

Structural Influence of the Carbon Chain Length in Hybrid Materials Obtained from Zirconium n-Propoxide and Diols

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Abstract. Zirconium n-propoxide $Zr(OPr^n)_4$ has been chemically modified by 1,3-propanediol and 1,3-butanediol with molar ratio $r = 0.5, 1$ and 2 . The properties of the hybrid organic-inorganic materials obtained after drying at 100°C for 24 hours have been measured by thermal analysis, X-ray diffraction, infra-red spectroscopy and ^{13}C NMR with cross-polarisation at magic angle spinning. Chemical modification of the zirconium precursor at a molecular level has been clearly detected, with a bridging coordination mode for both diols. If the coordination mode of the diols cannot be changed by increasing the carbon chain length, it was found using ^{13}C CP MAS NMR that the local order is much more well-defined when the reactivity of both OH groups are not the same. Thus, using 1,3-butanediol which has a primary and a secondary OH group, it is possible to obtain after complete modification ($r = 2$) a highly homogeneous hybrid polymer which transforms directly into tetragonal zirconia below 400°C . With other diols (1,2-ethanediol and 1,3-propanediol), the hybrid materials transform into tetragonal zirconia above 400°C through a decomposition process involving several steps. Then playing with the carbon chain length and/or the steric hindrance around the OH groups provides an easy way to monitor the ultrastructure of these hybrid materials, and allows a better control of the gel \rightarrow oxide transformation.

Keywords: zirconium alkoxides and glycoxides, carbon-13 CP-MAS NMR, hybrid sol-gel materials

1 Introduction

In a previous paper [1], chemical reactions between zirconium n-propoxide $Zr(OPr^n)_4$ and 1,2-ethanediol have been investigated. Structural characterisation of the as-prepared amorphous materials by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infra-red spectroscopy (FT-IR) and ^{13}C solid state NMR with cross-polarisation at magic angle spinning (CP-MAS), have shown that 1,2-ethanediol was able to remove n-propoxy groups from the zirconium coordination sphere with a preferential bridging coordination mode. Owing to this bridging conformation of the ligand, the

resulting zirconium glycoxides are highly entangled polymeric materials rather than well-defined molecular complexes such as those found with 2,4-pentanedione for instance [2]. This behavior of zirconium alkoxides contrasts with the case of boron alkoxides where chemical modification by 1,2-ethanediol leads to soluble monomeric complexes with chelating conformations for the glycols [3]. With silicon both coordination modes (bridging and chelating) can be observed in dimeric complexes [4]. In the case of silicon alkoxides, it has been shown that increasing the carbon chain length, or providing some steric hindrance around the hydroxyl groups, leads to less polymeric solids [5]. We have thus undertaken an investigation of two new zirconium-based hybrid materials. The first system involves 1,3-propanediol in order to look at the influence of the carbon chain length. The second system uses

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1,3-butanediol in order to have within the same molecule, two OH groups with different chemical environment. This paper reports our results concerning the structural characterisation of these two hybrid materials, following the same methodology already used in the case of 1,2-ethanediol [1]. These two diol were also chosen because they have not been used in the previous work of Saxena et al. describing the synthesis of various zirconium glycoxides [6].

2 Experimental Section

All preparations were made from zirconium n-propoxide $Zr(OPr^n)_4$ (Fluka 98%), 1,3-propanediol $HOCH_2CH_2CH_2OH$ (Prolabo 99.5%) and 1,3-butanediol $HOCH_2CH_2CHOHCH_3$ (Prolabo 99.5%) which were used without further purification. Upon mixing the zirconium alkoxide with the diol, opaque and white gels are immediately obtained for a molar ratio $r = n[\text{diol}]/n[Zr(OPr^n)_4] = 1$ and 2 (samples ZP10, ZP20 with 1,3-propanediol and ZB10, ZB20 with 1,3-butanediol). For $r = 0.5$, turbid and viscous solutions are obtained (samples ZP5 with 1,3-propanediol and ZB5 with 1,3-butanediol). After drying these solutions or gels at $T = 100^\circ\text{C}$ for 24 hours powders were prepared by grinding. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier Transform Infra-Red spectroscopy (FT-IR) and ^{13}C solid state NMR with cross-polarisation at Magic Angle Spinning (CP-MAS) measurements were made on the powders. XRD experiments were performed with a goniometer (Philips PW 1820) using the $\text{Cu K}\alpha$ radiation in reflection geometry. SEM micrographs (Cambridge Stereoscan instrument) were obtained after evaporation of a gold film onto the samples. TGA and DSC curves were recorded simultaneously under an oxygen atmosphere with a thermal analyser (Netzsch STA 409) from room temperature up to 1400°C with a DSC/TG4 sample carrier at $10\text{ K}\cdot\text{min}^{-1}$. FT-IR spectra were recorded on a spectrometer (Nicolet Magna-IR 550) as solids in KBr pellets or films of pure liquids. ^{13}C CP MAS NMR spectra were recorded on a spectrometer (Bruker MSL 400) operating at 100.62 MHz with a spinning rate of 8 kHz. The 90° -pulse width was $6\ \mu\text{s}$ with a contact time of 1 ms and a pulse repetition time of 5 s. Deconvolution of FT-IR and NMR spectra has been performed using the WINFIT software [7]. This leads to an average error on the reported FT-IR frequency of

$\pm 1\text{ cm}^{-1}$. For the NMR parameters similar spectral deconvolution leads to values having errors of $\pm 0.5\text{ ppm}$ for chemical shifts δ , $\pm 1\text{ ppm}$ for line widths $\Delta_{1/2}$ and $\pm 1\%$ for area A.

3 Results

All samples are amorphous by X-ray diffraction and display a smooth vitreous surface when observed by SEM.

3.1 Reaction with 1,3-Propanediol (ZP Series)

TGA total weight losses of samples ZP5, ZP10 and ZP20 are $38 \pm 1\%$, $46 \pm 1\%$ and $55 \pm 1\%$ respectively. TG derivative (DTG) curves of samples ZP5 and ZP10 show two weight losses around 100°C and another weight loss between 200°C and 380°C . Sample ZP20 display a quite different behavior with a first weight loss around 220°C [$T_{\text{eb}}^{760}(1,3\text{-propanediol}) = 213^\circ\text{C}$] and a second one between 330°C and 380°C . Figure 1 compares the recorded DSC curves for the three samples. Samples ZP5 is characterised by three exothermic phenomena at $228 \pm 1^\circ\text{C}$, $289 \pm 1^\circ\text{C}$ and $653 \pm 1^\circ\text{C}$. According to X-ray diffraction, the last phenomenon can be associated with the crystallisation of zirconia in the tetragonal phase ($t\text{-ZrO}_2$). For

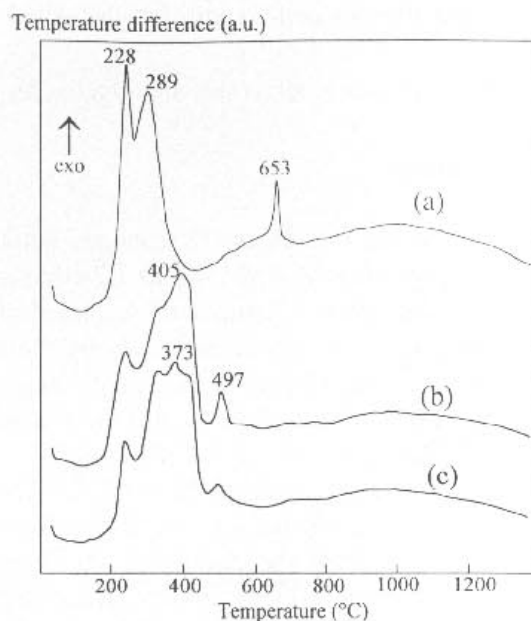


Fig. 1. DSC curves of the samples obtained by adding 1,3-propanediol to zirconium n-propoxide with (a) molar ratio $r = 0.5$ (ZP5), (b) $r = 1$ (ZP10) and (c) $r = 2$ (ZP20).

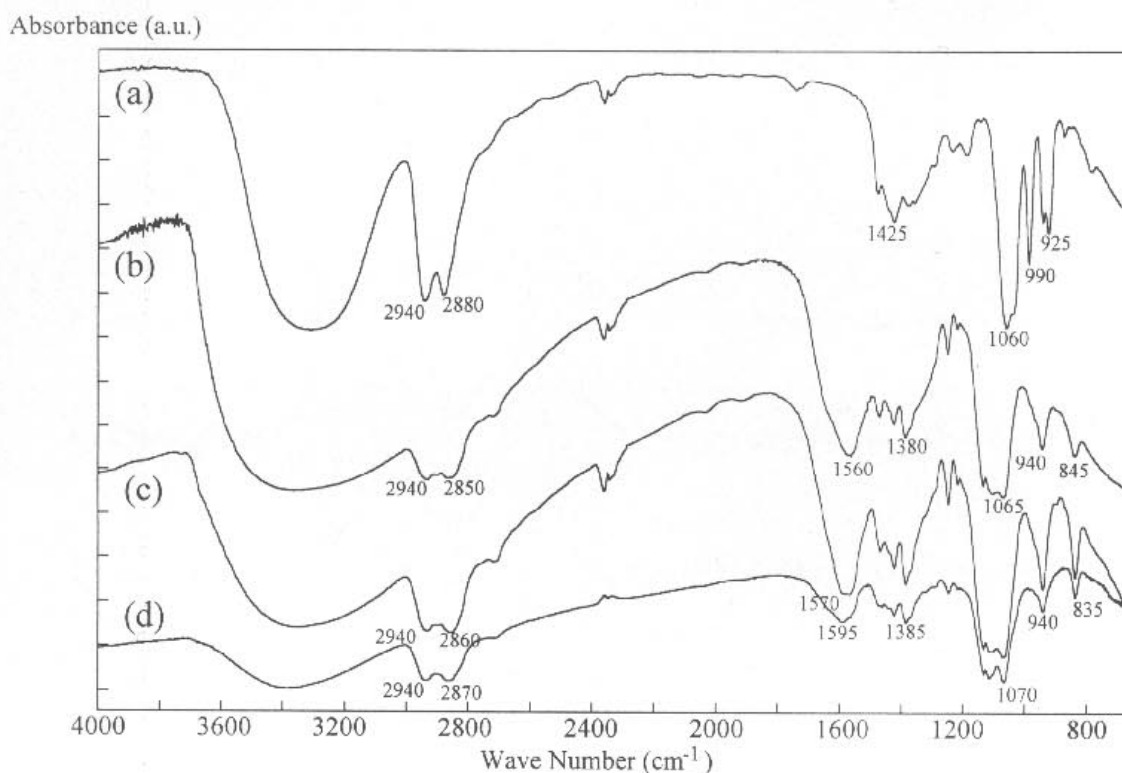


Fig. 2. FT-IR spectra of pure 1,3-propanediol (a) and of samples ZP5 (b), ZP10 (c) and ZE20 (d).

samples ZP10 and ZP20, the DSC trace is very similar to that of sample ZP5 below 300°C, but crystallisation of *t*-ZrO₂ occurs in both cases at 497 ± 1°C. Moreover, an additional rather intense exothermic phenomenon is observed at ca. 400°C, with a peak at 373 ± 1°C for sample ZP20. In all cases, the tetragonal to monoclinic (*m*-ZrO₂) transformation is observed between 600°C and 800°C, as weak deformations of the DSC-baseline.

Figure 2 compares the FT-IR spectra of samples ZP_{*n*} (*n* = 5, 10 and 20) with that of pure 1,3-propanediol. Strong modifications are observed in all characteristic regions: 2800–3000 cm⁻¹ (ν CH₂), 1300–1500 cm⁻¹ (δ CH₂), 900–1200 cm⁻¹ (ν C—O and ν C—C) and 400–800 cm⁻¹ (ν Zr—O). This means that 1,3-propanediol reacts with zirconium *n*-propoxide in all proportions. As already observed with 1,2-ethanediol, the IR spectra of three samples are very similar. However, it should be noticed that the frequency of the ν_s CH₂ band increases steadily with the modification ratio *r*. It occurs at 2834 cm⁻¹ in pure Zr(OPr^{*n*})₄ (*r* = 0), at 2852 cm⁻¹ in sample ZP5 (*r* = 0.5), at 2860 cm⁻¹ in sample ZP10 (*r* = 1), at 2870 cm⁻¹ in sample ZP20 (*r* = 2) and at 2884 cm⁻¹ in pure 1,3-propanediol (*r* → ∞).

According to literature the ¹³C chemical shifts of 1,3-propanediol are 60 ppm for the CH₂CO site and 36 ppm for the CH₂C₂ site with a 2:1 ratio and no solvent dependence [8]. Figure 3 gives the ¹³C CP-MAS NMR spectra of samples ZP5, ZP10 and ZP20. The spectrum of sample ZP5 is characterised by four main signals at δ = 68.0 ppm (*A* = 42%, $\Delta_{1/2}$ = 4 ppm), δ = 35.0 ppm (*A* = 30%, $\Delta_{1/2}$ = 6 ppm), δ = 27.0 ppm (*A* = 9%, $\Delta_{1/2}$ = 3 ppm), δ = 11.0 ppm (*A* = 9%, $\Delta_{1/2}$ = 2 ppm) and a shoulder at ca. 63 ppm (*A* = 10%, $\Delta_{1/2}$ = 3 ppm). The two shielded signals (11 and 27 ppm) are the signature of unreacted *n*-propoxy groups (CH₃C and CH₂C₂ sites respectively) [1]. From our previous study, we know that substitution of an hydrogen atom by a zirconium atom in bridging or terminal conformation leads to an upfield shift of at least 6 ppm for the carbon atom directly linked to the oxygen atom, a downfield shift of at most 2 ppm for the carbon in α position of the Zr—OC moiety and to an upfield shift of at most 0.5 ppm for a carbon atom in β position of the Zr—OC moiety [1]. Consequently, the two other signals (35 and 68 ppm) can be reasonably attributed to bridging 1,3-propanedioxy groups (Zr—OCH₂CH₂CH₂O—Zr), whereas the occurrence of the shoulder suggests some mixed bonding such as

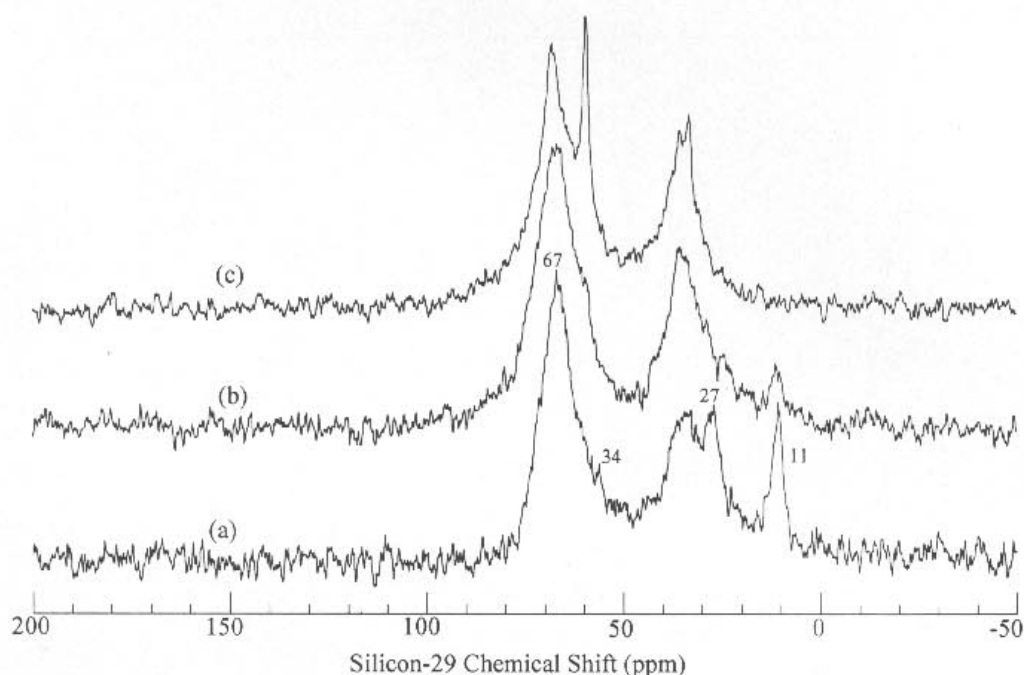


Fig. 3. ^{13}C 400 MHz CP-MAS NMR spectra of samples ZP5 (a), ZP10 (b) and ZP20 (c).

$\text{Zr}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{Zr}$ for instance. The same attribution can be made for the spectrum of sample ZP10 which displays also four signals at $\delta = 68.0$ ppm ($A = 51\%$, $\Delta_{1/2} = 6$ ppm), $\delta = 35.0$ ppm ($A = 29\%$, $\Delta_{1/2} = 5$ ppm), $\delta = 27.5$ ppm ($A = 5\%$, $\Delta_{1/2} = 4$ ppm), $\delta = 11.0$ ppm ($A = 5\%$, $\Delta_{1/2} = 2$ ppm) and a shoulder at ca. 62 ppm ($A = 10\%$, $\Delta_{1/2} = 5$ ppm). In sample ZP20 no pair of signals with a 1:1 ratio is observed at 27 and 11 ppm, showing that for $r = 2$, all alkoxy groups have been removed. Based on line widths and seeking for a characteristic 2:1 ratio, the four main signals can be separated into two groups: $\delta = 68.0$ ppm ($A = 48\%$, $\Delta_{1/2} = 4$ ppm) and $\delta = 36.0$ ppm ($A = 19\%$, $\Delta_{1/2} = 3$ ppm) on one hand, and $\delta = 59.5$ ppm ($A = 13\%$, $\Delta_{1/2} = 1$ ppm) $\delta = 33.5$ ppm ($A = 5\%$, $\Delta_{1/2} = 1$ ppm) on the other hand. The deviations from the theoretical 2:1 ratio are attributed to differences in the cross-polarisation rates for the various sites. The largest pair of signals (36 and 68 ppm) can be safely attributed as in sample ZP5 and ZP10 to bridging 1,3-propanedioxy groups ($\text{Zr}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-\text{Zr}$). The thinnest pair (33 and 60 ppm) displaying a chemical shift close to that of pure 1,3-propanediol for the CH_2CO site, can then be attributed to solvating 1,3-propanediol molecules ($\text{Zr} \leftarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{ZR}$ and/or $\text{Zr} \leftarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$). At this stage, only 85% of the experimental spectrum has been accounted for. The

remaining magnetisation (15%) appears to be distributed in the bottom of the lines and would lead to several additional peaks of large line widths and low intensity to account for the full spectra. Obviously such values are not very significant being subject to very large errors. Consequently, the only conclusion which may be drawn, is the existence of other coordination modes, different from bridging or solvating, which are in too low proportions to be characterised by the ^{13}C CP-MAS NMR technique.

3.2 Reaction with 1,3-Butanediol (ZB Series)

TGA total weight losses of samples ZB5, ZB10 and ZB20 are $39 \pm 1\%$, $48 \pm 1\%$ and $55 \pm 1\%$ respectively. These values are very close to that observed for the ZP series. Samples ZB5 and ZB10 show two important weight losses between 100°C and 400°C and another one around 700°C . In contrast sample ZB20 show no weight loss above 400°C . Figure 4 show the DSC traces of the three samples. DSC curves of samples ZB5 and ZB10 are rather similar with two exothermic phenomena at 250°C and 380°C and a another rather weak distortion of the baseline between 800 and 900°C . X-ray diffraction performed within that temperature range shows that the solids are undergoing a tetragonal to monoclinic phase transition. The DSC diagram of sample ZB20 is quite different, with a

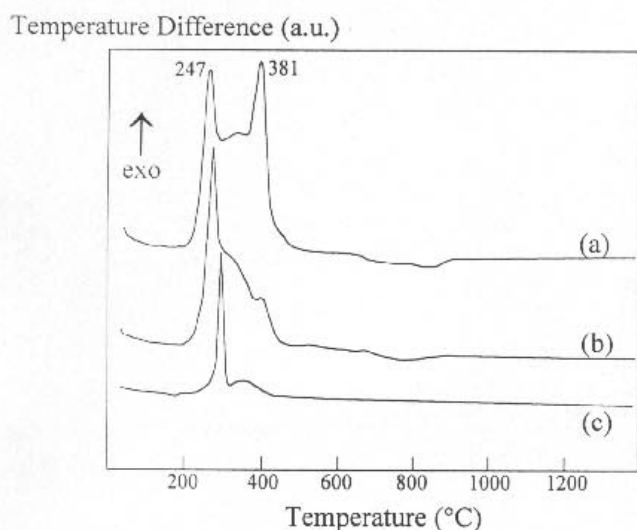


Fig. 4. DSC curves of the samples obtained by adding 1,3-butanediol to zirconium *n*-propoxide with (a) molar ratio $r = 0.5$ (ZB5), (b) $r = 1$ (ZB10) and (c) $r = 2$ (ZB20).

very strongly exothermic phenomenon at $T = 290^\circ\text{C}$ [$T_{\text{cb}}^{760}(\text{1,3-butanediol}) = 207^\circ\text{C}$] and a much broader one around 350°C . Above 400°C ZB20 appears to be crystallised in the tetragonal phase.

Figure 5 compares the FT-IR spectra of samples ZB5, ZB10 and ZB20 with that of pure 1,3-butanediol. As in the case of the ZP series, strong modifications are

observed in all domains ($\nu\text{-CH}_3$, $\nu\text{-CH}_2$, $\delta\text{-CH}_2$, $\nu\text{-CC}$, $\nu\text{-CO}$ and $\nu\text{-ZrO}$). Consequently, 1,3-butanediol like 1,2-ethanediol and 1,3-propanediol reacts with zirconium *n*-propoxide in all proportions. As already seen in the ZE and ZP series, the IR spectra of samples ZB5, ZB10 and ZB20 are qualitatively very similar. However, in contrast with the ZP series, no regular change is observed for the $\nu_s\text{-CH}_2$ band, probably owing to some mixing the $\nu_s\text{-CH}_3$ band.

Liquid ^{13}C NMR reveals that pure 1,3-butanediol is characterised by four signals of equal intensities at 24.0 ppm (CCH₃ site), 42.5 ppm (CC₂H₂ site), 60.0 ppm (CH₂CO site) and 65.5 ppm (CHC₂O site) with no solvent dependence [8]. Figure 6 gives the ^{13}C CP-MAS NMR spectra of the three ZB n samples ($n = 5, 10$ and 20).

The spectrum of sample ZB5 is characterised by five main signals occurring at $\delta = 73.0$ ppm ($A = 35\%$, $\Delta_{1/2} = 3$ ppm), $\delta = 66.0$ ppm ($A = 7\%$, $\Delta_{1/2} = 4$ ppm), $\delta = 41.0$ ppm ($A = 10\%$, $\Delta_{1/2} = 4$ ppm), $\delta = 27.0$ ppm ($A = 23\%$, $\Delta_{1/2} = 3$ ppm) and at $\delta = 11$ ppm ($A = 13\%$, $\Delta_{1/2} = 1$ ppm). If we assume again a minimum downfield shift of 6 ppm upon substitution of hydrogen by zirconium, we expect two signals around 66 and 72 ppm for 1,3-butanedioxy groups in bridging conformation. This means that it should be rather difficult to differentiate with NMR a free

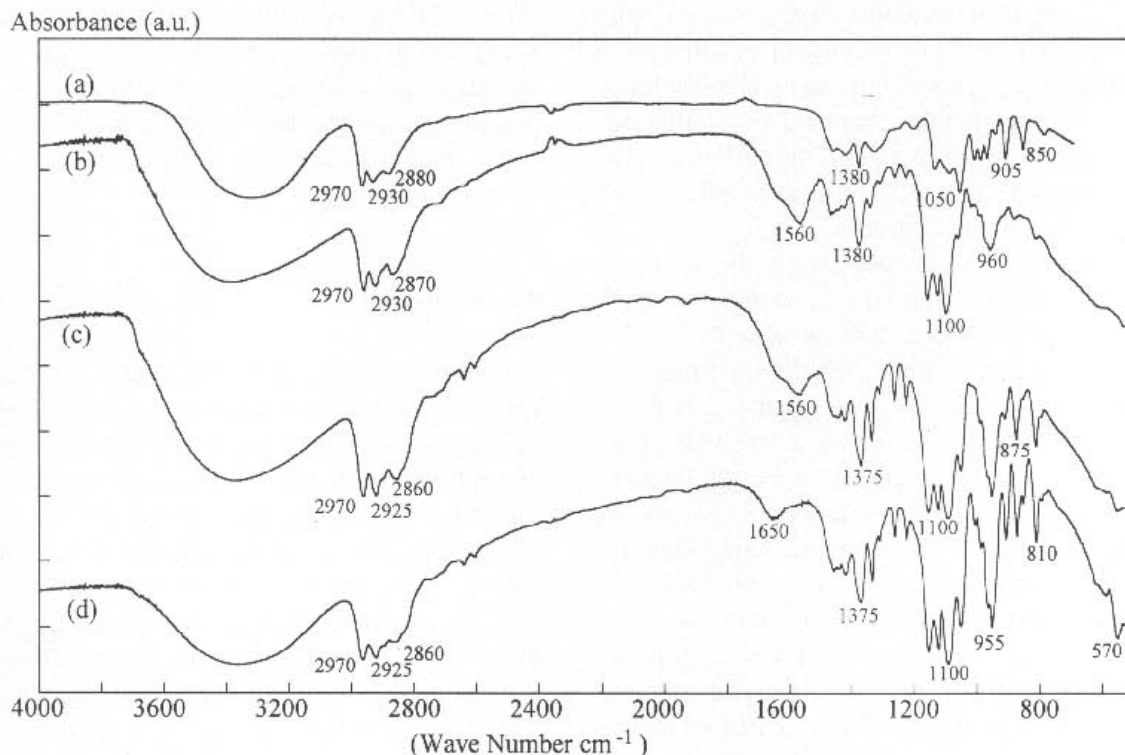


Fig. 5. FT-IR spectra of pure 1,3-butanediol (a) and of samples ZB5 (b), ZB10 (c) and ZB20 (d).

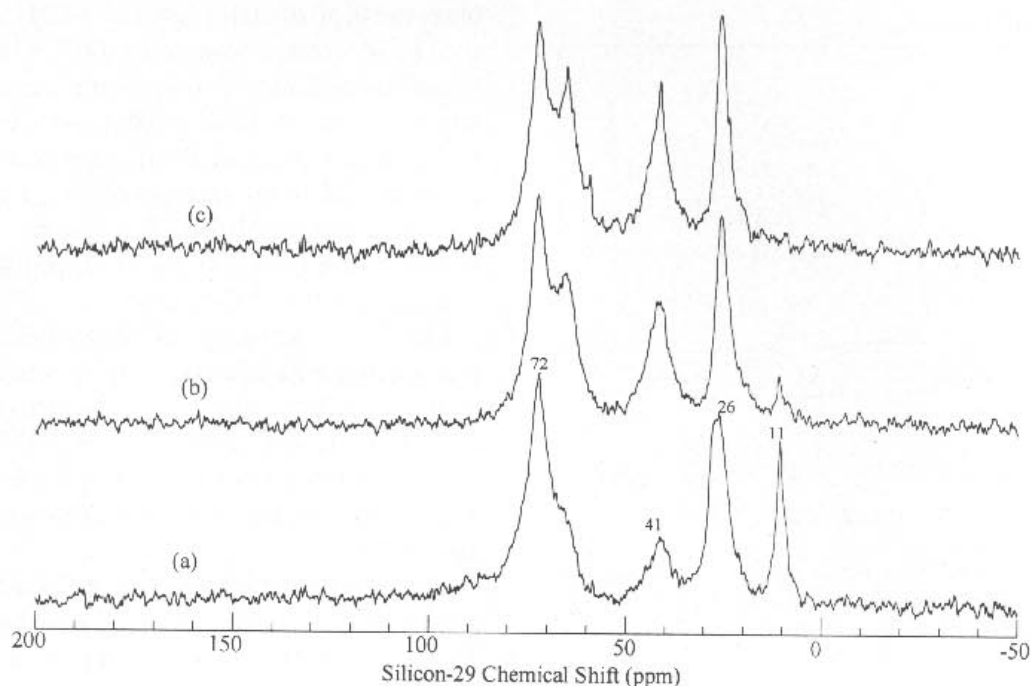


Fig. 6. ^{13}C 400 MHz CP-MAS NMR spectra of samples ZB5 (a), ZB10 (b) and ZB20 (c).

secondary C—OH group from a primary zirconium-bonded C—OZr group. With this restriction in mind, a possible assignment of the ZB5 spectrum is as follows: terminal alkoxy groups at 11 and 27 ppm (CH_3C and CH_2C_2 sites respectively) as in ZE and ZP series, and zirconium-bonded 1,3-butanedioxy groups at 73, 66, 41 and 27 ppm, most probably in bridging position owing to the polymerised nature of the as-prepared solids. Besides these strong signals, complete simulation of the ZB5 spectrum shows that 12% of the carbon atoms are not involved in such associations (terminal alkoxy or bridging 1,3-butanedioxy groups).

The spectrum of ZB10 is qualitatively the same as ZB5. The signal of the CH_3C site of terminal alkoxy groups ($\delta = 11.0$ ppm) has now an area $A = 3\%$ with $\Delta_{1/2} = 1$ ppm. Other signals are found at $\delta = 73.0$ ppm ($A = 27\%$, $\Delta_{1/2} = 3$ ppm), $\delta = 66.0$ ppm ($A = 24\%$, $\Delta_{1/2} = 4$ ppm), $\delta = 42.0$ ppm ($A = 21\%$, $\Delta_{1/2} = 4$ ppm) and $\delta = 26.0$ ppm ($A = 25\%$, $\Delta_{1/2} = 4$ ppm) in reasonable agreement with the expected 1:1:1:1 ratio. A fine simulation of the 24 ppm peak shows that it could be decomposed into two component having NMR parameters $\delta = 26.0$ ppm ($A = 14\%$, $\Delta_{1/2} = 2$ ppm) and $\delta = 23.0$ ppm ($A = 11\%$, $\Delta_{1/2} = 5$ ppm). If such a deconvolution is significant, this would mean that at least two kinds of methyl groups having quite different local environments occur in sample ZB10.

The $\delta = 11$ ppm peak is no more present in the ZB20 spectrum, while four main signals are observed at $\delta = 73.0$ ppm ($A = 29\%$, $\Delta_{1/2} = 3$ ppm), $\delta = 66.0$ ppm ($A = 18\%$, $\Delta_{1/2} = 2$ ppm), $\delta = 43.0$ ppm ($A = 18\%$, $\Delta_{1/2} = 2$ ppm) and $\delta = 27.0$ ppm ($A = 21\%$, $\Delta_{1/2} = 2$ ppm). As with sample ZB5, full simulation of the spectrum requires additional lines of low intensity and large line widths for a total area of 14%. Despite this fact, ZB20 appears to be the most homogeneous solid, from a local order point-of-view, of all so far investigated samples.

4 Discussion

Our results clearly show that zirconium *n*-propoxide reacts at a molecular level with 1,3-propanediol and 1,3-butanediol, leading to highly entangled polymeric amorphous solids having glycolate bridges. For the highest modification ratio ($r = 2$), all *n*-propoxy groups can be removed from the first coordination sphere of zirconium, while for lower modification ratio ($r = 1$ and 0.5), these groups remain trapped inside the polymeric network as dead-ends. This behavior is qualitatively quite similar to that already observed with 1,2-ethanediol [1]. However, from a local order point-of-view, the various materials appear to be quite different. If we look at the line widths of the most

deshielded NMR signals, which correspond to carbon atoms nearest neighbors of zirconium atoms, we get after averaging over the modification ratio r : $\Delta_{1/2} = 10$ ppm, $\delta = 71$ ppm for 1,2-ethanediol [1], $\Delta_{1/2} = 5$ ppm, $\delta = 68$ ppm for 1,3-propanediol and $\Delta_{1/2} = 3$ ppm, $\delta = 71$ ppm for 1,3-butanediol. As we attribute these peaks to bridging glycoxy groups, we check that the local disorder decreases as the carbon chain length increases. The thinnest signals are obtained with a glycol having two non-equivalent OH groups. This could be attributed to the rather strong dipole-dipole interactions between the two OH groups of 1,2-ethanediol, which inhibit relaxation of the disorder generated by the rapid mixing of two solutions (the alkoxide and the glycol). As the carbon chain length increases, some flexibility is introduced and the polymer can undergo a partial relaxation of the constraints induced by the syntheses, leading to a more well-defined local order. The most favorable case for this relaxation to occur is met when the glycol has two non-equivalent OH groups with a flexible carbon skeleton. OH groups undergoing the least steric hindrance (primary OH) can react first with zirconium alkoxide, while the other OH groups (secondary or tertiary) are still unreacted. The growing polymer has thus enough time to adopt the most favorable conformation before occurrence of reticulation which hinders further molecular reorientation process. The local homogeneity thus obtained is clearly seen on the DSC trace of sample ZB20 which shows a unique and sharp decomposition into zirconium oxide at $T = 290^\circ\text{C}$ and can be quantified using ^{13}C CP-MAS NMR.

Another challenge provided by these hybrid materials is the detection of chelating coordination mode for the glycoxy groups. Such a coordination mode has been clearly evidenced in the case of silicon but has not been yet reported for zirconium. Our results show that increasing the chain length, or introducing some steric hindrance into the carbon chain do not favor chelating over bridging coordination mode. Whereas we cannot say that these chelating groups are lacking in our samples, the highly insoluble nature of the as-prepared hybrid solids brings strong support to the bridging hypothesis. This may well be a size effect, as boron and silicon have ionic radii respectively six times and two times smaller than zirconium. We have to wait for other experiments involving aluminium or

titanium alkoxides for instance, as well as other glycols, to discuss more deeply this chelating versus bridging behavior.

5 Conclusion

Our study has shown that it was possible to perform chemical modification of zirconium n-propoxide with various diols. Diols bind to zirconium mainly through a bridging conformation, and we have been not able to detect unambiguously, the chelating conformation in our samples. Additional ^{13}C NMR structural characterisations with cations of smaller size (B^{3+} , Al^{3+} , Si^{4+} , Ti^{4+} . . .) and with other glycols are thus required. However, if the coordination mode cannot be changed from bridging towards chelating, it was possible to monitor the local order in these hybrid amorphous materials. By increasing the carbon chain length and providing some steric hindrance around the OH groups, it is possible to decorrelate the reactivity of the different kind of hydroxyl groups beard by the same molecule. Structural relaxation during polymer growth can then occur, leading to rather homogeneous hybrid materials which can decompose in a single step into crystalline oxides. This molecular monitoring of chemical reactivity should be of the utmost importance in the field of nanosized ceramics powder syntheses. With this respect ^{13}C CP-MAS NMR has proved to be a very valuable tool to follow these local order changes as a function of molecular environment.

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