that small absorbance bands due to alkoxide ligands are present in the freshly prepared titanium film solution (1 Ti(OPr^i)$_4$:9 valeric acid:1.5 water) spectra (not shown). The FTIR spectrum of a solution which has been aged for 24 h does not contain bands characteristic of alkoxide ligands.

Zirconium Solutions. Figure 3a shows the FTIR spectrum of Zr(OPr^n)$_4$ in n-propanol. When an equimolar amount of valeric acid is added to the alkoxide (Figure 3b), it reacts completely (no band at 1711 cm^{-1}) and forms valerate ligands (ν_{as}(COO) bands at 1562 and 1535 cm^{-1} with a 1600 cm^{-1} shoulder). As in the titanium solutions, the higher frequency bands are probably due to bidentate bridging ligands and the lower may be due to either bridging or chelating valerates. The relative intensity of alcohol bands between 1200 and 800 cm^{-1} also increases with respect to the alkoxide bands in this region of the

spectrum. This is consistent with the displacement of alkoxide ligands and formation of alcohol. Unlike titanium, none of the alkoxide (C–O)Zr features split, and their relative intensities do not appear to change with the addition of valerate ligands. This implies that alkoxide ligand coordination and oligomerization is unchanged by carboxylation. However, absorbance bands due to n-propanol also occur in this region of the spectrum making it difficult to say this unequivocally. The maximum intensity of the bands between 700 and 500 cm^{-1} is shifted to a slightly higher frequency than in the alkoxide spectrum. This is may be due to coordination with valerate ligands.[13]

The spectrum of the 1:2 mixture is shown in Figure 3c. Small bands at 1711 (unreacted valeric acid) and 1734 cm^{-1} (*vide infra*) are present. These bands are not present in the spectrum of a 1:1.5 mixture (not shown). Nearly two valerate ligands are readily coordinated to zirconium atoms in this solution. A broad band due to ν_{as}(COO) occurs between 1589 and 1535 cm^{-1} indicating valerate ligands with bidentate coordination only. In comparison to the 1:1 solution spectrum, the relative intensities of the alkoxide bands are decreased and the alcohol bands increased. This is most clearly seen by comparing the intensity of the alkoxide band at 1135 cm^{-1} with the alcohol bands in this region.

Figure 3d shows the spectrum of this solution after the addition of water. Unlike the titanium solutions, addition of water completely removes all alkoxide ligands from zirconium. Alkoxide bands at 1139, 1082, and 1007 cm^{-1} are not evident. Indeed, this portion of the spectrum resembles that of n-propanol (Figure 1e). The alkoxide bands between 600 and 450 cm^{-1} are also absent. Absorption bands at 635 and 471 cm^{-1} are probably due to ν(Zr–O) vibrations of oxy bridges formed upon condensation. As in titanium solutions, some of the valerate groups are hydrolyzed as well, as seen by the increase in the intensity of the band at 1711 cm^{-1}. ν_{as}(COO) bands are present in the same range as before the addition of water, indicating only bidentate coordination.

Comparison of Titanium and Zirconium Solution Reactions. The results of the FTIR analysis of Ti(OPr^i)$_4$–valeric acid and Zr(OPr^n)$_4$–valeric acid solution spectra are consistent with the three-step reaction scheme presented in the Introduction. However, our study has revealed that there are differences in the reactivity of the two alkoxides. In particular, Zr(OPr^n)$_4$ readily accepts a higher level of carboxylate ligands than Ti(OPr^i)$_4$ and Zr-(OPr^n)$_4$ alkoxide ligands are more rapidly hydrolyzed than those on Ti(OPr^i)$_4$. These differences can be related to both the chemical nature of the metal atoms and to steric factors associated with their ligands.

As stated in the Introduction, transition-metal alkoxides are more reactive toward nucleophilic substitution reactions than silicon alkoxides due to the more electropositive nature of transition metals and the ability to expand their coordination sphere. For analogous reasons, in general, zirconium alkoxides would be expected to be more reactive than titanium alkoxides. Zirconium is less electronegative than titanium, and zirconium is able to accommodate a larger coordination sphere than titanium. Coordination numbers of up to 8 are possible for zirconium, whereas the optimum coordination number for titanium is 6.[51]

(50) McDevitt, N. T.; Baun, W. L. *Spectrochim. Acta* **1964**, 20, 799.

(51) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.

The nature of the ligands on the metal center also affects the reactivity of a particular alkoxide. The reactivity of alkoxy ligands with respect to nucleophilic substitution decreases in the order tertiary > secondary > primary.[15] This is related to the ability of the alkoxide to form a good leaving group. Therefore, isopropyl ligands would be expected to be more reactive than n-propyl ligands in nucleophilic substitution reactions. The reactivity of alkoxy ligands is also influenced by the structure of the alkoxide compound. Monomeric alkoxides are more reactive than oligomeric alkoxides. For these reasons, Ti-$(OPr^i)_4$ is expected to be very reactive in nucleophilic substitution reactions. Indeed, 1:1 mixture of this alkoxide with valeric acid undergoes a strongly exothermic reaction producing an oligomer in which titanium has a coordination number of six.

Addition of a second valerate ligand apparently occurs more readily for the zirconium valerate alkoxide complex than for its titanium counterpart. Not only is zirconium larger than titanium, but it is coordinated with less bulky primary alkoxide ligands. It is also possible that the oligomeric nature of $Zr(OPr^n)_4$ is unchanged by reaction with valeric acid. Relatively labile solvate molecules, as well as alkoxide ligands, could be displaced in the substitution reaction to accommodate bidentate valerate ligands without a change in the oligomeric nature or coordination number. However, stable oligomeric titanium complexes would need to be broken in order to accommodate the addition of a second bidentate valerate ligand. Evidence of the inability of titanium to accommodate further carboxylate ligands is the presence of monodentate coordination in the 1:1:5 Ti$(OPr^i)_4$ valeric acid solution. No monodentate valerate ligands are apparent in the zirconium solution spectra.

Alkoxide ligands are evident in the titanium solution spectra after the addition of water. Aging of the film solutions for 24 h leads to the removal of the alkoxide ligands. In contrast, addition of water to the zirconium solutions results in the complete and immediate removal of all alkoxide ligands. This difference may be related the hydrolysis and/or condensation rate of the materials. Since carboxylates are more electronegative ligands than alkoxides there will be a higher partial charge on the highly carboxylated zirconium center than on titanium. Consequently, it would be expected to be more reactive in nucleophilic substitution reactions such as hydrolysis. The hydrolysis rate also depends upon the concentration of water. Sufficient water for complete hydrolysis is present only if condensation occurs as well. Therefore, if condensation is slow, it will in turn limit the hydrolysis rate.

The spectra of solutions containing unreacted valeric acid (Figures 2c,d and 3c,d) show an absorbance band at 1734 cm^{-1}. Bands of this frequency are commonly attributed to the presence of esters. Esterification is important in acetic acid transition-metal alkoxide sol-gel chemistry. However, higher order carboxylic acids (i.e., valeric acid) are known to form esters less readily than acetic acid.[52] Esterification is typically a slow reaction at room temperature and in the absence of an acid catalyst.[52] Though our solutions are warmed briefly by the exothermic reaction of the alkoxides with valeric acid, our solutions are not externally heated or allowed to stand for more than 24 h before casting.

(52) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1974.

To see how readily esters could be prepared and to identify absorbances due to esters, mixtures of valeric acid and the alcohols were prepared with concentrations similar to that in the solutions used to cast films (for purposes of this calculation only, it was assumed that all alkoxide groups react to form alcohol in solution). The alcohol-valeric acid mixtures were heated at 40 °C for 0.5 h with and without concentrated sulfuric acid catalyst. No changes were observed in the spectra of uncatalyzed mixtures. Spectra of the catalyzed mixtures contained new bands which could be attributed to the presence of esters. The most prominent new bands in the spectrum of the n-propanol mixture are at 1739 and 1180 cm^{-1} and are typical of $\nu(C=O)$ and $\nu(C—O)$ vibrations, respectively, in ester molecules.[41] Similarly, bands are observed at 1734 and 1183 cm^{-1} in the spectrum of the acid catalyzed isopropyl alcohol–valeric acid mixture.

The presence of an absorption band at 1734 cm^{-1} does not necessarily indicate the presence of esters in a solution. Very dilute solutions of valeric acid in both isopropyl alcohol and n-propanol were prepared and analyzed with FTIR. In the spectra of these solutions, a shoulder at 1734 cm^{-1} is evident on the C–O stretch band of dimeric valeric acid (1711 cm^{-1}). The shoulder is not present in the spectrum of a dilute solution of valeric acid in CCl$_4$. Heating and aging the valeric acid/alcohol mixtures did not change the relative intensity of the two bands. On the basis of these results, the band at 1734 cm^{-1} in these dilute solutions is not attributed to esters but to valeric acid which is involved in carbonyl–alcohol H bonds.[41]

We believe that the bands at 1734 cm^{-1} in the solution spectra (Figures 2 and 3) are also due to the presence H-bonded valeric acid–alcohol species. First, in these spectra and in all film solution spectra there was no evidence of corresponding $\nu(C–O)$ bands. Second, esters proved to be difficult to produce from valeric acid and these alcohols in the absence of an acid catalyst. Therefore, we do not believe that esterification plays a significant role in the chemistry of valeric acid–alkoxide solutions used to prepare the films.

FTIR Characterization of Valerate Films. The infrared spectra of titanium (Ti00 and Ti24) and zirconium (Zr00) valerate films are presented in Figure 4. All FTIR absorbance bands in film spectra can be assigned to valerate ligands, hydroxyl groups (either hydroxyl ligands or water), or to the metal–oxygen backbone. No film spectrum contains bands that can be attributed to alkoxide groups, valeric acid, or alcohols.

Valerate Ligands. The three bands observed at 2959, 2933, and 2873 cm^{-1} are identical in all titanium and zirconium films. The relative intensity and position of these peaks are similar to those observed for valeric acid (Figure 1a) and, therefore, are attributed to valerate ligands. Less intense bands observed in all film spectra at 1319, 1302, 1109, and 752 cm^{-1} are also due to valerate ligands.

The most intense absorbances in the film FTIR spectra are $\nu(COO)$ bands associated with valerate ligands (1650-1200 cm^{-1}). In the spectrum obtained for the Ti00 film (Figure 4a), $\nu_{as}(COO)$ and $\nu_s(COO)$ frequencies of comparable intensity are observed at 1530 cm^{-1} and 1448 cm^{-1}, respectively ($\Delta\nu$ = 82 cm^{-1}). For the Ti24 film (Figure 4b), the $\nu_{as}(COO)$ band is less intense than the $\nu_s(COO)$ band. In addition, the $\nu_{as}(COO)$ band in the spectrum of the Ti24 film consists of two distinct bands at 1559 and
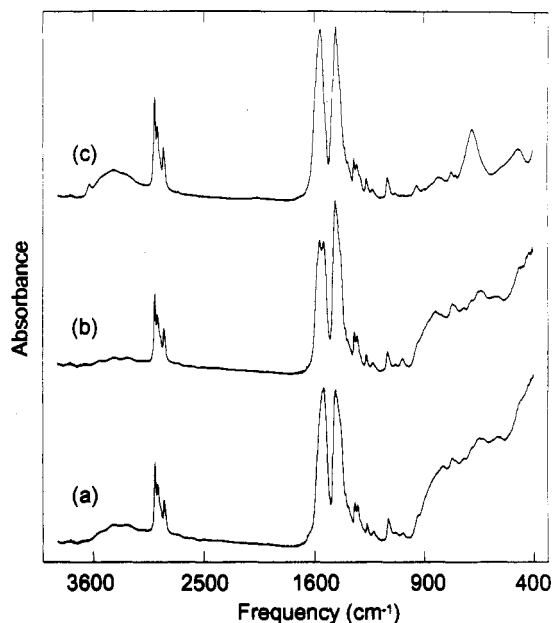
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Figure 4. FTIR spectra of (a) Ti00, (b) Ti24, and (c) Zr00 films.

1528 cm⁻¹ with a shoulder at 1577 cm⁻¹ ($\Delta\nu$ = 111, 80, and 129 cm⁻¹, respectively).[53] The frequency range spanned by the ν_{as}(COO) bands and ν_s(COO) bands are unchanged by solution aging. Thus we believe that solution aging does not necessarily lead to new valerate coordination configurations but rather to a different redistribution of ligands amongst configurations. Comparing these $\Delta\nu$ values with that in sodium valerate (141 cm⁻¹) suggests that titanium films contain only bidentate ligands. While the presence of chelating ligands cannot be ruled out, we believe it is possible that our films contain only bidentate bridging ligands which vary slightly in bond angle giving rise to several distinct maxima. Doeuff et al.[36] reported three distinct ν_{as}(COO) bands present in a crystalline acetate alkoxy titanium complex known to contain only bridging acetates of varying bond angle.

In the spectrum obtained for the Zr00 film (Figure 4c), the ν_{as}(COO) band at 1554 cm⁻¹ and ν_s(COO) band at 1447 cm⁻¹ are of similar intensity. Solution aging has little effect on the carboxylate stretch region of the FTIR spectra of the zirconium films. The spectrum obtained for the Zr24 film shows ν_{as}(COO) and ν_s(COO) bands at 1559 and 1445 cm⁻¹, respectively. $\Delta\nu$ values are 107 and 114 cm⁻¹ and indicate that the zirconium films contain only bidentate valerate ligands. Paul et al.[54] report values of 1540 and 1420 cm⁻¹ for the asymmetric and symmetric COO stretches of zirconium(IV) propionate ($\Delta\nu$ = 120 cm⁻¹) and ascribed these bands to the presence of bidentate ligands.

Spectra of solutions used to prepare these films (not shown) were also collected but, due to the presence of excess valeric acid and alcohol, they are of limited value in providing information about the polymer structure in solution. However, asymmetric carboxylate stretches can be readily seen in the solution spectra. Comparing this region of the solution spectra with that in the film spectra,
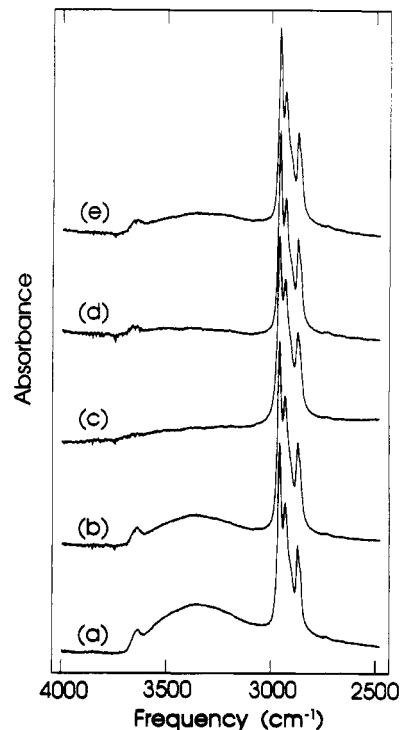

Figure 5. FTIR spectra of hydroxyl region: *in situ* heating of Zr00 film (a) before heating, (b) heated to 50 °C, (c) heated to 100 °C, (d) cooled to room temperature in dry nitrogen, (e) exposed to ambient air for 30 min.

suggests that carboxylate coordination modes are similar before and after spin casting.

Hydroxyl Groups. Broad bands due to H-bonded hydroxyl groups are observed near 3400 cm⁻¹ in the spectra of all films. The intensity of the hydroxyl stretch observed in the zirconium film spectra is essentially unchanged by solution aging and greater than that observed in the titanium film spectra. In zirconium films, the sharp band observed at 3639 cm⁻¹ is typical of "free" or non-H-bonded hydroxyl groups.[41] Water has a characteristic absorbance near 1600 cm⁻¹.[41] Unfortunately, the strong carboxylate absorbances in this region make it impossible to use this band to distinguish between hydroxyl ligands and water.

To determine whether these absorbances are associated with water or hydroxyl ligands, changes in the hydroxyl stretch absorbances were observed while heating titanium and zirconium films in dry nitrogen. Heating titanium films at 50 °C essentially removed the hydroxyl stretch band centered at 3400 cm⁻¹. This band is partially restored by exposure to ambient air after cooling. Hydroxyl groups should not be removed at such low temperatures, and, therefore, we ascribe the hydroxyl bands observed in the FTIR spectra of titanium films to sorbed water.

Figure 5 shows the effect of heating on the hydroxyl region of the Zr00 film spectrum. The intensity of the hydroxyl absorbances decreased upon heating slowly to 50 °C (Figure 5b); however, the hydroxyl bands are evident unless the film is heated to 100 °C (Figure 5c). Additionally, when the film is heated rapidly to 75 °C, the broad absorbance disappears before the loss of the sharp band (not shown). A small band at 3639 cm⁻¹ is restored upon cooling (Figure 5d), and exposure to ambient air for 30 min results in the partial restoration of the broad hydroxyl absorbance (Figure 5e). Continued exposure to ambient air did not cause any additional increase in the intensity of this band. Again, the low temperature required for

(53) In all film spectra, the ν_s(COO) band is as broad as the ν_{as}(COO) band; however, only one well-resolved maximum is observed. All $\Delta\nu$ values are reported with respect to this maximum which is on the high-energy side of the peak. Therefore, separations of the outer peaks may actually be greater that the values reported.

(54) Paul, R. C.; Baidya, O. B.; Kumar, R. C.; Kapoor, R. *Aust. J. Chem.* **1976**, *29*, 1605.

removal of the hydroxyl absorption bands indicates that water and not hydroxyl ligands is the primary source of the bands.

We tentatively ascribe the non-H-bonded hydroxyl absorbance to water coordinated to Zr centers. We attribute H-bonded hydroxyl absorbances to sorbed water. During slow heating an equilibrium is maintained between the two types of water. Rapid heating results indicate that non-H-bonded water is more difficult to remove, perhaps due to a combination of steric hindrance and coordination with Zr. It also may be energetically more stable since the sharp absorbance band returns first upon cooling. Partial restoration of the broad absorbance upon exposure to ambient air is further evidence that this band is due to sorbed water.

Water may be present due to condensation reactions occurring during spin casting or due to trapping of water present in precursor solutions. Water is probably also present due to exposure to ambient moisture during spin casting and drying. Zirconium can accommodate a larger coordination sphere than titanium. As a consequence, hydration of zirconium may occur leading to films with a higher water content than the titanium films. Factors such as porosity may also contribute to the extent of water sorption in the films.

Backbone. The low-frequency region of the Ti00 and Ti24 spectra (Figure 4a,b, respectively) contains a broad absorbance below 980 and 530 cm^{-1} that is commonly attributed to an envelope of phonon bands in the titanium oxide network.[50] Similar features have been reported by Doeuff et al.[22] in the spectra of titanium acetate gels and were also present in our solution spectrum (Figure 2d). Though the shape of this broad absorbance is essentially unchanged with increased precursor solution age, its relative intensity is decreased with respect to carboxylate absorbances. The low-frequency region of the FTIR spectra of the zirconium films (Figure 4c) show two major bands at 654 and 462 cm^{-1} which we attribute to backbone ν(Zr–O). These bands are similar to those in the solution spectra after the addition of water (Figure 3d). Atik and Aegerter[23] ascribed bands at 666 and 363 cm^{-1} to Zr–O–Zr stretches and Sanchez and In[55] attributed a broad band between 600 and 300 cm^{-1} to these vibrations in a zirconium oxide based network.

XPS Characterization of Valerate Films. The XPS metal core peak binding energies measured for titanium (Ti 2p$_{3/2}$ = 458.7 eV) and zirconium (Zr 3d$_{5/2}$ = 182.3 eV) are independent of solution aging and typical of values measured for tetravalent forms of the elements.[56] The XPS C 1s spectra measured for the films consist of peaks at 284.6 eV (reference peak) and 288.5 eV due to alkyl and carboxylate carbon, respectively. No features due to alkoxide carbon (~286 eV) are observed in the spectra which is consistent with the FTIR analysis of the films. The XPS O 1s spectra measured for the films consist of peaks at 530.0 and 531.7 eV that are attributed to backbone and ligand (carboxylate, hydroxyl, or water) oxygen, respectively. Figure 6 shows that XPS O 1s spectra of Ti00, Ti24, and Zr00 films. The relative intensity of the ligand oxygen peak increases with respect to that of the backbone oxygen peak with titanium solution aging. For
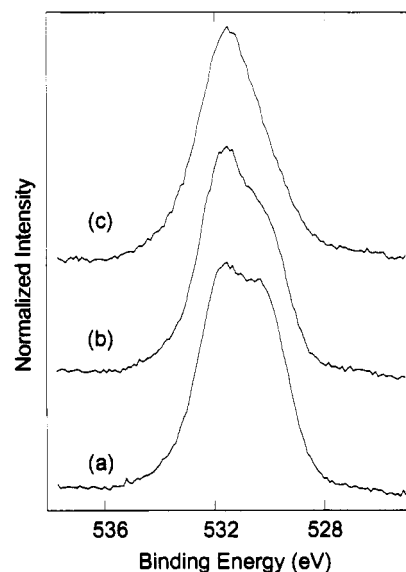
(55) Sanchez, C.; In, M. *J. Non-Cryst. Solids* **1992**, *147, 148*, 1.

(56) *Handbook of X-ray Photoelectron Spectroscopy*; Wagner, C. D., Riggs, W. M., Davis, L. E., Joulder, J. F., Muilenburg, G. E., Eds.; Perkin-Elmer, 1979.

Figure 6. Oxygen 1s photoelectron spectra measured for (a) Ti00, (b) Ti24, and (c) Zr00 films.

Table 1. Atomic Ratios of Carbon and Oxygen Species Calculated from XPS Intensity Ratios

	atomic ratios[a]			
	backbone oxygen	carboxyl carbon	ligand oxygen	ligand oxygen
film	metal	metal	metal	carboxyl carbon
Ti00	1.4	1.2	2.2	1.9
Ti24	1.1	1.4	2.6	1.8
Zr00	1.0	1.8	3.8	2.1
Zr24	1.0	1.9	3.9	2.0

[a] Relative standard deviations for atomic ratios are ≤±10%.

the zirconium films, the relative intensities of the backbone and ligand oxygen peaks are independent of the age of solution used to cast the film.

Atomic ratios derived from XPS intensity ratios are presented in Table 1. When combined with interpretation based upon the FTIR analysis of the films, these values provide a quantitative assessment of the chemical species present in the films. FTIR analysis indicates that the films consist primarily of a metal oxygen network with valerate ligands coordinated to metal centers. Water is also present in the films. The concentration of valerate ligands is indicated by carboxyl carbon/metal atomic ratios determined by the XPS analysis. Since each carboxylate carbon is associated with two ligand oxygens, a film containing only carboxylate ligands is expected to have a ligand oxygen/carboxyl carbon ratio close to two. Thus, ligand oxygen/carboxylate carbon values greater than two indicate the presence of water or hydroxyl groups in the films.

It is important to note that if water is present in valeric acid when it is mixed with the alkoxide, levels of carboxylation are lower. This is in agreement with the results of Doeuff et al.,[27] who found that adding titanium alkoxide to a mixture of water and acetic acid led to the formation of a gel with a low level of carboxylation. To achieve the level of carboxylation indicated by our results, the use of dry reactants is imperative.

Titanium Films. The concentration of valerate ligands in the films[57] increases from the Ti00 film (1.16 ± 0.10) to the Ti24 film (1.42 ± 0.05), indicating that these ligands add to titanium during solution aging. Accompanying the

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increase in valerate ligand content is a corresponding decrease in the backbone oxygen concentration with solution aging. Backbone oxygen to titanium atomic ratios decrease from 1.40 ± 0.01 for Ti00 films to 1.12 ± 0.03 for Ti24 films. The change in the relative concentrations of these two species is also apparent by comparing the FTIR spectra of the Ti00 and Ti24 films (Figure 4).

These changes can be understood based upon solution compositions. Recall that the FTIR spectra of freshly prepared titanium solutions contain absorbances due to alkoxide ligands. This indicates that hydrolysis and condensation reactions have not gone to completion in these solutions. We believe that the removal of the solvent that occurs during spin-casting and drying facilitates completion of these processes and the formation of backbone oxygen linkages. Because valerates are strong ligands, their presence limits the extent of condensation. In contrast, alkoxide groups are absent in the aged film solutions. Film solutions contain a large excess of valeric acid and during solution aging, valerate ligands may displace remaining alkoxide and/or hydroxyl ligands. The extent of carboxylation is increased while the extent of condensation has been accordingly decreased.

A slow rate of carboxylation for titanium valerate alkoxide complexes is consistent with their slow rate of hydrolysis since both are nucleophilic substitution reactions. Though isopropoxide ligands form good leaving groups, their bulkiness may hinder the approach of nucleophiles to titanium. In addition, solution studies indicated that a second valerate ligand was not readily added to titanium since it required the breaking of relatively stable oligomers. Bridging alkoxide ligands were preferentially hydrolyzed and subsequent condensation reactions led to completely new oligomeric structures. These species may be more easily carboxylated than the titanium valerate alkoxide dimers.

The ligand oxygen/carboxyl carbon ratio for titanium films is slightly less than two, indicating that little water is present in these films. Sorbed water evident in the FTIR spectra is pumped away in the vacuum required for XPS analysis. *In situ* FTIR heating experiments indicated that water is not strongly bound to the titanium films.

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(57) In this discussion, values are reported to two decimal places and the standard deviation of the values measured for three different films is given to indicate the actual precision of the measurements.

Zirconium Films. The compositions of zirconium films prepared from fresh and day-old solutions are nearly identical. This is consistent with FTIR results which indicate that aging has little effect on the structure of the films. The number of valerate ligands per zirconium is the same within experimental error in zirconium films prepared from fresh (1.80 ± 0.12) and aged (1.90 ± 0.15) solutions and all zirconium films have a backbone oxygen/metal atomic ratio of approximately one.

The ligand oxygen/carboxyl ratio for zirconium films is slightly greater than that for titanium films. However, its value also indicates that little water is present in these films. Again, sorbed water observed with FTIR is removed by the vacuum prior to XPS analysis. A small amount may remain in the zirconium films. This is consistent with the higher concentration of water in the zirconium films as indicated by the FTIR analysis and the higher temperature required for its removal. The presence of a small concentration of hydroxyl ligands cannot be ruled out.

Additional Comments. It should be noted that film compositions calculated using XPS intensity ratios have the appropriate number of ligands per metal center. Titanium and zirconium have +4 oxidation states, backbone oxygen has a –2 oxidation state, and a carboxylate group can be assigned a charge of –1. Using this accounting system, the anion charge calculated for the Ti00 film (1.4 backbone oxygens and 1.2 carboxylate species/metal center) is –4.0. Similar calculations for the Ti24, Zr00, and Zr24 films lead to charges of –3.7, –3.9, and –3.9, respectively. Within experimental error, these results indicate the formation of neutral polymers and further demonstrate the use of XPS to determine film composition.

The levels of carboxylation determined for the films are consistent with that observed in the solution studies. According to the solution studies, between 1 and 1.5 valerate ligands displace alkoxide ligands on $Ti(OPr^i)_4$. The Ti00 and Ti24 films contain 1.2 and 1.4 valerate ligands/metal center. $Zr(OPr^n)_4$ were shown to react readily with just under two valeric acid molecules which is the level of carboxylation measured in the zirconium films.