

# Transparent monolithic zirconia gels: effects of acetylacetonone content on gelation

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Transparent yttria-stabilized zirconia monolithic gels were synthesized under controlled conditions for hydrolysis and chemical polymerization. The influence of acetylacetonone on the previous chemical reactions was explored, and a plausible explanation was proposed concerning the outstanding role of this additive during the gelation process. Small-angle X-ray scattering was used to estimate the size of the polymeric species and to investigate the influence of acetylacetonone on the structure of the gels prepared.

## 1. Introduction

Considerable attention has been paid to the sol-gel synthesis of glasses and ceramics during recent years [1-4]. This technique affords, at least on laboratory scale, new possibilities to achieve unusual compositions of glasses as well as reactive ceramic powders with a submicronic size [5, 6]. Furthermore, the sol-gel process is a straightforward route to obtain homogeneous compositions when the individual constituents of a complex chemical formulation are nothing but high melting point and unreactive oxides.

As a part of our general study concerning zirconia- and fluoride-based materials [7], recent work has focused on the production of various compositions in the  $ZrO_2$ - $Y_2O_3$  phase diagram [8]. It is the purpose of the present paper to describe the elaboration of monolithic gels of yttria-doped zirconia using, as in the work of Debsikdar [9], a suitable additive, such as acetylacetonone, to control the kinetics of the reactions involved, then to elucidate the influence of this additive through small-angle X-ray scattering (SAXS) experiments.

## 2. Experimental techniques

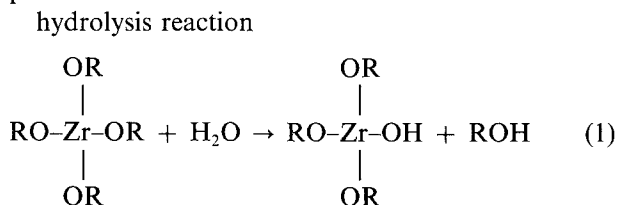
Zirconium *n*-propoxide (Alfa Products Danvers, MA 01923, USA) and yttrium nitrate (Rhone Poulenc, 92400, Courbevoie, France) were used as main precursors to prepare the sols, and isopropanol was used as solvent. Preliminary investigations demonstrated that under the present conditions, an acidic catalyst was necessary to achieve the hydrolysis reaction of the zirconium alkoxide. For this purpose, a small amount of concentrated nitric acid was added during the sol preparation. Several sols were investigated with variable concentrations of reagents in order to point out the general trends of the sol-gel transition and, more specifically, the time necessary to reach the gelation. The results of these investigations are reported in Table I.

SAXS data [10] were obtained with a point-like small-angle camera. Quartz monochromatic  $CuK\alpha$  radiation was used, and the detector was a position-

sensitive proportional counter with an effective length of 55 mm. The distance between the sample and the detector was 290 mm and the X-ray chamber was evacuated. Gel samples were thin slices cut from the massive gels with a thickness close to 1 mm. Experimental data were collected with an acquisition time of 30 min, then corrected for parasite scattering and normalized by a standard procedure to constant sample thickness and incident-beam intensity, according to the transmission coefficients measured under the same conditions.

## 3. General background on the gelation of alkoxy-derived zirconium compounds

Gelling occurs through the formation of a polymeric network following chemical reactions [11]. Starting from the simple case of a pure zirconium precursor, two simplified equations describe conveniently the overall gelation process within two successive steps that involve first the hydrolysis of the monomeric alkoxy and then the polymerization of the hydrolysis products



polymerization by condensation mechanism

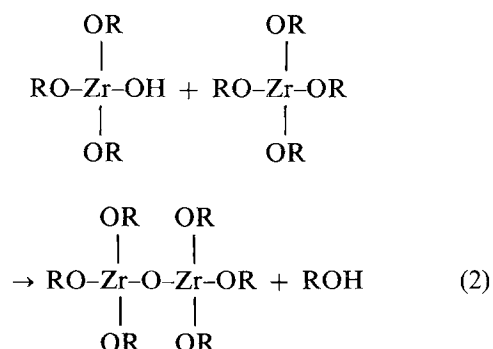


TABLE I The conditions for the preparation of the sols investigated

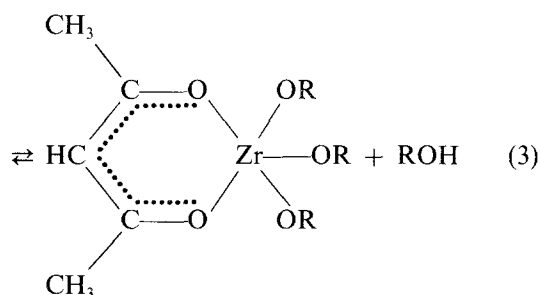
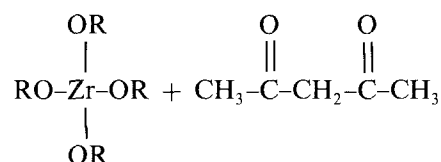
| Relative content of acetylacetonone | Acetylacetonone (ml) | Isopropanol (ml) | Yttrium nitrate (g) | Zirconium <i>n</i> -propoxide (ml) | Nitric acid (drops) | Water solution isopropanol + H <sub>2</sub> O (ml) |
|-------------------------------------|----------------------|------------------|---------------------|------------------------------------|---------------------|--|
| 0                                   | 0                    | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.237                               | 0.9                  | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.343                               | 1.31                 | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.49                                | 1.87                 | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.524                               | 1.98                 | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.537                               | 2.05                 | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.576                               | 2.2                  | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 0.808                               | 2.5                  | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 1                                   | 3.1                  | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |
| 1.21                                | 3.75                 | 12.5             | 0.74                | 11.25                              | 1                   | 6.25 + 1.975                                       |

where R is an alkyl group, i.e. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>- in the case of zirconium *n*-propoxide. Once hydrolysis has started, it is expected that both Reactions 1 and 2 progress more or less simultaneously. The resultant network structures are strongly affected by the respective kinetics of both reactions, which in turn depend on many parameters. It is known [12] that a polymeric gel is obtained if hydrolysis is much faster than the polymerization by condensation mechanism. On the other hand, if the kinetics of the two reactions become similar and fast enough, the resultant product is a gelatinous precipitate or a "colloidal gel".

Addition of a catalyst can modify the respective kinetics of Reactions 1 and 2 [11], but no satisfactory explanation has yet been proposed in the literature, to our knowledge, concerning the mechanism through which the catalyst operates. From an experimental point of view, drastic effects have been observed [11] both in the gelling time and the microstructure of the gel. Alternatively the dilution of reactants can also influence the gelling time and finally the gel structure, as expected from simple laws of chemical kinetics. Owing to the inherent complexity of the microscopic phenomena involved, and after some preliminary experiments which had demonstrated the benefits resulting from the addition of acetylacetonone in the production of monolithic gels, it has been deliberately chosen to keep the amount of catalyst constant throughout the present study and to focus on the role of the acetylacetonone.

Debsikdar has investigated the gelation of a similar

system [9]. He explained the influence of acetylacetonone on the kinetics of Reaction 1 by the enol form of acetylacetonone



This enol form produces a complex after reaction with the zirconium alkoxide (chelating effect), thus allowing a control of the zirconium alkoxide reactivity. First steric hindrance prevents a fast hydrolysis of the bonds between the metal and the acetylacetonone (acac) group. Then the kinetics of Reactions 1 and 2 are reduced because the bonds established with the less electronegative species are hydrolysed first, whereas the others made with the acac group are eliminated during the polymerization. This improves the formation of polymeric gels by anisotropic growth of oligomers.

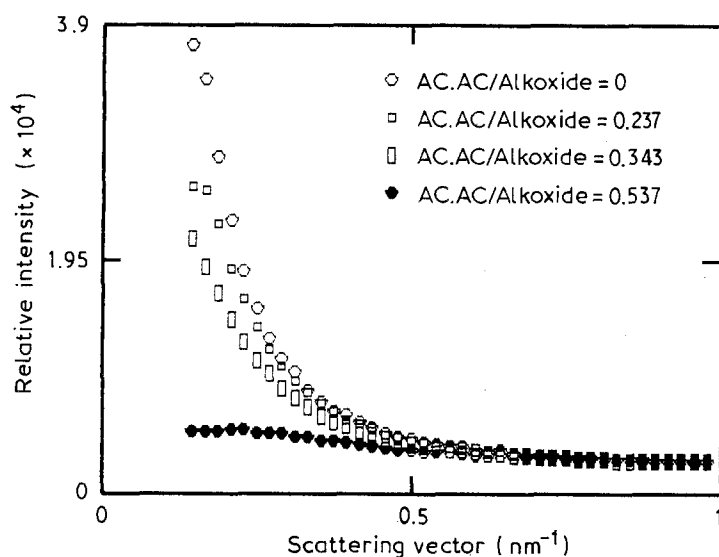


Figure 1 Scattering curves of the resultant products after gelation with different relative contents of acetylacetonone (the molar ratio [acacH]/[Zr + Y] is denoted AC.AC/Alkoxide on the plot).

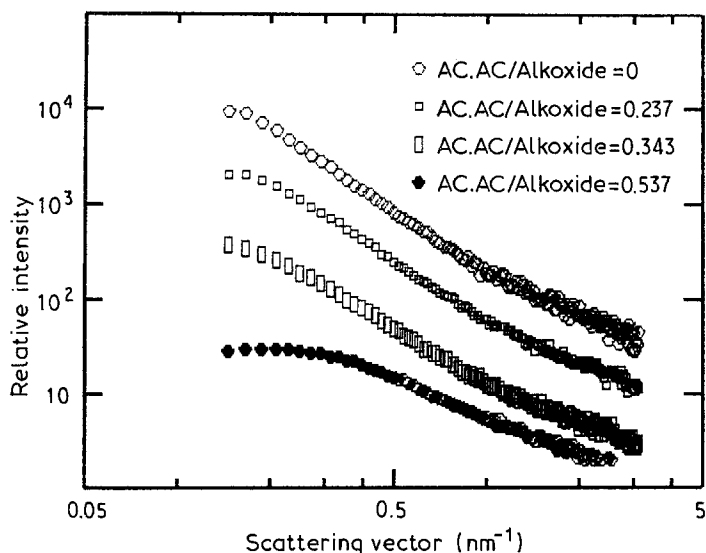


Figure 2 Log-log plots of relative scattering intensity against the scattering wave vector for gels with different relative content of acetylaceton. The slopes are measured for values of  $R_g$  ranging from 0.2 to 1 nm.

#### 4. Results

The gelling time for most of the sols is very short. Such a fast evolution after the mixing of products means that no information about the kinetics can be obtained by SAXS because the gelling time is shorter than the acquisition time. SAXS profiles of the resultant products after gelation are reported in Fig. 1.

In the case of high acacH concentration, where gelling time greatly increases, no significant change in the scattering profiles has been observed between the pre-gel (just before gelling) and the post-gel state. At low angles, the scattered intensity increases as the molar ratio  $[\text{acac}]/[\text{Zr} + \text{Y}]$  decreases, while it remains constant in all cases at large angles. All the gels with a molar ratio greater than 0.5 present the same scattering curve.

From the initial decay of the intensity, we evaluated the electronic radius of gyration through the Guinier's approximation, at low angles [13]

$$I(H) \sim n^2 N (1 - H^2 R_g^2 / 3) \quad (4)$$

where  $H = 4\pi \sin \theta / \lambda$  denotes the scattering wave vector,  $N$  is the number of scattering centres,  $n$  is the total number of excess electrons in each of the scattering centres, and  $R_g$  is the electronic radius of gyration of the scattering entities.

Other information about the internal structure of scattering entities can be obtained from the analysis of SAXS results at higher angles. A power law dependence of the scattered intensity is expected in the Porod region defined as  $HR_g \gg 1 \gg Ha$ ; where  $a$  is a typical chemical bond distance [14], and

$$I(H) \simeq H^{-x} \quad (5)$$

For uniform, dense particles with a smooth surface,  $x = 4$  and the Porod law is obeyed. For  $x < 4$ , the concept of fractal geometry [15] allows the characterization of random systems such as polymers, colloidal aggregates, rough surfaces, and porous materials [16].

Polymer-like structures lead to mass fractal objects with  $1 < x < 3$ . For such structures, the Porod exponent is the fractal dimension,  $D$ , which relates the size,  $R$ , of the object to its mass,  $M$

$$M \simeq R^D \quad (6)$$

in the present experiment  $R$  is the average radius of gyration  $R_g$ . The log-log plot of  $I(H)$  against the

scattering wave vector, reported in Fig. 2, exhibits a power law dependence in the range extending from  $2/R_g$  to  $1 \text{ nm}^{-1}$ . The slopes of the curves remain similar for the gels synthesized with a molar ratio smaller than 0.5 and their average value is close to 2.5, while for molar ratios larger than 0.5 the slopes decrease to 1.6.

#### 5. Discussion

The observation that the gel structure is influenced by the content of acetylaceton makes the concentration of the complexing agent an important experimental parameter for the synthesis of monolithic gels.

In Fig. 1 the gels synthesized with a molar ratio  $[\text{acacH}]/[\text{Zr} + \text{Y}] < 0.5$  present the same scattering profile and no significant variation is revealed from the initial curve. When the molar ratio increases beyond 0.5, the profile becomes different and exhibits an important change of the initial curvature. All the gels with a molar ratio larger than 0.5 behave similarly. This effect indicates that the local structure of gels drastically changes when the molar ratio crosses the value 0.5, probably because modifications of the kinetics of hydrolysis and polymerization Reactions 1 and 2 occur.

In Fig. 3 the variations of both  $R_g$  and gelling time plotted against the relative content of acetylaceton show three successive domains denoted I, II and III. In domain I ( $0 \leq [\text{acacH}]/[\text{Zr} + \text{Y}] \leq 0.5$ ) the relative content of acetylaceton with respect to metal cations is lower than 0.5. The sol-gel transition occurs almost instantaneously after addition of water, indicating that the kinetics of Reactions 1 and 2 are not time controlled. The radius of gyration of scattering entities amounts to 7.5 to 8 nm<sup>-1</sup>, and the Porod scale 2.5 indicates a mass fractal object which looks like a densely cross-linked polymer molecule [16]. In this domain the chelation of zirconium alkoxide molecules by acetylaceton is not large enough, on average, to control the reactivity of the system with respect to water. The polymeric species form quickly after fast hydrolysis of the non-chelated molecules followed by polymerization by condensation mechanism reactions. Consequently, the polymeric species also grow quickly and precipitation of the molecular aggregates of hydrated zirconium oxide is observed. In this domain, no transparent or monolithic gel could be obtained.

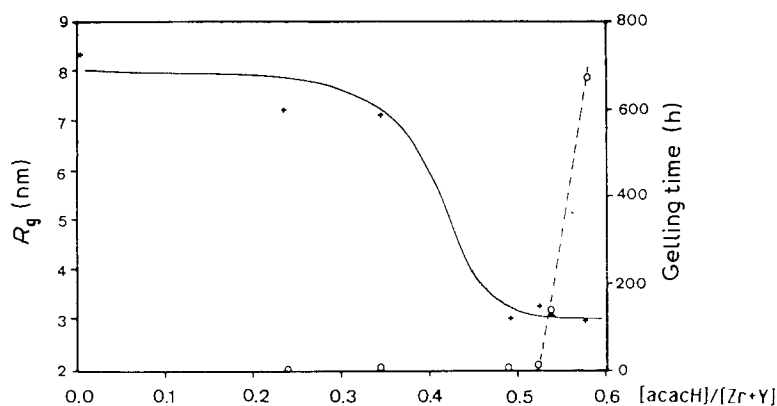
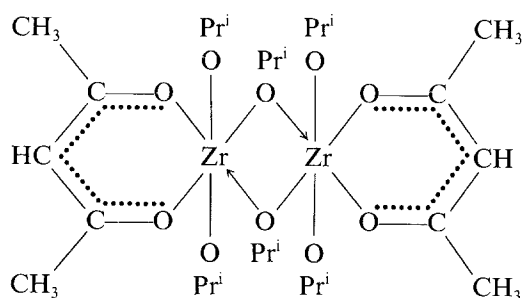


Figure 3 Plots of (—)  $R_g$  and (---) gelling time against the relative content of acetylacetonate.

In domain II ( $0.5 \leq [\text{acacH}]/[\text{Zr} + \text{Y}] \leq 0.8$ ) the situation becomes different. The resultant products are transparent and monolithic gels. The growth of polymeric species is limited to a size close to  $3 \text{ nm}^{-1}$  and the SAXS experiments indicate a Porod slope consistent with cross-linked polymer molecules [16]. The Porod slope of 1.6 suggests that the polymer molecules possess a highly open structure resulting, for example, from a cluster-cluster growth mechanism [16], and that the polymeric species formed are less dense than in domain I ( $M \approx R^D$ ).

It is worthwhile mentioning that the gelling time increases quickly with the relative content of acetylacetonate. The exact chemical role of acetylacetonate in this domain remains to be explained. If we refer to the simple presentation of the chelating effect of acacH which combines with zirconium alkoxide in 1:1 ratio as mentioned previously, a satisfactory mechanism cannot be found. In fact, the sols synthesized in this domain are expected to contain two kinds of molecular precursors: the chelated and the non-chelated molecules. The non-chelated zirconium alkoxide molecules are quite reactive and would normally lead to a behaviour similar to that of domain I. Thus the polymerization by a condensation mechanism of these molecules proceeds instantly and rapidly. For the chelated molecules, the polymerization kinetics are lower than for the others, and there is probably a larger concentration of chelated molecules on the surface of the oligomers formed initially than in the interior. The polymeric network develops between the species previously formed by a cluster-cluster aggregation, and if the number of chelated molecules on the cluster surface increases, the gelling time becomes longer.

When the relative content of acetylacetonate still increases the triisopropoxide mono- $\beta$ -diketonate zirconium probably appears which exhibits dimeric behaviour [17]. A hexacoordinated dimeric structure was proposed for this compound in which isopropoxy groups form bridges:



The hydrolytic reactivity of this triisopropoxide mono- $\beta$ -diketonate zirconium is still lower than the previous (steric effect) complex molecules. This explains the drastic increase of gelling time with the relative content of acetylacetonate.

Finally, in domain III, the hydrolysis reaction cannot proceed and gelation is not reached even after an extended period of time, i.e. after 4 months.

## 6. Conclusion

The role of acetylacetonate in the processing of zirconia gels from zirconium *n*-propoxide in isopropanol has been investigated. A ratio 1:1 of this additive alters the kinetics of reactions involved after introduction of water and allows the elaboration of monolithic gels. The effect has been explained in terms of chemical reactions between the zirconium alkoxide and acetylacetonate, that makes the hydrolysis step slower. Important experimental parameters, such as gelling time and size of polymeric species, have been taken into account.

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