# Microstructure of the ionic aggregates in telechelic ionomers

**Gilberto Vlaic* and Claudine E. Williams**
*LURE, Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, University of Paris-Sud, 91405, Orsay, France*

**and Robert Jérome**
*Macromolecular Chemistry and Organic Catalysis Laboratory, University of Liège, Sart-Tilman, 4000 Liège, Belgum*

**and Martin R. Tant† and Garth L. Wilkes**
*Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*
*(Received 5 June 1987; accepted 6 July 1987)*

Extended X-ray absorption fine structure (EXAFS) investigations of various types of zinc-neutralized telechelic ionomers have evidenced large differences in the degree of local order within the aggregates. Among the parameters influencing the microstructure, it is shown that the conditions of neutralization play an important role.

**(Keywords: ionomer; telechelic polymer; EXAFS; multiplet; microstructure)**

## INTRODUCTION

The viscoelastic properties of ionomers are well explained by a microphase separation between the ionizable repeat units and the non-polar portions of the chain, as driven by an attractive dipolar interaction. The ionic aggregates act as physical crosslinks and develop a three-dimensional polymeric network. However, a detailed description of these ionic regions in terms of composition, size or local arrangement of the ion pairs is still open to question. It is also not quite clear how the local order depends on the parameters which have been shown to influence the global structure or texture of the material, as revealed by small-angle X-ray scattering (SAXS) for instance.

In an attempt to shed light on this problem, we report on some EXAFS (extended X-ray absorption fine structure) experiments on zinc-neutralized telechelic ionomers which consider the influence of neutralization conditions. Specifically, the type of neutralizing agent and its excess will be considered. The possible presence of solvating agents will also be taken into account.

Telechelics are ionomers where the ionizable monomers are located only at the end points on the macromolecule. These have been used extensively as model 'ionomer' species for studying the processes of ion aggregation by various techniques. The sulphonated polyisobutylene and the carboxy-polybutadiene reported here are both made of short chains of similar flexibility and similar low dielectric constant. They differ only by the anion type, as will be specified.

EXAFS spectroscopy provides a description of the short range environment of selected atoms in terms of type and number of neighbours, distances, and thermal and static disorder in those distances without the need for long range order. Hence it is well adapted for the investigation of the local environment around the ionomer cations within a range of a few Ångström[1], and more specifically it has permitted the description of the short-range order within the aggregates of selected carboxylato-polybutadienes[2-5]. A comparative analysis of the EXAFS data as a function of neutralization parameters on the two types of telechelics mentioned above is presented below.

## EXPERIMENTAL

### *EXAFS spectroscopy: technique and data reduction*

The EXAFS data are obtained as a measurement of the X-ray linear absorption coefficient $\mu$ as a function of incident photon energy $E$. The structural information is deduced by relating the experimental modulation of $\mu$ above the absorption edge $E_0$, $\chi(k)$, to a theoretical description in the single-electron single-scattering approximation[6], where

$$\chi(k)=(1/k)\sum_i(N_i/R_i^2)F_i(k)\exp(-2\sigma_i^2k^2)\sin\{2kR_i+\Phi_i(k)\}$$

$k$ is the wave-vector of the ejected photoelectron, $N_i$ the number of neighbours at distance $R_i$ from the absorbing atom, $F_i(k)$ the amplitude of backscattering, $\sigma_i$ a Debye–Waller-like term and $\Phi_i(k)$ the total phaseshift experienced by the photoelectron for each coordination shell $i$. $\Phi_i$ is characteristic of a particular combination of absorbing atom and back-scattering shell, whereas $F_i$ is almost entirely dependent on the backscattering shell; both their values can be calculated theoretically[7] or

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* Present address: Istituto Guido Donegani SPA, 28100, Novara, Italy
† Present address: Bldg B-1218, Dow Chemical USA, Freeport, TX 77541, USA

0032-3861/88/010173-04$03.00

derived experimentally from reference compounds of known crystallographic structure. The latter procedure has been used here. Analysis of the EXAFS data has been carried out according to a standard procedure of Fourier filtering and fitting described elsewhere[8].

### *Measurements*

The EXAFS spectra were recorded in the transmission mode on the EXAFS-I station installed at LURE-DCI storage ring running at 1.85 GeV with positron currents of the order of 150 mA. The energy of the photon beam was selected by a Si220 channel-cut monochromator. The intensity of the beam was measured, before and after passing through the sample, with ionization chambers. The data were collected every 2 eV, for 2 s, over an energy range 260 eV below and 740 eV above the *K*-threshold of zinc at 9659 eV. Each experiment was repeated three times.

All samples were studied in air and at room temperature. Their thickness was adjusted so that the product of absorption and thickness above the edge was about 1.5. The ionomers were moulded and self-supporting (PIB) or contained between thin Kapton windows to prevent viscous deformation during experiment (PBD); the reference compounds were finely ground and deposited on thin membranes to form homogeneous films.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *α,ω-Dicarboxylato-polybutadiene*

The sample investigated was obtained by neutralization with zinc acetate of a commercially available dicarboxylic acid polybutadiene*, for which $\bar{M}_n = 4600$, $\bar{M}_w/\bar{M}_n = 1.8$, functionality = 2.01 and *cis*/*trans*/vinyl proportions were 20/65/15. For this purpose, dicarboxylic acid polybutadiene was dissolved in toluene (5 wt%) and added with the stoichiometric amount of zinc acetate previously dissolved in methanol ($5 \times 10^{-2}$ mol l$^{-1}$). The carboxylic acid end-groups were reacted with zinc acetate, resulting in formation of acetic acid. Both methanol and acetic acid were removed from the reaction medium by azeotropic solvent distillation. After three or four distillation runs of toluene, the absorption at 1710 cm$^{-1}$ characteristic of carboxylic acid had completely disappeared in favour of a new absorption at 1560 cm$^{-1}$ due to the carboxylate. Toluene was finally distilled off and the polymer was dried under vacuum to constant weight.

*Figure 1* shows the EXAFS spectra for the Zn–PBD material and for the reference compound, ZnO, which is characterized by a first tetrahedral shell of oxygen atoms at 1.977 Å and a second shell of 12 zinc atoms at 3.23 Å. The $k^3$-multiplied spectra were then Fourier-transformed in the 40–500 eV range using a Hanning window. The moduli which represent the radial distribution function in *R*-space are shown in *Figure 2*. Note that the peaks are shifted towards lower values of *R* than the real distances because of the *k* dependency of the phaseshift $\Phi_i$. Only one shell appears in the Fourier transform of PBD, which is attributed to Zn–O pairs. The amplitude and phase functions for that pair were calculated from the Fourier-filtered first peak of ZnO and transferred to the back-transformed peak of the ionomer. The structural parameters, as computed by a least-squares fitting, are noted in *Table 1*. For the fit, a variation $\Delta E_0$ of the threshold energy is introduced to take into account any approximation in chemical transferrability of amplitude and phase function. ($E_0$ was determined as the inflection point of the edge jump.) Also, $\sigma$ has only a relative value $\Delta\sigma$, compared to that of the reference compound. Both parameters are noted in *Table 1*. Note that the precision expected for the bond length is ±0.01 Å, whereas *N* has an accuracy of the order of 20%. These results show that, on average, each zinc atom is surrounded by 4.2 oxygen atoms at a distance of 1.984 Å, without much disorder. There is no other well defined shell at larger distances.

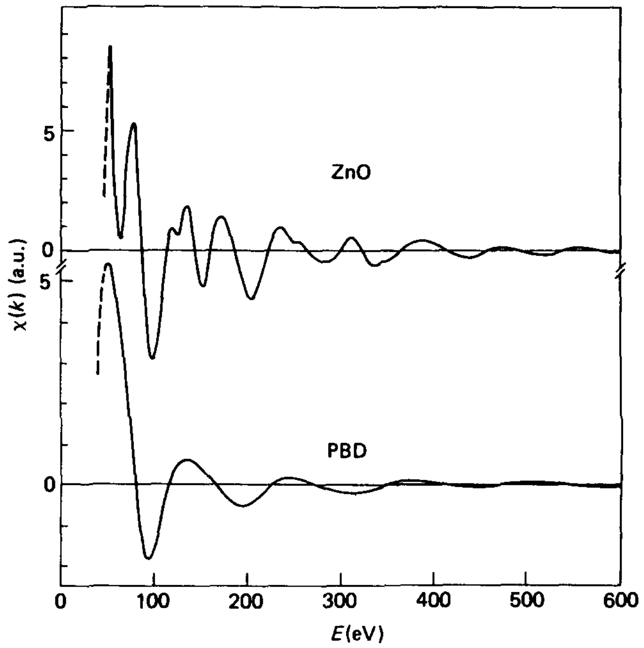

**Figure 1** $\chi(k)$ data deduced from X-ray absorption near the zinc *K* edge for the carboxy-polybutadiene sample PBD and the reference compound ZnO

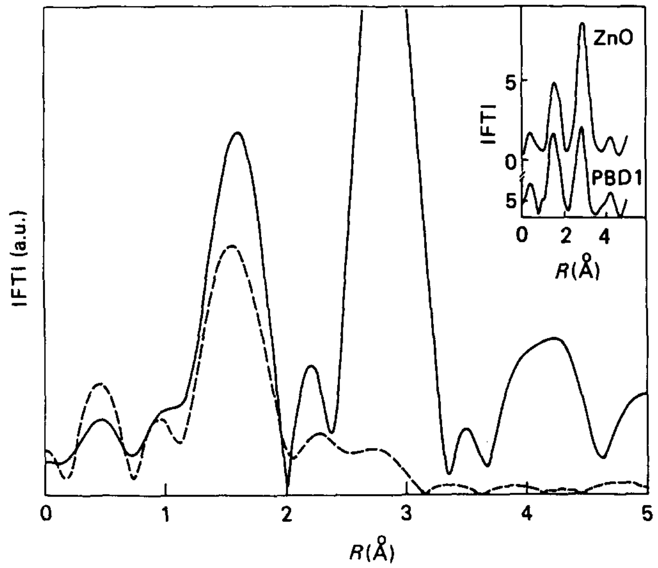

**Figure 2** Radial distribution function obtained as the amplitude of the Fourier transform of $k^3\chi(k)$ to real space for the telechelic polybutadiene PBD (– – –) and the reference compound ZnO (———). The insert shows data obtained previously[2] for a sample identical except for the conditions of neutralization

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* Hycar CTB 2000X 156, commercialized by B. F. Goodrich

**Table 1** Structural parameters deduced from EXAFS data on zinc-$\alpha,\omega$-dicarboxylato-polybutadiene

| Sample | Shell | $N$ | $R$ (Å) | $\Delta\sigma$ (Å) | $\Delta E_0$ (eV) |
|---|---|---|---|---|---|
| ZnO | 1 | 4 | 1.977 | – | – |
| | 2 | 12 | 3.23 | – | – |
| PBD | 1 | 4.2 | 1.984 | 0.060 | −5.7 |
| | 2 | – | – | – | – |
| PBD1[2] | 1 | 5.3 | 1.97 | 0.050 | −5 |
| | 2 | 4.8 | 3.22 | 0.008 | −2.3 |

*Table 1* also lists the results of a previous investigation[2] on an identical prepolymer, but neutralized under strictly anhydrous conditions with diethylzinc, an organometallic compound which reacts strongly with carboxylic acid to form the corresponding zinc carboxylate, with evolution of ethane and without the formation of a secondary reaction product. The formation of ion pairs and their aggregation are instantaneous and take place in the absence of any solvating agents such as water or alcohol. In that case a highly ordered structure has been observed with an average of five oxygen atoms as first neighbours at 1.97 Å *and* five zinc atoms in a second coordination shell at 3.22 Å. There is no trace of that second shell in the present investigation although the first distance is the same. This meaningful difference in local order could be tentatively rationalized by the solvation of the ion pairs when they form in the presence of polar compounds (water, alcohol or acetic acid). Even though these solvating agents could be completely removed when drying the polymer, any phase redistribution in the bulk material is expected to be largely prevented.

Although we do not attempt to give a detailed description of the microstructure within the ionic aggregates, it is clear from these data on two identical prepolymers, both neutralized with a proportion of one zinc atom per chain, that the reactivity of the neutralizing salt and the conditions of the neutralization are important parameters in the process of aggregation. They should be included in experimental reports if one wants to obtain meaningful comparisons between different investigations.

It is worth mentioning that both of the samples described showed a distinct SAXS peak, usually taken as a signature for ionic aggregation[9]. However, the associated characteristic length was unusually large for the polymer neutralized with diethyl zinc and was not reproducible from sample to sample. It appeared as if a non-equilibrium conformation may be trapped when the neutralization reaction is too rapid in the absence of any solvating agent.

### *Disulphonated polyisobutylene*

The polyisobutylene prepolymer was characterized by $\bar{M}_n = 10\,000$, polydispersity index 1.7 and functionality 2.0. The terminal sulphonic acid groups were neutralized in solution using a procedure described previously[10]. Briefly, the neutralization was carried out in tetrahydrofuran with aqueous zinc acetate. Direct titration with zinc acetate, a weak base, does not give a distinct end point. Therefore aliquots of the solution were titrated directly with a strong base, ethanolic potassium hydroxide, to determine the number of equivalents per gram of solution needed for stoichiometric neutralization. An equivalent normal amount of aqueous zinc acetate was then added to the non-neutralized solution, along with the desired excess amount. After neutralization, antioxidant (Irganox 1010) was added and films were cast in Teflon moulds. These films were then dried in a vacuum oven at 80°C for at least 24 h. These solution-cast materials were then compression moulded at 150–160°C for about 5 min to form the films used for EXAFS analysis.

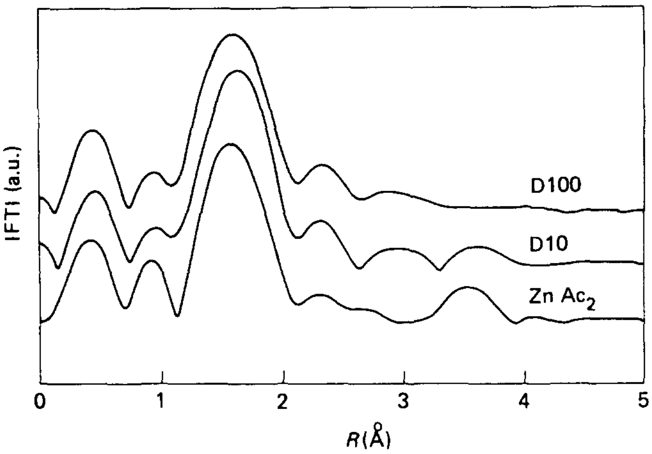

**Figure 3** Radial distribution function for the telechelic polyisobutylene samples D-10 and D-100 and for zinc acetate, ZnAc$_2$

Two samples were compared: one was neutralized to 10% excess (D-10–ZnAc-10 or D-10), the other to 100% excess (D-10–ZnAc-100 or D-100). Zinc oxide was also used as a reference compound for the EXAFS analysis, and a sample of zinc acetate* was also investigated. The analysis of the data was identical to the preceding one.

*Figure 3* shows the radial distribution function for the samples D-10, D-100 and zinc acetate (ZnAc$_2$) in arbitrary units. The best fit is illustrated in *Figure 4*, and the calculated structural parameters for the first shell are summarized in *Table 2*. Inspection of these experimental results shows that:

(1) Within experimental error, the environment of zinc is the same for both D-10 and D-100. One sees only one Zn–O distance of the order of 2.06 Å but no well defined Zn–S or Zn–Zn distance.

(2) There are no visible features of zinc acetate in the ionomeric samples, which, if present, could be a signature for the presence of residual microcrystals of the excess of neutralizing salt.

(3) We believe that Zn is in an octahedral site with six oxygen neighbours, four from SO$_3$ groups and two from residual water molecules, although the average number detected by the technique is near five.

This last statement deserves some comment. Based on the correlation found between the Zn–O bond length and the coordination number for compounds of known crystallographic structure, Pan *et al.*[13] suggested that the Zn–O distance is a sensitive probe of the coordination number. Since the precision on $N$ is only 20% or less if the sample thickness is not uniform, this method could

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* It is interesting to note here that zinc acetate dihydrate was first used as a reference compound for the study of dicarboxylato-polybutadiene since its chemical structure is similar to the one expected in the ionomer. However, in the course of the study it was discovered that the published crystallographic structure[11] is not correct. Indeed, when the phase and amplitude functions of ZnAc$_2$ were introduced into the data analysis of the experimental results for ZnO, the distances so deduced did not agree with the well established structure of ZnO, e.g. a Zn–O distance of 2.12 Å was found, compared to the correct value of 1.977 Å

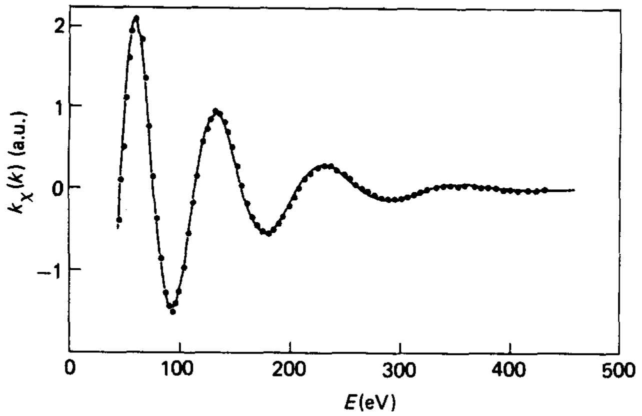

**Figure 4** Fourier back-transformed data (●) and best non-linear least squares fit (———) for sample D-100

**Table 2** Structural parameters for the first oxygen shell of disulphonated polyisobutylene and reference compounds

| Sample | $N$ | $R$ (Å) | $\Delta\sigma$ (Å) | $\Delta E_0$ (eV) |
|---|---|---|---|---|
| ZnO | 4 | 1.977 | – | – |
| D-10 | 4.7 | 2.06 | 0.070 | −4 |
| D-100 | 4.5 | 2.05 | 0.070 | −3 |
| $ZnAc_2$ | ?[a] | 2.04 | ?[a] | −2 |

[a] See footnote in this section

provide much more accurate results. In this case it gives $N=6$.

So the question is: why do we count only five neighbours? The same problem was encountered with a copper carboxypolybutadiene[3], where it was found that at room temperature the water molecules have such a high Debye–Waller factor that their contribution to the EXAFS spectra is smeared out. The same could be true here. Experiments at low temperature should provide the right coordination number.

To check if a shorter distance could fit the data and be compatible with the experimental value of $N=5$, we made a simulation with two distances, 2.03 and 2.06 Å, keeping all other parameters constant (*Figure 5*). Since the shift of the curves is not constant along the energy axis, it cannot be taken into account by a variation of $\Delta E_0$ and the distance found (2.06 Å) seems to be correct.

These results on two samples which differ only by the amount of neutralizing salt seem to suggest that the first associations formed with some degree of local order are independent of the amount of neutralizing agent. They contain very few dipoles. These further aggregate and incorporate the excess salt – since no trace of zinc acetate has been found – into disordered larger units which are responsible for the different mechanical and viscoelastic properties of the material[10]. Although increasing the amount of neutralizing agent strengthens and stabilizes the network, it appears to have no effect on the local environment of the metal.

## CONCLUSION

With this study on some zinc-neutralized telechelic ionomers, we have investigated the influence of the conditions of neutralization on the local environment of the metal cation. EXAFS spectroscopy was used to probe the degree of local order within a range of 1 to about 5 Å. Two prepolymers were used, polybutadiene and polyisobutylene, with similar molecular properties (molecular weight, flexibility, dielectric constant, etc.) but end-terminated with different anions, COO– and $SO_3$–, which is supposed to form stronger ionic associations.

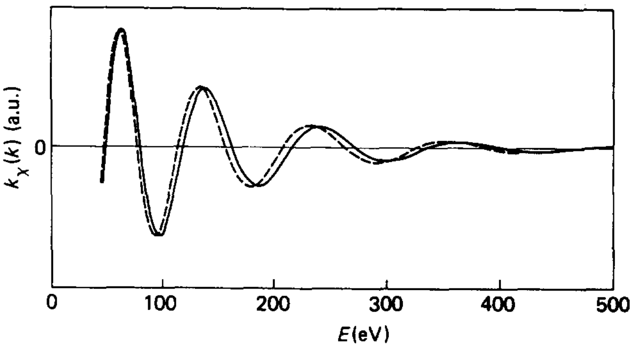

**Figure 5** Simulation of fits for two distances, all other parameters being kept constant: (———) $R=2.03$ Å; (– – –) $R=2.06$ Å

It was found that the nature and reactivity of the metallic reagent used to perform the neutralization and the presence of solvating agents during the process can drastically change the degree of local order. Since they also appear to influence the texture and long range structural properties of the material, an exact description of the conditions of neutralization are mandatory for complete sample characterization. On the other hand, the amount of neutralizing salt above the stoichiometric point does not seem to play a role in the very local structure around the cation, although it changes the viscoelastic and mechanical properties of the material. No trace of microcrystals of the excess neutralizing salt has been found. It is also interesting to note that the so-called 'strength' of ionic association does not seem to be related to a difference in local structure. One could wonder to what extent the local arrangement of the ion pairs is related to the more global structure of the material and ultimately to its mechanical properties.

## ACKNOWLEDGEMENTS

Thanks are due to the technical staff of LURE-DCI for providing the synchrotron beam and for assistance during the experiment. We also acknowledge interesting discussions with R. A. Register and S. L. Cooper on EXAFS data analysis.

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