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Organically Modified Zirconium Phosphate by Reaction with 1,2-Epoxydodecane as Host Material for Polymer Intercalation: Synthesis and Physicochemical Characterization

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Organically modified α-layered zirconium phosphate samples ($ZrP(C_{12})_x$) containing dodecyl groups bonded to the α-layers through P−O−C bonds have been prepared by reaction of 1,2-epoxydodecane solutions in tetrahydrofuran (THF) with gels of partially exfoliated zirconium phosphate in THF. Two dimensional correlation solid state NMR experiments for ^1H-^{13}C and ^1H-^{31}P nuclei have been used to prove the formation of P−O−C bonds arising from nucleophilic attack of POH mainly to carbon 1 and, to a lesser extent, to carbon 2 of epoxydodecane. $ZrP(C_{12})_x$ samples with *x* in the range from ∼0.5 to ∼2.0 are thermally stable up to at least 200 °C, and their interlayer distance increases continuously with *x* from ∼20 to ∼35 Å. On the basis of structural considerations, it has been suggested that samples with low *x* values could intercalate aliphatic polymers. Accordingly, preliminary results have shown that molten polyethylene is intercalated in $ZrP(C_{12})_{0.49}$ and $ZrP(C_{12})_{0.73}$. These materials can therefore be regarded as filler candidates for polymer matrixes.

1. Introduction

Monohydrogen zirconium phosphate of α-type, $Zr(HPO_4)_2 \cdot H_2O$ (hereafter ZrP), is a well-known inorganic ion exchanger whose structure[1] is built up by the packing of zirconium atom planes that are sandwiched between monohydrogen phosphate groups in such a way that each group is bonded to three zirconium atoms of the plane. The layers are held together by weak van der Waals interactions,[2] and this allows to exfoliate ZrP by intercalating short chain amines.[3]

In recent years, increasing attention has been devoted to the use of ZrP as a filler of neutral and charged polymers not only because of its good thermal stability and chemical inertia but also because of the possibility to exfoliate the ZrP microcrystals and to control the aspect ratio of the particles arising from exfoliation.[4]

The presence of hydrophilic POH functions on both layer sides has made ZrP an attractive filler of charged polymers and in particular of sulfonated polymer membranes for low temperature fuel cells.[5−10] On the other hand, to be used as a filler of neutral polymers, ZrP must be functionalized with coupling agents assuring sufficiently strong interaction with the polymer matrix. To this end, the intercalation of suitable amines, such as propylamine,[4] amino alcohols,[11] Jeffamine[12−17]

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and a mixture of ciclohexylamine and dodecylamine[18] were used to functionalize the ZrP layers and to exfoliate the functionalized material within the polymeric matrix as well.

A different synthetic approach to ZrP functionalization consists in the preparation of zirconium phosphonates, that is, compounds with general formula $Zr(HPO_4)_{2-x}(RPO_3)_x$ where R is a suitable organic group serving as coupling agent. In spite of the large variety of groups that can be bonded to the phosphorus atom, only few examples of polymer composites filled with zirconium phosphonates are reported in the literature.[19-22]

Another approach, allowing bonding of covalently organic groups to the ZrP layers, is based on the reaction of the monohydrogen phosphate group with epoxides leading to the formation of P−O−C bonds. Although this approach is in principle fairly simple, only reactions of ethylene oxide with ZrP were reported to date.[23] It was shown that with highly crystalline samples reaction takes place only at the microcrystal surface. However, if the interlayer distance is first increased so that ethylene oxide can diffuse into the interior, complete reaction ensues. On the other hand, less crystalline samples react directly with ethylene oxide either as a gas or as a solution (similar reactions with ethylene oxide and propylene oxide were also reported for γ-zirconium phosphate, $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$[24,25]). The higher reactivity of poorly crystalline ZrP was attributed to its larger surface area and to the fact that the interlayer spacing may be larger as the state of hydration is greater.

On the basis of these considerations, it was of interest to investigate the reactivity toward epoxides of ZrP gels in organic solvents obtained by intercalation−deintercalation of propylamine in crystalline ZrP as they contain partially exfoliated ZrP with high surface area.[4] The main difference between this type of gel and those made of amorphous ZrP lies in the morphology of the solid phase. The intercalation−deintercalation process does not alter the size of the ZrP layers so that the size of the particles of the gels prepared from crystalline ZrP depends on the size of the ZrP microcrystals.[4] Thus, a suitable choice of the starting material allows control of the aspect ratio of the gel particles, and this is of great importance in view of use of ZrP as a filler of polymer composites.[7,15]

In the present paper, organically modified ZrP was synthesized by reaction of 1,2-epoxydodecane ($C_{12}H_{24}O$) with gels of ZrP in tetrahydrofuran (THF). The organic derivatives thus obtained were characterized by thermogravimetric analysis, solid state NMR, and powder X-ray diffraction (XRD). Preliminary experiments were also performed to test the ability of these compounds to intercalate molten polyethylene (PE).

2. Experimental Section

2.1. Chemicals. Zirconium(IV) oxide chloride octahydrate ($ZrOCl_2\cdot 8H_2O$) was supplied by Merck. All other reagents were supplied by Aldrich and were used as received without further purification.

2.2. Preparation of Organically Modified ZrP by Reaction with $C_{12}H_{24}O$. Crystalline ZrP was prepared by the direct precipitation method in the presence of hydrofluoric acid.[26] A colloidal dispersion of ZrP intercalated with propylamine (ZrP·PrN, where PrN = $C_3H_7NH_2$) in water was prepared according to ref 3 by adding 16.6 mL of 0.1 M propylamine to a suspension of 0.5 g of ZrP in 33 mL of water. The dispersion was treated with 6 mL of 1 M HCl (final pH < 2) so as to regenerate the hydrogen form of zirconium phosphate. The solid was separated from the solution and washed with water under vigorous stirring. A gelatinous precipitate settled by centrifugation at 3000 rpm. Washing was repeated up to the elimination of the chloride ions. The gel thus obtained contained 1.5−2.5 wt % anhydrous ZrP.

The ZrP gel in water was washed three times with four times excess of THF. After each washing, the ZrP gel was separated from the solution by centrifuging at 3000 rpm. Functionalization of ZrP with $C_{12}H_{24}O$ was carried out by adding a suitable volume of 0.1−3.0 M solution of $C_{12}H_{24}O$ in THF to the ZrP gel in THF with $C_{12}H_{24}O$/ZrP molar ratios in the range 0.5−10. The samples, in Teflon bottles, were stirred magnetically overnight at room temperature and then heated at 70 °C in an oven for 48 h. The resulting gelatinous precipitate was separated from the solution by centrifuging at 3000 rpm and washed under vigorous stirring 3 times with a suitable volume of THF to remove unreacted $C_{12}H_{24}O$. The samples were dried at 80 °C.

2.3. Techniques. XRD patterns of powders and composite films were collected with a Philips X-Pert PW 3710 powder diffractometer using the Cu Kα radiation source. Thermogravimetric determinations were carried out by a NETZSCH STA 449 Jupiter thermal analyzer connected to a NETZSCH TASC 414/3 A controller at a heating rate of 10 °C min^{-1}, with an air flow of about 30 mL min^{-1}. Elemental analysis was carried out by a FISONS Mod. EA 1108 CHN analyzer.

Solid state NMR experiments were performed on a Bruker Avance 400 spectrometer at resonance frequencies of 400.13 MHz for ^1H, 161.97 MHz for ^{31}P and 100.61 MHz for ^{13}C. Powdered samples were packed into 4 mm zirconia rotors and sealed with Kel-F caps. The spin-rate was 9794 Hz. ^{31}P MAS NMR spectra were performed with a recycle delay of 140 s, the $\pi/2$ pulse width was 3.5 μs; 1200 scans were collected. The deconvolution of ^{31}P MAS spectra was performed using the dm2006 program.[27] The Gaussian/Lorentzian model was selected. Each resonance was characterized by the amplitude, the resonance frequency in parts per million (ppm), and the width at half-height.

^{31}P CP-MAS spectra were performed with a recycle delay of 3s, the $\pi/2$ pulse width was 3.0 μs, the contact time was 2 ms, and 800 scans were collected. ^{13}C CP-MAS spectra were performed with a recycle delay of 3s, the $\pi/2$ pulse width was 3.0 μs, the contact time was 1 ms, and 1600 scans were collected. The cross-polarization was performed applying the variable spin-lock sequence RAMP-CP-MAS,[28] the RAMP was applied on the ^1H channel, and during the contact time the amplitude of the RAMP was increased from 50 to 100% of its maximum value. All spectra were acquired using 1024 data points in the time

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domain, zero filled, and Fourier transformed with a size of 2048 data points.

The heteronuclear ^{13}C-^{1}H and ^{31}P-^{1}H dipolar-correlation experiments were performed with frequency-switched Lee–Goldburg homonuclear decoupling.[29] The duration of the successive FS-LG pulses was optimized to 10.2 μs, the magic angle pulse length was 2.13 μs.

The ^{13}C-^{1}H HETCOR experiment was acquired with 80 slices in the t_1 dimension, and the number of scans was 64. A very short contact time, 80 μs, was used to obtain correlation only between carbons and directly bonded protons. ^{1}H and ^{13}C chemical shifts were internally referenced to the methyl resonance at 14.1 (^{13}C) and 0.88 (^{1}H) ppm with respect to tetramethylsilane (TMS).

The ^{31}P-^{1}H HETCOR experiment was acquired with 64 slices in the t_1 dimension, and the number of scans was 32. ^{1}H and ^{13}P chemical shifts were referenced to glucose 6-phosphate which was added as internal reference. Glucose 6-phosphate was previously solubilized in D_2O and frozen dried to convert all exchangeable OH groups to OD groups. The phosphorus resonance of glucose 6-phosphate was set at 3.8 ppm from H_3PO_4 95% and H6, H6′ protons of glucose 6-phosphate were set to 4 ppm from TMS.

3. Results and Discussion

In preliminary experiments, gels of ZrP in THF were put in contact with 0.1 M $C_{12}H_{24}O$ solutions in THF at 70 °C, with $C_{12}H_{24}O$/ZrP molar ratios ranging from 0.5 to 10. After 2 days of equilibration, the resulting solids (hereafter ZrP-$(C_{12})_x$) were dried at 80 °C, stored at 53% relative humidity, and analyzed by thermogravimetric determinations in the range 20–1000 °C. In all cases cubic ZrP_2O_7 was the final decomposition product, but the overall weight loss (from ~34 to ~55%) was much larger than that expected for the formation of ZrP_2O_7 from monohydrated ZrP (i.e., 12%) thus indicating the uptake of $C_{12}H_{24}O$.

Typical weight loss curves for ZrP$(C_{12})_x$ samples (Figure.1) show three steps in the ranges 20–150 °C, 200–350 °C and 350–700 °C. The first step starts just above room temperature and may arise from the loss of intercalated water and/or residual THF weakly interacting with the ZrP layers. The fact that the second step starts above 200 °C is consistent with the incipient decomposition of alkyl chains covalently bonded to the phosphorus atoms of ZrP through P–O–C bridges arising from the nucleophilic attack of ≡POH to carbon 1 or 2 of epoxydodecane (Scheme 1). On the other hand, the third step is in all cases larger than that expected for the formation of ZrP_2O_7 from ZrP, thus indicating that the removal of the organic component is not complete in the second step and needs a temperature above 350 °C. A similar thermal behavior was also reported for the compounds obtained by reaction of ZrP with ethylene oxide.[23]

On the basis of the above considerations, the overall weight loss corresponding to the second and third step of the thermogravimetric curve was used to calculate the number (x) of alkyl chains per Zr atom. The composition of some ZrP$(C_{12})_x$ samples is reported in Table 1 as a function of the molar ratio $C_{12}H_{24}O$/ZrP in the starting 0.1 M $C_{12}H_{24}O$ solutions. For ratios ranging from 0.5 to 2, the x values increased from ~0.5 to ~1.4, while no appreciable change in x was observed even for $C_{12}H_{24}O$/ZrP ratio as high as 10. With the latter reactant ratio, x values around 2 were obtained by increasing the epoxide concentration to 0.3 M, and no further increase in x was found for concentrations up to 3 M. The carbon and hydrogen weight percentages of some samples were determined by elemental analysis and turned out to be in good agreement with the corresponding data calculated from thermogravimetric analysis (TGA), (Table 1).

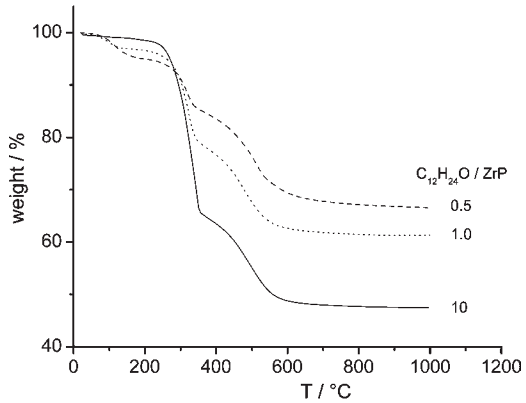

Figure 1. Thermogravimetric curves for samples prepared by reaction of ZrP/THF gels and 0.1 M $C_{12}H_{24}O$ with the indicated $C_{12}H_{24}O$/ZrP molar ratios.

Scheme 1. Expected Products for the Reaction between ZrP and $C_{12}H_{24}O$

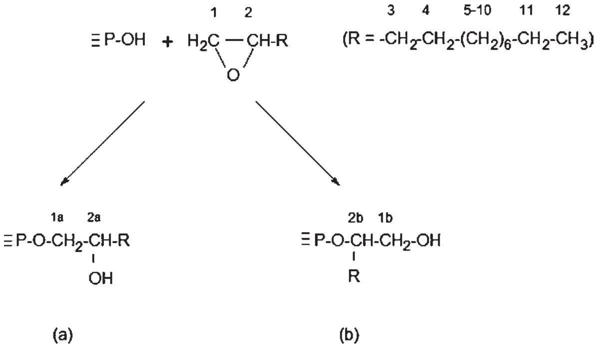

Table 1. Composition (x), Obtained from Thermogravimetric Determinations, and Interlayer Distance (d) for ZrP$(C_{12})_x$ Samples As a Function of the Initial Reactant Molar Ratio ($C_{12}H_{24}O$/ZrP)[a]

			% H		% C		
$C_{12}H_{24}O$/ ZrP	$C_{12}H_{24}O$ conc. (M)	x	TGA	elemental analysis	TGA	elemental analysis	d(Å)
0.5	0.1	0.49	3.7	4.1	18.9	17.2	19.5
1.0	0.1	0.73					24.8
1.5	0.1	0.94	5.2	5.7	29.7	27.7	28.4
2.0	0.1	1.43	6.8	6.8	37.8	36.9	31.9
10	0.1	1.45					30.8
10	0.3	1.96					34.0
10	1.0	2.07	7.8	7.9	44.9	44.7	35.1

[a] The hydrogen and carbon weight percentage, calculated on the basis of TGA data and determined by elemental analysis, is also reported for some compounds.

The kinetics of the reaction of ZrP gels with 0.1 and 0.3 M $C_{12}H_{24}O$ solutions and with $C_{12}H_{24}O$/ZrP = 10 was also investigated (Figure.2). In both cases x reaches values of 0.6–0.75 in less than 5 h while the reaction is nearly complete in 2 days.

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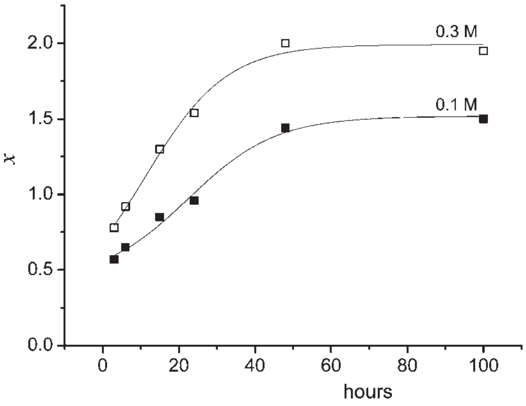

Figure 2. Composition (x) as a function of time for $ZrP(C_{12})_x$ samples obtained by reaction of ZrP with 0.1 and 0.3 M $C_{12}H_{24}O$.

3.1. NMR Determinations. To prove that the reaction between epoxydodecane and the ZrP gels leads to the formation of P−O−C bonds it will be shown that (1) $ZrP(C_{12})_x$ samples are free of unreacted epoxide, (2) according to the proposed reaction scheme, an increase in the number of alkyl chain (x) is associated with a decrease in the number of monohydrogen phosphate groups, and (3) phosphorus atoms not belonging to monohydrogen phosphate groups are coupled with hydrogen atoms of the alkyl chains. To this end, ^{13}C CP-MAS, ^{31}P MAS, and CP-MAS NMR, as well as solid state two-dimensional ^{1}H-^{13}C and ^{1}H-^{31}P correlation experiments were carried out. In the correlation experiments the contact time for the cross-polarization was purposely tailored to obtain only correlations between carbon and directly bonded hydrogen atoms and between phosphorus and the neighbor hydrogen atoms, respectively.

The ^{13}C CP-MAS spectra of all samples are very similar. As an example, the ^{13}C CP-MAS spectrum of sample $ZrP(C_{12})_{1.96}$ is shown in Figure 3 as projection in the f2 frequency domain of the 2D ^{1}H-^{13}C correlation spectrum. The resonance of the terminal methyl of the fatty chain is observed at 14.1 (^{13}C) and 0.88 (^{1}H) ppm, the resonance of methylene carbons 11 and 4 are observed at 23.6 (^{13}C) and 1.0 (^{1}H) ppm, the resonance of methylene carbon C3 is observed at 35.31 (^{13}C) and 1.265 (^{1}H) ppm, whereas the resonances of the other methylene carbons C5−C10 are overlapped at 27.5 (^{13}C) and 1.2 (^{1}H) ppm and at 31.7 (^{13}C) and 1.2 (^{1}H) ppm. It is worth noting that the absence of carbon resonances at about 52 and 48 ppm, which are characteristic of the carbon atoms of the three membered ring of epoxydodecane, allows the assessment that unreacted epoxydodecane is not present in the investigated compound.

In the case of the reaction occurring according to Scheme 1a, the resonance observed at 61.6 (^{13}C) and 3.6 (^{1}H) ppm is assigned to methylene carbon 1a, and the resonance observed at 71.2 (^{13}C) and 3.3 (^{1}H) ppm to methine carbon 2a. The presence of the resonance at 79.6 (^{13}C) and 3.6 (^{1}H) ppm might reveal that the reaction between monohydrogen phosphate and epoxydodecane also occurs at the position of methine carbon 2, giving rise to the structure reported in Scheme 1b, where the methine and the methylene carbons are now reported as 2b and 1b, respectively. According to Scheme 1b, the resonance of methylene carbon 1b possibly overlaps to the resonance ascribed to methine 2a, and the resonance at 79.6 ppm might be ascribed to methine carbon 2b.

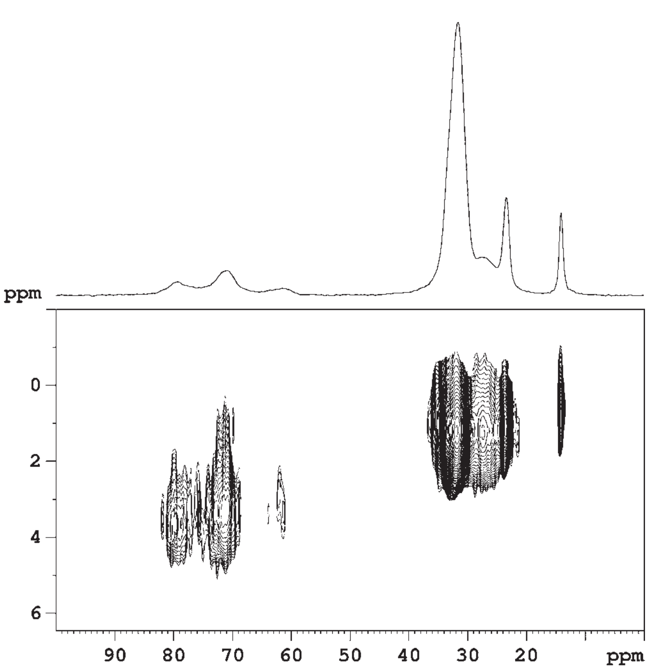

Figure 3. 2D solid state ^{1}H-^{13}C correlation experiment for sample $ZrP(C_{12})_{1.96}$; the ^{13}C CP-MAS spectrum is shown as projection.

To prove that an increase in the number of alkyl chains (x) is associated with a decrease in the number of monohydrogen phosphate groups, 2D ^{1}H-^{31}P correlation experiments were performed on samples of ZrP, $ZrP(C_{12})_{1.45}$ and $ZrP(C_{12})_{1.96}$.

To assign the ^{1}H chemical shifts of OH groups belonging to unreacted phosphate groups a 2D ^{1}H-^{31}P correlation experiment was performed on a sample of ZrP after drying in an oven at 140 °C for 24 h to remove the crystallization water, see Figure 4. The ^{31}P CP-MAS spectrum is reported as a projection in the f2 dimension, whereas the calculated ^{1}H projection of the ^{1}H-^{31}P correlation spectrum is reported in the f1 dimension. The intense cross peak centered at −18.81 ppm (^{31}P) and 7.36 ppm (^{1}H) evidences the correlation occurring between the phosphorus and the acid hydrogen atoms of the monohydrogen phosphate group. Similar chemical shift values were reported in the literature for monohydrated ZrP.[30,31] On the basis of this assignment it was established that the acid hydrogen atoms resonate at 7.36 ppm. It is worth noting that this cross peak shows a rather broad shoulder at low field. The very weak cross peak centered at −18.81 ppm (^{31}P) and 5 ppm (^{1}H) is due to a low amount of residual water.

In Figure 5 the 2D ^{1}H-^{31}P correlation spectra of samples $ZrP(C_{12})_{1.96}$ (a) and $ZrP(C_{12})_{1.45}$ (b) are reported; the corresponding ^{31}P CP-MAS spectra are also reported as projections in the f2 dimension. On the basis of the above assignment the cross peak at −19.0 ppm (^{31}P) and 7.36 ppm (^{1}H) appearing in the spectrum of sample

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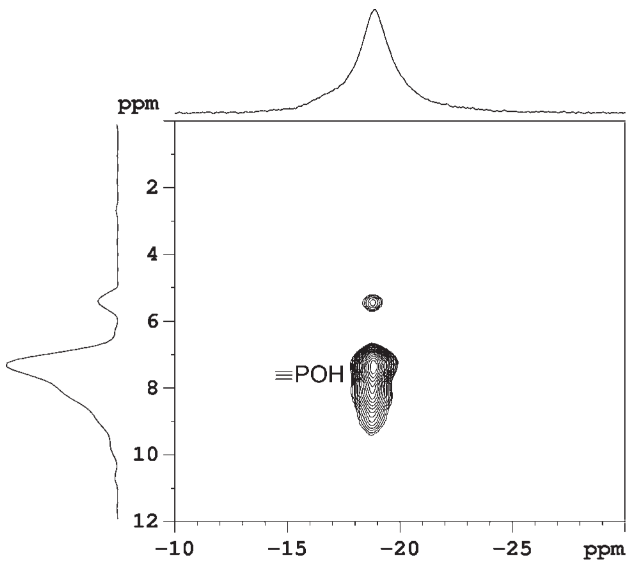

Figure 4. 2D solid state ^{31}P-^{1}H correlation spectrum, obtained with a very short contact time, on a ZrP sample dried in an oven at 140 °C. The ^{31}P CP-MAS spectrum is reported as a projection in the f2 dimension whereas the calculated ^{1}H projection of the 2D spectrum is reported in the f1 dimension.

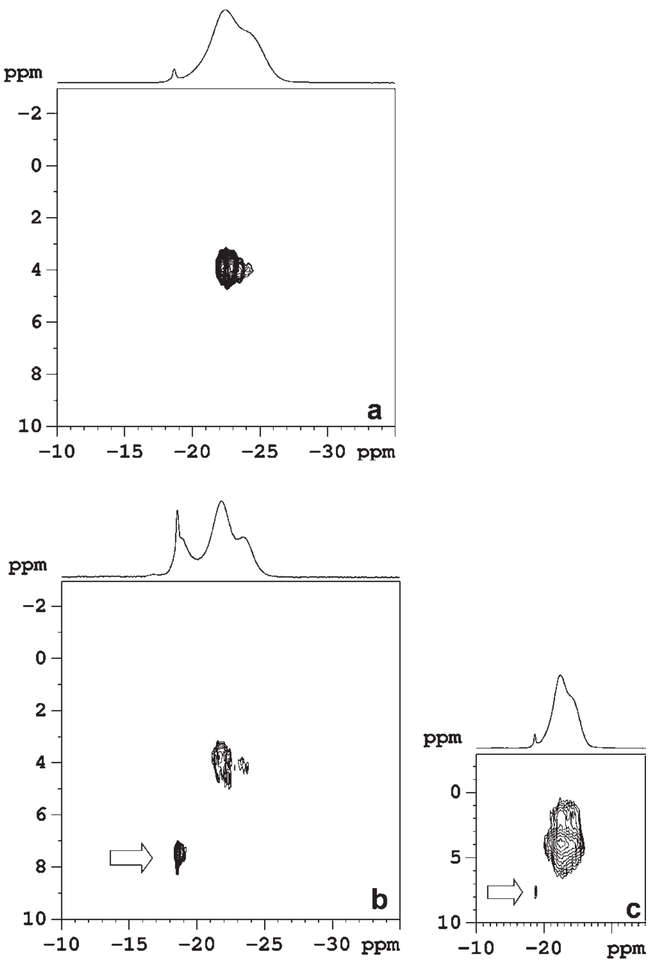

Figure 5. 2D solid state ^{31}P-^{1}H correlation spectra, obtained with a very short contact time, of $ZrP(C_{12})_{1.96}$ (a) and of $ZrP(C_{12})_{1.45}$ (b); the ^{31}P CP-MAS spectra are reported as projections in the f2 dimension. In (c) the correlation spectrum reported in (a) is shown with an 8 times vertical multiplication. The cross peak due to the correlation between the phosphorus and the acid hydrogen atoms of the monohydrogen phosphate group is evidenced with an arrow.

$ZrP(C_{12})_{1.45}$, see Figure 5b, must be assigned to the correlation between the phosphorus and the acid hydrogen atoms of the monohydrogen phosphate groups. As a matter of fact, this cross peak is observed when unreacted monohydrogen phosphate groups are present. The same cross peak with a definitely lower intensity is also present in the spectrum of $ZrP(C_{12})_{1.96}$, see Figure 5c, thus indicating that the number of unreacted phosphate groups decreases with increasing x and vanishes as x approaches 2. Note that the correlation spectrum reported in Figure 5c is shown with an 8 times vertical multiplication compared to that shown in Figure 5a.

In 2D ^{1}H-^{31}P correlation spectra reported in Figure 5a and 5b, an intense cross peak representing the correlation between P atoms (resonating at −22.6 and −24.7 ppm) and H atoms (resonating at about 3.5 ppm) is also clearly observed. The chemical shift of these H atoms not only is too upfield shifted to be assigned to H atoms belonging to acid ≡POH groups, but it is also the same as that of the H atoms bonded to carbon 1a and carbon 2b. The fact that the P atoms resonating at −22.6 and −24.7 ppm are coupled with H atoms of the alkyl chain is consistent with the presence of P−O−C bonds arising from the reaction between ZrP and epoxydodecane. In this connection, it can be observed that the change in the chemical shift of the phosphorus atom associated with the formation of $ZrP(C_{12})_x$ compounds (from −19.0 ppm to −22.6 and −24.7 ppm) is similar to that (from −8.90 ppm to −13.24 ppm) reported for the reaction of the dihydrogen phosphate group of γ-zirconium phosphate with ethylene oxide.[32]

In Figure.6 the ^{31}P MAS spectrum of $ZrP(C_{12})_{1.96}$ is reported along with the spectral deconvolution. As obtained from the deconvolution procedure, the integral of the resonance at −22.6 ppm accounts for 72% of the total integral, whereas the integral of the resonance at −24.7 ppm accounts for 27.5% of the total integral. The integral of the weak resonance at −19 ppm accounts for 0.5% of the total integral. Since in 1,2-epoxydodecane position 1 is less sterically hindered than position 2, it can be reasonably hypothesized that the resonance at −22.6 ppm is due to the phosphate groups bonded to carbon 1a, whereas the resonance at −24.7 ppm is due to the phosphate groups bonded to carbon 2b.

It can be finally observed that the only alternative to the formation of P−O−C bonds could be an oligomerization reaction of the $C_{12}H_{24}O$ monomers catalyzed by the acid ≡POH groups. As a consequence, a fairly large amount of unreacted ≡POH groups should be present even in $ZrP(C_{12})_{1.96}$, but this is not the case.

3.2. XRD Determinations. XRD powder patterns were collected on materials dried overnight at 80 °C. Figure.7 shows the patterns of $ZrP(C_{12})_x$ samples with $x = 0.49$, 0.94, 1.45, and 2.07 together with the pattern of the dry starting gel. The common feature to all these patterns is a weak reflection which shifts from $2\theta = 33.9°$ to $2\theta = 33.5°$ with the increase of x. The corresponding interplanar distances change from 2.64 to 2.67 Å. A reflection at $2\theta = 33.8°$ is also found in microcrystalline α-ZrP[1] with

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(32) Nakano, H.; Ohno, T.; Yamanka, S. *Chem. Lett.* **1994**, *23*, 9–12.

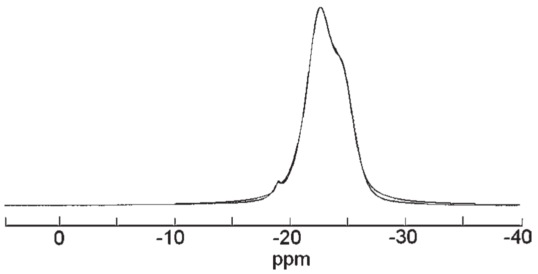


Figure 6. ^{31}P MAS experimental and deconvoluted spectra for sample $ZrP(C_{12})_{1.96}$.

Miller indexes 020, and the associated interplanar distance is half the separation between neighboring Zr atoms in the α-layer (5.297 Å). As a consequence, the position of the 020 reflection of ZrP remains unaltered if reactions and/or intercalation processes occurring in the interlayer region of α-ZrP do not alter the Zr−O−P framework of the α-layer. If it is reasonably assumed that in $ZrP(C_{12})_x$ too the reflection at 33.5−33.9° is associated with the Zr atom separation, then it can be concluded that the reaction between $C_{12}H_{24}O$ and ZrP leaves substantially unaltered the structure of the α-layer.

The XRD powder patterns of $ZrP(C_{12})_x$ samples (Figure.7) show the strongest reflection in the 2θ range 2.5−3.7° followed by the second and, in some cases, by the third order reflections. While the starting gel is nearly XRD amorphous, the intensity of these reflections increases with x thus indicating that the presence of long alkyl chains bonded to phosphate groups favors an ordered packing of the α-layers.

XRD patterns collected during kinetics experiments with 0.1 and 0.3 M $C_{12}H_{24}O$ solutions also show quite a sharp reflection corresponding to an interlayer distance of 7.5 Å which can be assigned to anhydrous α-ZrP. This reflection, which is already present after 3 h, becomes progressively weaker as time elapses and, in most cases, disappears after 2 days (a very weak peak is still visible in the patterns of the samples with $x = 0.49$ and 1.45). Thus, no crystalline phase other than that originating the peaks in the 2θ range 2.5−3.7° seems to be present at the equilibrium. On the other hand, the presence of amorphous unreacted ZrP cannot be excluded in $ZrP(C_{12})_x$ samples with $x < 2$.

Interlayer distances (d) for all compounds were calculated from the position of the first reflection of the XRD pattern after a 2 day reaction. Figure.8 shows that d values increase continuously with x from $d = 19.5$ Å for $x = 0.49$ up to $d = 35.1$ Å for $x = 2.07$. A continuous increase in d was also observed during the kinetic experiments (Figure.9) carried out with an initial $C_{12}H_{24}O$/ZrP molar ratio of 10.

This behavior is substantially different from that of a large part of the intercalation compounds of α-zirconium phosphate, $ZrP \cdot A_x$, where the guest species (A) is a cation or a neutral molecule. In most cases the coefficient x can only assume few and well-defined values so that attempts to change the A content in a given $ZrP \cdot A_x$ phase lead to the formation of a new phase with different x and d values. More specifically, a progressive change in the A content is generally associated with the concomitant change in the relative amount of the two phases, but not in their composition and interlayer spacing. By contrast, only one crystalline phase is revealed by the XRD pattern of the epoxy-functionalized gels, and its interlayer spacing changes with the C/Zr molar ratio without any discontinuity.

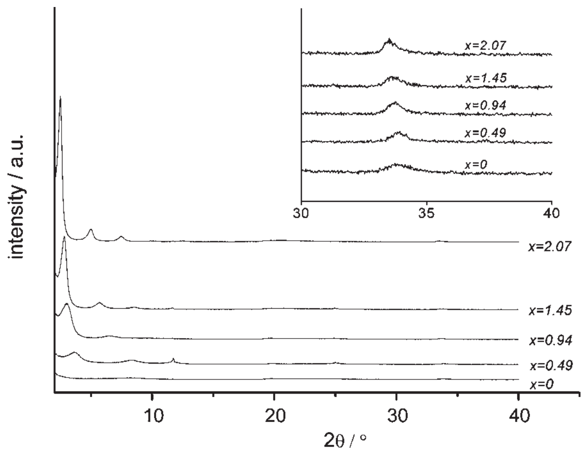


Figure 7. XRD powder patterns of $ZrP(C_{12})_x$ samples. Curves were translated to avoid overlapping. The inset shows a pattern magnification in the 2θ range 30 to 40°.

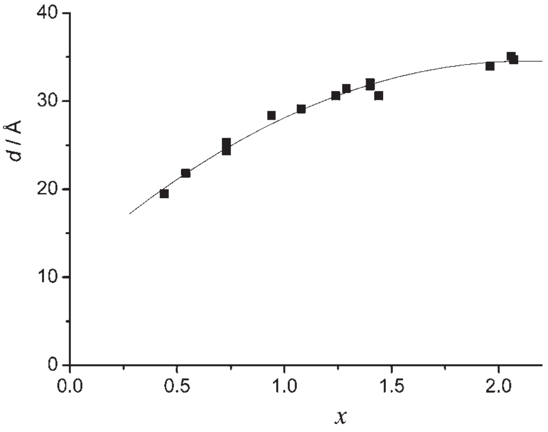


Figure 8. Interlayer distance (d) of $ZrP(C_{12})_x$ samples as a function of x.

3.3. Structural Considerations. It is interesting to compare the epoxy derivative $ZrP(C_{12})_2$ with the corresponding intercalation compound of zirconium phosphate with n-dodecylamine ($ZrP \cdot 2CH_3(CH_2)_{11}NH_2$) with regard to the density of the alkyl chain packing in the interlayer space (ρ_C). In terms of number of carbon atoms per unit volume of the alkyl chain film, ρ_C is given by the following equation:

$$\rho_C = \frac{R}{Sd_C} \tag{1}$$

where R is the C/Zr molar ratio, d_C is the thickness of the alkyl chain film, and S the area of the Zr atom plane associated with each Zr atom. If d' is the thickness of the layer portion which does not contain carbon atoms, then $d_C = d - d'$. Moreover, under the assumption that amine intercalation and epoxy functionalization leave the structure of the α-layer substantially unaltered, the value of S is the same as for monohydrogen zirconium phosphate[1] ($S = 24$ Å^2).

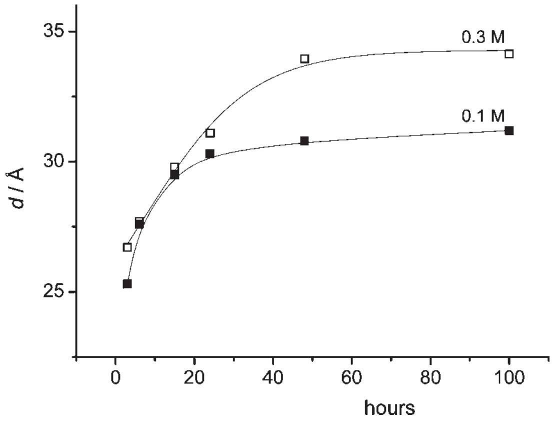


Figure 9. Interlayer distance (*d*) as a function of time for samples obtained by reaction of ZrP with 0.1 and 0.3 M $C_{12}H_{24}O$.

For the dodecylamine intercalation compound, the d' value can be obtained taking into account that, for R up to 28, the interlayer distance of intercalation compounds of zirconium phosphate with *n*-alkylamines ($ZrP\cdot 2CH_3(CH_2)_{n-1}NH_2$) depends linearly on n[33] and consequently on R, according to the relation

$$d(\text{Å}) = 10 + 2.22n = 10 + 1.11R \qquad (2)$$

where $R = 2n$. Assuming $d' = 10$ Å (i.e., the d value for $R = 0$), d_C turns out to be $1.11R$ so that $\rho_C = (1.11S)^{-1} = 0.0375$ carbon atoms/Å^3, independent of R. This value is close to the packing density of trans−trans alkyl chains (0.0406 carbon atoms/Å^3) calculated from the cell parameters of $C_{29}H_{60}$.[34]

On the basis of the structural features of α-zirconium phosphate,[1] the d' value for the epoxy derivatives can be roughly estimated to be around 6.3 Å, which is twice the distance between the zirconium atom plane and the barycenter of the oxygen atom bridging phosphorus and carbon atoms (Scheme 2). Taking into account that $d = 34.5$ Å for $x = 2.0$ (Figure.8), the corresponding ρ_C value is 0.035 carbon atoms/Å^3. It should be pointed out that the ρ_C value is only weakly affected by the uncertainty on d' as $d \gg d'$.

Since $ZrP(C_{12})_2$ and the dodecylamine intercalation compound are characterized by about the same ρ_C value and the same C/Zr molar ratio, the lower interlayer distance of $ZrP(C_{12})_2$ ($d = 34.5$ Å) in comparison with the intercalation compound ($d = 37.6$ Å) is due to the fact that, while in the epoxy derivative the alkyl chain is bonded directly to the oxygen of the phosphate group, in the intercalation compound it is separated from the phosphate by an ammonium group.

Because of the possible presence of amorphous unreacted ZrP, the calculation of ρ_C is not possible for $ZrP(C_{12})_x$ samples with $x < 2$. However, the available data allow to discuss two limit situations where (i) unreacted ZrP is absent, or (ii) unreacted ZrP is present and the alkyl chains are packed with the same density as in $ZrP(C_{12})_2$.

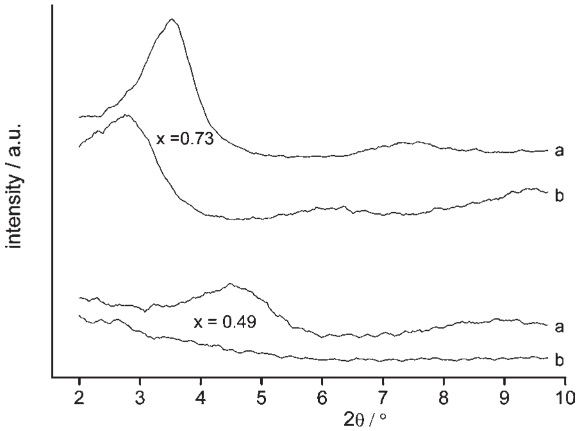
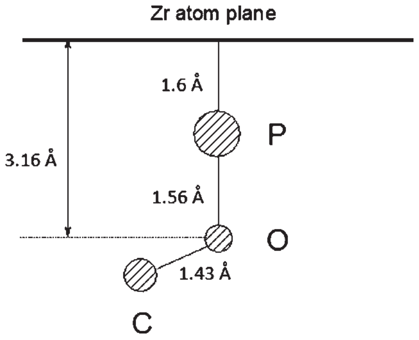


Figure 10. XRD powder patterns collected at room temperature for mixtures of PE + 5 wt % $ZrP(C_{12})_x$ before (a) and after (b) PE melting.

Scheme 2. Schematic Representation of the C−O−P Bonds in $ZrP(_{12})_x$ Samples



In the first case the packing density of a uniform distribution of alkyl chains (ρ_C^*) can be obtained by means of eq 1. The results of this calculation show that ρ_C^* is nearly halved when R decreases from 24 to 6. This low density chain packing is expected to favor intercalation processes and possible exfoliation of the host material.

In the second case, the organically modified phase would have a higher C/Zr molar ratio (R^*) than that (R) determined analytically. R^* values are calculated by eq 1 using the d values plotted in Figure.8 and Table 1, setting $\rho_C = 0.035$. With decreasing d from 35.1 to 19.5 Å, R^* becomes progressively larger in comparison with R, in particular, for $d = 19.5$ Å and $R = 5.9$, R^* turns out to be ~11. This means that the organically modified phase would have the formula $ZrP(C_{12})_{0.92}$ so that less than half of the phosphate groups would be bonded to the alkyl chains. In this case a suitable chain arrangement could create enough room in the interlayer region for intercalation reactions.

3.4. Polyethylene Intercalation. To test the ability to intercalate aliphatic polymers, $ZrP(C_{12})_x$ samples with x in the range 0.5−2.0 were ball-milled together with medium density PE, and the resulting mixtures were heated overnight at 130 °C. Under these conditions the polymer is in the molten state and could be intercalated into $ZrP(C_{12})_x$.

The XRD powder patterns of physical mixtures containing 5 wt % $ZrP(C_{12})_x$ were collected before and after heating at 130 °C. While the thermal treatment did not alter the pattern of $ZrP(C_{12})_{1.96}$ and $ZrP(C_{12})_{1.40}$, the first

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(33) Clearfield, A.; Costantino, U. *Two and Three-Dimensional Inorganic Networks*; Alberti G., Bein, T., Eds.; Pergamon, Elsevier Science ltd Press: Oxford, 1996; Vol. 7, Chapter 4, pp 107−149.

(34) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; pp 48−61.

reflection of $ZrP(C_{12})_{0.73}$ was shifted toward lower 2θ values by 0.8° (Figure.10). Correspondingly, the interlayer distance changed from 24.8 to 32.0 Å, the latter value being about the same as that of $ZrP(C_{12})_{1.40}$.

The increase in the interlayer distance as a consequence of PE melting proves that PE was intercalated into $ZrP(C_{12})_{0.73}$. Moreover, no reflection in the 2θ range from 2 to 10° was observed in the pattern of $ZrP(C_{12})_{0.49}$. The disappearence of the first reflection of $ZrP(C_{12})_{0.49}$ indicates undoubtedly the occurrence of a big change in the layer arrangement which can arise from either formation of an intercalation compound whose first reflection would fall below 2° (i.e., interlayer distance higher >44.1 Å) or even the exfoliation of $ZrP(C_{12})_{0.49}$ and its dispersion in the PE matrix.

4. Conclusion

The reaction between gels of ZrP in THF and 1,2-epoxydodecane allowed the covalent bonding of long hydrophobic alkyl chains to the ZrP layers, as proved by two-dimensional correlation solid state NMR experiments. Structural considerations suggested that a suitable chain arrangement in $ZrP(C_{12})_x$ samples with low content of dodecyl groups could create enough room in the interlayer region for intercalation reactions, and preliminary tests showed indeed that molten PE is intercalated in $ZrP(C_{12})_{0.49}$ and $ZrP(C_{12})_{0.73}$.

The synthetic approach here presented, being based on the modification of preformed ZrP, allows an easy control of the morphology of the organically modified material by suitable choice of the morphology of the starting ZrP microcrystals. From this point of view the new synthetic approach is much more versatile than the conventional precipitation of zirconium phosphonates from Z(IV) and phosphonic acid solutions. In addition, since different types of epoxide are expected to give similar reactions with zirconium phosphate gels, the reaction between epoxides and ZrP gels should clear the way for the synthesis of a large variety of "taylor made" organically modified zirconium phosphates. Research is in progress in our laboratory on the development of composite materials based on aliphatic polymers and ZrP alkyl esters obtained by reaction of ZrP with epoxides.

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