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# MORPHOLOGY OF INORGANIC-ORGANIC HYBRID MATERIALS DERIVED FROM TRIETHOXYSILYLATED DIETHYLENETRIAMINE AND TETRAMETHOXYSILANE

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# MORPHOLOGY OF INORGANIC-ORGANIC HYBRID MATERIALS DERIVED FROM TRIETHOXYSILYLATED DIETHYLENETRIAMINE AND TETRAMETHOXYSILANE

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Key Words: Inorganic-Organic Hybrid Materials, Sol-Gel Processes, Morphology

## ABSTRACT

Triethoxysilylated diethylenetriamine (f-DETA) and its mixtures with tetramethoxysilane (TMOS) have been hydrolyzed and condensed to form abrasion resistant coatings for optical plastics such as bisphenol-A polycarbonate and CR39. In this paper, the influences of the pH and water concentration on the morphology of gels derived from f-DETA alone (f-DETA100) or equal weights of f-DETA and TMOS (f-DETA50TMOS50) were studied. For the f-DETA50TMOS50 system, with an equivalent ratio (**r**) of water to alkoxysilane (OH/SiOR) of 4.4, sol-gel reactions

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at pH 0-2 often led to a particulate gel structure. However, if the reaction was carried out pH 4-5, the resulting gel often had a uniform compact structure although some particulate features were found on the surface. For the f-DETA100 system at pH 0-2, as **r** increased from zero, the resulting f-DETA gels exhibited a morphological transition from a monolithic uniform structure, to a porous particulate structure, and then to a compact fine particulate structure. A similar transition also existed in the binary system f-DETA50TMOS50, but the particle size was much smaller and no obvious porous stage was observed. The aging time and drying rate were also important factors influencing the structure of the f-DETA/TMOS coatings.

## INTRODUCTION

During the past few years, our laboratory has been developing abrasion resistant coatings for optical plastics by hydrolysis and condensation (or sol-gel reactions) of a tetraalkoxysilane and an organic compound containing multiple triethoxysilane groups [1-9]. F-DETA, the reaction product of 3-iso-cyanato-propyl-triethoxysilane (3-ICPTES) with diethylenetriamine (DETA) (Figure 1) [1-3], is one of the trialkoxysilylated compounds that have received extensive studies during the past few years [1-9]. Inorganic-organic hybrid coatings derived from this compound alone or its mixtures with metal alkoxides, especially tetramethoxysilane (TMOS), have been formed on polymer substrates such as bisphenol-A polycarbonate and CR39 [7-9] and metal substrates such as aluminum, copper, brass and stainless steel [10-13]. These coatings are very effective in controlling wear of these materials. To apply these coatings on a selected substrate, a mixture of f-DETA and TMOS is hydrolyzed in an alcoholic medium (Figure 1). During this process, the triethoxysilane groups in f-DETA and tetramethoxysilane gradually hydrolyze and condense by eliminating water, methanol or ethanol to form a sol containing clusters of various molecular weights. This resulting sol is applied on the substrate to be protected as a thin layer. After the solvent evaporates, it is thermally cured into a compact, transparent, abrasion resistant coating.

The morphology of a sol-gel film usually depends on the structure of the clusters generated during the hydrolysis and condensation process. According to the literature [14], primary clusters formed during the sol-gel process usually have a highly irregular structure, which is dependent on the pH value and the equivalent ratio (**r**) of water to metal or semi-metal alkoxide in the system. In

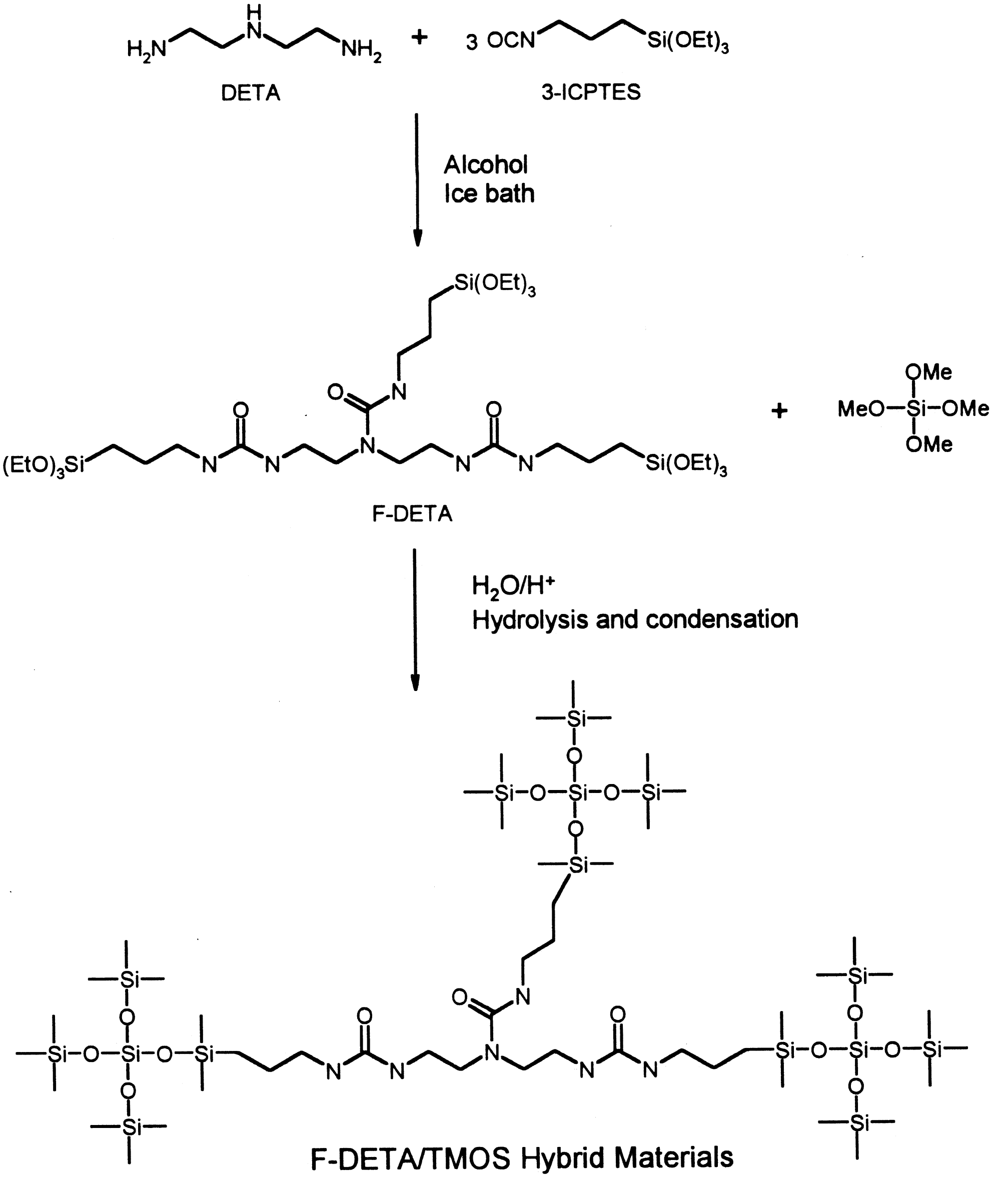

**Figure 1.** Inorganic-organic hybrid materials based on triethoxysilylated diethylenetriamine and tetramethoxysilane.

strong acid media with a small **r** (ca. 1), silica sols developed from tetraethoxysilane usually consist of extended primary clusters, and may be capable of drawing fibers [15]. Still in acid media, but with a high **r** (ca. 20), the resulting sols include less extended clusters, and are not spinnable. Furthermore, sols developed in basic media are often particulate, not spinnable, and tend to form a porous gel [15].

The structure of sol-gel derived clusters can often be described by mass fractal geometry [16, 17]. The space filling ability of the cluster can be reflected by the mass fractal dimension $D_{mass}$, which is determined by the power law relationship between the mass (M) of the cluster within any randomly selected region and the radius (R) or a characteristic size of that region (Equation 1):

$$M \propto R^{D_{mass}} \; 0 \leq D_{mass} \leq 3 \tag{1}$$

according to Equation 1, extended primary clusters should have a lower fractal dimension while condensed clusters should have a higher fractal dimension. The fractal dimension of silica primary clusters developed from TEOS in an acid medium have a mass fractal dimension of 1.8-2.0, while in a basic medium, the silica primary clusters have a mass fractal dimension of 2.8-3.0 [18, 19]. Clearly, the mass fractal dimension quantitatively reflects how the structural openness of the silica clusters varies with the pH of the medium.

The porosity and surface smoothness of a thin film deposited from a sol are related to not only the primary clusters in the sol, but also the subsequent aggregation and drying processes. According to Brinker *et al.* [20, 21] during film formation, the primary clusters in a layer of sol aggregate as solvent evaporates. Subsequently, these aggregated clusters interpenetrate into one another and collapse under the capillary forces exerted during the final stage of drying. The extent of cluster interpenetration depends on the mass fractal dimension of the clusters. According to Mandelbrot [17], the mean number of intersections ($M_{1,2}$) for two clusters of radius R and mass fractal dimension of $D_{mass}$ to occupy the same position of three dimensional space is (Equation 2):

$$M_{1,2} \propto R^{2D_{mass}-3} \tag{2}$$

According to Equation 2, if the clusters have a fractal dimension of less than 1.5, the mean number of intersections between two clusters approaches zero as R infinitely increases. This means the clusters are mutually “transparent”, and can move through each other freely. On the other hand, if the fractal dimension of the clusters is greater than 1.5, the mean number of intersections increases infinitely with R. This means the clusters are mutually “opaque”, and overlap of clusters is not possible. In fact, real clusters are finite in size, so clusters should never be completely “transparent” nor completely “opaque”. Based on these analyses, silica sols formed in acidic media usually contain clusters of low fractal dimensions, and hence tend to form smooth and structurally compact films. In contrast, sols formed in basic media often include clusters of higher fractal dimensions, and hence are more likely to form rough and porous coatings.

Similar to the sol-gel process of tetraethoxysilane, the f-DETA/TMOS system is also based on hydrolysis and condensation of alkoxysilanes and silanols except that this system is essentially a binary system of alkyltriethoxysilane (T) and tetraalkoxysilane (Q). Due to the inductive effect of the alkyl group, the sol-gel reactions of the alkyltriethoxysilane group is expected to show a somewhat different response to the pH of the medium. In addition, the presence of the nine Si-OEt groups in each f-DETA molecule may also change the mode of cluster formation. This paper provides a general comparison of the pH-dependence of condensation reactivity between the T and Q species and then discusses the influences of the condensation reactivity order of T & Q on the morphology of the final f-DETA/TMOS gel. Small angle X-ray scattering (SAXS), atomic force microscopy (AFM), and scanning electron microscopy (SEM) are utilized to reveal the influences of pH, **r**, aging of the gel and evaporation of the solvent on the morphology of the resulting f-DETA/TMOS coatings.

## EXPERIMENTAL

### Materials and Surface Treatments

Diethylenetriamine (DETA, 98%), 3-aminopropyltriethoxysilane (3-APS, 99%), tetramethyoxysilane (TMOS, 99+%) and 3-isocyanatopropyltri-ethoxysilane (3-ICPTES, 95%) were purchased from Aldrich Chemical Company and used without further purification. F-DETA was prepared by reaction of DETA with 3-ICPTES (mole ratio 1:3.15) in the solvent 2-propanol or ethanol. The material prepared by this method was a 70 wt% solution in 2-propanol ($^i$PrOH) or ethanol (EtOH).

Coating recipes were formulated using f-DETA, TMOS, water (W), $^i$PrOH or EtOH, and an acid catalyst. The acid catalyst was hydrochloric acid, phosphoric acid, or acetic acid and these acids will be abbreviated as HCL, HPO and HAC, respectively, in the nomenclature. The coating recipe is named according to the concentrations of the coating components, but the alcohol part is often omitted in the nomenclature. The concentration of each major component is given as a weight percentage based on the total weight of the four major components, which include f-DETA, TMOS, water and the alcohol solvent. The acid catalyst concentration is given as millimoles per kilogram of the recipe excluding the catalyst (mmol/kg), and it is separated in the nomenclature from the major components by a dash. For example, in a 2-propanol based recipe f-DETA31TMOS31W5-HCL27, the system includes 31 wt% f-DETA, 31 wt% TMOS, 5 wt% water and 33 wt% 2-propanol, and the concentration of the hydrochloric acid catalyst is 27 mmol/kg. Since the weight percentage concentration of water does not reflect the stoichiometry of the system, the equivalent ratio between water and alkxoxysilane (**r**) is often used to address the influence of water concentration on the gel morphology.

Among the four major components in the f-DETA/TMOS system, water is only partially miscible with f-DETA and TMOS, while any other two components are completely miscible. However, either heterogeneous or homogeneous mixtures can be hydrolyzed to transparent sols in the presence of an acid catalyst. During the coating formulation, pH was measured using a pH glass electrode calibrated using a standard buffer solution (pH=4). Recipes including equal weights of f-DETA and TMOS (f-DETA50TMOS50) usually had a gelation time of from 5-15 minutes at pH 0-2, to about 8 hours at pH 4-5. These formulae were generally allowed to pre-hydrolyze for a certain period of time (0.6-0.8 times the gelation time) so that transparent sols were obtained. During the sol-gel process, the acetic acid catalyst also reacted with the alcohol solvent to form an ester. However, the influence of this reaction should be negligible because only a small amount of acetic acid was used. For SEM and SAXS experiments, gel samples were prepared by casting these sols into polystyrene dishes as films. The film thickness was 1-2 mm for SEM experiments and 0.1-0.5 mm thick for SAXS experiments. For AFM experiments, smooth coating samples (2-4 μm thick) were prepared by spin-coating these sols onto bisphenol-A polycarbonate substrates. However, as will be indicated later in this paper, the gel morphology may exhibit some dependence on the thickness of the film. Therefore, even derived from the same recipe, samples for AFM, SAXS, and SEM, which had relatively large differences in film thickness, could exhibit different gel morphologies.

## Characterization

Specific surface areas were measured under a static process by means of a Micromeritics ASAP 2010 instrument. The specific surface area was calculated by the BET method and the average pore size was calculated by the method proposed by Barrett, Joyner and Halenda (the BJH method) [22].

Scanning electron microscopy was conducted on a Cambridge 200 Stereoscan microscope. The gels were broken into fragments of ca. 1 mm in diameter, dried at 170°C for 4 hours., and adhered to SEM mounts with graphite double-sided tapes. Treatment at 170°C was required so that condensation induced by electron bombardment would not affect imaging. The sample along with the SEM mount was sputtered with a thin layer of gold to impart the sample surface with electrical conductivity.

Small angle X-ray scattering (SAXS) studies were conducted to study the morphology of gels (in film form) of f-DETA or its mixtures with TMOS. The method can detect electron density fluctuactions on the length scale of 5-300 Å. A Philips X-ray generator (model PW1729) was used to provide Cu $K_\alpha$ radiation (1.54Å) and the X-ray was filtered by a nickel filter and collimated by a slit. The experiments were carried out in vacuum and a Kratky-Siemens camera and an M Braun positive-sensitive detector was used. The angular dependence of scattering intensity I(s) was plotted as relative scattering intensity, (I), vs. the scattering vector, s, defined by (Equation 3):

$$s = \frac{2}{\lambda} \sin \frac{\theta}{2} \tag{3}$$

where θ is the radial scattering angle.

Atomic force microscopy (AFM) was conducted by the tapping mode using a Digital Instrument's DI dimensional 3000 instrument and a tapping mode etched silicon probe. A height image and a phase image were obtained for each sample. In the height images, bright areas usually correspond to protrusions, while for phase images, they correspond to harder regions.

## RESULTS AND DISCUSSION

### The pH-Dependence of Condensation Reactivity for T and Q

The sol-gel process of an f-DETA/TMOS system includes self-condensation T-T and Q-Q as well as cross-condensation T-Q. Here T and Q, respectively, represent $-Si(OEt)_3$ groups and tetramethoxysilane plus their corresponding derivatives. The relative reaction rates are expected to influence the distribution of the f-DETA and TMOS (i.e. residuals after condensation) in the gel. However, the OH/OR substituents of the same silicon atom usually have unequal reactivities and hence the rate of condensation depends on the extent of reaction. Consequently, it is not possible to estimate the sequence distribution of the monomers in the gel by the statistical method used for linear or slightly crosslinked organic copolymers. To date, little information is available regarding the kinetics of co-condensation between the T and Q monomers. To help understand the morphology of the f-DETA/TMOS gel, we attempt to analyze the pH-dependence of reactivity of T and Q toward self-condensation utilizing the inductive effect of the substituents of the silicon central atoms.

The condensation for a tetraalkoxysilane has been known qualitatively in the whole pH region [14]. The overall condensation rate is governed by three major reactions: 1) acid catalyzed condensation, 2) base catalyzed condensation, and 3) dissolution of siloxane bonds (reverse reactions of condensation). A minimal condensation rate is usually observed at ca. pH 2, which is close to the point of zero surface charge (PZC) of silica. The condensation below pH 2 occurs predominantly by acid-catalysis, so the reaction rate decreases as pH increases in this range. However, within the range of pH 2-8, base catalyzed condensation becomes predominant and hence, the condensation rate increases steadily with pH. The dissolution rate of siloxane bonds are generally unimportant within pH 0-4, but increases distinctly at pH>7. Because of this, the overall condensation rate drops sharply at pH>8. The relationship between the condensation reactivity of TMOS and the pH is illustrated in Figure 2 [14].

Due to the presence of the electron-donating alkyl group, the silicon atom of T has a slightly higher electron density than that of Q. In the transition state, the silicon atom bears a partial positive charge and a negative charge in the acid catalysis mechanism [23] and base catalysis mechanism, [24] respectively. Therefore, T should be more reactive than Q towards the acid-catalyzed condensation, but less reactive than the latter towards base-catalyzed condensation. These inductive effects have been supported by a few experiments. For example, Pohl *et al.* [23] have studied the pH-dependence of the dimerization rate of 3-aminopropyldimethylsilanol, 3-glycidoxypropylmethylsilanediol, and 3-glycidoxypropylsilanetriol, which have three, two and one alkyl substituents at the central silicon atoms, respectively. The dimerization rates of these three compounds occurred at minimal rates at pH 6.5, pH 5.8, and pH 4.5, respectively. Hence, as the number of alkyl substituents increased, the silanol increasingly preferred to undergo the acid-catalyzed reaction. Pkarakar *et al*. have studied the condensation of ethylsilanetriol and orthosilicic acid formed during hydrolysis of ethyltriethoxysilane and tetraethoxysilane [25]. At pH 1.7 and pH 2.2, the self-condensation of T was greater than cross-condensation between T and Q,

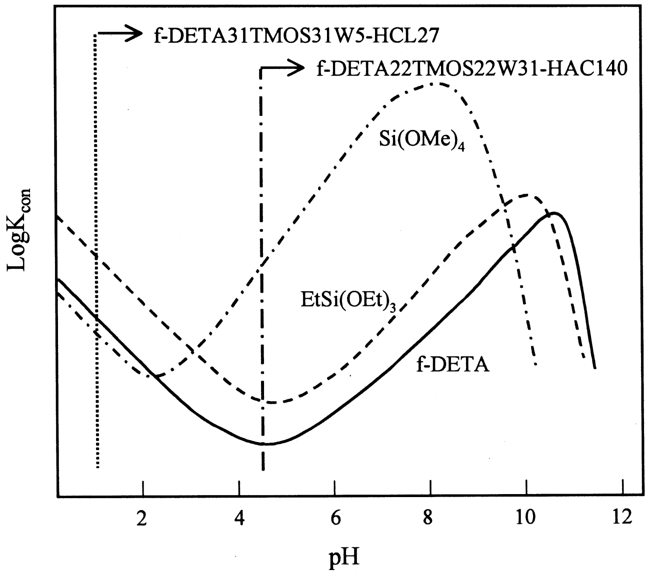

**Figure 2.** The suggested approximate pH-dependence of the condensation rates for TMOS, $EtSi(OEt)_3$ and f-DETA.

which was in turn greater than the self-condensation of Q. We have studied the sol-gel processes of the 3-methacryloxypropyltriethoxysilane (3-MPTES)/ TMOS, the [N-(3-triethoxysilyl)propyl-N'N'-diethyl]urea (UREA) /TMOS system, and f-DETA/TMOS system using [29] Si NMR spectroscopy. At pH 0-2, T in all three systems condensed as fast as or even faster than Q; However, at pH 4-5, Q condensed much faster than T. These experiments are obviously in accord with predictions based on inductive effects.

According to the similarity between the T and Q species, inductive effects, and experimental evidence, the pH-dependence of condensation reactivity of T is illustrated in Figure 2. The condensation reactivity of the T species shows similar pH-dependence to that of the Q species. However, due to inductive effect, T condenses at a minimum rate at ca. pH 4.5, so the reactivity curve of T is expected to be roughly that of Q shifted to the right side by ca. 2.5 pH units. Ethyltriethoxysilane (T) has little steric hindrance from the ethyl group, so it should condense faster than Q of TMOS within pH 0-2. However, with a bulk alkyl group, f-DETA (T) may condense slightly slower than TMOS (Q) due to the steric hindrance. At pH 4-5, ethyltriethoxysilane and f-DETA condenses nearly at its minimal rates. However, at this pH, TMOS condenses predominantly by base-catalysis. Its overall condensation rate is expected to be much faster than its minimum rate at ca. pH 2.0 as well as the condensation rate of the two T species within pH 4-5.

Compared to a normal triethoxysilane, the uniqueness of f-DETA is that the compound has three triethoxysilane groups (9 Si-OEt groups) in each molecule. Assuming all silanol/alkoxysilane groups in f-DETA have equal reactivity in a sol-gel reaction, according to the Flory & Stockmayer theory (ignoring closed-loop condensation) [26], the critical extent of condensation for the system to reach gelation is 12.5% (critical extent of reaction $p_c$). Even if only one of the three Si-OEt groups in each T unit forms a Si-O-Si bond in the reaction, conversion of 50% of T will lead to the gelation of the system. Therefore, at the same reaction conditions, a solution of f-DETA usually reaches the point of gelation much earlier than an ethyltriethoxysilane solution containing the same concentration of T.

## The Influence of pH on the Morphology

The pH and **r** value in the recipe are two important factors influencing the gel morphology. Sol-gel reactions of the f-DETA50TMOS50 system were carried out at several different pH levels (Table 1). Smooth transparent coating films could be formed easily within the range of pH 0-5. However, with a pH>5, the system often quickly formed a white precipitate, and hence, was not suitable for coating applications. The white precipitate is believed to be silica-rich since

TABLE 1. F-DETA50TMOS50 Recipes Formulated Using Different Catalysts and pH Values

| # | Catalyst | pH | Comments |
|---|---|---|---|
| 1 | HCL | 0.5-2 | Smooth and transparent coating could be prepared by dip coating and spin coating |
| 2 | HPO | 2.4-2.7 | |
| 3 | HAC | 4.0-4.2 | |
| 4 | HAC and TMAAC (1:1) | ~5 | Often forms precipitation of silica |
| 5 | TMAOH | ~11 | |

HCL: hydrochloric acid
HPO: phosphoric acid
HAC: acetic acid
TMAAC: tetramethylammonium acetate
TMAOH: tetramethylammonium hydroxide

TMOS (Q) condenses rather fast in this pH range. Although f-DEDA alone formed a transparent sol at pH 11, it formed hazy particulate coatings, which are inappropriate for optical coatings. For this reason, we only compared the morphology of films or coatings obtained by hydrolyzing and condensing f-DETA50TMOS50 recipes at pH 0-5.

Small angle X-ray scattering (SAXS) was conducted on gels derived from the following recipes: 1) f-DETA22TMOS22W31-HCL20 (**r**=4.4, pH= 1.7), 2) f-DETA31TMOS31W5-HCL27 (**r**=0.55, pH=0.5), 3) f-DETA22 TMOS22W31-HPO20 (**r**=4.4, pH=2.5), and 4) f-DETA22TMOS22W31-HAC140 (**r**=4.4, pH= 4.2). All these recipes were prepared using 2-propanol as a solvent. These recipes were pre-hydrolyzed for 5 minutes, 5 minutes, 30 minutes, and 6 hours, which correspond to 0.6-0.8 times of the gelation time of the respective recipe. The resulting sols were cast in polystyrene dishes and slowly dried over a three-day period at room temperature. In the following discussion, these gels will be simply mentioned by the catalyst portion of their recipe nomenclature. For example, gel HAC140 refers to a gel derived from recipe f-DETA22 TMOS22W31-HAC140.

Generally, due to shrinkage caused by syneresis (continuous condensation) and capillary forces during aging, drying, and curing processes, the primary clusters developed before gelation become interpenetrated and aggregated. Hence, the mass fractal dimensions of the primary clusters cannot be obtained by a SAXS analysis of the gel, but pores or concentration fluctuations of any components in the nanometer scale can still be detected. Figure 3 shows the SAXS profiles for the four film (0.2-0.3 mm thick) samples mentioned above. Among the four samples, gels HCL20 and HPO20, which were derived from water-abundant recipes (**r** = 4.4) at pH 1.7 and pH 2.5, respectively, exhibited relatively strong scattering in the range of s = 0-0.01 $Å^{-1}$ in their SAXS profiles. For gels HCL27 and HAC140, however, the scattering intensity in this angular region is as weak as that in the higher angular region (s = 0.01-0.8 $Å^{-1}$). Therefore, gels HCL20 and HPO20 likely include particulate features, pores and/or uneven distribution of f-DETA on the length scale > 100 Å; whereas gels HCL27 and HAC140 seem to be relatively morphologically homogeneous on the length region of 5-300 Å.

Similar SAXS experiments were also conducted for f-DETA100 gels. These gels were prepared by hydrolyzing and condensing f-DETA using a hydrochloric acid catalyst (pH=0-2) or an acetic acid catalyst (pH=4-5). The gels prepared at pH 0-2 showed obviously stronger scattering than those prepared at

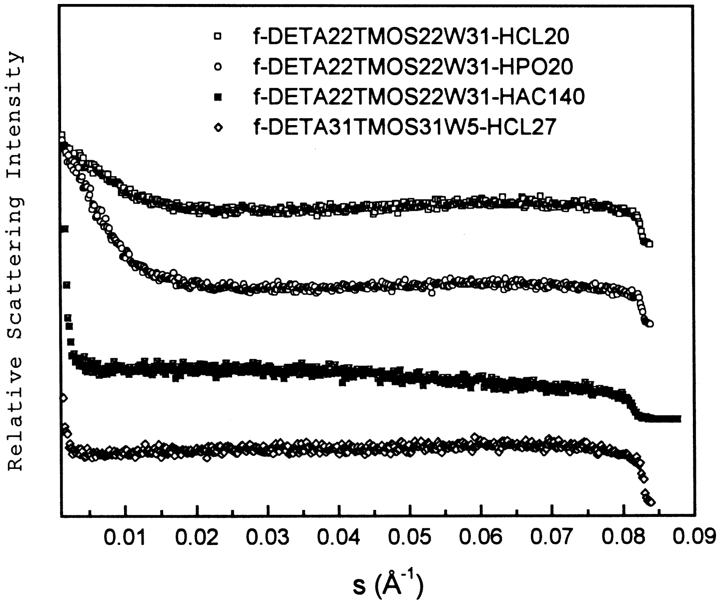

**Figure 3.** Small angle X-ray scattering profiles (arbitrarily shifted along the y-axis) for 0.2-0.3 mm thick f-DETA/TMOS films derived from different acid catalysts.

pH 4-5 in the range of s=0-2x10$^{-3}$ Å$^{-1}$ of the SAXS profiles. Therefore, the former gels may have contained some particulate features, pores, or structural nonuniformity on the length scale of ca. 500 Å. However, as correlation distances of this magnitude are near the upper limit of measurable length scale for our SAXS instrument, no further comments will be made based on these results.

Figures 4-6 show the AFM tapping mode height images of gels HCL27 (**r**=0.5), HCL20 (**r**=4.4) and HAC140 (**r**=4.4), respectively. The AFM samples were prepared by spin-coating the related pre-hydrolyzed recipes on bis-A PC substrates, followed by curing at 125°C for 4 hours. Figure 4 indicates that the continuous matrix of gel HCL27 was rather structurally homogeneous although particles of 0.1-0.2 µm in diameter were present. Both the radius of gyration of these particles and the distances between the particles were ca. 0.1-0.2 µm and 1 µm, respectively, which is beyond the effective range for SAXS analysis. Therefore, the SAXS profile stated earlier is unable to reflect morphological features of this length scale. Gels HCL27 and HCL20 were prepared in a water-deficient condition (r=0.5) and a water abundant condition (**r**=4.4), respectively. The latter gel exhibited completely different morphology as indicated by the

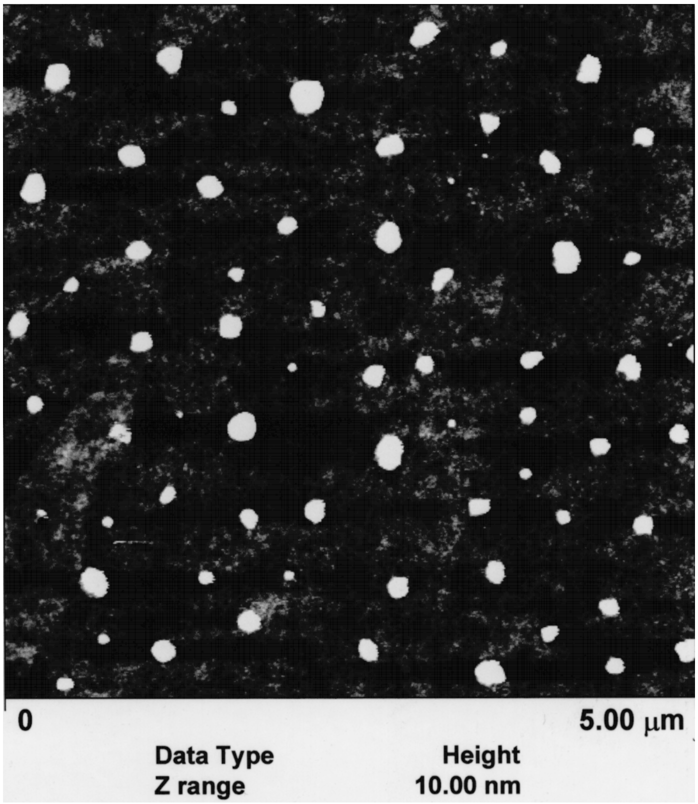

**Figure 4.** AFM tapping mode images showing surface features of an f-DETA22TMOS22 W31-HCL27 coating.

height image in Figure 5. According to the phase image, gel HCL20, unlike gel HCL27, was composed of hard spherical particles of ca. 50 nm in diameter in a softer continuous matrix. Gel HAC140 was prepared using the same amount of water as was gel HCL20; however, the former was prepared at ca. pH 4.2 using an acetic acid catalyst. As indicated by Figure 6, gel HAC140 also had a particulate morphology, however, it was composed of smaller (ca. 20 nm) and less regular particles. The SAXS profile for this type of gel (Figure 2) did not show any peak or shoulder (compared to the background) within the range of s=0.002-0.08 $Å^{-1}$, suggesting the particulate feature may exist only on the surface of the gel.

The SAXS and AFM results can be rationalized through the pH-dependence of condensation reactivity of f-DETA and TMOS and the higher molecular weight of f-DETA. With a high condensation rate of f-DETA at pH 0-2, the

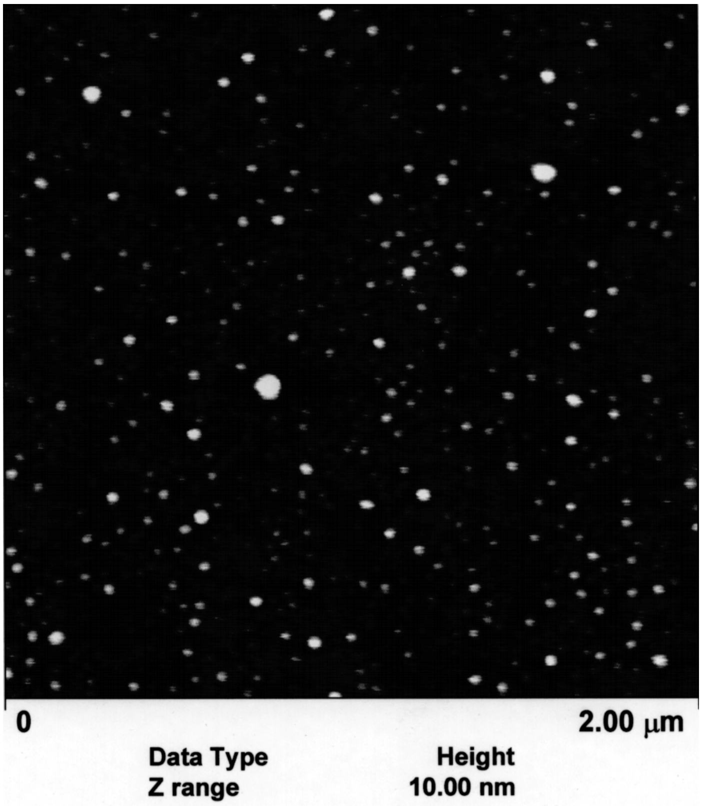

**Figure 5.** AFM tapping mode images showing surface features of an f-DETA22TMOS22 W31-HCL20 coating.

f-DETA or f-DETA-rich clusters can grow at a faster rate. Under a water-deficient condition, not all Si-OR groups can be hydrolyzed, so f-DETA-rich clusters can grow to relatively large sizes without collapsing, leading to relatively large soft domains. Under a water-abundant condition, however, the hydrolysis is rather complete and the resulting clusters tend to undergo extensive closed-loop condensation (intra-cluster condensation), leading to the collapse of the clusters and formation of relatively dense and rigid f-DETA or f-DETA-rich particles (a larger $D_{mass}$). After the solvent evaporates, these particles become embedded into a continuous matrix formed by low molecular weight species. During the process, pores may remain between these particles, moreover, the particles and matrix may also differ in the concentration of f-DETA and TMOS. On the other hand, if the sol-gel reaction is carried out at pH 4-5, the condensation rate of f-DETA is much lower and hence, it is more likely to form a extended cluster

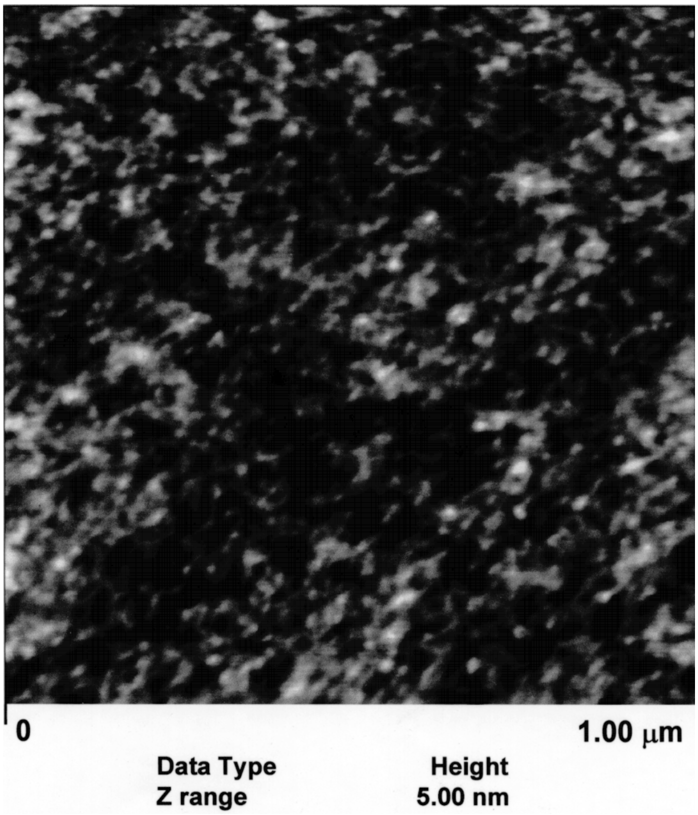

**Figure 6.** AFM tapping mode images showing surface features of an f-DETA22TMOS22 W31-HAC140 coating.

structure. The condensation of TMOS is relatively fast under this condition. However, due to the low molecular weight of TMOS, the growth of silica particles should be limited because of its condensation reaction with bulky and less reactive f-DETA molecules. As these extended clusters later can interpenetrate one another easily during the drying and curing processes, a more chemically uniform and less porous gel is formed.

## The Influence of the Water Concentration on Gel Morphology

In general, increasing water concentration in a sol-gel system can promote hydrolysis of alkoxysilane groups, thus raising the average functionality of the monomer and the mass fractal dimension of the resulting clusters.

Six f-DETA100 gels were prepared by adding water to 4 grams of 46 wt% f-DETA in 2-propanol acidified by hydrochloric acid. In these systems, pH

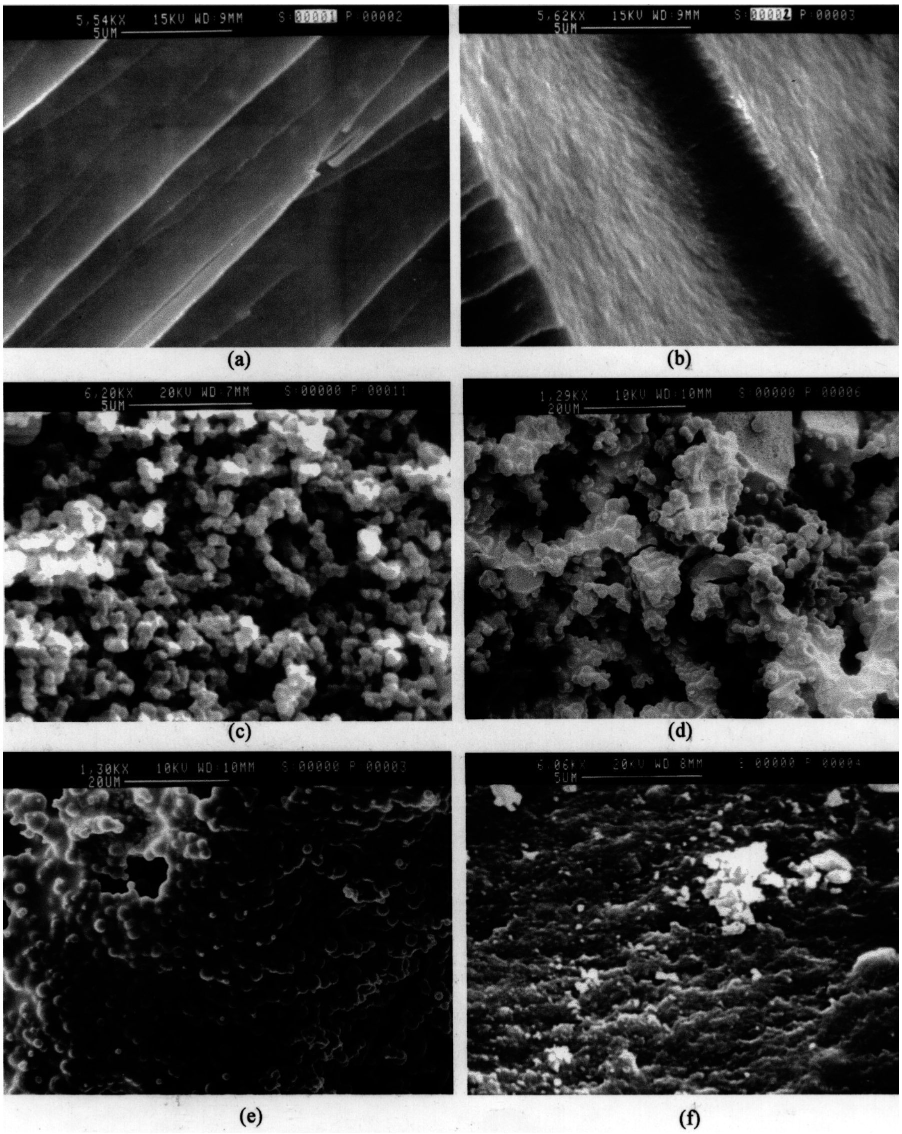

**Figure 7.** SEM micrographs of f-DETA gels derived in 2-propanol using HCL catalyst at pH ~0-2. (a) **r**=0.47, (b) **r**=0.93, (c) **r**=1.86, (d) **r**=3.72 (e) **r**=7.44, and (f) **r**=14.9.

was controlled to between 0-2 and the water concentration was gradually increased so that **r** in these recipes was 0.46, 0.92, 1.8, 3.6, 7.2 or 14.9, respectively. By this formulation method, the increase of **r** was accompanied by a slight decrease in the f-DETA concentration. Figure 7 shows the SEM micrographs for the fracture surfaces of the resulting six gels. Generally, when **r** was 0.46 and 0.92, transparent gels were obtained. SEM micrographs showed that the gel with **r** = 0.46 had smooth fracture surfaces (Figure 7**a**). As **r** increased to 0.92, the fracture surface topography became slightly rough (Figure 7**b**), indicating an increase in the particulate feature in the gel. As **r** further increased to 1.8, 3.6, and 7.2, white porous f-DETA particulate gels were formed instead. The particle sizes in these gels are ~0.4 μm in Figure 7**c**, ~2 μm in Figure 7**d**, and ~2 μm in Figure 7**e**, respectively. As **r** further increased to 14.9, a nearly transparent gel (Figure 7**f**) was obtained again. This gel distinctly had a more compact structure; however, fine particulate features could still be resolved by SEM. Under this water-abundant condition, it is assumed that the silanol groups were stabilized by water, so the growth of clusters occurred at a slow rate and hence smaller clusters were obtained during the pre-hydrolysis process. Since the particle size was well below the wavelength of visible light, the film obtained was nearly transparent. The stabilization of the system by water could be visualized by the immediate flocculation and precipitation of the transparent sols of f-DETA or f-DETA/TMOS when 2-propanol or ethanol was added to this pre-hydrolyzed system.

Similar experiments were conducted for f-DETA solutions in ethanol (pH 0-2) by adjusting **r** to 0.46, 0.93, 1.8, 3.6, 7.2, and 14.9. In these systems, the concentration of f-DETA was maintained constant at 18 wt% by controlling the ethanol concentration. As **r** increased, this series of gels also exhibited the same morphological transition as in the case of Figure 7a-f. It is believed that as **r** increases, both the silanol concentration and the polarity of the medium are increased. The former accelerates the cluster growth rate and intra-cluster condensation, while the latter stabilizes the silanol groups and decreases the cluster growth rate. The former effect is expected to be more important at a small **r**. However, after **r** increases to beyond a critical value**,** the latter effect can significantly offset the influence of the former, thus leading to formation of smaller particles.

F-DETA100 gels were also prepared using an acetic acid catalyst (pH~4.0) and a value of **r** changing from 2.2, 4.5, 8.9, 17.8, or 35.6. The series did not include the conditions of **r** = 0.46 and 0.93 since the hydrolysis rate under these conditions was very slow. Highly transparent gels of f-DETA were obtained under all conditions except for **r**=2.2, in which case a translucent gel was obtained. The gels developed at ca. pH 4 with an acetic acid catalyst differed from those developed at pH 0-2 with a hydrochloric acid catalyst. In the latter cases, **r** values of 1.86, 3.72 and 7.44 corresponded to porous particulate gels. indicates that the translucence of the gel with **r** = 2.2 was not caused by the particles, but by the remaining pores, especially pores on the surfaces. In this case, gradual condensation in the gel (often called microsyneresis) seems to have led to the formation of large pores that could not be collapsed by capillary forces (Note this gel was slowly dried at room temperature).

The influence of **r** on the morphology of the f-DETA50TMOS50 gel at pH 0-2 using a hydrochloric acid catalyst was also systematically studied. Gels of f-DETA50TMOS50 prepared using an **r** value of 0.5 had been characterized earlier by SAXS (Figure 2) and AFM (Figure 3). Under this condition, a more structurally uniform gel was obtained although some large f-DETA rich particles were shown in the AFM images. However, at **r** = 2.0, an obvious particulate gel was formed as revealed by the SEM image in Figure 10. As **r** was further increased to 4.4, no particulate features could be observed by SEM because of the limited resolution. However, the AFM result mentioned earlier in Figure 4 revealed that a highly transparent but still particulate gel was formed in this case. It is believed that at pH 0-2, the cross-condensation between TMOS with f-DETA blocks some reactive T units, thus slowing the growth of the cluster. Therefore, the particle size in an f-DETA/TMOS system is often much smaller than in the case of a pure f-DETA system. The dependence of gel particle size on the **r** may be utilized to control the pore size in the system and hence improve the abrasion resistance of the two component coating.

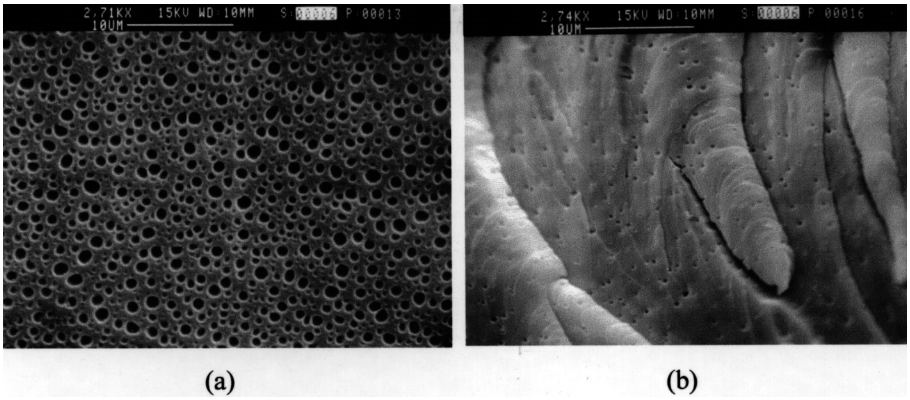

**Figure 8.** SEM micrographs for gel f-DETA23W33-HAC138 (r=2.2) (a) the gel surface; (b) internal fracture surface of the gel.

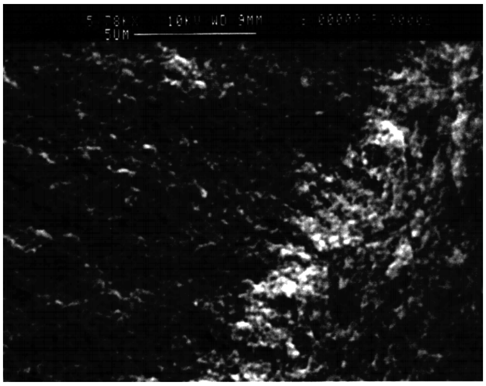

**Figure 9.** SEM micrograph for the fracture surface of gel f-DETA26 TMOS26W19-HCL24 (**r**=2.2).

### The Influence of Drying Speed on the Morphology

When a pre-hydrolyzed sol is spread on a substrate, it includes high molecular weight clusters or particles, low molecular weight polymers, and non-hydrolyzed or partly hydrolyzed monomers. As the solvent evaporates, all these species aggregate, interpenetrate each other, and undergo further sol-gel condensation. At the final stages of drying, the pores between clusters or particles are collapsed by capillary forces and hence a monolithic film is then formed on the substrate [20, 21].

Cluster interpenetration is a diffusion process. As the solvent evaporation is typically accompanied by an increase in the condensation rate, so a slow solvent evaporation rate may be beneficial to interpenetration of structurally dense primary clusters, especially for sols developed in basic media. For example, when f-DETA was hydrolyzed using tetramethylammonium hydroxide as the catalyst (ca. pH 12) at **r**=14.9, a transparent sol was formed after ca. 10 hours. of hydrolysis. As this sol was spread on a bis-A PC substrate, the solvent quickly evaporated and a white powdery material was left on the substrate. However, when the sol was slowly dried in a polystyrene dish, a highly transparent gel was obtained. In this example, the f-DETA sol contained structurally dense primary clusters (a large $D_{mass}$), which were unable to interpenetrate into each other in a short period. However, interpenetration and collapse of pores became possible if the drying process was sufficiently slow.

On the other hand, if the condensation or microsyneresis is so fast that it may significantly vary the gel structure during the drying process, a fast drying

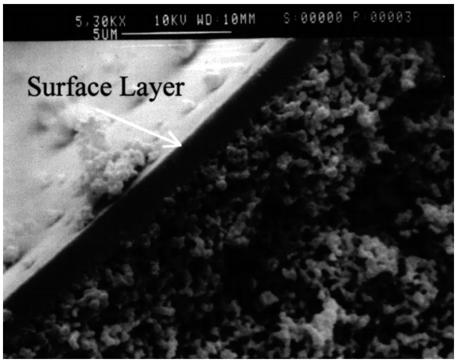

**Figure 10.** A sectional view of a 0.9-mm thick gel of f-DETA43W8-HCL38 gel showing a structurally compact surface layer.

rate may be helpful for reducing the porosity of the film. Recipe f-DETA43W8-HCL38 (**r**=1.9) usually formed a porous gel. However, if the sol was spread and desolvented before big particles had formed, then it was still possible to form transparent films. Figure 10 shows a sectional view of a 0.9-mm thick film of this gel. The gel has a structurally compact surface layer although its core remains porous. During the film formation, the surface layer desolvented quickly, thus clusters within this layer collapsed and formed a structurally compact layer. Inside the gel, however, the solvent is removed at a much slower rate due to a surface "skin" so that clusters or particles continued to grow, which eventually led to separation of the solvent from the gel and formation of porous structure.

In general, when prepared at pH 0-2 using a hydrochloric acid catalyst, f-DETA50TMOS50 usually formed a structurally compact gel at a low water concentration (**r**<1) or a high water concentration (**r**>4). Under similar conditions, compact gels of f-DETA or its mixture with TMOS could be formed more easily if acetic acid was used as the catalyst. Note: the structural compactness of a gel was mainly defined by the absence of any pores on SEM micrographs of the gel fracture surface. As SEM typically has a resolution of ca. 0.1 μm, it cannot provide any information about pores of nanometer sizes. For these reasons, the specific surface areas and pore sizes were measured for powders of gels made from f-DETA31TMOS31W5-HCL27, f-DETA22TMOS22 W31-HCL20, f-DETA28W40-HAC166, f-DETA26TMOS31W35-HAC144 and f-DETA22 TMOS22W31-HAC166. The results indicated that these samples had a specific surface area of only ca. 3-9 $m^2$/g, a pore volume of ca. 0.004-0.007 $cm^3$/g and average pore diameters about 60-100Å. Therefore, f-DETA/TMOS gels derived under these conditions can be considered to be densely packed. The low pore density of these gels helps to explain why the corresponding coatings are useful in protecting some substrates from the attack of organic solvents and some corrosive chemicals.

## CONCLUSION

The influence of the pH on the morphology of the gels f-DETA100 and f-DETA50 TMOS50 has been discussed based on the relative reactivities of T and Q. Due to induction effects, the condensation of T is as fast as or even faster than that of TMOS at pH 0-2, but is slower than the latter at pH 4-5. For these reasons, systems including f-DETA or both f-DETA and TMOS tended to form relatively large clusters in strong acid media and those clusters would collapse to form relatively dense rigid particles under water-abundant conditions. On the other hand, if the sol-gel reactions were carried out at pH 4-5, the condensation of f-DETA was rather slow, so the resulting clusters were structurally more extended, and less likely to collapse to dense rigid particles. These loose clusters could well interpenetrate one another during the drying and curing process, thus forming more structurally homogeneous films although these gels still showed some particulate features on the surface.

The influence of the water concentration (**r**) to the morphology has also been discussed. At pH 0-2, the sol-gel reactions of only f-DETA tended to form gels with morphology changing from mainly a monolithic structure, to porous particulate structure, and to a compact particulate structure as **r** gradually increased. Similar behavior was observed for the f-DETA50TMOS50 system, however, this system rarely formed porous particulate gels as in the case of f-DETA100 gel. In addition, the particle size in the f-DETA50TMOS50 system was generally much smaller. The observed phenomena are believed to be due to the blocking of some of the reactive T units by the Q units, which slows cluster growth.

Finally, during the film formation, the solvent evaporation rate with respect to condensation rate could influence the structure of f-DETA/TMOS gels. Lengthening aging time might promote interpenetration of primary particles, leading to a low porosity; however, it might also promote syneresis, leading to further particle growth and pore formation. The specific surface areas and pore sizes have been measured for several f-DETA/TMOS gels, and the results indicated these gels were structurally compact. Therefore, these f-DETA/TMOS gels can serve as protective coatings for polymers and metals if good films can be formed on these substrates and strong adhesion can be established. If they are used to protect optically clear polymers, then it is also necessary that the coating process does not cause turbidity.

## ACKNOWLEDGEMENTS

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