polymer papers

Microstructure of iron(III) α,ω-dicarboxylatopolybutadiene

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α,ω-Dicarboxylatopolybutadiene has been prepared and neutralized to varying extents, on either side of stoichiometry, using iron(III) 2-propoxide under anhydrous conditions. These samples have been characterized by extended X-ray absorption fine structure (EXAFS) measurements, and by magnetic measurements and Mössbauer spectroscopy as a function of temperature. It is deduced from EXAFS data, by comparison with iron(III) glycine, that most of the iron is present as μ_3-oxo-triion complexes which bond to six polybutadiene chain ends. Static magnetic measurements are consistent with the presence of antiferromagnetic triangular trimers with an $S \simeq 1/2$ ground state. There is some evidence from Mössbauer spectroscopy of the presence of superparamagnetic fine particles with a blocking temperature of at most 7 K, implying the association of some (> 10) of these trimers to give larger clusters.

(Keywords: microstructure; polybutadiene; dicarboxylatopolybutadiene; EXAFS; Mössbauer spectroscopy)

INTRODUCTION

Polymer chains with an acid group at each extremity but with no sidegroups are excellent model compounds for examining the influence of ionic bonds on polymer properties. On converting the telechelic polymer to the salt form by displacing the protons with metal atoms it is found that the ions tend to form small clusters. The problem is to define this microstructure, and to relate it to the physical properties. Pineri, Levelut and coworkers[1,2] used small-angle X-ray scattering to infer a cluster size of about 30 cations, which was independent of the degree of neutralization or the nature of the ion for Na^+, K^+, Cs^+ or Mn^{2+}. They suggested that the ionic aggregates may be lamellar in form. In another series of studies, Broze, Jérome, Teyssié and Marco focussed attention on the viscoelastic behaviour of alkaline earth telechelics, both in solution[3] and in the solid state[4–6]. Their conclusion is that small numbers of ions, 3–9, form aggregates, or multiplets in Eisenberg's terminology[7], although a recent EXAFS study of zinc α,ω-dicarboxylatopolybutadiene[8] indicated that the number of zinc ions present in the aggregates is significantly greater. The thermal, dynamic mechanical and dielectric behaviour has also been examined in specimens containing an excess of neutralizing salts[9]. A multiplet cluster description of these systems has been given, the excess salt being assumed to be in the ionically concentrated phase.

In the present paper several experimental techniques, Mössbauer spectroscopy, magnetic measurements and X-ray absorption fine structure (EXAFS) measurements, are combined to build up a picture of the microstructure of ferric α,ω-dicarboxylatopolybutadiene, including its dependence on the degree of neutralization. In an earlier Mössbauer study of this type of material much of the iron appeared to have hydrolysed to ferric hydroxide[11]. We therefore took precautions to exclude excess water during the sample preparation. Our principal conclusion is that most of the iron is present as μ_3-oxo-triion complexes which bond to six polybutadiene chain ends.

A detailed picture of the ionic dispersion in Cu^{2+} telechelic has also been obtained in a parallel study by combining magnetic, e.p.r. and EXAFS data[10]. Roughly one quarter of the copper there is present as isolated Cu^{2+} ions, while the remainder forms dimers with a cubic structure with the copper in square planar coordination. The ends of four polybutadiene chains are bonded at each of these centres.

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EXPERIMENTAL RESULTS

Preparation of samples

Samples were prepared by neutralizing a commercial carboxy-telechelic polybutadiene with iron(III) 2-propoxide. The polybutadiene[12]

$$HOOC\text{-}[CH_2CH{=}CH\text{-}CH_2]_n\text{-}COOH$$

had $n \simeq 88$, $\bar{M}_n = 4600$ and $\bar{M}_w/\bar{M}_n = 1.8$. The chains each contained a mean number of 2.01 carboxylic acid groups and the *cis/trans*/vinyl ratio was 20/65/15. Five samples were prepared, with different degrees of neutralization of the carboxylic acid groups by iron(III), using the following procedure: The carboxy-telechelic polybutadiene was initially dried by three successive azeotropic distillations of benzene and finally dissolved in toluene (5% wt/vol) previously dried by refluxing over calcium hydride. Iron(III) 2-propoxide in solution in benzene (dried in the same way as toluene) was added dropwise into the prepolymer solution in order to neutralize the carboxylic acid end-groups at various well-defined degrees. The solvent was partly distilled off under reduced pressure. Freshly dried toluene was added into the reaction medium and a further distillation run was carried out to ensure the complete elimination of the 2-propanol reaction subproduct. Whatever its degree of neutralization, the polymer was finally dissolved in nonanhydrous toluene (excess water compared to the polymer end-groups) in order to hydrolyse the unreacted alkoxy groups when used in excess. All samples underwent the same chemical treatment and any residual reactive alkoxy group was transformed into more stable oxo-hydroxide functions. Iron(III) carboxylate-containing polybutadienes were dried under vacuum to constant weight and moulded at 100°C.

Iron(III) 2-propoxide was prepared by bubbling ammonia into a solution of anhydrous ferric chloride in a mixture of dry benzene (60% v/v) and 2-propanol (40% v/v), at 0°C (ref. 13). After completion of the exothermic reaction and storage for 12 h at room temperature, the volatile components were evaporated off under reduced pressure. The residue of iron(III) 2-propoxide and ammonium chloride was extracted with dry benzene. After the evaporation of the benzene, a dark brown crystalline solid was obtained; it was finally dissolved in dry benzene in a ratio of 5×10^{-2} mol l^{-1}. 2-Propanol was dried by refluxing over sodium.

In addition a sixth sample was prepared following the same procedure except that the polybutadiene used, $\bar{M}_n = 90\,000$, did not have acid end groups. U.v. irradiation was necessary in this case to obtain a rigid material. The samples are listed in *Table 1*.

Table 1 Telechelic samples studied

Sample	% Fe by weight	Fe/PBD	Charge stoichiometry
1	0.41	0.33	0.50
2	0.61	0.50	0.75
3	0.81	0.67	1.00
4	1.20	1.00	1.50
5	1.79	1.50	2.25
6	0.81	0.67	–

Table 2 Mössbauer fit parameters for spectra at 80 K

Sample	Isomer shift δ (mm/s)	Quadrupole splitting Δ (mm/s)
1	0.52 (1)	0.57 (2)
2	0.51	0.63
3	0.50	0.71
4	0.50	0.81
5	0.48	0.83
Fe–glycine	0.51	0.53

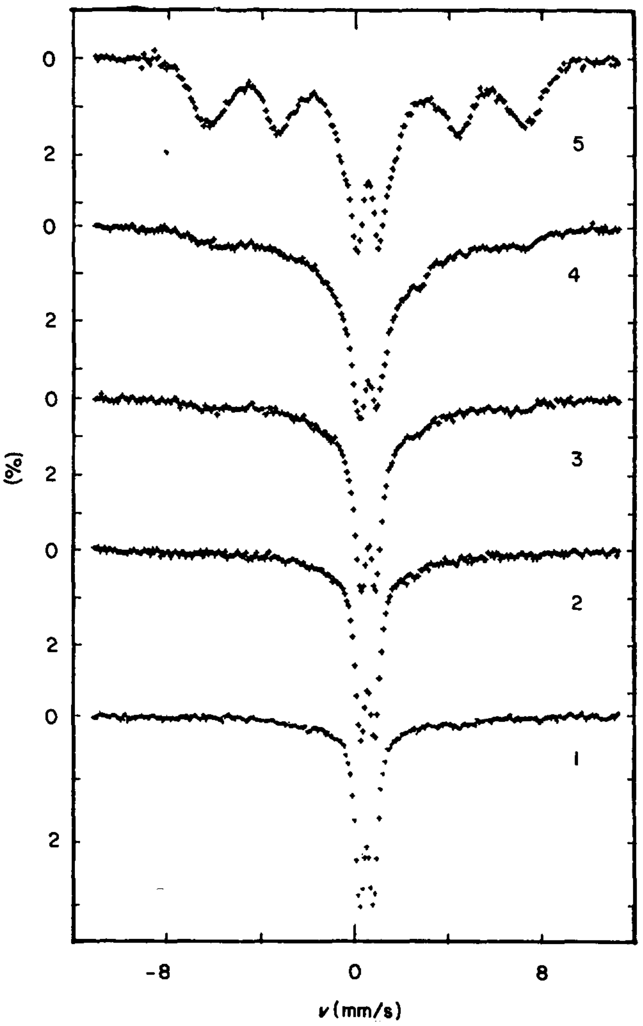

Figure 1 Mössbauer spectra at 4.2 K of Fe^{3+} telechelics for samples 1–5

Mössbauer measurements

Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using a source of ^{57}Co in Rh. Absorbers were discs approximately 20 mm in diameter and 8 mm thick. Isomer shifts are quoted relative to the αFe absorber used for calibration.

There is no Mössbauer absorption for any of the iron-neutralized telechelics at room temperature because it is well above the glass transition of the polymer, T_g = 195 K (ref. 14). At 80 K, a quadrupole doublet appears for all samples, and the least-squares fit parameters are listed in *Table 2*. The isomer shift is typical of Fe^{3+} octahedrally coordinated by oxygen. Extrapolated parameters for the dilute limit are $\delta = 0.52$ (1) mm/s and $\Delta = 0.52$ (2) mm/s, in agreement with those of ferric glycine at the same temperature. $[Fe_3O(C_2H_5O_2N)_6 3H_2O](CO_4)_7$ was taken as reference material for the EXAFS measurements as its crystal structure is known[15].

Spectra at 4.2 K for the series of samples are shown in *Figure 1*. Besides the central quadrupole doublet, which is due to a paramagnetic mono- or polynuclear species, there appears a broad central component which develops into a magnetically split spectrum with increasing neutralization. It is most clearly visible for the overneutralized sample 5. The temperature dependence of the spectrum of this sample, illustrated in *Figure 2*, is typical of superparamagnetic fine particles with an average Mössbauer blocking temperature of about 7 K. The hyperfine field extrapolated to 0 K is 450 kG. Similar behaviour has been found for a range of other polymers containing iron(III)[16-18] and it is likely to be associated with the formation of tiny clusters of amorphous ferric hydroxide. Nevertheless, it should be noted that the hyperfine field for sample 6 is 480 kG at 4.2 K, which suggests that the superparamagnetic species in samples 1–5 is either much more finely divided or else differs in composition or morphology from that in the unneutralized sample 6. In view of the lamellar morphology proposed for the ionic clusters in telechelics[2,4], it is worth noting that the hyperfine field in 2-dimensional antiferromagnetic Fe^{3+} compounds tends to be reduced with respect to that of their 3-dimensional counterparts[16].

Magnetization

Magnetization measurements give a more precise idea about the nature of the iron complexes. Magnetization curves for samples 1–5 obtained on a vibrating-sample magnetometer operating with a 70 kG superconducting magnet are shown in *Figure 3*, and the temperature dependence of the inverse susceptibility (defined as B/M, with $B = 2$ kG) is shown in *Figure 4*. It is apparent from these data that practially all the iron ions are subject to strong antiferromagnetic interactions. The magnetization of isolated iron ions would follow a Brillouin function with $S = 5/2$ saturating at $M = 5\ \mu_B$/Fe. The magnetization data of *Figure 3* show that no more than 5% of the iron can be in this form. Furthermore, since the broad or magnetically split component in the spectra of *Figure 1* far exceeds 5% of the total absorption, it follows that it must be attributed to incipient magnetic order in iron clusters rather than paramagnetic hyperfine splitting of isolated ferric ions. The quadrupole doublet, which accounts for the major part of the absorption in samples 1–3, has to be attributed to a polynuclear complex. We have therefore

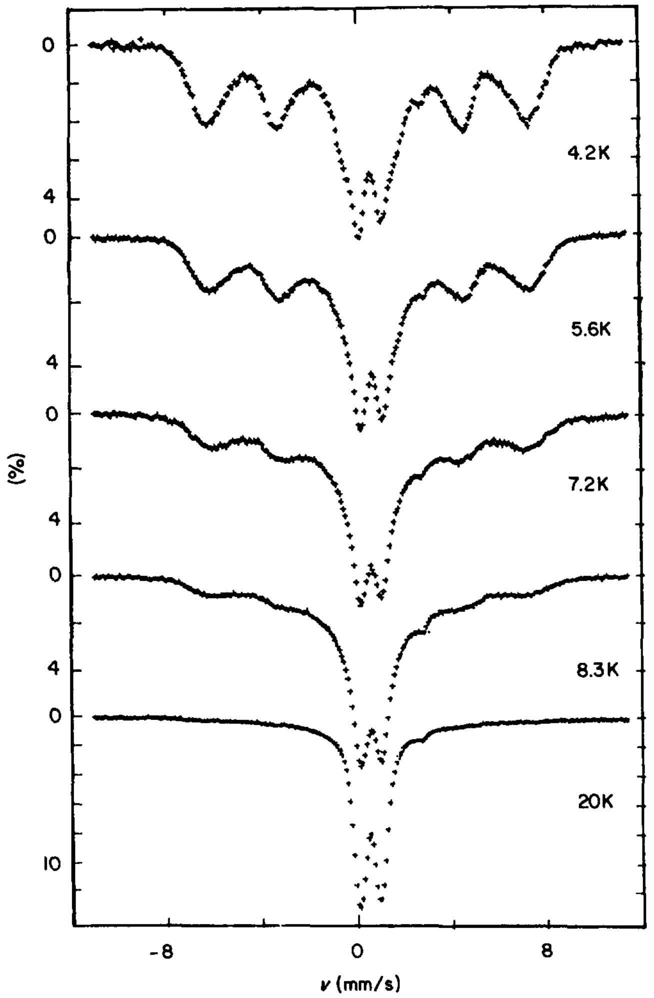

Figure 2 Mössbauer spectra as a function of temperature for the overneutralized sample 5 at 4.2–20 K

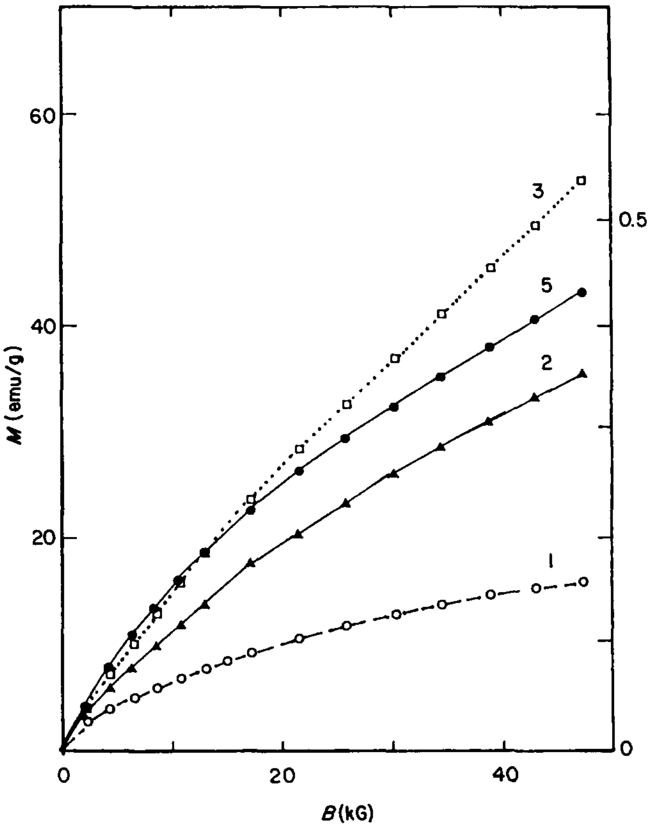

Figure 3 Magnetization curves for the Fe^{3+} telechelics at 4.2 K. Magnetization is expressed in emu/g of iron on the left and in μ_B/iron atom on the right hand side

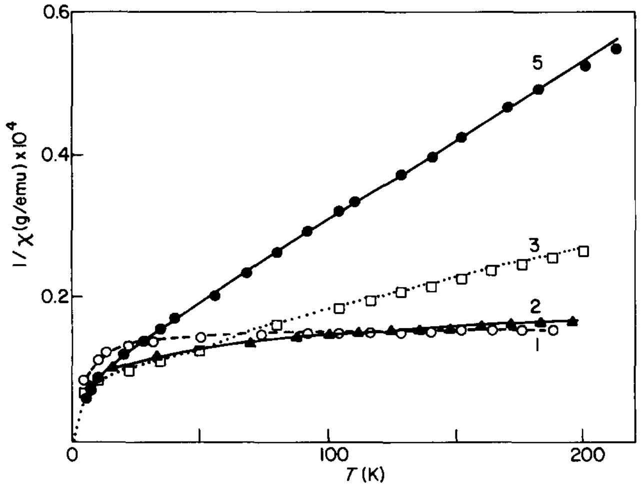

Figure 4 Temperature dependence of the inverse susceptibility, measured at 2 kG

calculated the magnetization and susceptibility expected for complexes containing 2, 3 or 4 iron atoms using the hamiltonian

$$H=-\sum_{ij}J\vec{S}_i\cdot\vec{S}_j-g\mu_B\vec{B}\cdot\vec{S}'_z \qquad (1)$$

where $S'=\Sigma S$. Results are shown in *Figures 5* and *6*, where J was chosen, for illustrative purposes as 1 K or 40 K. The latter is a typical value for an oxo-bridged dimer or trimer[17]. No species with an $S'=0$ ground state has the correct temperature of $1/\chi$, which does not diverge at low temperature, but turns down instead. Furthermore, species with $S'=5/2$ can also be ruled out as major iron constituents because their magnetization would be too great. In fact the best agreement with the magnetic data of sample 1 for a *single* polynuclear species is obtained for a triangular trimer with $J=\sim 4$ K. Oxo-bridged trimeric clusters have been observed in many ferric carboxylic or dicarboxylic acid complexes[17–20] including the ferric glycine[15]. However, the possibility of minor amounts of other species such as dimers, isolated ions, quadrimers or larger antiferromagnetically coupled clusters cannot be excluded and addition of a small amount of weakly antiferromagnetic dimer will reproduce the observed inverse susceptibility over the whole range of temperature.

Extended X-ray absorption fine structure

X-ray absorption measurements were made on the EXAFS I spectrometer at the Synchrotron radiation facility at Orsay (LURE)[21]. In the following sections we first present the technique in general terms, then the experimental details at LURE and finally the results on the ferric telechelics.

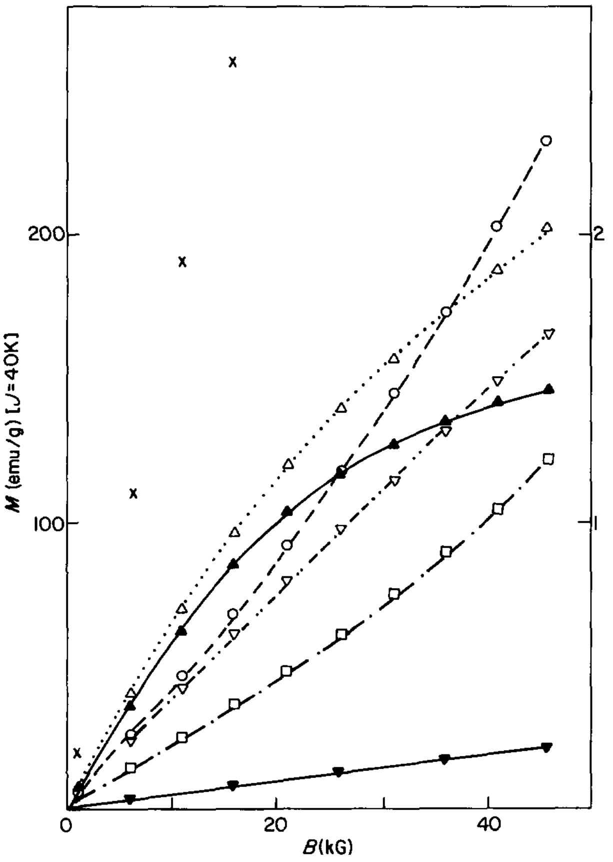

Figure 5 Calculated 4.2 K magnetization curves for isolated ions (×), dimers (○), triangular trimers (▽), linear trimers (△) and quadrimers (□). Open symbols are for $J=1$ K, solid symbols are for $J=40$ K

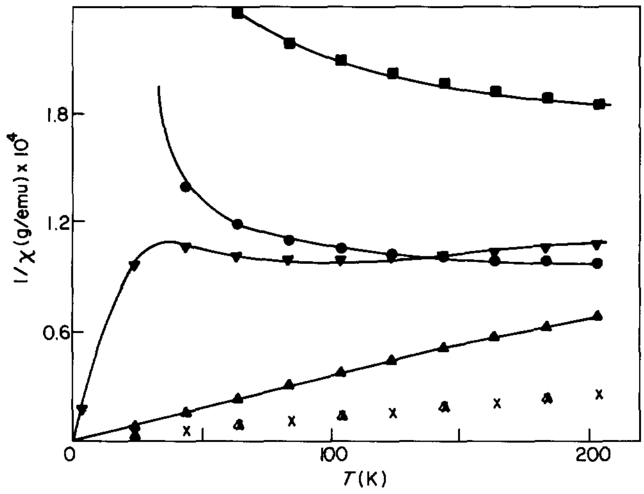

Figure 6 Calculated temperature dependence of the inverse susceptibility, measured at 2 kG. Symbols have the same meaning as for *Figure 5*

EXAFS method. The EXAFS method involves a measurement of the linear absorption coefficient μ as a function of phoelectron wave vector $k=[2m(E-E_0)/h^2]^{1/2}$. E is the incident photon energy and E_0 is the photoelectron binding energy. μ is defined by $\mu x=\ln(I_0/I)$, where x is the sample thickness, and I_0 and I are the incident and transmitted intensities of the photon beam. The EXAFS signal is given by

$$\chi(k)=\frac{\mu(k)-\mu_b(k)-\mu_0(k)}{\mu_0(k)} \qquad (2)$$

where μ_b is the background originating beyond the absorption edge and μ_0 is the smooth atom-like contribution. The standard backscattering theory[22] relates $\chi(k)$ to the structural parameters.

$$\chi(k)=\frac{1}{k}\sum_i^{N_i}R_i^2e^{-2\sigma_i^2k^2}F_i(k)\sin(2kR_i+\phi_i(k)) \qquad (3)$$

where R_i is the average distance between the absorbing atom and the N_i neighbours which define the ith shell. The root mean square (rms) deviation in R_i is σ_i, including both statistical and thermal distortion of the equilibrium structure. EXAFS measurements were made at room temperature where the Debye–Waller factor $\exp(-2\sigma_i^2k^2)$ is non-zero although the corresponding Lamb–Mössbauer factor $\exp(-k^2\gamma\langle x^2\rangle)$ is zero because the characteristic time involved in the Mössbauer experiment, the ^{57}Fe excited state nuclear lifetime (10^{-7} s), is much longer than that of the EXAFS experiment, the lifetime of the atomic excited state ($\sim 10^{-15}$ s). $F_i(k)$ and $\phi_i(k)$ are the amplitude back scattering factor and phase shift, respectively. They are characteristic of a particular combination of absorbing atom and backscattering shell, i. The $F_i(k)$ term includes a factor taking into account inelastic processes, normally written as $\exp(-2R_i/\lambda)$. Data processing was carried out using procedures described elsewhere[23].

EXAFS measurement. All samples were studied in air at room temperature, after moulding into homogeneous tablets 3 mm thick and 8 mm in diameter. Known amounts of finely ground $Fe(C_5H_7O_2)_3$ and $[Fe_3O(C_2H_5O_2N)_6(H_2O)_3](ClO_4)$ were used as reference compounds of known crystallographic structures[15,24]. Powders were supported on Scotch tape to form homogeneous films.

The EXAFS spectra were recorded in the transmission mode using a Si(220) channel-cut monochromator, with the DCI storage ring working at the energy of 1.56 GeV (in order to minimize the presence of harmonics) with current of the order of 100 mA. The data were collected at 2 eV intervals (1.5 s per step) over an energy range of 1 keV (6.9 to 7.9 keV) above the K-edge of iron. The entrance slit was 2 mm, and the transverse dimension of the beam was adjusted to be smaller than the sample size. The first ionization chamber was filled with a He–Ne mixture, while the second one was kept in air.

Data analysis and discussion. The data analysis has been carried out using standard procedures for obtaining the EXAFS modulation, Fourier filtering and fitting. First estimates of damping terms due to disorder and inelastic processes were made using theoretical phase shifts for the model compounds. Then the acetylacetone and glycine were used to extract experimental phase shifts respectively for the first shell (Fe–O) and second shell (Fe–Fe). The EXAFS oscillations for all compounds are presented as $\chi(k)$–k in *Figure 7* (k being the photoelectron wavevector); Fourier transforms taken in the same way are exhibited in *Figure 8*. A double peak structure is clearly seen in all cases, corresponding to the Fe–O and Fe–Fe distances. Curve fitting of Fourier-filtered EXAFS has been carried out. The results are exhibited in *Table 3*.

It should be noted that the number of iron neighbours in the second shell is close to 2, as in the Fe–glycine model compound, and the iron–iron distances are quite similar. This indicates a triangular trimeric structure of the iron complexes in the iron(III) dicarboxylatopolybutadiene.

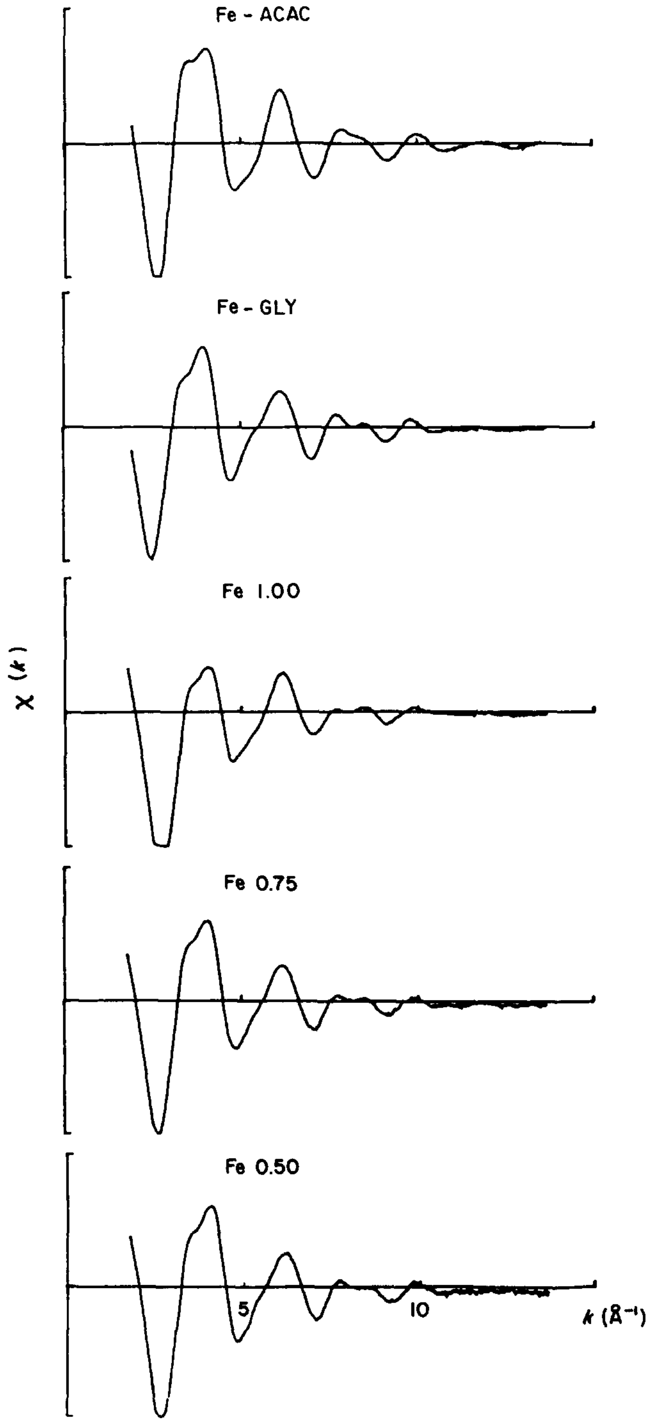

Figure 7 $\chi(k)$ data deduced from the X-ray absorption near the iron K-edge for the telechelic samples 1–3 and two model compounds

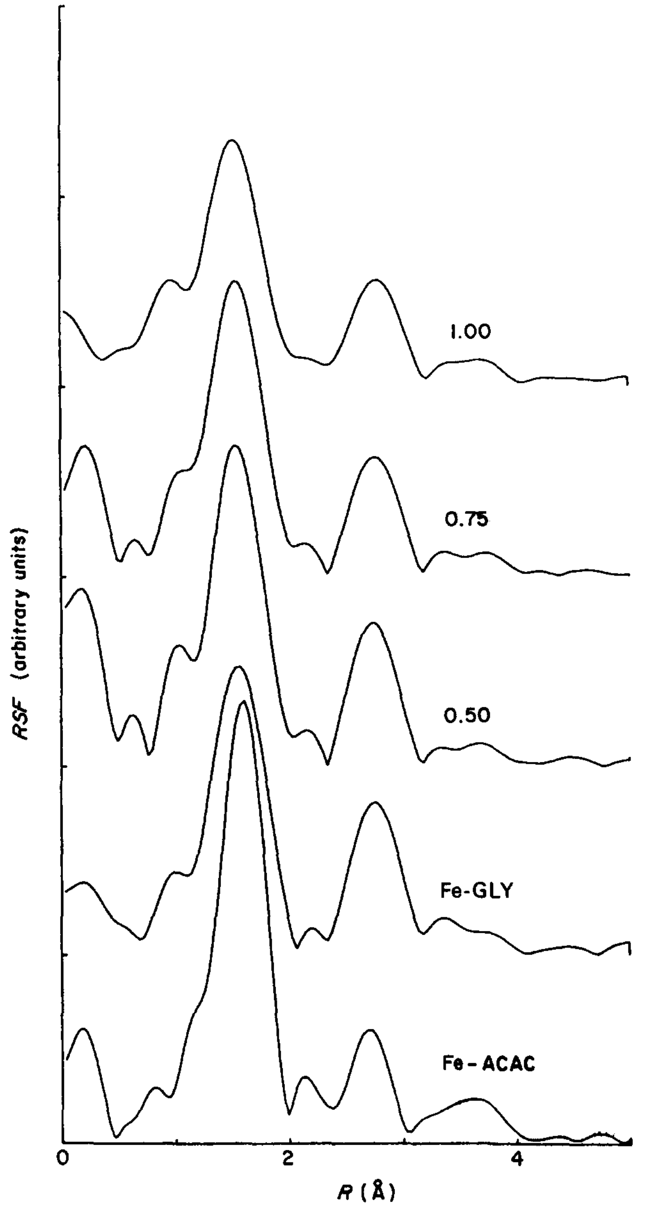

Figure 8 Radial structure functions deduced from EXFAS data on telechelic samples 1–3, and the two model compounds

Table 3 Structural parameters deduced from EXAFS data on model compounds and Fe-telechelics

	First shell, Fe–O			Second shell, Fe–Fe		
Sample	N_1	σ_1 (Å)	R_1 (Å)	N_2	σ_2 (Å)	R_2 (Å)
Fe–AcAc	6	0.021	1.999		–	
Fe–Gly				2	0.079	3.30
1	6.0 (1.0)	0.066 (10)	1.991 (10)	2.2 (2)	0.088 (10)	3.30 (1)
2	6.0 (1.0)	0.072 (10)	1.995 (10)	2.0 (2)	0.093 (10)	3.32 (1)
3	4.8 (1.0)	0.073 (10)	1.981 (10)	1.5 (2)	0.085 (10)	3.34 (1)

A strong correlation generally exists between the coordination number and the damping parameter due to inelastic effects. We have used here a mean free path $\lambda = \frac{1}{\Gamma}$. The important point is that the Γ parameter could be kept constant along the series of telechelics (Fe 0.50, Fe 0.75, Fe 1.00); for other shells the Γ value was 0.30 $Å^{-1}$. In this way, the coordination number was found nearly constant ($N_1 = 6$, $N_2 = 2$) for Fe 0.50 and Fe 0.75; however for Fe 1.00, a marked decrease has been found for both shells.

The Debye–Waller factors were found with good accuracy; they are of the same order for the Fe–O shell as in the glycine reference compound. From this we can infer that the static disorder is similar to that of the glycine reference compound. Little can be said about distances for the first shell, although a small increase is observed in the second shell for the series of samples.

CONCLUSIONS

All data are in accord with the idea that iron in stoichiometric and underneutralized Fe^{3+} telechelics is present as triangular oxygen-bridged clusters, similar to those in ferric glycine. The trinuclear iron centre is illustrated in *Figure 9*. Strong antiferromagnetic superexchange results from ~120° Fe–O–Fe bonds.

As shown, the iron centre bonds to six chain ends and is positively charged. As the iron in samples with charge stoichiometry up to 1.50 might be accommodated in this form, and the water content of the polymer deduced from the desorption isotherms[25] is sufficient to provide the necessary $1H_2O/Fe^{3+}$, the positive charge of the trinuclear centre could be neutralized by binding a seventh chain, or by protonation of the bridging oxygen.

The Mössbauer spectra at 4.2 K indicated aggregation of some of the iron, which increases with increasing iron content. Signs of large scale inhomogeneity have also been detected in small-angle X-ray scattering experiments[26]. This aggregation can be achieved if the outer H_2O molecules (or OH^- ions) are common to two trinuclear centres. Growth of these aggregates will ultimately be impeded by the bulk of the polymer chains that they entrain. The superparamagnetic blocking behaviour suggests that the aggregates involve at least ten trinuclear centres. There may also be a tendency towards hydrolysis of ferric iron, particularly in the overneutralized samples, but comparison with the uncarboxylated sample 6, where iron almost certainly forms aggregates of poorly crystallized ferric hydroxide[27], indicates that this tendency is not complete in any of the ferric telechelics studied.

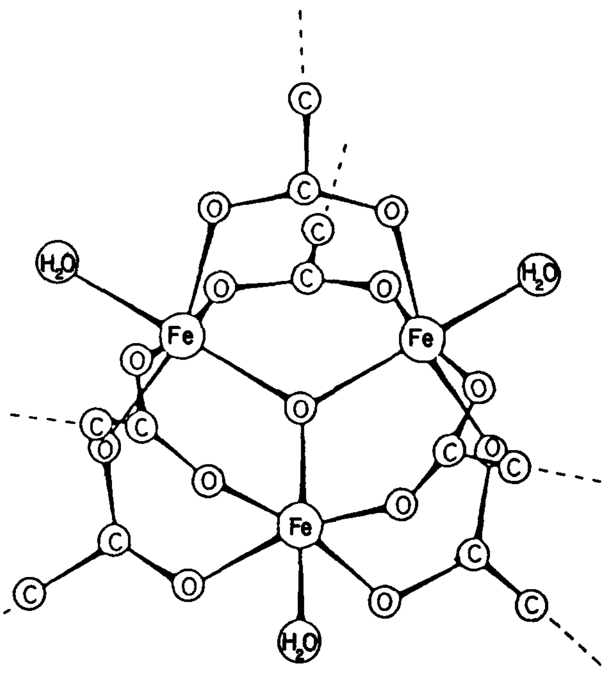

Figure 9 Trinuclear iron centre proposed for Fe^{3+} telechelics. Broken lines represent the polybutadiene chairs which are attached to the six carboxylate groups

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