EXAFS evidence for non-ionic crosslinks in some halato-telechelic polymers

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Two types of titanium–oxygen bonds have been evidenced by EXAFS spectroscopy in a carboxylato-telechelic polymer neutralized with an excess of titanium isopropoxide in the presence of water. This confirms the presence of Ti–O–Ti intramolecular bonds, as suggested by the chemistry involved in the preparation, and shows the unique microstructure of the aggregates in these ionomers. A detailed model for the microstructure is presented.

(Keywords: ionomer; EXAFS; telechelic polymer; aggregates; microstructure)

INTRODUCTION

Short polymeric chains terminated by metallic salt groups at each end, known as halato-telechelic polymers (HTPs), constitute a class of ionomers with well-controlled molecular characteristics. In the bulk, a thermoreversible crosslinked material is produced by aggregation of the chain ends, effected by the attractive dipolar interaction between the ionic groups. Usually, the strong influence of the polarity of the medium on the aggregation requires strictly anhydrous conditions and removal of any polar reaction side product during preparation and neutralization of the HTPs[1]. This is particularly the case for α,ω-carboxylato-polymers neutralized with monovalent and divalent metals where the carboxy–metal bond has a strongly ionic character. However, it has been found recently[2] that if the neutralization is carried out with group IVb metal ions, such as titanium, the presence of water is necessary to produce an efficiently crosslinked material, as shown by its viscoelastic properties[3]. On the basis of these findings and of the chemistry involved in the preparation, it was postulated that formation of Ti–O–Ti intermolecular bridges takes place, in competition with neutralization of the chain ends, in an α,ω-carboxylato-polybutadiene neutralized with titanium. In order to test this hypothesis, we have used EXAFS (extended X-ray absorption fine structure) spectroscopy to probe the local environment around the titanium atoms and to give a picture of the microstructure within the aggregates.

SAMPLE PREPARATION

Samples were prepared by neutralizing in toluene with titanium isopropoxide, a commercially available[2] carboxy-telechelic polybutadiene with $\bar{M}_n = 4600$, $\bar{M}_w/\bar{M}_n = 1.8$, functionality = 2.01 and *cis/trans*/vinyl ratio = 20:65:15. Titanium alkoxide was used in excess of the carboxylic acid end groups. The unreacted alkoxy groups attached at the chain ends were hydrolysed into metal oxohydroxide moieties before removing the solvent and drying the polymer to constant weight. For this investigation, two samples were prepared, corresponding to 2 titanium atoms per chain (sample 1) or 3 titanium atoms per chain (sample 2).

The polymers were then moulded at 110°C into discs whose thickness was adjusted to give the best signal-to-noise ratio in the EXAFS experiment (absorption μ times thickness of the order of 2).

THE EXAFS TECHNIQUE: EXPERIMENTAL AND DATA ANALYSIS

The EXAFS spectra, obtained as the sample linear absorption coefficient μ vs. incident photon energy, were recorded on the EXAFS I station installed at LURE-DCI storage ring (Orsay, France) running at 1.56 GeV with positron currents of the order of 100 mA. At the energy of the titanium K-edge of 4965 eV, a Si 111 channel-cut monochromator was used so that no second-order harmonics were present in the monochromatic beam. Experiments were conducted in air at room temperature. The data points were collected every 2 eV, for 2 s, over the energy range 4750–5650 eV and each spectrum was measured three times.

Extraction of the EXAFS signal, i.e. modulation of the absorption above the edge, followed our standard procedures[4,5]. Let us recall that the $x(k)$ EXAFS signal can be described as[6]:

$$x(k) = 1/k\Sigma_i N_i/R_i^2 F_i(k) \cdot e^{-2\sigma_i^2 K^2} \sin[2kR_i + \Phi_i(k)]$$

where N_i is the number of neighbours at distance R_i from the absorber, k is the wave vector of the ejected photoelectron, $F_i(k)$ is the amplitude of backscattering, σ_i is a Debye–Waller-like term and $\Phi_i(k)$ is the total phase shift experienced by the photoelectron.

To extract the experimental amplitude and phase functions for the Ti–O and Ti–Ti pairs, TiO_2 (anatase

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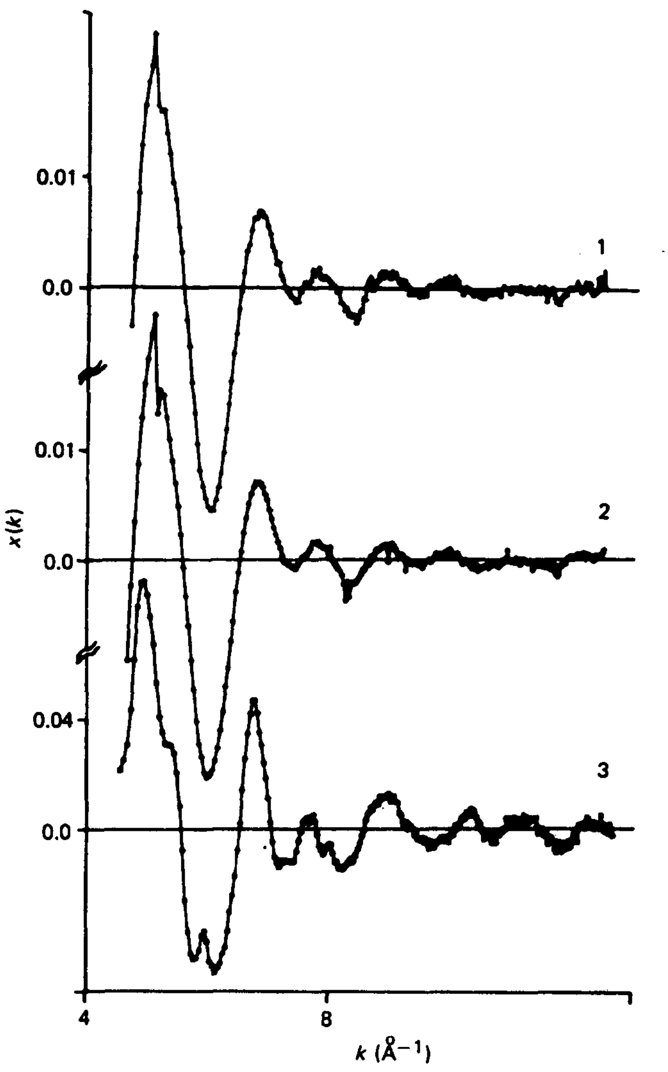

Figure 1 Experimental EXAFS signals for Ti-neutralized HTP samples 1 and 2 and for anatase (curve 3). Note the change of scale on the vertical axis for TiO_2

form) was used as a model compound. For this purpose a known amount of TiO_2 was deposited by filtration on a polycarbonate membrane (Nucleopore), 15 mm diameter, 10 μm thick, so that the absorption coefficient was 1.2 after the edge.

Figure 1 shows the EXAFS spectra for the two ionomers and the model compound. The k^3 multiplied spectra were then Fourier transformed in the domain 4.6–12.5 Å^{-1}, after application of a Gaussian window. The moduli are shown in *Figure 2*. They are dominated by two distinct peaks, easily attributed to Ti–O and Ti–Ti atom pairs.

RESULTS

Provided that the $F_i(k)$ and $\Phi_i(k)$ functions are known, the structural parameters N_i, R_i and σ_i can be determined for a given compound. Therefore, the first two peaks of anatase were separately Fourier filtered and $F(k)$ and $\Phi(k)$ were calculated for the Ti–O and Ti–Ti atoms pairs on the basis of its well-characterized crystallographic structure (each Ti is surrounded by 6 oxygen atoms at a mean distance of 1.95 Å and 4 Ti atoms at 3.04 Å)[7]. Note that in this procedure the exponential of σ remains convoluted with $F(k)$ so that the calculated values for the other samples have a relative value only, noted as $\Delta\sigma$. The experimental functions were then transferred to the simultaneously back-transformed first two peaks of ionomers, and the structural parameters were then computed by least-squares fitting.

As the back Fourier transforms of the two polymer samples were absolutely superposable, the fit was conducted only on the first sample.

The best fit is illustrated in *Figure 3*, and the calculated structural parameters are summarized in *Table 1*. During the fit we allowed a variation of k to take into account any approximation in chemical transferability of amplitude and phase functions. The adjusted wave vector is $k' = (k^2 + 0.262467\,\Delta E_0)^{1/2}$. The main experimental results derived from this EXAFS analysis are fourfold.

(1) On average, each Ti atom is surrounded by *two* shells of oxygen atoms at distances of 1.89 Å and 2.45 ± 0.02 Å. All attempts at fitting with only one Ti–O distance were unsuccessful.

(2) A third shell of Ti atoms is clearly visible containing an average number of 0.8 atom: this shows that most Ti atoms appear as dimers, although some are isolated or in highly disordered aggregates.

(3) The local structure is identical whether the ratio [Ti]/[chain] is 2 or 3.

(4) The structural parameters are consistent with the

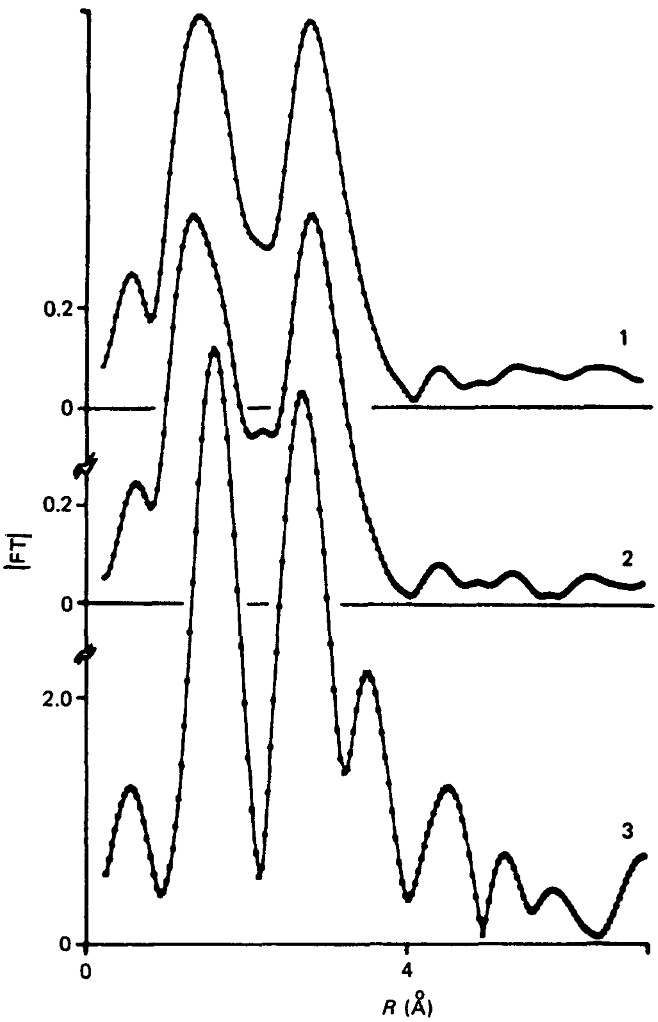

Figure 2 Moduli of Fourier transforms for Ti-neutralized HTP 1 and 2 samples and for TiO_2 (curve 3). Note the change of scale on the vertical axis for anatase

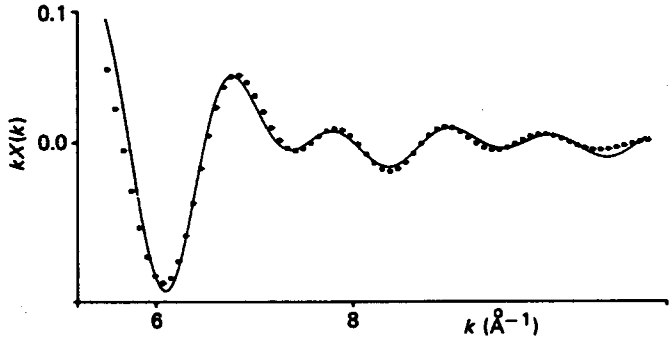

Figure 3 Fit (continuous line) of the Fourier filtered first two peaks (dotted line) for Ti-neutralized HTP sample 1

Table 1 Structural parameters

Sample	Neighbour	N	R(Å)	$\Delta\sigma$(Å)	E_0(eV)	ΔE_0(eV)
TiO_2	O	6.0	1.95	–	4968	–
	Ti	4.0	3.04	–	4968	–
Ti HTP	O	2.1	1.89	0.076	4967	1.9
	O	2.3	2.45	0.082	4967	0.0
	Ti	0.8	3.08	0.000	4967	−5.0

dimeric model shown in *Figure 4*, where the Ti–O–Ti angle is 109°, compared with 101.93° in anatase. We were not able to devise other suitable structures: isolated Ti neutralized chain-ends or more complicated Ti-linked networks could not describe the data. However, since the EXAFS data result from an average of all existing situations, one can conclude that, if they exist, other structures contribute little to the total signal and that most of the titanium atoms are included in these dimeric units.

DISCUSSION AND CONCLUSION

Of importance is the fact that two types of Ti–O bonds exist in these ionomers, clearly evidenced by two bond lengths. Furthermore, the data are consistent with a model of titanium dimers linked by two oxygen bridges. These are presumably bonded to either hydroxyl groups or to carboxyl groups on the polybutadiene chains, depending on the proportion of Ti in the sample. In this respect it is worth recalling that the EXAFS technique only probes the local environment of each Ti atom and as such does not generally provide crystallographic data nor does it count chemical species.

This model is consistent with the chemistry involved in the neutralization of the α,ω-carboxylato-polybutadiene. In a first step, each carboxylic acid is capped with a Ti atom carrying the unreacted alkoxide groups used in excess. Upon subsequent hydrolysis, these Ti–OR groups give rise to Ti–OH functions which condense with a non-hydrolysed Ti–OR to form Ti–O–Ti bridges. An excess of Ti–OH groups is expected to remain unchanged during the moulding process at 110°C for a few minutes.

Although the majority of Ti atoms are included in dimer units (see the quality of the fit) some monomers are also present and trimers are not excluded, as long as the average number of Ti atoms seen by each Ti is 0.8.

Relaxation of the Ti–O–Ti angle, compared with that in TiO_2 is not surprising, since a dimeric species is compared to a three-dimensional regular structure where each Ti is at an octahedral site and is surrounded by oxygen atoms.

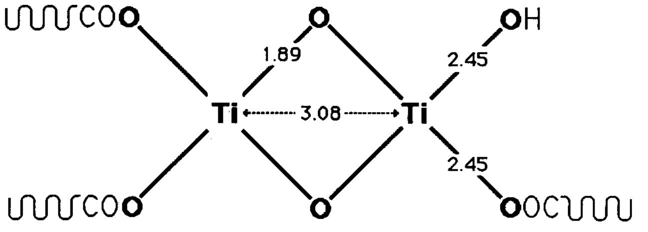

Figure 4 Model of the local structure within the aggregates. Only the bold symbols are seen by the technique and each end-oxygen can belong to either a hydroxyl or a carboxyl group, depending on the proportion of Ti in the sample

These conclusions differentiate the α,ω-carboxylato polybutadiene neutralized with an excess of titanium in the presence of water from those neutralized with Zn[8], Cu[9], Fe[10] or Ba[11] under anhydrous conditions and also investigated by EXAFS. Indeed, the latter ones show only *one* oxygen–metal distance; generally a well-defined metal–metal distance is also observed.

Although the microstructure within the aggregates of this new type of ionomers is markedly different, the macrostructure, revealed by small-angle X-ray scattering[12] is characterized by the same features: whatever the cation or the method of neutralization, the salt groups tend to aggregate into small domains of radius of gyration < 10 Å. These are distributed in the organic matrix with an organization governed mainly by the molecular characteristics of the polymeric chain.

Finally, let us add that the conclusions of this EXAFS investigation have recently been supported by an X-ray photoelectron spectroscopy (ESCA) study which shows that the O1s core level spectrum of carboxylic acid neutralized with a metal(IV) alkoxide (Zr in this case) has two components when an excess of alkoxide is used[13]. The formation of an extra peak promoted by hydrolysis of the alkoxide excess is further experimental evidence for the existence of metal(IV) oxohydroxide groups.

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