

Electrochemical investigations on the sol–gel polymerization of transition-metal alkoxides

H. Cattetey,^a P. Audebert,^{*a} C. Sanchez^b and P. Hapiot^c

^aLaboratoire de Chimie et Electrochimie Moléculaire, Université de Franche Comté, La Bouloie, Route de Gray, 25030, Besançon, France

^bLaboratoire de Chimie de la Matière Condensée, URA CNRS no. 1466, Université Pierre et Marie Curie, 2 Place Jussieu, 75005, Paris, France

^cLaboratoire d'Electrochimie Moléculaire, URA CNRS no. 438, Université Denis Diderot, 2 Place Jussieu, 75005, Paris, France

The kinetics of polymerization of zirconium propoxide has been studied under various conditions using an original electrochemical method. The alkoxides were complexed with bidentate ligands some of which were functionalized by ferrocene electroactive moieties. The bound electroactive ferrocene component diffusion is used as a probe for determining the mass variation of the oligomers formed through the hydrolysis–condensation process. Chronoamperometry provided a means for studying diffusion kinetics. In this way polymerization kinetics can be followed with a fair precision on a real timescale, provided that the electroactive probe binds irreversibly to the polymerizing zirconium species. Two organic complexants, acetylacetonate and ethyl acetoacetate, have been used in this study, in order to obtain gels from the highly reactive zirconium *n*-propoxide. The binding part of the electroactive probe was the strongly complexant salicylate ligand. The electrochemical results reveal the kinetics of polymerization, and give in addition an estimation of the mobile species present once the system has reached a stable state. The results have been confirmed by several other techniques including SEM, elemental analysis, light diffusion and BET specific surface determination on the resulting xerogels.

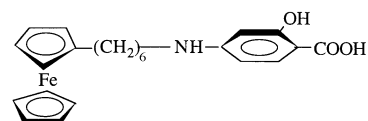
While the polymerization mechanisms of silicon alkoxides are relatively well known, the more complex case of transition-metal alkoxides has only been investigated to a limited extent,¹ especially with organic complexants.^{1a} Most of the previously performed *in situ* studies rely on NMR experiments.² NMR is an adequate tool to follow kinetics when they are slow but NMR studies are expensive and the equipment is not always available. As a consequence, most NMR data has been devoted to study the hydrolysis–condensation behaviour of silicon alkoxides. The hydrolysis of transition-metal alkoxides displays much faster kinetics, due to their usually higher reactivity, and their study is thus more difficult.

We recently introduced a new electrochemical approach to investigate the microviscosity of the sols and gels obtained through the hydrolysis of silicon and titanium alkoxides, based on the *in situ* determination of diffusion coefficients of a electroactive species embedded in zirconia or silica gels,^{3a} or anchored to the molecular precursors of zirconia, silica or titania gels.^{3b} This work addresses a further development of this method, using ferrocene species strongly bonded to a zirconium alkoxide.

Since transition-metal alkoxides are very reactive, complexation of the metal is commonly used to tune the reactivity. In this way, a polymer network can be generated instead of a precipitate.⁴ Exchange of one propylate group by a bidentate ligand such as acetylacetonate increases the coordination of a zirconium species and diminishes the reactivity^{4b} to enable the formation of transparent sols and gels. The propylate moiety is always hydrolysed before a coordinated bidentate ligand such as acetylacetonate. Therefore it is possible to bind irreversibly electroactive moieties to zirconium alkoxides and to the resulting condensed species after the hydrolysis–condensation process has begun, using a strong bidentate complexant functionalized with a ferrocenic electroactive probe. The diffusion kinetics of the functionalized complexant can be followed by chronoamperometry, and information can be extracted on the

average size of the polymers or aggregates to which the functionalized complexant has bound.

For zirconium, the complexing power is in the following order: salicylate \gg acac $>$ alkyl acetoacetate, and therefore salicylic acid is one of the best complexants for zirconium and titanium alkoxides.⁵ We have also prepared the functionalized complexant Fc-sal, where a ferrocenyl group is covalently bound to a salicylate moiety.



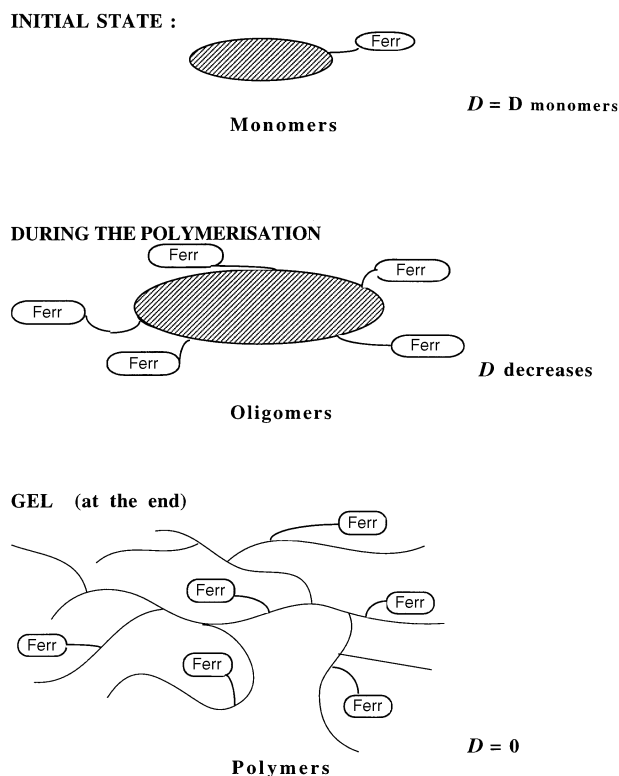
This irreversibly bound^{5b} electrochemical probe has been used to investigate the polymerization of zirconium *n*-propoxide in the presence of either acetylacetonate or ethyl acetoacetate as the main (weaker) complexant, with various hydrolysis ratios. Scheme 1 illustrates our working hypothesis.

Experimental

Synthesis of ligands

The Fc-sal ligand is made from 1-(6-bromohexyl)ferrocene, which was produced in two steps from ferrocene, according to the following sequence.

(a) Preparation of 1-(6-bromohexanoyl)ferrocene. AlCl₃ (8.72 g, 6.54 $\times 10^{-2}$ mol) was added at 5 °C under N₂ to 13.37 g (7.19 $\times 10^{-2}$ mol) of ferrocene dissolved in CH₂Cl₂ (ca. 200 ml). 10 ml (6.53 $\times 10^{-2}$ mol) of 6-bromohexanoyl chloride dissolved in CH₂Cl₂ (about 50 ml) was then added dropwise to the above mixture. The solution was stirred for 10 min, and then allowed to warm to ambient temperature. 1-(6-Bromohexanoyl)ferrocene is obtained as an orange oil after hydrolysis in an ice/water mixture. Extraction with CH₂Cl₂



Scheme 1 Polymerization via the sol-gel process, with functionalized monomers. The ferrocene species bind progressively to higher oligomers and to the main polymeric network.

and chromatography [pentane-diethylether (1/1)] gave a yield of 6%, $F = 33^\circ\text{C}$, $^1\text{H NMR}$: δ 4–5.5 (m, 9H, ferrocenyl protons), 3.4 (t, 2H, CH_2Br), 2.75 (t, CH_2CO), 1.90 (q, $\text{CH}_2\text{CH}_2\text{Br}$), 1.70 (q, $\text{CH}_2\text{CH}_2\text{CO}$), 1.50 (q, central CH_2).

(b) Preparation of 1-(6-bromohexyl)ferrocene. A standard Clemmensen reduction procedure was followed: 6.10 g (2.25×10^{-2} mol) of HgCl_2 , 50 ml of distilled water and 8 ml of concentrated HCl were mixed before introducing 79.15 g (1.21 mol) of activated zinc powder. The solution was stirred for five min and decanted. A mixture of 25 ml of water, 30 ml of concentrated HCl and 60 ml of cyclohexane was added under strong stirring. Then 14.59 g (4.02×10^{-2} mol) of 1-(6-bromohexanoyl)ferrocene were added and the mixture was heated at 100°C for 6 h. Care should be taken to maintain strong agitation, or extensive deacylation may occur as a side-reaction. 1-(6-Bromohexyl)ferrocene, as an orange oil, was obtained after extraction with CH_2Cl_2 and flash chromatography (pure pentane). Yield (after chromatography): 64%, $F = 33^\circ\text{C}$, $^1\text{H NMR}$: δ 4 (m, 9H, ferrocenyl protons), 3.4 (t, 2H, CH_2Br), 2.35 (t, CH_2Fc), 1.90 (q, $\text{CH}_2\text{CH}_2\text{Br}$), 1.30–1.60 (m, 6H, central CH_2 groups).

(c) Synthesis of 4-[6-amino(1-ferrocenyl)hexyl]salicylic acid (Fc-sal). Salicylic acid 0.41 g (2.68×10^{-3} mol) was dissolved in 3 ml of dry acetonitrile dried over 3 \AA molecular sieves, and 0.82 g (6.77×10^{-3} mol) of 2,4,6-trimethylpyridine and 0.85 g (2.43×10^{-3} mol) of 1-(6-bromohexyl)ferrocene were added (addition of a few tenths mg of oven-dried magnesium sulfate may be required). The mixture was heated for 6–8 days with agitation at 55°C . The solution was extracted by diethyl ether and washed several times with acidic water. The product was obtained as an orange solid after separation by flash chromatography (100% pentane then dichloromethane was progressively added up to 100%) in 11% yield. $^1\text{H NMR}$: δ 11.05 (s, 1H, NH), 6–7.65 (3H, benzene ring), 4.25 (t, 2H, CH_2NH), 4.1 (m,

9H, ferrocenyl protons), 2.25 (t, CH_2Fc), 1.75 (q, $\text{CH}_2\text{CH}_2\text{NH}$), 1.30–1.60 (m, 6H, central CH_2 groups).

All structures were confirmed by ^{13}C NMR and also by mass spectroscopy for Fc-sal.

Acetylacetonone (acac) and ethyl acetoacetate (etacac) were purchased (Aldrich Chemicals) and used as received.

Preparation of gels

In a typical experiment to 5 ml of a 70% $\text{Zr}(\text{OPr}^n)_4$ –30% isopropyl alcohol solution x equivalents of complexant (acac or etacac), in acetonitrile–propanol (1:1, v/v, typically 15 ml); and 0.2 g lithium perchlorate were added in a tube-shaped thermostatted cell. Fc-sal (10^{-3} M) was then added and cyclic voltammetry and a chronoamperogram were performed immediately. Then a given amount of a water–propanol (1:9, v/v) hydrolysis solution was added with stirring {the amount of water is defined by the hydrolysis ratio h = number moles of water/number moles of $\text{Zr}(\text{OPr}^n)_4$ }; since h was allowed to vary, the volume of the solution also varied, and therefore concentration corrections were made in the diffusion coefficient determinations.

The gelification diagram of the systems $\text{Zr}(\text{OPr}^n)_4$ –acac and $\text{Zr}(\text{OPr}^n)_4$ –etacac have not been reported in the literature and have been determined from a separate set of similar experiments, quoting the gelation times and nature (sols, clear gels, turbid gels or precipitates) but without any electroactive probe and the results are shown in Fig. 1. Gels were qualified as ‘slow’ when the gelation time was > 1 h, otherwise they were quoted as ‘fast’ gels. Usually, slow gelling times lead to transparent gels, while fast gelling times lead to opalescent or turbid gels. In addition it was verified in a few selected cases that the small amount of electroactive probe did not affect the gelation process.

Electrochemistry

The electrochemical device and methodology used was previously described in ref. 3(b). The electrochemical study was commenced as soon as the addition of water had been completed (about 20 s). For the majority of our studies, the electrochemical set-up consisted of a 1.2 mm diameter glassy carbon electrode, a platinum counter electrode, and a calomel

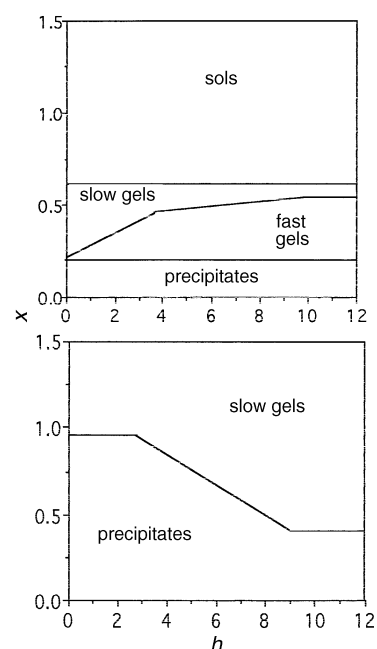


Fig. 1 The two gelification diagrams according to the complexant used: upper, acetylacetonone (acac); lower, ethyl acetoacetate (etacac)

electrode connected to a home-made potentiostat⁶ equipped with an ohmic drop compensation device.

The chronoamperometry experiments were performed stepping from 0 to +0.7 V (>200 mV beyond the potential peaks of the ferrocenyl in the sols). The data were collected on a Nicolet 350 digital oscilloscope, the duration of the experiment (data acquisition) being usually 1 or 2 s. A typical chronoamperometric curve is shown in Fig. 2, and attests to both the linearity of the Cottrell plot⁷ and the adequate choice of the timescale.

Several experiments were conducted in parallel using ultramicroelectrodes instead of conventional microelectrodes. In this case, the electrodes were 10 or 20 μm gold microdiscs, and the oscilloscope for data acquisition was a Nicolet 3094 c with a 5 ns sampling time. The data after digitalisation were transferred to a PC computer for treatment. The diffusion coefficients were extracted using the equation devised by Shoup and Szabo (see Discussion and ref. 8). Other experimental conditions (solvents, *etc.*) were identical to the those in conventional experiments.

Miscellaneous

Gas adsorption (BET) experiments were performed on dry xerogels on a Micromeritics 2100 A rapid surface area analyser using N_2 as the adsorbed gas.

SEM (scanning electronic microscopy) images were taken with a Cambridge Instruments Stereoscan 120, on gold coated substrates. Gels taken at a given stage were dried under vacuum to the corresponding xerogel state and coated in vacuum.

Elemental analyses were performed on several xerogels after stabilization of the system and drying in air.

Results and Discussion

Theoretical background

A few basic questions underly the analysis of our work, among which the first is the relation between the electrochemical current obtained from a chronoamperometry experiment in the presence of a collection of electroactive species. Of course

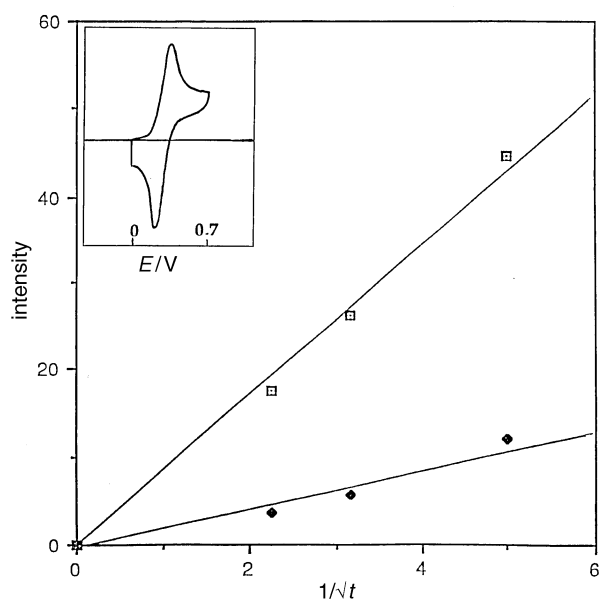


Fig. 2 Cottrell straight plots obtained by chronoamperometry in the case of the system Fc-sal-etacac for $x=0.37$ and $h=2$. The upper curve represents the evolution of the diffusion coefficient at the beginning of the polymerization reaction, and the lower curve at the end of the polymerization. The insert shows the voltamogram of the corresponding system obtained at 1 V s^{-1} .

a certain distribution of diffusion coefficients D should be assumed, and consideration of the charges of the species. The complete answer to this question raises both the problem of the definition of a mean diffusion coefficient, and of the possibilities of complications arising from homogeneous charge transfer between species diffusing at different rates. This somewhat complicated problem will be examined in a forthcoming paper.⁹ It was shown in ref. 8 that with a centred distribution, and provided that the Stokes–Einstein law is followed, the experimentally determined average D value accurately enough reflects the real average D value. The linearity of the plots in Fig. 2 provides confirmatory support.

However, in order to override possible problems resulting from a concomitant variation of both the concentration and the diffusion coefficient of the electroactive species, experiments on ultramicroelectrodes were performed. The determination of the diffusion coefficients can be obtained independently from the concentration of the electroactive species according to the equation $i=(8/\pi^2)FAD^{1/2}C/(\pi t)^{1/2}+4FDCr$, r being the electrode radius and the other symbols having their usual meaning.⁸ Separation of terms D and C arises from the simultaneous determination of the slope and the intercept of the $i=f(t^{-1/2})$ plot. Comparison between several identical systems showed that identical D values were obtained, and both methods were therefore valid.

Another possible problem would be the existence of an equilibrium between the functionalized electroactive complexant and the growing zirconium species. The choice of the salicylate functionality to bind the electroactive species certainly inhibits its release. Also, the solubility of the free species is low in water-containing solvents. Salicylic acid totally exchanges with monomeric zirconium alkoxides to form stoichiometric bis-salicylate and is not released, even in pure water, as shown by previous studies.^{5a} Analyses were also made on xerogels where salicylic acid was the main complexant. With gels prepared using *p*-aminosalicylic acid, with a complexant/ $\text{Zr}(\text{OPr}^n)_4$ ratio equal to 0.5, the formula of the resulting xerogels show that 100% of the salicylate is found in the resulting xerogel.^{5b}

As a final precaution, to avoid any possible interference arising from the main complexant (polymerization controller), we always chose a more weakly reacting ligand than the electroactive complexant; hence no competition occurs with the grafting of the electroactive probe.

Behaviour of the systems

Earlier works have shown that acetylacetonate (acac)^{4b,5} and salicylic acid (sal)⁶ were very efficient ligands, which exchanged readily with the propylate moieties on zirconium alkoxides.¹⁰ Ethyl acetoacetate (etacac), which has been proven to be a weaker complexant than acac, has only been rarely used to control zirconium alkoxide polymerization.¹⁰ Previous NMR and chemical studies^{4a,b,10a} have shown that the complexation strength increases in the order $\text{etacac} < \text{acac} < \text{sal}$; while EtOAc binds reversibly, acac binds irreversibly (however it is released to some extent by excess water). Two sol–gel systems were investigated here, $\text{Zr}(\text{OPr}^n)_4$ -etacac and $\text{Zr}(\text{OPr}^n)_4$ -acac. This fulfilled two requirements: first, to control a few parameters tuning the aggregation kinetics and second, as previously mentioned, to make sure that no competition occurred between the fixation of the main ligand and of the electroactive probe.

Gelification diagrams

Prior to the electrochemical study, it was necessary to determine the gelification diagram of the zirconium propoxide in the presence of the two complexants that we used, namely etacac (weak complexant) and acac (strong complexant), in acetonitrile–propanol. No reports were available in the former case, but even with acac, although some reports exist,^{4,5b,11} the

use of a slightly different solvent mixture made it useful to determine the gelification parameters under precise conditions.

Fig. 1 shows the results obtained in the case of the two systems studied; it is clear that both systems behave as previously noted in analogous cases,¹⁰ with precipitation of zirconium oxopolymers in all cases with a small complexing ratio x (x = number of moles of complexant/number of moles of $[\text{Zr}(\text{OPr}^n)_4]$) and, on the contrary, stable sols above a given value of x . However, the intermediate gel zone shows a difference between the two systems. While there is no detectable influence of the hydrolysis ratio h in the case of the strong complexant acac, on the contrary, h influences gelification/precipitation in the case of etacac, as a probable consequence of the easier hydrolysis of this weaker ligand.

Electrochemistry results

Several h and x values were investigated, both in the sol and gel regions. It has been verified (Fig. 2) that the electrochemical response of the sols and gels is classically diffusion controlled as has been previously shown with analogous systems.³ As expected, the chronoamperometry currents decrease upon sol ageing and in the course of the gel formation.

Separate macroscopic viscosity measurements were performed in the sol state with the help of a classical flow-rate viscosimeter. In all cases it was observed that the macroscopic viscosity displayed only very small variations within the time range of the drop of diffusion coefficient. Therefore the variations in D observed through the electrochemistry experiments are unrelated to macroscopic viscosity effects and are only due to variations in the diffusion rate of the mobile electroactive species.

In all cases a very fast initial current decrease is observed, followed by a plateau. This initial behaviour shows that the hydrolysis of the alkoxide is extremely fast, and that the condensation process starts within seconds after the water addition. The plateau current must be linked to the size of the polymers present in the sol or gel, since the probe cannot be removed from the zirconium polymers. This point is discussed further below.

Sol behaviour. The two upper curves in Fig. 3 show the variation of the diffusion coefficients of stable sols with etacac or acac as ligand. It can be seen that the diffusion coefficient variation is small and occurs always within short time ranges.

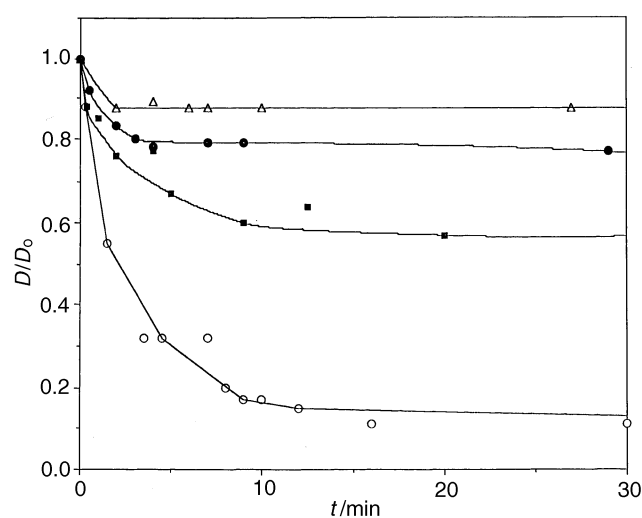


Fig. 3 Variation of diffusion coefficients with time (from classical electrochemical measurements), obtained with the two complexants, etacac or acac, for different complexation and hydrolysis rates; (Δ) acac, $x=1.25$, $h=2$, (\bullet) etacac, $x=0.75$, $h=12$, (\blacksquare) etacac, $x=1.25$, $h=12$, (\circ) acac, $x=0.37$, $h=2$

This suggests the formation of molecular clusters and short oligomers, such that the values of D do not decrease appreciably. It should be emphasized that the expected variation of D with the mass of the electroactive species is that D is proportional to $M^{1/3}$, from the Stokes–Einstein law. In any case the expected variation should be weak, so that the influence of the formation of small molecular clusters should fall within the experimental error of measurement of D .

Gel behaviour. When working in the gel domain, however, the lower curves of Fig. 3 and 4 show that an appreciable decrease in the diffusion coefficient is found in each case. It is also obvious that the characteristics of the system influences both the kinetics of the variation of D and its final value.

Fig. 4 clearly shows the influence of the ligand; when acac is used instead of etacac, in identical proportions and with the same hydrolysis ratio, the polycondensation process is slower. Besides, the plateau in D is much lower in the case of EtOAc, showing that in this case larger condensed species are formed, as expected.

Fig. 3 clearly shows the importance of the complexation ratio. The D plateau values are different, with the lowest plateau corresponding to the smallest complexation ratio. This result again confirms that the polymer size is governed by the complexant/zirconium ratio x ; the smaller the value of x , the larger the polymers formed. As expected, the stronger complexant acac leads to smaller condensed species than etacac. On the contrary, only a weak influence of the hydrolysis ratio h was observed on the D plateaus, and therefore on the oligomer size. This is in accordance with a very fast hydrolysis step of the propylate moieties, followed by condensation processes with kinetics governed only by the value of x even if some incidental water is present.

The electrochemistry experiments display only weak variations in the cases where the system remains in the sol state, and therefore scarcely detectable from the experimental error. On the contrary, it is clear that in gelling systems, the drop in D experienced by chronoamperometry is strong enough to provide quantitative information on both the evolution and the final state of the systems. These data can be discussed in relation with BET data and observations by SEM.

Surface area measurements, elemental analysis and SEM microscopy

Gas adsorption experiments allow the determination of specific surface area values of the dried xerogels and results are given

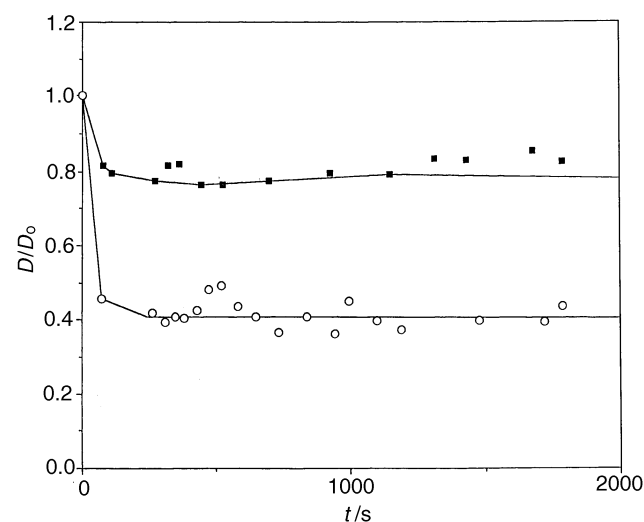


Fig. 4 Influence on D values of the complexants (from ultramicroelectrode measurements), for identical complexation and hydrolysis ratios; (\blacksquare) acac, $x=0.75$, $h=10$, (\circ) etacac, $x=0.75$, $h=10$

Table 1 BET results of several xerogels

| complexant | complexation ratio | hydrolysis ratio | BET surface area /m ² g ⁻¹ |
|------------|--------------------|------------------|--|
| acac | 0.50 | 2 | 82 |
| | 0.50 | 4 | 140 |
| | 0.50 | 10 | 231 |
| etacac | 0.58 | 10 | 73 |
| | 0.69 | 10 | 105 |
| | 0.96 | 10 | 92 |

in Table 1, and show that the BET specific surface area values of the xerogels are around 100 m² g⁻¹. There is an increase with the hydrolysis ratio in the case of a good complexant like acac; on the other hand the surface area is practically constant, whatever the value of h with the weak complexant etacac, confirming the weak influence of h in this kind of system. The results of elemental analysis on carbon and hydrogen clearly show that most ligands remain inside the xerogels, while on the contrary, all propylate moieties are hydrolysed and the propanol formed is then evaporated out of the final xerogel (because of the presence of a little residual water, oxygen content does not provide reliable data). 90–100% of the strongly bound acac and 100% of the Fc-sal type ligands are retained in the dry xerogel. The more labile etacac ligand is partially released, 60–80% of etacac remaining in the final dry xerogel, according to the initial x and h values. SEM micrographs of the gels show a granular structure (Fig. 5) with grains ranging in size from a few micrometres to much lower values. The appearance of the gel is in accordance with a

structure made of bridged oxopolymers aggregates with a size distribution allowing the existence of lower mass species.

Discussion

Although the morphology of the dried gel is certainly different from the wet gel, the average surface of a zirconium aggregate in a porous xerogel can be roughly estimated from the free internal surface experienced by N₂ in BET experiments, divided by the number of aggregates. Therefore, it is possible to propose a comparison between the BET data and the average final size of the polymers as measured by electrochemistry. The estimated size of an aggregate, from the extreme BET values in Table 1, falls between $r_{\max}=100$ Å and $r_{\min}=30$ Å (The calculation was performed on the basis of a compact stacking of spherical aggregates, which of course gives only an approximate value.)

We can analyse the electrochemistry data in terms of mass induced variations of D . The value of the plateau current shows probably that in the wet gels, even upon ageing, most of the oligomeric species are still free to diffuse in the structure. The D plateau values given by electrochemistry allow the estimation of the average oligomer size, assuming that the Stokes–Einstein law is obeyed. We can take $(D_f/D_i)^3 = M_i/M_f$ [$= (d_i/d_f)^3$] for freely diffusing oligomers [D , M and d representing respectively the diffusion coefficient, the average mass and the average diameter of the oligomers, with subscripts i for initial (monomer) and f for final]. Since the drop in the values of D are between 10 and 85% (Fig. 3 and 4), the average mass of the oligomers should be between 10 and 1000 times

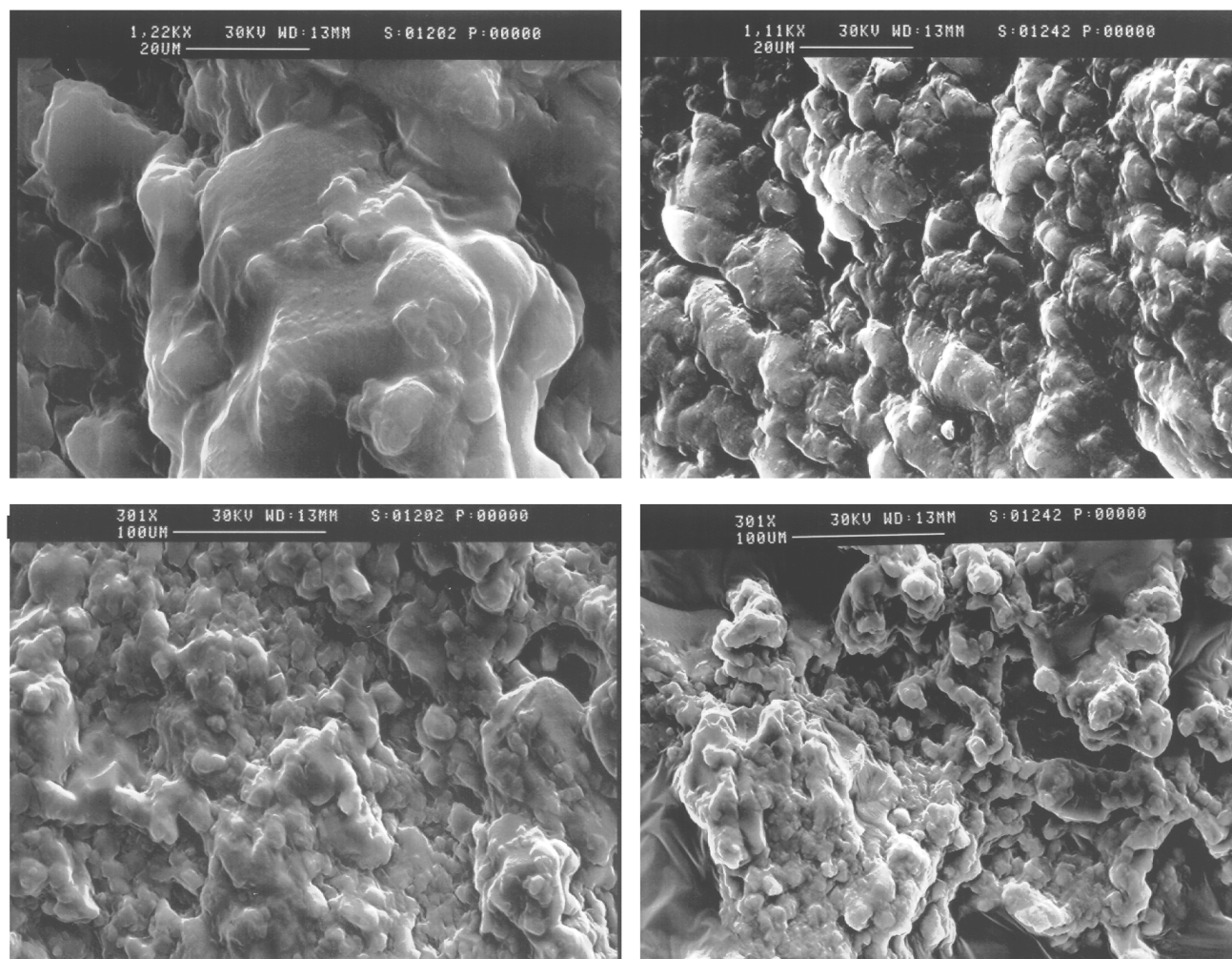


Fig. 5 SEM images of dynamically dried gels, magnification *ca.* 1200 \times . Left, Fc-sal-etacac and right, Fc-sal-acac.

the mass of the functionalized monomer (according to the hydrolysis conditions), *i.e.*, between 3000 and 3×10^5 g mol⁻¹. Previous authors have determined that the average molecular mass (on the basis of light diffusion measurements) was between 10^4 and 10^5 g mol⁻¹ on closely related systems,¹² in accord with our results.

Although the electroactive ferrocene is not a spherical molecule, it can be considered in terms of an equivalent sphere of diameter 20–25 Å, based on diffusion measurements. Given this, the average diameter of the oligomeric aggregates formed would be between 25 and 250 Å. These values fall in the range estimated from BET data.

Conclusion

It has been shown that with transition metal sols and gels, electrochemical techniques associated with functionalization of growing inorganic species can bring valuable information on the dynamics of such systems. It has been proposed in particular that the interpretation of electrochemical data and BET data leads to concordant values for the effective average size of oligomers formed. From the interpretation of results from both techniques, we can estimate the average size of the oxo species formed to be between 30 and 150 Å depending on the nature and ratio of the main complexant used. It was also reconfirmed from the comparison of plateau currents, that etacac led, as expected, to more condensed species than acac when used in identical proportions.

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