



**HAL**  
open science

## Microstructure of halato telechelic polymers bearing group IVb metal carboxylate end-groups

Jean-René Regnard, Pierre Lagarde, Claudine E. Williams, Gilberto Vlaic, Pascal Charlier, Robert J. Jérôme

► **To cite this version:**

Jean-René Regnard, Pierre Lagarde, Claudine E. Williams, Gilberto Vlaic, Pascal Charlier, et al.. Microstructure of halato telechelic polymers bearing group IVb metal carboxylate end-groups. *Journal de Physique*, 1990, 51 (16), pp.1721-1731. 10.1051/jphys:0199000510160172100 . jpa-00212482

**HAL Id: jpa-00212482**

**<https://hal.science/jpa-00212482v1>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

61.40K — 81.20S

## Microstructure of halato telechelic polymers bearing group IVb metal carboxylate end-groups

Jean-René Regnard <sup>(1,\*)</sup>, Pierre Lagarde <sup>(1)</sup>, Claudine E. Williams <sup>(1)</sup>, Gilberto Vlaic <sup>(2)</sup>, Pascal Charlier <sup>(3)</sup> and Robert J. Jérôme <sup>(3)</sup>

<sup>(1)</sup> LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique), CNRS-CEA-MEN, University of Paris-Sud, 91405 Orsay, France

<sup>(2)</sup> Dipartimento di Scienze Chimiche, Università di Cagliari, 09124, Cagliari, Italy

<sup>(3)</sup> Macromolecular Chemistry and Organic catalysis Laboratory, University of Liège, Sart Tilman, B6, 4000 Liège, Belgium

(Received in February 1st, 1990, accepted on April 26, 1990)

**Résumé.** — On a analysé, par spectroscopie EXAFS, la structure locale des agrégats d'ionomères carboxylato-téléchéliques neutralisés par un excès de zirconium. La présence de liaisons Zr-O-Zr explique la grande stabilité du matériau aux solvants polaires. L'augmentation du nombre de voisins zirconium avec la quantité d'agent de neutralisation indique une croissance des agrégats avec le taux de neutralisation. On propose un modèle compatible avec les propriétés mécaniques de ces matériaux.

**Abstract.** — The local structure within the ionic aggregates of a carboxylato-telechelic ionomer neutralized with an excess of zirconium has been investigated by EXAFS spectroscopy. The presence of non-ionic Zr-O-Zr intramolecular bonds explains the great stability of the material towards polar compounds. The number of Zr neighbours in the aggregates has been found to increase with the total amount of zirconium in the sample. A model consistent with the unique mechanical properties of the resulting material is proposed.

### Introduction.

Ionomers are materials in which ion pairs, randomly spaced along a nonpolar polymeric backbone, associate into microdomains responsible for a thermoreversible network [1-4]. Halato-telechelic polymers (HTP's) form a class of model ionomers since they consist of short chains selectively terminated by a salt group which may be either a neutralized acidic, a neutralized basic or a quaternized amino group [5-8]. The network junction points are now situated at the chain ends and thus separated by a well-defined characteristic distance.

Both the quantitative functionalization of a carboxy-telechelic polymer and the complete neutralization of the acid end-groups are key parameters for the contribution of all chain

---

(\*) *Permanent address* : Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, B.P. 85X, F38041 Grenoble Cedex.

segments to the load-bearing capability of the material. A highly controlled method for neutralization of these carboxy-telechelic polymer has been reported using stoichiometric amounts of very reactive alkaline or alkaline-earth metal alcoxides [5]. This technique requires that the alcohol formed as a byproduct is completely eliminated in order to displace the reaction equilibrium and also to avoid the ion pair solvation. The related metal carboxylates promote the formation of highly interacting ion pairs [5, 7, 8]. Provided the chain length is uniform, there is complete microphase separation between the chain segments and the ionic groups which are incorporated into multiplets [9]. These domains are surrounded by a volume from which other ionic domains are excluded, and arranged in a liquid-like manner in space. In these materials, there is no evidence for ionic clusters as postulated in the more classical ionomers [9]. However the contribution of the ionic aggregates as physical cross-links and fillers, although important, is not sufficient to account for the small-strain tensile moduli of carboxy-telechelic polyisoprenes and the modulus enhancement has been attributed to entanglements in the form of interlocking loops formed when both ends of a telechelic chain are located in the same aggregate [10]. It has also been shown that the ionic microdomains in materials with a higher modulus are more ordered, as shown by Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). It is indeed observed that metal  $\alpha$ ,  $\omega$ -carboxylato polyisoprenes are able to strain-harden more as the coordination number of the metal atom increases. Furthermore the degree of local order strongly depends on the neutralization pathway, all other conditions being identical [11, 12]. So, when an  $\alpha$ ,  $\omega$ -carboxylic acid polybutadiene (PBD) is quantitatively neutralized by Zn in such a way that no byproduct which could solvate the ion pairs is produced, a highly ordered structure is observed. A coordination of shell of five Zn atoms at 3.22 Å is indeed reported which disappears when the Zn carboxylate ion pairs are formed in the presence of a solvating agent. An exact description of the conditions of neutralization is therefore mandatory for complete sample characterization.

On the other hand, when telechelics are neutralized with tetravalent transition metals, the resulting material has unique properties related to the different nature of the metal-carboxylate bond. Indeed in contrast to alkaline and alkaline-earth metals, elements such as titanium and zirconium form bonds which are mainly covalent and their dipolar interaction is noticeably weaker. A cross-linking effect is observed only when an excess of alkoxide groups is used in the neutralization steps and subsequently hydrolyzed [13, 14], an observation which led to believe that the network is stabilized by carboxylato-metal-oxohydroxide groups [8, 14]. The resulting material contains small inorganic domains and shows a great stability towards polar compounds, which contrasts with that of alkaline telechelics. Indeed no structural change is seen by small-angle-neutron scattering when Ti-PBD has been immersed in deuterated water whereas an increase in the domain size corresponding to hydration of the metal by D<sub>2</sub>O is observed for Na-PBD [15].

The nature of the tetravalent metal also influences the mechanical properties. Dynamic mechanical measurements have shown that oxy-Zr-carboxylates form bigger although less stable aggregates than the Ti counterparts and that  $\alpha$ ,  $\omega$ -carboxylic acid PBD exhibits a more complex viscoelastic behaviour when neutralized by Zr instead of Ti. This has been tentatively attributed to the nonequilibrium aggregation of the oxymetal carboxylates and/or to the occurrence of at least two different thermally activated processes in the Zr containing polymer [14]. The surface composition of the ionomer, as analysed by ESCA, is also different: for Ti-PBD the surface layer contains no Ti and is followed by a large concentration gradient towards the bulk whereas the Zr-containing domains tend to be randomly distributed in the PBD-Zr matrix [16]. Quite interestingly, ESCA has provided the first experimental evidence for the formation of carboxylato metal oxohydroxide moieties

upon the hydrolysis of the metal alkoxide groups used in excess [16]. EXAFS spectroscopy of an  $\alpha$ ,  $\omega$ -carboxylic acid PBD neutralized with an excess of Ti isopropoxide (400 and 600 %) in the presence of water has also confirmed the existence of Ti-O-Ti intermolecular bonds and has shown that the majority of the Ti atoms are included in dimer and trimer units. Two different Ti-O bond lengths have thus been measured [17].

Since the Zr behaviour contrasts in some aspect with that of Ti, it is of interest to probe the local environment around Zr atoms in order to compare the microstructure within the aggregates of oxy-Ti and oxy-Zr carboxylates. For this purpose, EXAFS spectroscopy has been used to provide a description of the short range order around Zr in terms of type and number of neighbours, distances and thermal and static disorder in these distances.

### Experimental.

**SAMPLE PREPARATION.** — The samples investigated were obtained by neutralization with zirconium isopropoxide of a dicarboxylic acid polybutadiene (Hycar CTNB 2000 X 156), commercialized by BF Goodrich, of molecular characteristics as follows:  $\bar{M}_n = 4\,600$ ;  $\bar{M}_w/\bar{M}_n = 1.8$ ; functionality = 2.01 and cis/trans/vinyl ratio = 20/65/15. A five wt % solution of the carboxy-telechelic polybutadiene was prepared in toluene previously dried by refluxing over calcium hydride. The polymer was then dried by three successive azeotropic distillations of toluene and an appropriate amount of Zr isopropoxide ( $0.1 \text{ mol L}^{-1}$  solution in toluene) was added to the final 5 wt % solution of the polymer. Zr alkoxide was used in the stoichiometric ratio but also in various excess to the carboxylic acid end-groups. Samples called ZR1, ZR2, ZR4 and ZR6 correspond to an alkoxide/acid molar ratio of 1, 2, 4 and 6, i.e. to a degree of neutralization of 100, 200, 400 et 600 %, respectively. The neutralization reaction was driven to completion by azeotropic distillation of the isopropanol formed as a reaction byproduct. When ca. 20 % of the toluene volume was distilled off under reduced pressure, it was replaced by fresh solvent and a further distillation run was carried out. After three distillation runs, the 20 % of distilled toluene was replaced by toluene saturated by water in order to hydrolyze the unreacted Zr alkoxide functions. Again three distillation runs were achieved under these particular conditions. Toluene was finally distilled off completely and the polymer was dried to constant weight under vacuum at 65 °C. It was molded at 120 °C (150 °C for ZR6) into disks whose thickness was adjusted to get the best signal-to-noise ratio in the EXAFS experiment (absorption coefficient times thickness on the order of 2).

**THE EXAFS TECHNIQUE, EXPERIMENTAL AND DATA ANALYSIS.** — All samples were studied in air and at room temperature on the EXAFS I station at LURE-DCI. The storage ring was run at 1.85 GeV with positron currents of about 250 mA. For scanning the energy range around the Zr K-edge at 17 998 eV, a Si 331 channel cut monochromator was used. The EXAFS spectra were recorded in the transmission mode at 2 eV intervals over the energy range 17 800-18 800 eV using two ionization chambers filled with argon. Each data point was collected for 2 seconds and each complete spectrum was measured 5 times for the highest Zr-content (ZR4 and ZR6) and 7 times for the lowest concentrations (ZR2 and ZR1). The experimental amplitude and phase functions for the Zr-O pair were obtained from the cubic perovskite  $\text{BaZrO}_3$  ( $d_{\text{Zr-O}} = 2.095 \text{ \AA}$ ,  $N(\text{O}) = 6$ ).

The EXAFS modulation of the linear absorption coefficient  $\mu$  as a function of the photoelectron wave-vector  $k$ , above an absorption edge  $E_0$  is :

$$\chi(k) = \frac{\mu(k) - \mu_B - \mu_0(k)}{\mu_0(k)} \quad (1)$$

where  $\mu_0$  is the smooth atomic like contribution above the edge and  $\mu_B$  the background originating from pre-edge absorption processes.

For a K-edge, the simple back-scattering theory gives the relationship between the EXAFS signal  $\chi(k)$  and the structural parameters [18]:

$$k \cdot \chi(k) = \sum_i \frac{N_i}{R_i^2} \exp \frac{-2 R_i}{\lambda(k)} F_i(k) \exp(-2 \sigma_i^2 k^2) \sin [2 k R_i + \Phi_i(k)] \quad (2)$$

where  $R_i$  is the average distance which separates the absorbing atom from the  $N_i$  neighbouring atoms defining the  $i$ th shell, with a r.m.s. deviation  $\sigma_i$ ;  $\exp(-2 \sigma_i^2 k^2)$  is an effective Debye-Waller factor resulting from the statistical and thermal distortion of the equilibrium structure.  $F_i(k)$  and  $\phi_i(k)$  are the amplitude of back-scattering and the total phase shift, respectively, characteristic of the selected (absorbing atom)/(back scattering shell  $i$ ) pair, and  $\lambda(k)$  is the photoelectron mean free path.

Data processing was carried out on a VAX 730 computer according to a standard procedure [19] that is only briefly summarized here:

$\mu_B$  is extrapolated from the pre-edge region fitted with a Victoreen function ( $\mu_B x = c\lambda^3 + D\lambda^4$ ) and then subtracted from the experimental data.  $\mu_0(k)$  is obtained from a smoothing procedure (200 iterations) of the EXAFS oscillations starting 50 eV above the edge. The slow residual oscillations of  $\chi(k)$  are then eliminated by a multi-iterative process which affects only the very small  $R$ -values (typically  $R < 1 \text{ \AA}$ ) of the modulus of the Fourier transform.

$E_0$  was arbitrarily chosen as the inflection point of the Zr K-edge in the selected model compound  $\text{BaZrO}_3$  ( $E_0 = 18\,006 \text{ eV}$ ). The reduced data for the model compound and the ionomers are shown in figure 1. The  $k^3$  multiplied spectra were then Fourier transformed in the domain [51, 680] eV after application of a Hanning window, yielding the moduli |FT| shown in figure 2. The main feature of these radial distribution functions (RDF) is the presence of two distinct peaks for each ionomer, attributed to Zr-O and Zr-Zr atom pairs, whose intensities vary systematically with Zr-content without much change in position [20]. The broadening of the first peak for sample ZR1 could not be reasonably explained.

## Results and discussion

Provided that the  $F_i(k)$  and  $\phi_i(k)$  functions are known, the structural parameters  $N_i$ ,  $R_i$  and  $\sigma_i$  can be determined for a given compound. We use a semi-empirical approach: the first peak of  $\text{BaZrO}_3$  was Fourier filtered and the experimental phase function was extracted on the basis of its well characterized crystallographic structure (each Zr is surrounded by 6 oxygen atoms at the distance of 2.095 Å). Subsequently, the filtered signal was fitted using experimental phase and theoretical [21] amplitude functions to evaluate the  $\lambda$  and  $\sigma$  parameters of equation (3) ( $N$  being fixed at 6.0). Finally we calculated the experimental amplitude not convoluted with the Debye-Waller term, but still convoluted with the mean free path term. The experimental functions were then transferred to the back-transformed first peak of the four ionomers, and the structural parameters of the first shell were obtained by a least square fitting of the data in the interval between 70 and 600 eV. During the fit, a variation of  $k$  was allowed to take into account any approximation in chemical transferability of amplitude and phase functions. The adjusted wave vector is  $k' = (k^2 + 0.2624 \Delta E_0)^{1/2}$ . The best fits are reported in figure 3 and the calculated structural parameters are listed in Table I.

The first important conclusion is that it is impossible to fit the data with only one Zr-O distance: two subshells of oxygen atoms at distances 2.10 and  $2.25 \pm 0.02 \text{ \AA}$  have to be

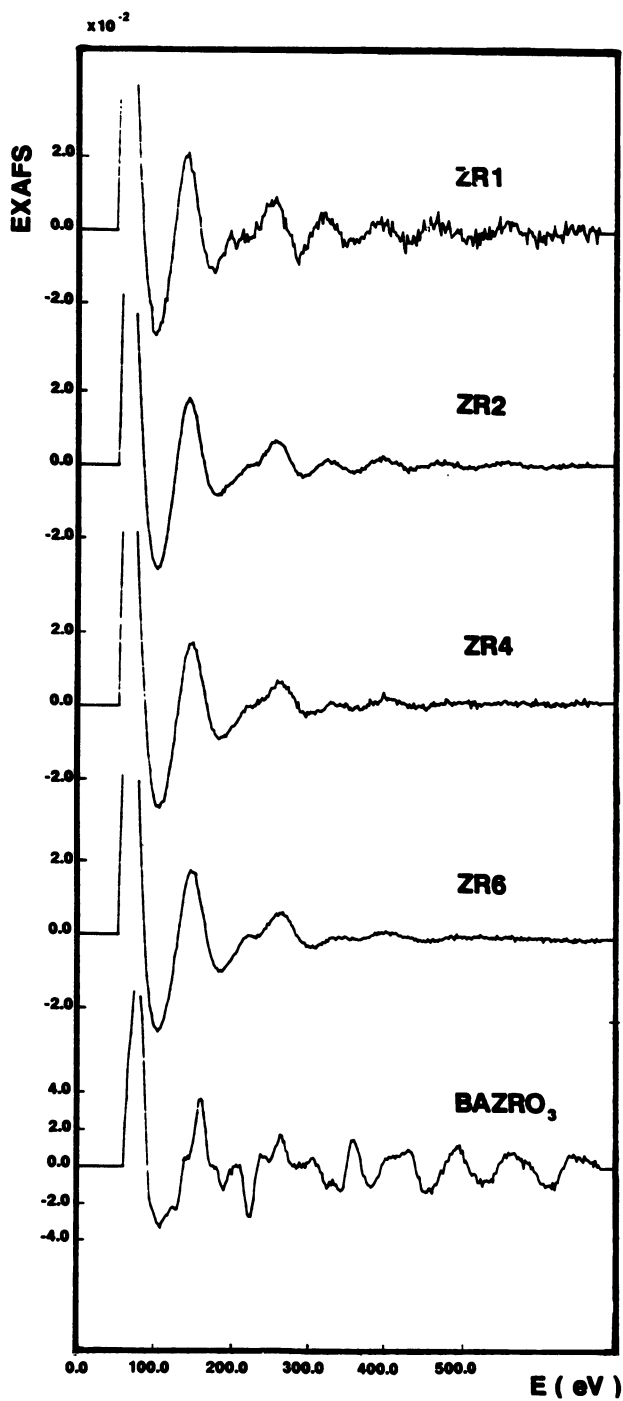


Fig. 1. — Experimental EXAFS  $\chi(E)$  vs.  $E$  for the four zirconium-neutralized  $\alpha$ ,  $\omega$  carboxypolybutadiene samples labeled ZR1, ZR2, ZR4, ZR6 and for the model compound BaZrO<sub>3</sub>. Note the change of scale on the vertical axis for BaZrO<sub>3</sub>.

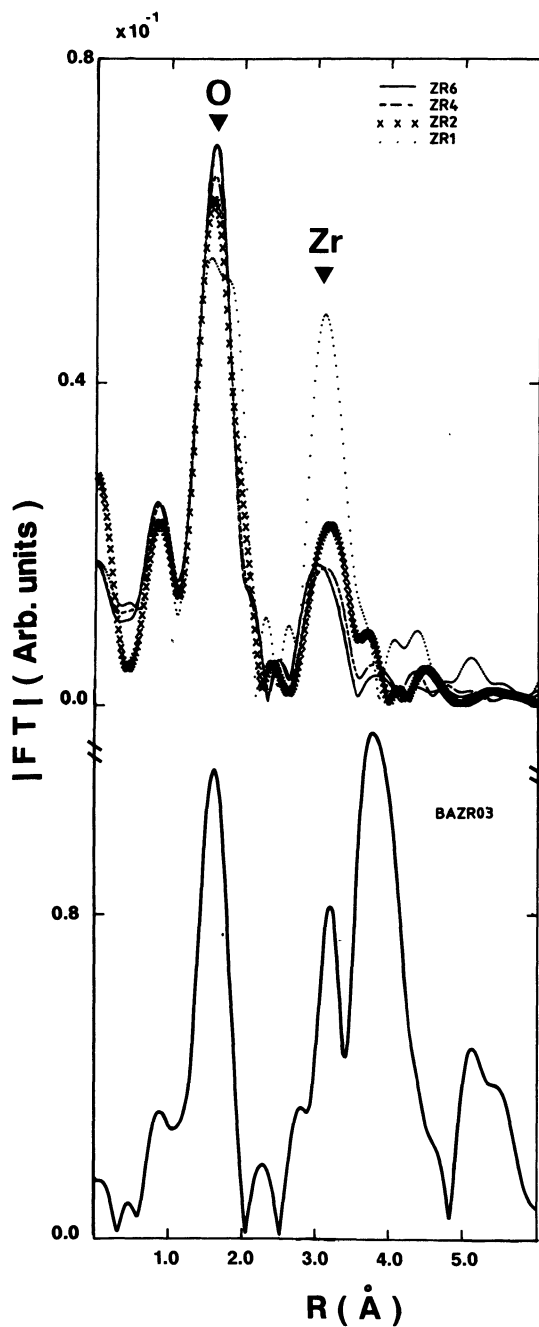


Fig. 2. — Amplitude of the Fourier transforms  $|FT|$  of  $k^3 \cdot \chi(k)$  for the four ionomers with increasing Zr content showing the 2 peaks attributed to oxygen and zirconium coordination shells. The data for  $BaZrO_3$  is also shown with a change of scale of the amplitude.

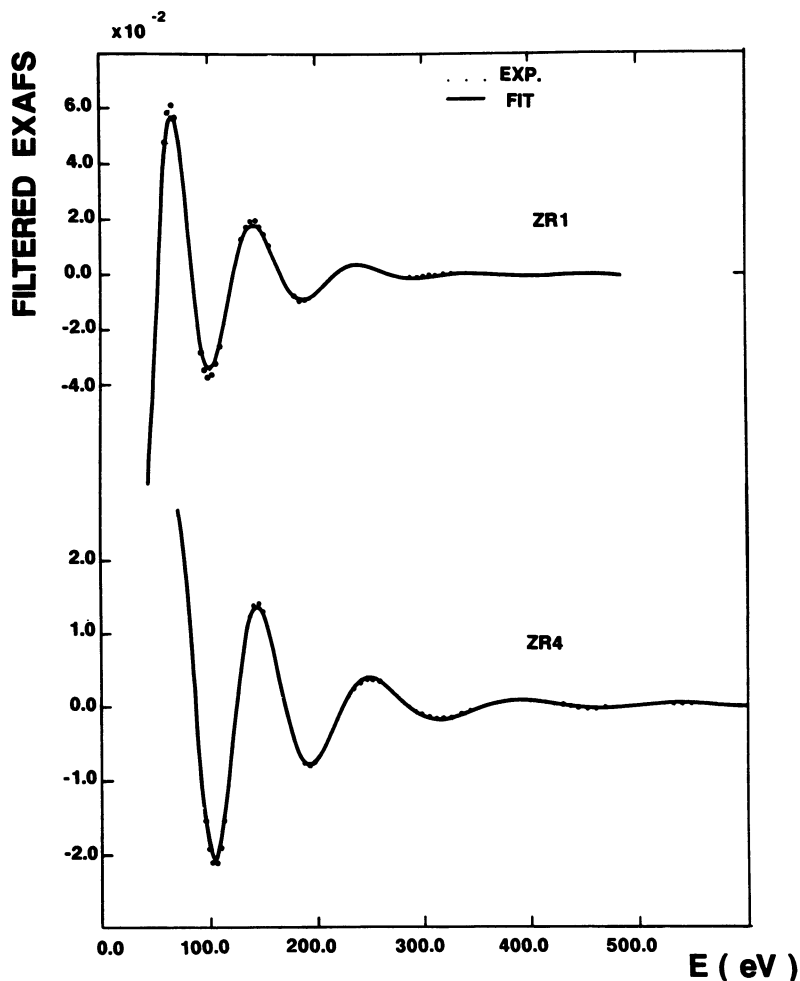


Fig. 3. — Fit (full line) of the Fourier filtered first peak (dotted line) for the ZR1 and ZR4 ionomers.

Table I. — Parameters of the first coordination shell split in 2 subshells noted *a* and *b* for the four Zr-neutralized HTP samples.

Sample	$N_a$	$R_a$ (Å)	$\Delta\sigma_a$ (Å)	$N_b$	$R_b$ (Å)	$\Delta\sigma_b$ (Å)	$\Delta E_0$ (eV)	$N_{tot}$
BaZrO <sub>3</sub>	6.0	2.095	0.080	—	—	—	—	6
ZR1 (100 %)	2.3	2.07	0.058	4.0	2.23	0.069	- 3.0	6.3
ZR2 (200 %)	2.7	2.10	0.068	3.2	2.26	0.081	- 1.0	5.9
ZR4 (400 %)	3.2	2.09	0.080	3.0	2.23	0.086	- 2.0	6.2
ZR6 (600 %)	3.2	2.09	0.081	2.9	2.25	0.090	- 2.0	6.1



introduced. It is interpreted as showing the existence of 2 types of Zr-O bonds. The total number of oxygen atoms is constant for all samples with an average value of  $6.0 \pm 0.5$  but they are not distributed equally between the 2 subshells : in the inner subshells at  $2.10 \text{ \AA}$ , the number increases with the degree of neutralization up to 400 %, whereas it decreases in the outer subshell at  $2.25 \text{ \AA}$ . The samples containing a proportion of 2 or 3 Zr per chain (ZR4 and ZR6) have almost the same local structure of oxygen atoms.

Attempts to fit the back-Fourier-transformed second peak (Zr-Zr pairs) of the ionomer RDF with amplitude and phase shifts extracted from tetragonal yttrium-stabilized  $\text{ZrO}_2$  [22] as a model compound were unsuccessful. Hence for the second shell, a comparison within the series of samples was carried out and two different analyses of the data were performed. First we used the method proposed by Sayers *et al.* [23]. If it is assumed that the Zr-Zr distances are similar in the four ionomers, then the ratio between the envelopes  $A(k)$  of the EXAFS signal, relative to the second shell of two samples  $i$  and  $j$  is :

$$\ln \frac{A_i(k)}{A_j(k)} = \ln \frac{N_i}{N_j} + 2(\sigma_j^2 - \sigma_i^2) k^2. \quad (3)$$

A plot of  $\ln \frac{A_i(k)}{A_j(k)}$  vs.  $k^2$  should be linear and give the ratio of the coordination numbers and the  $\sigma^2$  values. As an example of this procedure, figure 4 shows the plot of  $\ln (A_4/A_6)$  as a function of  $k^2$ . A satisfactory linear behaviour was obtained for all combinations and the results are noted as « Method I » in table II. The second method uses one of the samples as a reference compound : the experimental phase and amplitude for the Zr-Zr atom pair are calculated by backtransforming the second peak of the ZR1 sample Fourier transform, arbitrarily setting  $N = 1$  and  $R = 3.5 \text{ \AA}$  (a reasonable value from Fig. 2). Then the fit of the back Fourier transform of the second peak of the other ionomers was achieved with these functions. An example of these fits is shown in figure 5. As reported in table II, both methods give results in good agreement. Note that on average, each Zr atom is surrounded by an

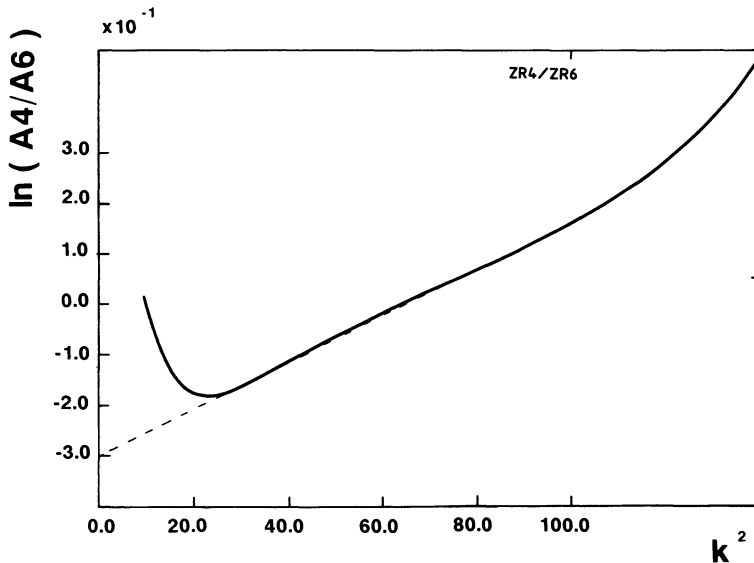


Fig. 4. — Ratio of the EXAFS amplitudes for the ZR4 and ZR6 ionomers plotted logarithmically versus  $k^2$ .

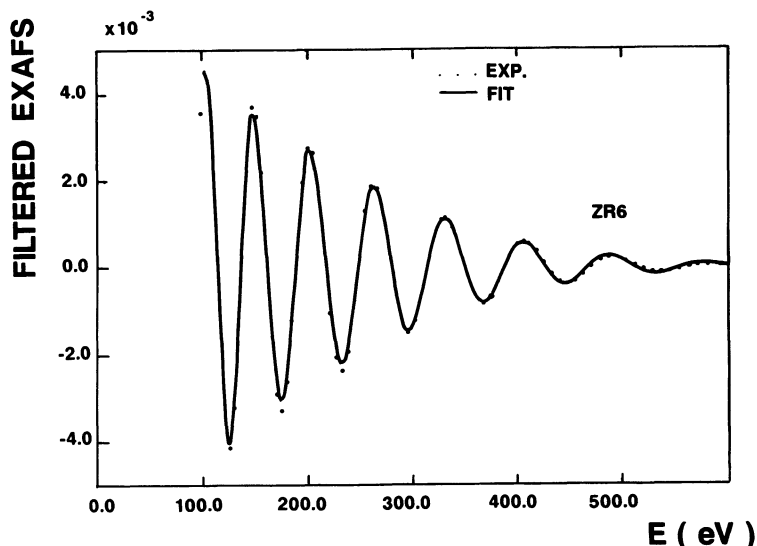
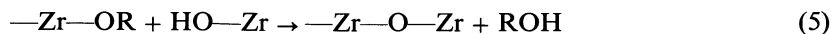
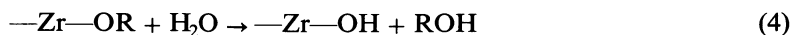


Fig. 5. — Fit (full line) of the Fourier filtered second peak (dotted line) for the ZR6 ionomer.

Table II. — Evolution of the relative coordination number, the effective Debye-Waller factor and the Zr-Zr distance in the Zr-neutralized HTP compared to sample ZR1.

Sample	Method I			Method II		
	$N_i/N_1$	$\sigma_i^2 - \sigma_1^2 (\text{\AA}^2)$	$N_i/N_1$	$R (\text{\AA})$	$\sigma_i^2 - \sigma_1^2 (\text{\AA}^2)$	$\Delta E_0 (\text{eV})$
ZR1	1	—	1	3.50	—	—
ZR2	1.2	0.0050	1.1	3.50	0.0048	4
ZR4	1.4	0.0075	1.3	3.47	0.0076	4
ZR6	1.8	0.0100	1.6	3.44	0.0096	3

increasing number of Zr neighbours in the second shell when the total amount of Zr in the ionomer increases, but with a higher degree of disorder. We believe that this is due to an increasing static disorder from ZR1 to ZR6. Low temperature investigations are planned to elucidate this point; they will be reported in a forthcoming paper. It is interesting to remark here that a casual glance at the moduli of the Fourier transforms (Fig. 2) would hint the opposite conclusion since the intensity of the second peak decreased with increasing ion-content. The conclusion that the average number of Zr neighbours increases is supported by the chemistry of the system. Indeed the hydrolysis of an increasing amount of unreacted zirconium alkoxides should lead to a more extended network of Zr-O-Zr bonds as

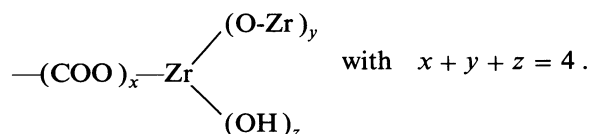


where OR is the alkoxide group.

## Conclusions

Three main conclusions can be drawn from this experimental investigation. First two types of Zr-O bonds exist in the aggregates of  $\alpha$ ,  $\omega$  carboxylic acid polybutadiene neutralized at and above stoichiometry with Zr isopropoxide followed by the hydrolysis of the unreacted alkoxide groups. Indeed, two coordination shells have been found around each Zr atom at 2.10 and  $2.25 \pm 0.02$  Å, that one can reasonably assign to Zr-O-Zr and Zr-carboxylate (-COOZr) and/or Zr-OH bonds, respectively. This observation is consistent with the chemistry involved in the neutralization process (Eqs. (4) and (5)). It also confirms the results of the ESCA analysis of octanoic acid neutralized with various amounts of Zr alkoxide followed by hydrolysis of the unreacted functions [16]. The  $O_1$  core level peak, that is unimodal when the octanoic acid is neutralized at stoichiometry, shows clearly two components when an excess of Zr alkoxide is used. The extra peak has been assessed to the Zr-O-Zr bonds (Eq. (5)). Note that the same conclusion has been reached when the carboxy-telechelic PBD was neutralized with an excess of Ti isopropoxide in the presence of water [17]; two O-Ti distances were also measured by EXAFS spectroscopy.

Second, when the amount of neutralizing agent increases from stoichiometry (ZR1) to a six fold molar excess (ZR6), the relative proportion of oxygen atoms in oxy-bridges (first oxygen subshell) increases whereas the total number of oxygen stays constant. This observation means that, whatever the OR/COOH molar ratio, each Zr involved in a carboxylato-oxhydroxide aggregate is surrounded by approximately the same number of near neighbour oxygen atoms, which can be expressed as



The main change in the local structure of the end-group aggregates as promoted by an increasing departure from stoichiometry has to be found in the relative proportion of oxygen atoms in the two subshells. That the population of oxygen atoms in oxy-bridges ( $R = 2.1$  Å) increases at the expense of those contributing to carboxylate and/or hydroxyde groups when the excess of hydrolyzable Zr alkoxide increases, means that the cross-linking of PBD extremities gets more efficient.

Finally this trend is supported by results concerning the third shell populated by an increasing number of Zr atoms when the total amount of Zr in the sample increases (Table II). It is thus likely that the size of the aggregates increases. However, as the basic unit grows in size, it becomes more disordered as shown by the large Debye-Waller factor. It is difficult at this point to devise a more detailed model of the actual structure.

As already pointed out, qualitatively similar results are obtained when  $\alpha$ ,  $\omega$ -carboxylic acid PBD is neutralized to 400 and 600 % by Ti isopropoxide [17]. The total number of oxygen atoms is however smaller (4.4 compared to 6) and a dimer of Ti has been proposed as the basic entity whose characteristics are constant in the range of the molar excess used (400 to 600 %). In that case, the coordination number of Ti is close to one (0.8) and the short range order is high.

The results reported in this study are consistent with previous viscoelastic measurements, and particularly with the steady-flow viscosity of a  $10 \text{ g} \cdot \text{dl}^{-1}$  solution of  $\alpha$ ,  $\omega$ -carboxylic acid PBD neutralized with Zr alkoxide [15]. A viscous solution is observed at the stoichiometry of the neutralization reaction.

The viscosity increases when a larger excess of Zr alkoxide is used for neutralization and

ultimately an elastic gel is formed. This change in the solution viscosity can only be accounted for by a more efficient cross-linking of PBD. It is also worth recalling that the bulk  $\alpha$ ,  $\omega$ -carboxylic acid PBD neutralized with a fourfold excess of Ti or Zr alkoxide, exhibits a rubber-like plateau in the viscoelastic measurements but the modulus is higher for Zr than for Ti [15]. Thus, at a constant degree of neutralization (i.e. 400 %), the mean number of chain ends attached to an aggregate of oxohydroxide metal carboxylate is higher for Zr. This is in qualitative agreement with the EXAFS observations which conclude to a higher coordination number of Zr compared to Ti, all other conditions being kept constant.

### References

- [1] EISENBERG A. and KING M., *Ion-Containing Polymers*, Polymer Physics Ed. Stein R., Vol. 2 (Academic Press, New York) 1977.
- [2] MCKNIGHT W. T. and EARNEST T. E., *J. Polym. Sci. Macromol. Rev.* **16** (1981) 41.
- [3] LONGWORTH R., *Developments in Ionic Polymers 1*, Applied Science (London) 1983, Ch. 3.
- [4] FITZGERALD J. J. and WEISS R. A., *J. Macromol. Sci. Macromol. Rev.* **C28** (1988).
- [5] BROZE G., JÉRÔME R. and TEYSSIÉ Ph., *Macromolecules* **15** (1982) 920 and 1300 ; **16** (1983) 996 and 1771.
- [6] BROZE G., JÉRÔME R., TEYSSIÉ Ph. and MARCO C., *J. Polym. Sci. Polym. Phys. Ed.* **21** (1983) 2205.
- [7] JÉRÔME R., BROZE G. and TEYSSIÉ Ph., *Microdomains in Polymer Solutions*, Ed. P. Dubin (Plenum, New York) 1985, p. 243.
- [8] JÉRÔME R. and BROZE G., *Rubb. Chem. Technol.* **58** (1985) 223.
- [9] WILLIAMS C. E., RUSSELL T. P., JÉRÔME R. and HORRION J., *Macromolecules* **19** (1986) 2877.
- [10] REGISTER R. A., FOUCART M., JÉRÔME R., DING Y. S. and COOPER S. L., *Macromolecules* **21** (1988) 1009.
- [11] JÉRÔME R., VLAIC G. and WILLIAMS C. E., *J. Phys. Lett. France* **44** (1983) L-717.
- [12] VLAIC G., WILLIAMS C. E., JÉRÔME R., TANT M. R. and WILKES G. L., *Polymer* **29** (1988) 173.
- [13] BROZE G., JÉRÔME R. and TEYSSIÉ Ph., *J. Polym. Sci., Polym. Lett. Ed.* **21** (1983) 237.
- [14] BROZE G., JÉRÔME R., TEYSSIÉ Ph. and MARCO C., *Macromolecules* **18** (1985) 1376.
- [15] JÉRÔME R., TEIXEIRA J. and WILLIAMS C. E., unpublished results.
- [16] JÉRÔME R., TEYSSIÉ Ph., PIREAUX J. J. and VERBIST J. J., *Appl. Surf. Sci.* **27** (1986) 93.
- [17] VLAIC G., WILLIAMS C. E. and JÉRÔME R., *Polymer* **28** (1987) 1566 ;  
and CHARLIER P., CORRIAS A., JÉRÔME R., REGNARD J. R., VLAIC G. and WILLIAMS C. E., *Nuovo Cimento*, to be published (Proceedings of the 2nd European International Conference on Progress in X-ray Synchrotron Radiation Research, 1989).
- [18] STERN E. A., SAYERS D. E. and LYTLE F. W., *Phys. Rev. B* **11** (1975) 4836.
- [19] LAGARDE P., *Rayonnement Synchrotron dans le domaine des rayons X*, Proceedings of the Aussois summer school, Septembre 1986, Editions du CNRS, Paris (1987).
- [20] Note that the features below the first peak have not been taken into account since they should have no physical significance for a light back-scatterer like oxygen ; the shouldering could be due to a low frequency component that has not been filtered out of the EXAFS signal. The features below and above the second peak have been taken as « ripples » due to the limited  $k$ -space used for the Fourier-Transform.
- [21] TEO B. K. and LEE P. A., *J. Am. Chem. Soc.* **101** (1979) 2815.
- [22] TUILLIER M. H., DEXPERT-GHYS J., DEXPERT H. and LAGARDE P., *J. Solid State Chem.* **69** (1987) 153.
- [23] SAYERS D. E., STERN E. A. and LYTLE F. W., *Phys. Rev. Lett.* **35** (1975) 584.