Microstructure of copper(II) α,ω-dicarboxylato polybutadiene

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α,ω-Dicarboxylato polybutadiene has been neutralized to varying extents below stoichiometry by using Cu^{2+} isopropoxide under anhydrous conditions. These samples have been characterized by extended X-ray absorption fine structure (EXAFS) measurements and by magnetic measurements and electron paramagnetic resonance (e.p.r.). It is deduced from EXAFS data by comparison with Cu(II) acetate that part of the copper ions are present as dimeric Cu–Cu complexes, which bond to the ends of four polybutadiene chains. A detailed description of these complexes has been obtained from e.p.r. results. The relative percentages of these different species (isolated Cu^{2+} and dimers) are given from the static magnetic measurements.

(Keywords: ionomers; electron paramagnetic resonance; extended X-ray absorption fine structure; magnetic measurements; Cu^{2+} ionomers)

INTRODUCTION

This article, like the preceding one[1], concerns the local structure of the multiplets formed by ionic associations in α,ω-dicarboxylato polybutadiene of relatively low molecular weight (~4600). Here we are concerned with polymers neutralized with copper(II) salts. As already emphasized[1], halato telechelic polymers constitute a model for studying the general problem of ionic associations in ionomers[2-4]. It has been shown from extended X-ray absorption fine structure (EXAFS) and magnetic measurements[3] that, in the ferric salts of these α,ω-dicarboxylato polybutadienes, the iron Fe^{3+} ions tend to form oxo-bridged trimers which constitute hexafunctional crosslinking points. Clustering of these primary multiplets permits an explanation of the Mössbauer and small-angle scattering results. These conclusions were made possible by the combination of the different techniques already mentioned.

The aim of this article is also to use several experimental techniques to obtain a consistent structure for the ionic associations formed after neutralization of the above-mentioned materials by copper salts. Cu^{2+} cations introduce the possibility of studying their relative interactions through electron paramagnetic resonance (e.p.r.) and static magnetic measurements. In addition to these two techniques, EXAFS has been used.

Some preliminary electron spin resonance (e.s.r.) results on these Cu^{2+} salts of carboxy telechelic polybutadiene polymers have already shown the presence of both isolated Cu^{2+} and $Cu^{2+}\ldots Cu^{2+}$ pairs[5,6]. Here we present a quantitative analysis of the species present in two samples with different copper contents and we give a detailed description of the structure of the dimer.

EXPERIMENTAL

Sample preparation

Carboxy telechelic polybutadiene commercially available from B. F. Goodrich (Hycar CTB 200 × 156) was neutralized in dry toluene by adding appropriate amounts

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of Cu(II) isopropoxide under strictly anhydrous conditions. The main molecular features of the prepolymer were $M_n = 4600$, $M_w/M_n \simeq 1.8$, mean number of carboxylic acid groups per chain = 2.01 and *cis*/*trans*/vinyl ratio = 20/65/15. 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. A suspension of Cu(II) isopropoxide in dry isopropanol was added dropwise to the prepolymer solution in order to neutralize the carboxylic acid endgroups to an extent of 50% and 75%, respectively. The solvent was partly distilled off under reduced pressure. Freshly dried toluene was added to the reaction medium and a further distillation run was carried out to ensure complete elimination of the isopropanol reaction subproduct. Cu(II) carboxylate-containing polybutadiene was dried under vacuum to constant weight and moulded at 100°C.

Cu(II) isopropoxide was prepared by reacting completely dehydrated copper(II) chloride[7] with a stoichiometric amount of lithium isopropoxide in anhydrous isopropanol[8]. A green precipitate of copper isopropoxide formed, which turned blue as the mixture was shaken. The supernatant solution was removed under nitrogen atmosphere (through a rubber septum and stainless-steel capillary) and the precipitate repeatedly washed with dry isopropanol (the LiCl reaction subproduct was soluble in isopropanol). Copper isopropoxide was used as a suspension in dry isopropanol (10^{-1} mol l^{-1}). Isopropanol was dried by refluxing over sodium. Lithium isopropoxide was freshly prepared just before use by reaction of pure lithium with anhydrous isopropanol used in large excess.

Two different samples have been prepared, designated Cu 0.50 and Cu 0.75, which correspond respectively to 50% and 75% neutralization.

Electron paramagnetic resonance

The apparatus used in this study was a Varian E4 working at 9500 MHz with a variable field from 0 to 6000 G. Between 77 and 295 K, the temperature was measured within ±2 K. Experiments in Q band were performed by means of a Varian E110 working at 35 GHz with a variable field from 0 to 20 000 G. The sample holder was a small cylinder of poly(methyl methacrylate) fixed onto the metallic bottom of the resonant cavity. This metallic part may be cooled by thermal contact with liquid nitrogen.

Magnetic susceptibility measurements

All these measurements were performed using a superconducting quantum interference device (SQUID) susceptometer[9] (S.H.E. Corporation). The essence of this technique is to use the high sensitivity of a superconductor with a weak link ring to any flux variation for measuring the magnetic moment induced in the sample by the stable, homogeneous field of a superconducting solenoid. This moment is the result of three contributions:

(a) moment of the sample holder;
(b) moment resulting from the diamagnetism of the polymer chains and also of the residual carboxylic acid endgroups; and
(c) moment associated with divalent copper ions.

A correction for the first two contributions has been made using unneutralized telechelic polymer.

The polarizing applied magnetic field was 40 000 G and, for each sample (about 100 mg), 30 measurements were performed in the temperature range 6–300 K.

The magnetometer was completely monitored by a microcomputer. The experimental magnetic susceptibility function obtained was fitted to the expected theoretical law using a mean square procedure to get the parameters of interest.

EXAFS

All samples were studied in air at room temperature after moulding into very homogeneous 3 mm thick platelets, 8 mm in diameter. A known amount of finely ground copper acetate $Cu(CH_3COO)_2 \cdot 2H_2O$, used as a reference compound of known crystallographic structure[10], was supported by a 10 μm thick polycarbonate membrane to form a homogeneous film, following a standard procedure.

The EXAFS spectra were recorded in a transmission mode at the French LURE facility (EXAFS I Station). The monochromator used was a Si (220) cut channel, the harmonics content being minimized by the working energy $E = 1.5$ GeV of the DCI storage ring[11].

Additional information concerning this experiment can be found in the preceding paper[1].

RESULTS

Sample characterization

No change in the glass transition has been observed upon neutralization for these Cu salts in either d.s.c. or ~0.1 Hz dynamic mechanical measurements. In *Figure 1* are shown the changes in modulus and damping *versus* temperature for the Cu 0.75 sample. The reference

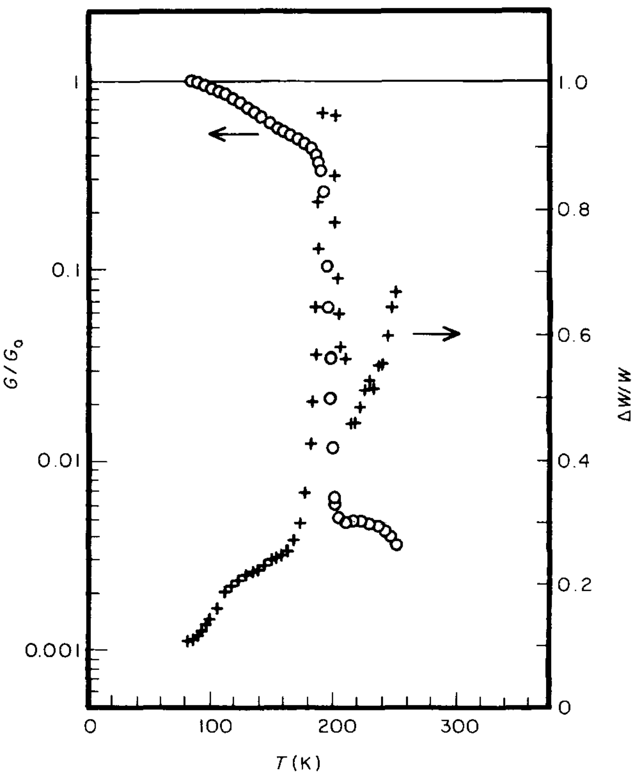


Figure 1 Changes in modulus G/G_0 (○) and damping $\Delta W/W$ (+) *versus* temperature for the Cu 0.75 sample

modulus is the 77 K modulus. The sharp decrease in modulus between 190 and 200 K is associated with the glass transition. The appearance of a plateau between 200 and 250 K is evidence for chain extension and crosslinking of the starting material. The flow associated with an increase in damping begins to occur above 250 K and may be interpreted as due to chemical exchange, with a lifetime of the order of the pseudo-period of oscillation (~10 s). Similar behaviour has been observed for the Cu 0.50 sample.

Water contents have been measured by using a Sartorius suspension balance. At ambient humidity conditions, around 2 wt% is present in the Cu 0.50 sample, involving the presence of several water molecules per Cu^{2+} ion.

Electron paramagnetic resonance

The e.p.r. spectrum of the Cu 0.75 sample as observed in Q band (*Figure 2*) exhibits three lines: a central line ($g = 2.1$) attributed to isolated divalent Cu^{2+} ions and two side lines clearly due to a magnetic species of spin $S = 1$, which will be shown to correspond to Cu^{2+}–Cu^{2+} pairs; the splitting between these two lines is about 3700 G (fine structure parameter D equal to $0.35\ cm^{-1}$). At low temperature, the side lines are much weaker than at room temperature, implying that the exchange interaction in the copper dimers is antiferromagnetic. The ground state is a singlet state ($S = 0$) and the observed magnetic triplet state ($S = 1$) is an excited state populated only by thermal excitation. Let us define the dimerization ratio x as the ratio of the mass of the copper ions involved in copper pairs to the total copper mass, J as the exchange energy, and I_M and I_D as the respective intensities of the central and side lines. The temperature dependence of the spectrum may then be described by the following law:

$$\frac{I_D}{I_M} = A\frac{x}{1-x}\frac{4}{3+e^{J/kT}} \tag{1}$$

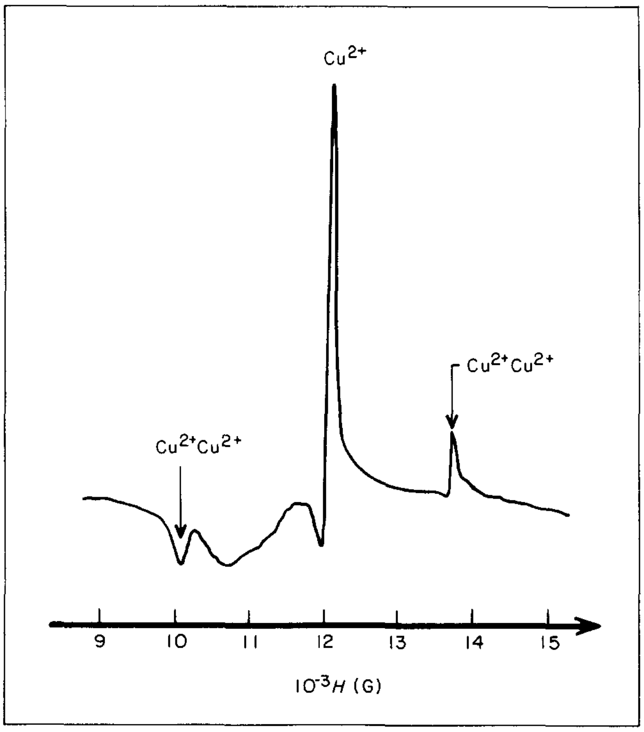


Figure 2 Spectrum at 35 G of sample Cu 0.75 obtained at $T \sim 150$ K

in which k is the Boltzmann constant, and A is a proportionality factor, which is a complicated function of the parameters of the spin Hamiltonian and also of the e.p.r. lineshape and linewidth. On the basis of experiments reported in the following sections, J is roughly estimated as 450 K. A rough estimation of A has been obtained by computer simulation of the powder spectrum observed. A first evaluation of the dimerization ratio was therefore obtained:

$$0.8 \leqslant x \leqslant 0.7 \qquad \text{for Cu 0.75 sample}$$

The e.p.r. spectra obtained in X band, observed many years ago on similar polymers[6] and on styrene[12] or butadiene[6] methacrylic copolymers, are consistent with these results. They exhibit a strong e.p.r. band at $g = 2.1$ and a weaker one at higher magnetic field; this weak line belongs to the high-field side line observed in Q band but the corresponding low-field one is no longer observable in X band. Again this line is strongly temperature-dependent and practically disappears at 77 K.

The interesting new feature of the X band spectrum is that structure is observed on the low-field side of the line. This structure is poorly resolved at room temperature but well resolved if the temperature is lower than T_g. This structure is due to the hyperfine interaction of the electronic spin of Cu^{2+} with the nuclear spin ($I = 3/2$) of the two isotopes ^{63}Cu and ^{65}Cu. The hyperfine constant observed is $A \simeq 0.015\ cm^{-1}$. For $T \geqslant T_g$ the e.p.r. linewidth increases as a consequence of the motion, and the hyperfine structure disappears. For $T \leqslant T_g$ it may be reasonably expected that the large residual linewidth (150 G) does not depend on temperature and, in this case, the temperature-dependent intensity ratio I_D/I_M may be related only to the theoretical population factor of the triplet state:

$$\frac{I_D}{I_M} \approx \frac{4}{3+e^{J/kT}} \tag{2}$$

However, experimental investigation of this law may be performed only in a narrow range of temperature below T_g because I_D becomes difficult to measure below 145 K.

Only two spectra (145 and 175 K) have therefore been used to estimate J: 450 ± 70 K ($310\ cm^{-1}$).

Magnetic susceptibility measurements

In the preceding section we have discussed the dependence of I_D and I_M on e.p.r. parameters such as linewidth and lineshape; as a consequence the estimation of x, the dimerization ratio, so far obtained is rather approximate. It is possible to obtain a more accurate value of x from static magnetic susceptibility measurements. We report now results obtained with this technique.

The contribution of the two types of copper ions (isolated and dimers) to the magnetic susceptibility χ may be described, to a first approximation, by the following expression:

$$\chi = \chi_M + \chi_D = \frac{C}{T}(1-x) + \frac{Cx}{T}\frac{4}{3+e^{J/kT}} \tag{3}$$

Here χ_M and χ_D refer to monomer and dimer respectively, and C is the Curie constant given by the expression:

$$C=\frac{[\mathrm{Cu}]g^2\beta^2}{4k}$$

where [Cu] is the number of Cu^{2+} ions per gram, β the Bohr magneton, k the Boltzmann constant and g the spectroscopic factor (measured by e.p.r.). Finally the only parameters in a fitting procedure are x (dimerization ratio) and J (exchange energy).

In the low-temperature range ($6 \leqslant T \leqslant 70$ K), the dimer contribution χ_D is negligible:

$$\chi \simeq \chi_M = \frac{C}{T}(1-x)$$

This is the Curie law, involving only x as a parameter. We see that x is directly measured in this temperature range, even if we do not know J. In the high-temperature range ($70 \leqslant T \leqslant 300$ K) dimerized copper ions have to be taken into account; they indeed induce a weak but observable deviation from the Curie law (*Figure 3*). The computer mean square procedure permits one to obtain J (470 K or 320 cm^{-1}). The precision of this measure of J is low; however, these results corroborate the value first obtained by the e.p.r. technique. In fact, as a consequence of the low temperature (6 K) and of the high applied magnetic field (40 kG), the Curie law is only a rough approximation. Actually, the fitting procedure was performed using a Brillouin law in place of the simpler Curie law:

$$\chi_M+\chi_D=-C(1-x)\frac{2k}{g\beta H}\left[2\coth\left(\frac{-g\beta H}{kT}\right)-\coth\left(\frac{-g\beta H}{2kT}\right)\right]+\frac{Cx}{T}\frac{4}{3+e^{J/kT}} \qquad (4)$$

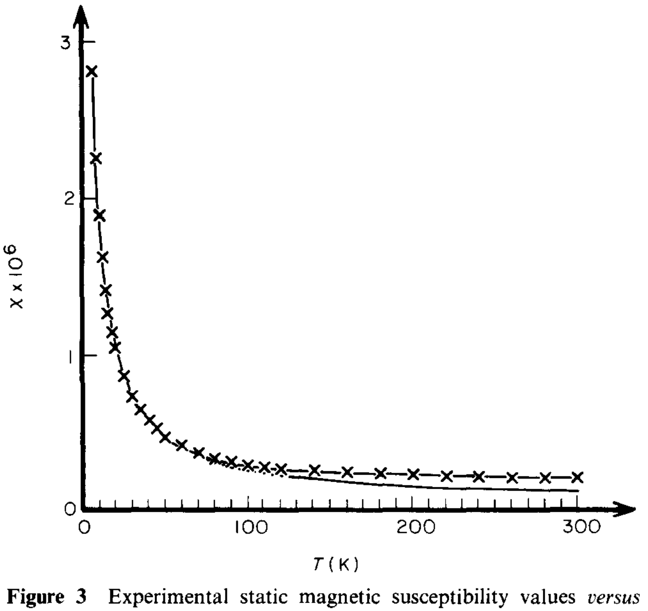


Figure 3 Experimental static magnetic susceptibility values *versus* temperature for the Cu 0.75 specimen (×). The lower full curve corresponds to a Brillouin law associated with the isolated copper ions. The upper full curve corresponds to the best fit when adding to this isolated contribution the dimer contribution according to equation (4)

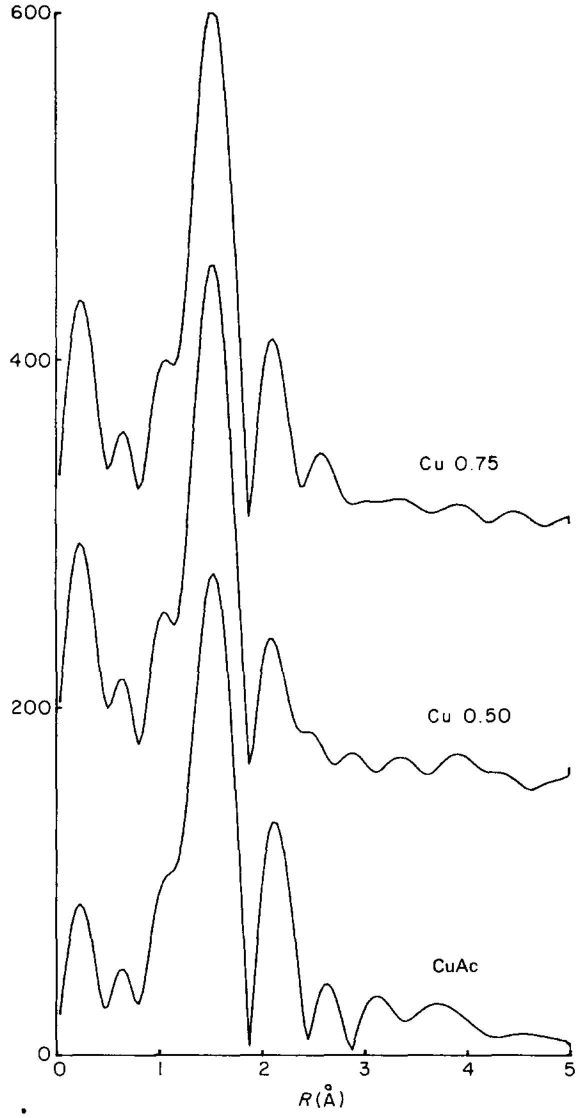


Figure 4 Fourier transform data of $k^3\chi(k)$ for the corresponding samples

The x values obtained from such a fitting procedure are respectively 0.7 for Cu 0.75 and 0.78 for Cu 0.50.

EXAFS

Data processing similar to that described in the preceding publication[1] on Fe^{3+} salts has been used for these Cu^{2+} salts. The Fourier transform moduli of the k^3 weighted EXAFS spectra are shown in *Figure 4*. Two well separated peaks are easily assigned to copper–oxygen and copper–copper bonds. Back-transformation to the k-space of each peak and of both peaks simultaneously have given excellent fits when using the experimental phaseshifts extracted from the CuAc reference compound. The deduced structural parameters (R_i, N_i, σ_i) for the two neighbouring shells are listed in *Table 1*.

The coordination number of the first shell, corresponding to the oxygen atoms, is the same for the Cu 0.50, Cu 0.75 and copper acetate samples. A decrease in the coordination number is observed for the second shell when increasing the extent of neutralization. This second shell is associated with the Cu–Cu pairs in copper acetate. A parallel change is observed for the Debye–Waller factor values. The influence of annealing has been studied for the Cu 0.75 sample. A decrease in the number of neighbours is observed for the first shell upon annealing.

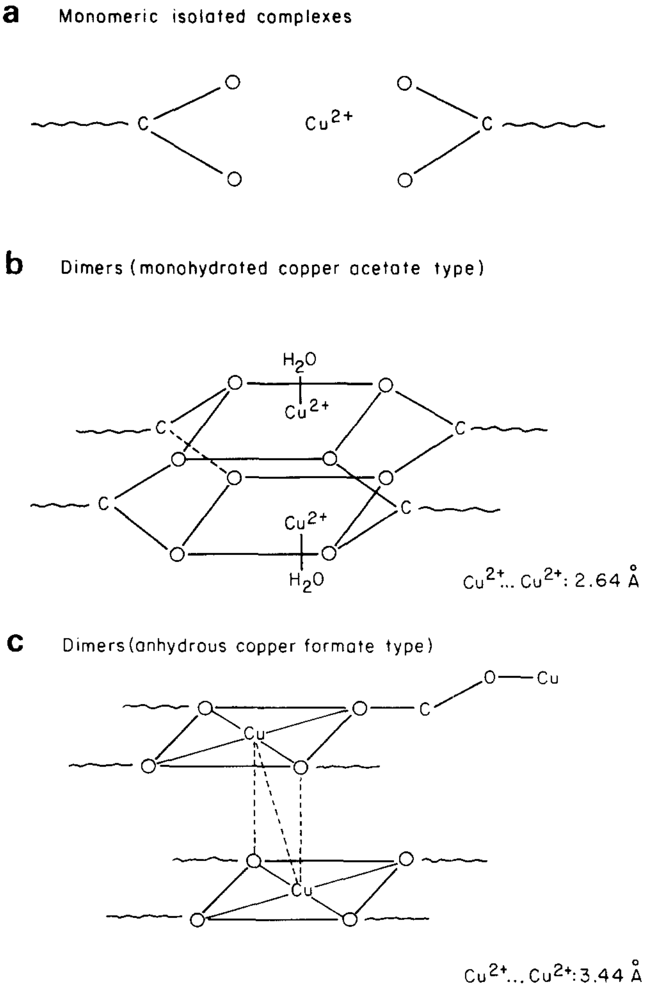
Table 1 EXAFS parameters obtained from *Figure 4*. N_{Cu-O} is the number of oxygen atoms in the first shell, R_{Cu-O} is the corresponding distance and σ_{Cu-O} is the Debye–Waller factor. N_{Cu-Cu}, R_{Cu-Cu} and σ_{Cu-Cu} are the corresponding values for the second shell associated with Cu

Sample	N_{Cu-O}	R_{Cu-O} (Å)	σ_{Cu-O} (Å)	N_{Cu-Cu}	R_{Cu-Cu} (Å)	σ_{Cu-Cu} (Å)	E_0 (eV)	ΔE_0 (eV)
CuAc	4.0	1.97	0.00	1.0	2.64	0.000	8988.0	0.0
Cu 0.50	4.0±0.4	1.97±0.01	0.00±0.02	1.0±0.2	2.63±0.02	0.074±0.02	8991.0	0.0±1.0
Cu 0.75	4.1±0.4	1.97±0.01	0.00±0.02	0.7±0.2	2.64±0.02	0.031±0.02	8991.0	0.0±1.0

DISCUSSION AND CONCLUSION

The local structures existing in these copper-neutralized carboxy telechelic polymers consist of both isolated and dimeric copper complexes, as shown in *Figure 5*, the proportion of each species depending on the total copper concentration. The exchange energy (measured by J) and its anisotropic part (measured by D) for these dimeric copper complexes have been found to be quite close to the values obatined for the corresponding dimers in copper acetates[13]. The dimer structure formed by the Cu^{2+} ions and the carboxylate endgroups therefore have a very similar structure to these acetate copper complexes[14–16]. There is no evidence of any third species from our data, an excellent fit of the e.p.r. results being obtained with the two copper species. Such a result is also confirmed by the EXAFS fits. Another point to be discussed is a possible association of the isolated ions of Cu^{2+} dimers to form ionic clusters. If we suppose a statistical distribution of the copper ions in the form of isolated species, we would have average distances, respectively, of ~22 and 25 Å for the Cu 0.75 and Cu 0.50 samples. The hyperfine structure observed for both specimens is not consistent with Cu–Cu distances ≤ 4 Å[17] with the presence of ionic clusters formed from the isolated Cu^{2+} ions. No information concerning possible aggregation of the Cu^{2+} dimers is obtained from these e.s.r. and EXAFS experiments. Clustering of Cu^{2+} ions has been suggested from small-angle X-ray scattering experiments[18], from which the distance between the scattering domains derived from a Bragg analysis of the maximum appearing at low q is ~50 Å. A radius of ~6 Å was obtained by a Porod–Debye analysis of the asymptotic form of the scattered intensity. Such a result therefore implies association of dimers to give larger ionic scattering particles.

These results have also to be compared with those obtained on styrene–methacrylic acid copolymers neutralized with copper[12]. From e.p.r. experiments on a partially neutralized 4.4 mol% acid, the authors have shown the presence of three different kinds of copper complexes. Similar isolated Cu^{2+} and dimeric $Cu^{2+} \ldots Cu^{2+}$ complexes were characterized as in our halato telechelic samples. A third species has been proposed corresponding to dimers with larger $Cu^{2+} \ldots Cu^{2+}$ distances and giving complexes with the COO^- structure of anhydrous copper formate type (*Figure 5*). The magnetic properties of these different copper(II) complexes have been extensively described elsewhere[19]. No evidence of the lines associated with this third species has been found in these halato telechelic polymers.


a Monomeric isolated complexes

b Dimers (monohydrated copper acetate type)

c Dimers (anhydrous copper formate type)

Figure 5 Structures of Cu^{2+} carboxylate salts

Another result to be stressed is the relative decrease, observed from both magnetic and EXAFS measurements, in the number of Cu^{2+} dimers when increasing the percentage of neutralization. Formation of the Cu^{2+} dimers involves the association of four carboxylic endgroups. When increasing the extent of neutralization, such a structure may be more difficult to form, mainly because of viscosity problems, than the simple $Cu^{2+}(COO^-)_2$ complexes.

This last result may be contrasted with recent e.p.r. observations on manganese salts of sulphonated polystyrene ionomers[20]. Six well resolved absorption lines have been associated with isolated Mn^{2+} ions and a single-line spectrum associated with Mn^{2+} in multiplets. The proportion of these different Mn^{2+} ions was then obtained from a simulation of the observed spectra. The relative percentage of ions in multiplets has been found to increase when increasing the overall ion concentration. This result, however, concerns samples that have not been annealed at temperatures higher than T_g and are not in thermodynamic equilibrium. No information is given concerning the kinds of complexes forming these multiplets.

Such analysis in terms of isolated ions or ions with exchange interactions has already been performed in ethylene acrylic copolymers[21] neutralized with Mn^{2+} and in perfluorinated membranes exchanged[22] with Cu^{2+}. In the acrylic copolymers, when increasing the degree of neutralization, the authors found an increase in the relative number of Mn^{2+} in clusters or multiplets with a Mn^{2+} ... Mn^{2+} distance less than 10 Å. In the ion-exchange membrane similar behaviour has been analysed as corresponding to a continuous change in local concentrations of Cu^{2+} ions in a phase containing mainly the water molecules and the Cu^{2+} and SO$_3^-$ ions.

The general conclusion resulting from our data is therefore the importance of the anion and/or cation in the structure of the complex. The local structure of the Cu^{2+}–carboxylate complexes has been found to be the same in these telechelic compounds as in polybutadiene or polystyrene copolymers in which the COO$^-$ are statistically dispersed along the polymer backbone[5]. The fact that the Cu^{2+} dimer found in these two systems has the same geometrical parameters as in the acetate salts emphasizes the importance of the ions in the formation of the basic ionomer complexes. A possible association of these dimers may form the larger ionic scattering particles observed in SAXS.

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