1556 *Chem. Mater.* **1994**, *6*, 1556–1562

Application of Controlled Hydrolysis of Titanium(IV) Isopropoxide to Produce Sol–Gel-Derived Thin Films

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Received February 4, 1994. Revised Manuscript Received May 18, 1994[®]

A variety of porous optically transparent titanium carboxylate films that can be supported on silicate glass substrates have been developed. These films were made by spin casting polymeric solutions of titanium carboxylates processed using sol–gel techniques. The stability and the quality of these films have been qualitatively correlated to the extent of control of hydrolysis exerted by carboxylate modification of the precursor titanium(IV) isopropoxide. A series of carboxylic acids ranging from acetic acid to myristic acid has been used, and their effects on film quality and stability are presented.

1. Introduction

Under controlled conditions, solution precursors of sol–gel systems can be prevented from forming gels.[1] Stable solutions thus obtained can be used to make thin films supported on various substrates using dipping, spin casting, and deposition techniques. These thin films, although processed differently, retain the structural integrity characteristic of porous sol–gel glasses along with high internal surface area and favorable optical properties.

Development of the sol–gel process has paved the way to processing novel materials having a variety of chemical and physical properties suitable to many applications including optical test strips. The sol–gel technique, in addition to providing stable, optically transparent and porous material, offers a multitude of modifying techniques[1–7] that may be necessary to sustain foreign molecular probes in good optical condition. In our current work, it was our intention to produce films that are suited for the construction of optical test strips.

Controlled hydrolysis[1–7] in sol–gel systems is the key to making thin films. Probably the most promising technique available for the control of hydrolysis of highly reactive alkoxides (for example titanium(IV) alkoxide) is to use chelating organic ligands such as glycols,[8,9] organic acids,[7,10,11] and β-diketones.[6,12] These chelating ligands effectively occupy some of the coordination sites of the alkoxide, thereby lowering the rate and extent of hydrolysis. A series of thin films that are porous, optically transparent, thermally stable and resistant to aqueous and organic solvents were produced by controlled hydrolysis of titanium(IV)isopropoxide using carboxylic acids of varying chain length as the chelating ligands. Spin casting was used exclusively to produce the films. Following this work, the utility of these films toward fabricating optical test strips was investigated. Detailed accounts of such work are given elsewhere.[13–15]

2. Background

1. Sol–Gel Solutions. Most transition-metal alkoxides hydrolyze upon contact with water resulting in metal hydroxide precipitates.[3,4] In the case of sol–gel-produced gels, films, and fibers, precipitation leads to inhomogeneity in the final structure. Therefore, preparation of homogeneous solutions by controlling precipitation is essential to process high-quality products.

Hydrolysis is the reaction that initiates the sol–gel process. However, rates at which reactions take place and the extends to which reactions proceed may vary significantly depending on the molecular nature of the metal alkoxide precursor. This will in turn determine the relative changes that can be expected in the processed materials.

Hydrolysis of metal alkoxides and subsequent product forms have received much attention in the literature. Many product forms and formulations for systems under varying conditions have been proposed.[16,17] Titanium

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[®] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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0897-4756/94/2806-1556$04.50/0

alkoxides, according to most of these studies, react very fast with water followed by slower rates of polycondensation. Lowering the rate of hydrolysis is of primary importance to the synthesis of homogeneous material. The attempt at controlling the rate and extent of hydrolysis in many studies has been successful. The rate of hydrolysis of titanium alkoxides, in general, is lower when the alkyl chain length of the alkoxy group is longer and when the alkyl group is secondary or tertiary.[8] This trend is attributed to the bulkiness of longer chains and nonprimary structures that inhibit hydrolysis through steric effects. Kamia et al.[18] have also presented a controlled hydrolysis method used to obtain preferential molecular structure for the preparation of TiO_2 fibers.

Addition of nucleophilic reagents such as glycols,[8,9] organic acids,[7,10,11] and β-diketones[6,12] to alkoxides and substitution of alkoxy groups of alkoxides by nucleophilic reagents can reduce the degree of hydrolysis and the rate of hydrolysis. The degree of hydrolysis is reduced as a result of these reagents occupying the coordination sites of the alkoxides. The hydrolysis rate reduction occurs due to modifying nucleophilic reagents having higher resitance to substitution by hydroxy groups. Consequently, hydrolysis and therefore precipitation are better controlled leading to desired material properties.

2. Sol–Gel Processed Thin Films. Once hydrolysis of the alkoxide precursor is initiated, the molecular precursors are transformed to oligomers and then to polymers that eventually congeal into homogeneous gels. However, controlled hydrolysis techniques briefly discussed above also allow the preparation of stable intermediate polymeric solutions that do not proceed to gel formation. These solutions—provided they possess suitable viscous properties—can be used to make coatings, generally in thin film form, using coating techniques such as dipping, deposition, or spin casting.[1,6] Sufficient control of compositions and conditions can lead to thin films of desired properties: homogeneous films without cracking or flaking, porous, optically transparent, good adhesion with chemical and thermal stability, solvent resistant, and structural distributions favoring stability of incorporated reagents.

All film-making techniques involve evaporation of solvent, excess precursors, and byproducts resulting in a volume reduction of the film.[6] In pure inorganic systems, relaxation along with the volume reduction is difficult due to prevalent excessive cross-linking. The brittleness of these materials leads to high shear stresses, and as a consequence the materials generally demonstrate poor adhesion properties. Sol–gel processing can be effectively used to reduce cross-linking and allow easier relaxation properties. The introduction of organic groups to the inorganic matrix of sol–gel material can increase the elasticity of the material.[6] This in turn can improve the ability of film formation of sol–gel polymeric solutions.

As discussed earlier, lengthy organic groups can be attached to alkoxide precursors. These groups occupy coordination sites of the metal reducing the amount of inorganic cross-linking. Therefore relaxation along with the volume reduction is easily accomplished. The organic groups having sufficient mobility also follow the shrinkage. Monodentate chelating ligands can act as flexible links between inorganic units. With relevance to sol–gel processed thin films supported on silicate glasses, adhesion is strenghtened by Si–O–M coupling where M is the metal of the alkoxide precursor used.

Schmidt et al.,[6] working with aluminum alkoxides, showed two cases where organic ligands were used to improve the film formation ability of sol–gel solutions. Aluminum alkoxides modified by both glycerol and acetylacetone led to crack-free coatings. TEM (transmission electron microscopy) analysis showed that increased homogeneity of the microstructure relates to better film quality.

Stable coating solutions are of considerable importance in film processing. Stability can be achieved by control techniques where hydrolysis/condensation sites are blocked by nonhydrolyzable moieties or by chelating ligands that are more resistant to hydrolysis compared to alkoxy groups. In general, such modifications prevent gelation or increase gelation time allowing a higher usable lifetime of the coating solutions.[1]

3. Materials and Methods

1. Materials and Instrumentation. Titanium(IV) isopropoxide and carboxylic acids were purchased from Aldrich Chemical Co. and used with no further purification. Water deionized with a resistance of 18 MΩ was used. VWR precleaned microscope slides (3 × 1 in., 1.2 mm) were used as substrates for films and were cleaned prior to usage. A Scientific Industries Vortex Genie 2 stirrer was used to agitate the reaction mixtures. The reaction mixtures were contained in Research Products Int. Corp. screw-top liquid scintillation glass vials. An International Clinical Centrifuge (Model CL 26802 M) was used for spin-casting films. The film thicknesses were measured on a DEKTAK IIA profilometer.

2. Processing. (I) *Sols*: Titanium(IV) isopropoxide was added to the carboxylic acid placed in a screw-top vial at ambient conditions. The mixture was stirred vigorously. Water was added to the resulting solution and the mixture was stirred vigorously as before. When carboxylic acids in solid form were used they were added to titanium(IV) isopropoxide placed in screw-top vials and were melted at 60 °C and stirred to form homogeneous solutions. Compositions of the solutions were measured in terms of molar ratios with respect to the alkoxide. Specific details are given in section 4.

(II) *Films*: Films were made by spin-casting solutions on microscope slides taped to the clinical centrifuge. The solutions were used for coating within the first half-hour from preparation. The coating solution (film solution) was placed on the microscope slide using a Pasteur pipet, and the solution was spread evenly over the slide using the same pipet. The films were spun immediately to remove excess solution. Each film was spun for 3 min at room temperature (24 °C) exposed to ambient conditions and stored in a dust-free chamber for observation also at ambient conditions. Casting was carried out in a ventilated environment.

Film Thickness Measurements. Films cast on microscope slides were etched using a fine blade at the center of the slide perpendicular to the longer dimension of the slide. The film surface was scanned with the DEKTAK IIA profilometer along the longer dimension of the slide across the "microcrevice" indented by the blade. Thickness was obtained by measuring the profile of the crevice generated by the instrument.

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4. Results and Discussion

Controlled hydrolysis of alkoxide precursors is the key to making thin films using the sol–gel process. In the work presented herein, the feasibility of a series of carboxylic acids as hydrolysis-controlling reagents in a titanium-based sol–gel system was investigated. The series of carboxylic acids studied included, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, octanoic acid, lauric acid, and myristic acid. Also, the effect of the relative amount of carboxylic acid introduced to the sol–gel system on film quality was studied. The relative amount of carboxylic acid used was measured in terms of the molar ratio between the acid and the titanium alkoxide (R_a) and the ratio ranged from 3 to 10. The molar ratio of water to alkoxide (R_w) was 1.5.

(I) Sols. The reactions between the titanium alkoxide and acids, in each case, were exothermic and yielded a range of colorless to yellow homogeneous and transparent solutions depending on the acid. Upon the addition of water to the reaction mixtures of acetic and propionic acid, an immediate phase separation in the form of a white precipitate was observed throughout the range of R_a values studied. The formation of the white precipitate and therefore the phase separation was confined to a limited volume that somewhat reflected the volume of the added water. White precipitates observed in these systems are hydroxides that form as a result of the facile substitution of alkoxy groups of alkoxides by hydroxy groups. An instantaneous heterogeneous reaction facilitated by the bulk introduction of water to the modified precursor may have caused the phase separation. Similar effects were observed by Kamia et al.[18]

When the reaction mixtures of the propionic acid system, at high R_a values, were stirred vigorously, the precipitate dissolved in the bulk solution readily and a homogeneous solution resulted. At lower R_a values, the solids required more time and stirring for dissolution. However, agitation of the acetic acid system formed an insoluble bulk white precipitate. Both butyric and valeric acids yielded a solid only at low R_a values that dissolved easily. At higher R_a values, water was not miscible in the bulk solution and remained as a separate suspended liquid phase until the system was stirred. In the reaction mixtures containing hexanoic and octanoic acids, only a separate suspended liquid phase was observed upon the addition of water throughout the range of R_a values studied. The suspension easily dissipated upon stirring. All acids, except acetic acid, gave colorless to yellow transparent and homogeneous solutions upon vigorous stirring.

Bradley et al.[8] observed that the reaction rate of normal titanium alkoxides decreases with the increase of the length or the bulkiness of alkoxy groups. Alkoxy groups having nonprimary structures also contribute to slower reaction rates. Steric effects of lengthy or bulky groups tend to hinder the susceptibility of the titanium atom to nucleophilic attack by potential reagents. Experiments with the modified reagents also seem to conform to this trend. As the length of the substituting carboxylic acid chain and the relative amount of carboxylic acid added are increased, the occurrence of precipitation upon the addition of water gradually decreased. At the same time a progressive increase in the appearance of the unreacted aqueous suspension is observed. Both these trends suggest that titanium alkoxides substituted with carboxylic acids of shorter chain length are relatively more reactive compared to those substituted with acids of longer chain length (the number of carbon atoms in the primary alkyl group of the acids was varied from 1 to 6). Fast reactions were reflected by the instantaneous precipitation of the white hydroxide suspension. Conversely, the appearance of an unreacted aqueous suspension was reflective of the resistance of the modified species to hydrolysis. It is plausible to rationalize that, in our scheme of reactions, the steric effects of longer carboxy ligands were responsible for the reduction in the rate of hydrolysis. Acetic acid, in agreement with these results that produced a completely insoluble hydroxide, is expected to offer the least resistance to hydrolysis of the remaining alkoxy groups.

Alkoxy groups are more facile; thus, coordination sites occupied by them are much more susceptible to hydrolysis than are sites occupied by carboxy ligands. Substitution of some of the coordination sites by carboxy ligands does not entirely prevent the hydrolysis of the sites occupied by the remaining alkoxy groups. Carboxy ligands or any other related chelating agents only lower the rate and extent of hydrolysis. They do so by occupying some of the coordination sites through less hydrolyzable bonds or by other physically restrictive impedances such as steric effects that effectively hinder the hydrolysis of alkoxy groups. Note that within an environment where external heat or pressure is not applied, it is unlikely that more than two of the alkoxy groups on the titanium(IV) alkoxide are replaced by acid groups;[19] i.e., at least two easily hydrolyzable sites are available in each alkoxide molecule.

Earlier work[19] established that the extent of substitution by carboxylic acids is proportional to the R_a value. Therefore, at low R_a values a low extent of substitution is expected. The work extent is used in the following context; the amount of alkoxide molecules subjected to substitution. That is, at higher R_a values more and more of the alkoxide molecules attain a level of saturation governed by the reaction conditions (temperature, pressure, etc). At ambient conditions it is unlikely that more than two molecules of acid would react with one molecule of alkoxide. It follows that the reactivity of modified alkoxide precursors toward hydrolysis should be lower at higher R_a values, since then, many of the sites otherwise available for hydrolysis would be occupied by more stable carboxy ligands. In the case of propionic, butyric and valeric acids, the tendency toward hydroxide precipitation decreased as the R_a value was increased. The observed trend is in compliance with the above argument.

Dilution of the alkoxide may also be a factor that contributes toward lower rates of hydrolysis at high R_a values. At higher R_a values, excess carboxylic acid dilutes the modified precursor significantly. Consequently, contact between water and alkoxide is minimized.

(II) Films. Films were characterized qualitatively in terms of optical (visible light) transparency, brittleness reflected by cracks in the film structure, and adherence to the substrate. Films that demonstrated

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(19) U.S. Patent 2,621,193 (assigned to E. I. Dupont De Nemours and Co., Inc.), June 27, 1950.

Table 1. Dependence of Film Stability on Composition

R_a	$R_{w/a}$	stability time before cracking,[a] min
(a) Propionic Acid, $R_w = 1.5$		
3.0	0.51	0
4.0	0.38	0
5.2	0.29	0
6.0	0.25	0
7.0	0.22	0
8.0	0.19	0
9.0	0.17	0
10.0	0.15	30
(b) Butyric Acid, $R_w = 1.5$		
3.0	0.51	5
4.0	0.38	10
5.2	0.29	30
6.0	0.25	720
7.0	0.22	720
8.0	0.19	720
9.0	0.17	stable
10.0	0.15	stable
(c) Valeric Acid, $R_w = 1.5$		
3.0	0.51	20
4.0	0.38	40
5.2	0.29	stable
6.0	0.25	stable
7.0	0.22	stable
8.0	0.19	stable
9.0	0.17	stable
10.0	0.15	stable

[a] The classification denoted "time before cracking" is an approximate measurement of the time unstable films were observed to commence cracking, counted immediately after 3 min of casting. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide. $R_{w/a}$: molar ratio of water to acid.

a tendency to crack were considered unstable. Optically transparent films with excellent adhesion properties and structural integrity (no cracking) were considered stable and of good quality.

A series of results, in terms of film quality, was obtained using propionic, butyric and valeric acid. The results are tabulated in Table 1 (note that the classification denoted "time before cracking" is an approximate measurement of the time unstable films were observed to commence cracking, counted immediately after 3 min of casting).

The widest range (in terms of R_a) of stable films resulted from solutions containing precursors modified by valeric acid. The range decreased drastically from valeric acid to butyric acid to propionic acid. Solutions that contained polymeric systems derivatized by hexanoic acid and octanoic acid possessed extremely poor adhesion properties and they failed to produce quality films.

Earlier in this discussion it was established that carboxylic acids of longer chain length and higher R_a values contribute to reduced rates of hydrolysis. Evidently, the reduced rates of hydrolysis can be correlated to improved film quality. Higher R_a values of both butyric and valeric acids produce stable films. The data show that the films approach stability in ascending order of R_a, most likely reflecting the gradual decrease in the rate and the extent of hydrolysis of the alkoxide derivative. Even though propionic acid does not produce stable films, the extent of cracking decreases as the R_a is increased and the trend is in general agreement with the other two acids. The widest range of stable films was produced by valeric acid film solutions followed by butyric acid. The trend is in accordance with slower rates and lower extents of hydrolysis resulting from increased steric effects of the longer chain carboxylic acid.

The impedance of hydrolysis by steric effects is expected to be most pronounced in systems modified by hexanoic and octanoic acid. Hydrolysis of the alkoxide initiates the polymerization process that compounds the structure of the sols and subsequently the structure of the films. If hydrolysis is hindered to an extent that only smaller oligomeric units are formed, it is reasonable to conceptualize that such systems would not produce continuous films due to the lack of linear and cross-linked matrix formation. The inability of systems modified by hexanoic and octanoic acids to produce film solutions with good adherence properties seem to suggest that these systems behave in compliance with the reasoning presented above.

One could argue that the higher hydrophobicity of hexanoic and octanoic acid effectively blocks the hydrophilic metal–oxygen–metal coupling between the substrate and the film. As a consequence, good adherence properties could be negated. However, in an experiment in which hydrophobic polystyrene surfaces were coated with the same modified film solutions, the trend in adherence properties was observed to be similar to that on silicate glass substrates. This behavior implies that poor adhesion properties enforced by hydrophobic effects can be discounted as a possible explanation. If hydrophobic effects were important, at least a crude reversal in the trend in coating properties should have occurred. Inadequate polymerization of less hydrolyzable modified precursors seems to be the likely explanation for the exhibited inconsistency in coating properties of film solutions made of longer chain hexanoic and octanoic acids.

Following the reaction between the alkoxide and the carboxylic acid, the excess acid and the alchol byproduct may react to form the corresponding ester.[20] The reaction is usually catalyzed by mineral acids. However, titanium can also exert a catalytic effect for the reaction. Earlier work[21] shows evidence for the formation of esters in a similar system. The water generated by the esterification reaction may induce hydrolysis and subsequent polymerization prior to the external addition of water. The inadequacy of the water so generated for hydrolyzing the modified precursors was tested. Butyric acid films at $R_a = 9.8$ and $R_w = 0$ (no water added) were unstable demonstrating that internally generated water alone is not capable of inducing the formation of a polymer matrix with the structural integrity necessary to remain stable as a uniform film. Variation of R_w over the range from 1 to 5 has no effect on film quality at a macroscopic level. Nevertheless, the importance of additional water is clear.

It was observed that longer chain carboxylic acids reacted at elevated temperatures in combination with shorter chain carboxylic acids are capable of stabilizing otherwise unstable films. The series of film solutions modified by propionic acid was preferred to study the stabilizing effect since the films they produced were not stable through the range. Lauric and myristic were the

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Table 2. Dependence of Film Stability on Added Long-Chain Carboxylic Acids

components in film solution	composition R_a	stability time before cracking,[a]
propionic acid	8	0
lauric acid	0.0	
propionic acid	8	0
myristic acid	0.0	
propionic acid	8	24 hr
lauric acid	0.36	
propionic acid	8	24 hr
myristic acid	0.31	
propionic acid	16	Stable
lauric acid	0.36	
propionic acid	16	Stable
myristic acid	0.31	

[a] The classification denoted "time before cracking" is an approximate measurement of the time unstable films were observed to commence cracking, counted immediately after 3 min of casting. R_w: molar ratio of water to alkoxide = 1.5. R_a: molar ratio of acid to alkoxide.

longer chain carboxylic acids utilized in this experiment. The process sequence was as follows: The longer chain carboxylic acid, $R_a = 0.36$ for lauric acid and $R_a = 0.31$ for myristic acid, was added to the titanium(IV) alkoxide placed in a screw-top vial. The heterogeneous mixture was heated at 60 °C until the solid melted to form a homogeneous solution. The shorter chain carboxylic acid was added to the well-stirred mixture and was stirred again. This step was followed by the introduction of water, $R_w = 1.5$, and thorough stirring. The results are tabulated in Table 2.

At $R_a = 8$, without the incorporation of a longer chain carboxylic acid, the propionic acid film solution produced a film in which cracking was observed upon casting for 3 min. However, the introduction of a small amount of lauric or myristic acid resulted in a film in which cracking was observed much later. The effect was much more pronounced at $R_a = 16$, in which case the addition of either lauric or myristic acid enabled the production of a stable film. The stabilizing effect of lauric and myristic acids was just as effective in low-R_a films of both butyric and valeric acids.

Preceding arguments established that precursors modified by shorter chain length carboxylic acids were susceptible to faster and greater hydrolysis compared to that modified by relatively longer chain carboxylic acids. Accordingly, controlled hydrolysis was correlated to the formation of stable films. The observations just presented seem to further confirm the argument. Addition of a small amount of lauric or myristic acid to an unstable shorter chain system produces a stable film. The stability of these films is likely due to the disposition of the system to produce polymer matrices of favorable structural integrity at low rates and low extents of hydrolysis. Lower rates and extents of hydrolysis upon annexation of longer chain lauric or myristic acids to shorter chain systems are expected due to increased steric effects.

The control imparted by shorter chain carboxylic acids or low R_a values or both on rates and extents of hydrolysis can be relatively low in magnitude leading to excessively cross-linked polymer matrices. Relaxation of the polymer strands along with the solvent evaporation that accompanies casting and drying of films is made difficult by the structural rigidity of excessively cross-linked matrices. Such systems are likely to yield brittle layers that crack upon drying as those conceivably produced by film solutions modified by propionic acid and others at low R_a values. Modification of the alkoxide precursor by longer chain carboxylic acids that reduce the extent of hydrolysis and thus cross-linking, should allow easier relaxation for the polymer strands leading to stable and continuous films. This behavior was striking in the stabilizing effect demonstrated by both lauric and myristic acids on unstable propionic acid systems.

Table 3. Film Thickness Measurements

type of film	film thickness,[a] Å
propionic acid	4900 ± 200
butyric acid	2500 ± 200
valeric acid	1400 ± 200

[a] Film thicknesses were measured as described in the experimental section. Films made with solutions at $R_a = 10$ and $R_w = 1.5$ were used in this experiment. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide.

Table 4. Film Thickness Measurements

type of film	R_a	film thickness,[a] Å
propionic acid	11.9	3600 ± 175
butyric acid	9.8	2600 ± 150
valeric acid	8.2	1900 ± 75

[a] Film thicknesses were measured as described in the experimental section. Films made with solutions at $R_w = 1.5$ were used in this experiment. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide.

Film thickness measurements are tabulated in Table 3. The R_a value of the film solutions was 10 in all cases. Thickness of the films decreased in the following order: propionic acid > butyric acid > valeric acid. These measurements also suggest that extensive polymerization initiated by less controlled hydrolysis is prevalent in films modified by propionic acid. The opportunity to polymerize extensively can lead to thicker matrices held by cross-linking. In addition, a greater extent of cross-linking is likely to produce solutions of higher viscosity leading to thicker film depositions upon casting.

It was noted that comparisons made solely based on the film thicknesses measured at a constant R_a value—in comparing propionic, butyric and valeric acids—would lead to erroneous conclusions. This is likely since higher molecular weight acids are accompanied by a volume increase in order to maintain the constant R_a. This in turn increases the total volume of the film solution. Consequently, water is diluted in the reaction mixture and its access to sites of hydrolysis may be limited. This unavoidable circumstance can effectively reduce the extent of hydrolysis and produce thinner films. The effect progressively increases from propionic to butyric to valeric acid. However, the film thickness measurements presented in Table 4 supports the former argument that the progressive reduction in thickness from propionic to valeric acid, at least in part, is due to control of hydrolysis exerted by steric effects. In this experiment the total volume of each film solution was kept constant by using the same volume amounts of alkoxide, acid, and water. At constant total volume, thinner films

Table 5. Film Thickness Measurements of Valeric Acid Films

R_a	film thickness,[a] Å
6	2950 ± 75
8	2300 ± 40
10	1600 ± 60

[a] Film thicknesses were measured as described in the experimental section. Films made with solutions at $R_w = 1.5$ were used in this experiment. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide.

were produced by longer chain length carboxylic acids. This suggests that even though the effect of dilution of water cannot be discounted, the steric effects imparted by carboxylic acids play a profound role on control of hydrolysis leading to films of favorable quality.

The data presented in Table 5 compare thickness of valeric acid films at different R_a values. The thickness decreases with increasing R_a. In this case it is possible that both higher R_a and dilution in combination are affecting the desired control. At higher R_a more of the alkoxide molecules are substituted by carboxy groups, thereby limiting hydrolysis, and dilution limits the amount of water available for hydrolysis. Experiments to determine the relative contributions from the two phenomena were not conducted.

It is conceivable that dilution of the polymer in excess acid can lead to thinner films. However, the trends established in this work suggest that the relative contribution of the bulk dilution toward film thicknesses is quite low in the range experimentally covered. In this range, the reduction in film thickness is accompanied by an improvement in film quality. In Table 4 the quality of films improved (not shown) with increasing carboxylic acid chain length and in Table 5 the quality of the films improved (not shown) with increasing R_a. This is unquestionably a consequence of a chemically induced alteration, thus, a chemical phenomenon.

Carboxylic acids are present in large excess in these systems. Indeed, physical properties of these acids such as viscosity and surface tension influence the coating properties of the film solutions. However, the current results strongly suggest that chemical restructuring of the polymer network due to controlled hydrolysis has a profound effect on the quality of the films. Therefore, although physical properties of film solutions are important considerations, it is our contention that controlled hydrolysis is more fundamental to the production of quality films and thus it could be exploited to obtain desired material properties. The formation of polymeric carboxylates and compositional changes was confirmed in a detailed parallel study using Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy.[22]

Stability of the films to external elements such as solvents, varied pH conditions, and thermal treatment was tested using a valeric acid film ($R_a = 9$). The film was insoluble in water and organic solvents (methanol, acetone, acetonitrile, benzene, xylene, chloroform, and carbon tetrachloride). The effect of solutions (HCl/NaOH) with pH ranging from 1 to 10 on films is tabulated in Table 6. To observe the effects of thermal treatment, films were stored in an oven at 300 °C for 2 h. Upon thermal treatment, the quality of the films remained unchanged; i.e., the films remained transparent and free of cracking and flaking. However, the loss of organic matter due to heat treatment transformed the hydrophobic films to hydrophilic ones.

Table 6. Stability of Films in Aqueous Solutions at Different pH Values

solution pH (HCl/NaOH)	stability of films[a]
1	dissolved within 1 h
4	stable
7	stable
10	etched after 1–2 weeks

[a] Valeric acid films made with a solution at $R_a = 10$ and $R_w = 1.5$ were used in this experiment. The films were immerced in the respective solutions for a period of 1 month. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide.

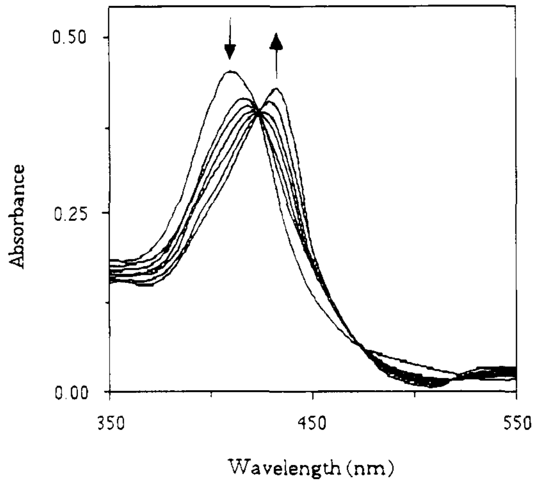

Figure 1. Spectral dynamics of tetrakis(pentafluorophenyl)porphine–Fe^{III}Cl entrapped in a valeric acid film upon contacting the film surface with an aqueous cyanide solution. Film solution parameters are as follows: $R_a = 9$, $R_w = 1.5$, $R_e = 40$, $R_p = 0.008$. The presented changes in the porphyrin spectrum took place over a 15-min period. The initial bulk cyanide ion concentration was 400 ppm. The scan time for each spectrum was approximately 1.6 min. R_a: molar ratio of acid to alkoxide. R_w: molar ratio of water to alkoxide. R_e: molar ratio of ethanol to alkoxide. R_p: molar ratio of porphyrin to alkoxide.

Development of the sol–gel process has paved the way to processing novel materials having a variety of chemical and physical properties suitable to many applications including optical sensors. The sol–gel technique, in addition to providing stable, transparent, and porous material, offers a multitude of modifying techniques that may be necessary to sustain foreign molecular probes in good optical condition. The porous matrix should be such that it accommodates the probe molecules with ideally no excretion but at the same time allowing maximum access for detectable species to the immobilized probe through favorable diffusion properties that minimize barriers to mass transport. The sol–gel process allows adjustment of diffusion properties through structural modifications.

The feasibility of using the titanium-based thin films developed in this work toward the fabrication of optical test strips was investigated using a model probe/analyte combination. The optical transparency (UV/vis absorption spectra of films were free of strong absorption bands in the region of interest, 325–750 nm) and the porosity of these films were exploited in fabricating the sensor

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(22) Severin, K. G.; Torgerson, B. A.; Berglund, K. A.; Ledford, J. S. Submitted for publication in *Chem. Mater.*

strip. An iron(III) porphyrin was entrapped within films supported on glass by direct dissolution of the porphyrin in the film solution. Contact of these films with aqueous cyanide produced a characteristic change in the absorption spectrum of the porphyrin upon its reaction with the diffusing cyanide ions. Spectral changes are illustrated in Figure 1. The spectral changes were calibrated to measure free cyanide ion concentrations ranging from 40 to 25 000 ppm. A detailed account of this work was submitted for publication.[15]

5. Conclusions

The routine sol–gel process can be successfully modified to produce thin films. Control of hydrolysis has a profound effect on the production of films. The judicious choice of modifying reagents leads to quality films having productive properties such as optical transparency, porosity, thermal stability, resistance to aqueous and organic solvents, excellent adhesion, and uniformity. Films thus produced can be utilized to fabricate optical sensors.

Acknowledgment. The authors acknowledge financial support from the Cooperative State Research Service (Grant No. 90-24189-5014) of the United States Department of Agriculture and the Crop and Food Bioprocessing Center/Research Excellence Fund at Michigan State University. Salary support for K.A.B. from the Michigan Agricultural Experiment Station is also acknowledged.