blend compositions on the binodal line could be extracted from the diffusion profiles at various annealing temperatures. The other blend composition always was too close to unity to be measurable. The Flory–Huggins interaction parameter, calculated from the measured blend composition, is in good agreement with SAXS measurements on similar blends of PS and PBr_xS.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft (SFB 60). F.B. thanks the Graduiertenkolleg Polymerwissenschaften at the University of Freiburg, FRG.

Registry No. Polystyrene, 9003-53-6.

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An EPR Study of Copper(II) Complexes of Poly(L-ornithine) and Poly(L-2,4-diaminobutyric acid)

Yue Zou and Frederick T. Greenaway*

Department of Chemistry, Clark University, Worcester, Massachusetts 01610

Jonathon P. Pease

Damon Biotech, Inc., 119 Fourth Avenue, Needham Heights, Massachusetts 02194.

Received February 16, 1989; Revised Manuscript Received May 9, 1989

ABSTRACT: The interactions of poly(L-ornithine) and poly(L-2,4-diaminobutyric acid) with copper(II) in aqueous solution have been investigated by using EPR and electronic spectroscopy and potentiometric titration as a function of pH between 2 and 13. As with the copper(II)–poly(L-lysine) system, many more complexes are found to be in pH-dependent equilibrium than previous reports for these systems have indicated. The complexes correspond to progressive replacement of the inner-sphere water molecules of the Cu(II) ion as the pH is raised, first by side-chain amines, then by deprotonated peptide nitrogens, and finally by hydroxide ligands. The length of the side chain strongly affects these equilibria. This is most noticeable in the unusual stability of the chelate of poly(L-2,4-diaminobutyric acid), where two amine and two deprotonated peptide ligands are bound to the copper even at pH values as low as 5. This provides evidence for a chelate effect indicating that adjacent Cu(II) ligands are nitrogen atoms from amine and peptide groups of the same amino acid residue, binding to form a six-membered ring. The similarity between the EPR parameters for the three systems indicates similar ligand environments in contrast to previous suggestions that deprotonated peptide nitrogens are adjacent ligands in the copper(II)–poly(ornithine) system.

Introduction

The interactions of copper(II) ions with polylysine, $(Lys)_n$, polyornithine, $(Orn)_n$, and poly(diaminobutyric acid), $(Dab)_n$, have been studied by a variety of techniques.[1-16] Although it is clear that the nature of the species present in solution depends strongly on pH, details of the structures of these species has remained elusive. We have previously reported the results of an investigation of the $Cu(Lys)_n$ system using EPR spectroscopy,[16] where we identified a series of pH-dependent equilibria that helped explain differences in interpretation of many previous experiments. We now report the extension of these studies to the polyornithine and polydiaminobutyric acid systems, whose side chains have one and two fewer CH_2 groups, respectively.

Experimental Details

Poly(L-lysine) hydrobromide of molecular mass 4000–15 000 and 70 000–150 000 was purchased from Sigma Chemical Co. Poly(L-ornithine) hydrobromide and poly(L-2,4-diaminobutyric acid) hydrobromide of molecular weight 40 000–75 000 and 8000–12 000, respectively, were prepared according to published methods.[17] The polymers were dissolved in deionized water. Copper(II) was added as a concentrated solution of the perchlorate salt (Aldrich Chemical Co., Inc.), and pH was adjusted by addition of small volumes of concentrated $HClO_4$ or NaOH solutions. Replacement of perchlorate by chloride had no effect on the results. Solutions were 0.005 M in amino acid residues for the EPR, absorption, and potentiometric work. In order to have a more rapid attainment of equilibrium and thus more reliable

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* To whom correspondence should be addressed.

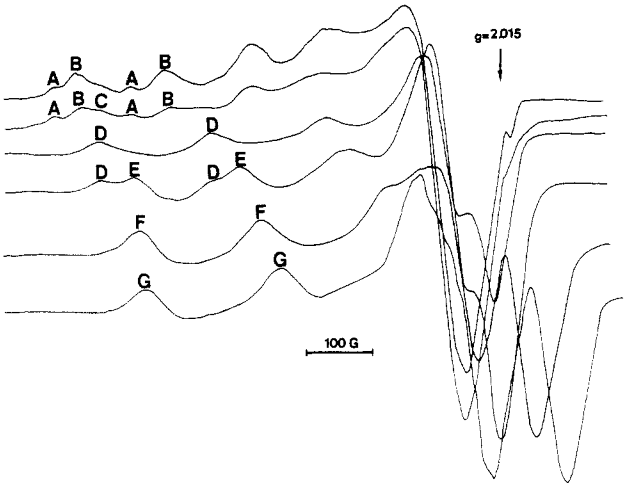

Figure 1. Representative X-band EPR spectra of 30:1 Orn:Cu frozen aqueous solutions at 110 K: microwave power, 20 mW; modulation amplitude, 5 G. The parallel copper hyperfine lines are identified by using the labels of Table I.

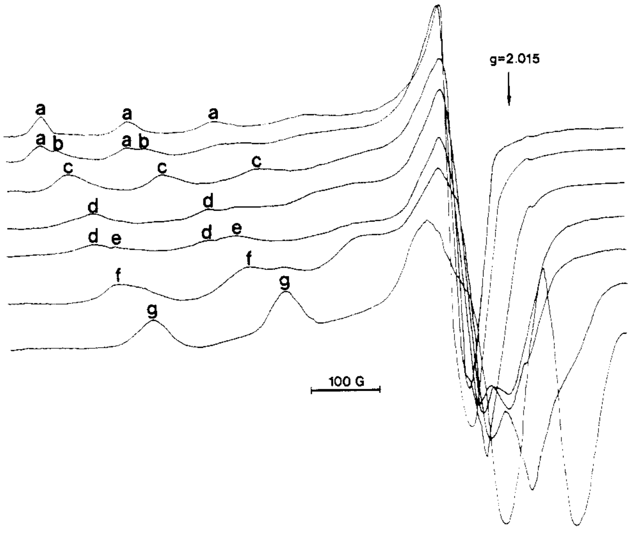

Figure 2. Representative X-band EPR spectra of 30:1 Dab:Cu. Conditions are the same as those for Figure 1.

results, the pH of the poly(amino acid) solutions was always raised to 13 first and then reduced to the desired pH by using acid.

EPR spectra were recorded by using a Varian E-9 EPR spectrometer operating at 9.1 GHz with 100-kHz modulation. Temperatures between 110 and 300 K were achieved by means of a nitrogen flow Dewar. The magnetic field was calibrated by using a Magnion gaussmeter, and the frequency was measured on a Hewlett-Packard frequency counter. Absorption spectra of solutions at 298 K were recorded on a Perkin-Elmer Lambda-3B spectrophotometer. Potentiometric titrations were made by using a Corning 130 pH meter with a combination Ag/AgCl glass electrode.

Results and Discussion

X-band EPR spectra of frozen solutions of Cu(Orn)$_n$ and Cu(Dab)$_n$ at 110 K (Figures 1 and 2) were typical of tetragonally elongated octahedrally coordinated Cu(II) with $g_\parallel > g_\perp$. As with Cu(Lys)$_n$,[16] we found no evidence of differences in the nature of the species present in solutions at 300 and 110 K, which validates comparisons between frozen solution EPR studies and liquid solution studies at 300 K. Eight Cu(II) species are observed in both systems. Since several species coexist at most pH values, the values of $A_\parallel$(Cu) and $g_\parallel$ given in Table I are quoted to fewer significant figures than is usual in such studies. When these parameters are plotted against one another, following the method of Peisach and Blumberg,[18] the results are found to be similar to those found for the Cu(Lys)$_n$ system.[16] Although in most cases no nitrogen superhyperfine structure was observed, the $A_\parallel/g_\parallel$ correlation and the widths of the parallel copper hyperfine lines that are dependent on the number of unresolved nitrogen superhyperfine lines were used to assign the ligand environments of the copper(II) ion.

The pH dependencies of the absorption spectra are shown in Figures 3–5 for Cu(Orn)$_n$ and Cu(Dab)$_n$. These compare well with the results of Phan et al.[11] for Cu(PLO)$_n$ but less well with the results of Palumbo et al.[8] probably because the solutions had not reached equilibrium in the latter case. Both the EPR and the absorption spectro-

Table I
EPR Parameters for Cu(Lys)$_n$, Cu(Orn)$_n$, and Cu(Dab)$_n$[a]

species	pH	$g_\parallel$	$A_\parallel$(Cu), cm^{-1}	assigned struct
A	<2	2.40	0.013	$[Cu(H_2O)_6]^{2+}$
B	2–3	2.34	0.014	$[Cu(H_2O)_5(LysNH_2)]^{2+}$
	2–4	2.34	0.014	$[Cu(H_2O)_5(OrnNH_2)]^{2+}$
	2–4	2.37	0.015	$[Cu(H_2O)_5(DabNH_2)]^{2+}$
C	3–5	2.33	0.015	$[Cu(H_2O)_4(LysNH_2)_2]^{2+}$
	3–5	2.33	0.015	$[Cu(H_2O)_4(OrnNH_2)_2]^{2+}$
	3–5	2.35	0.016	$[Cu(H_2O)_4(DabNH_2)_2]^{2+}$
D	5–6	2.30	0.015	$[Cu(H_2O)_3(LysNH_2)_3]^{2+}$
	4–6	2.27	0.018	$[Cu(H_2O)_3(OrnNH_2)_3]^{2+}$
	4–5	2.28	0.018	$[Cu(H_2O)_3(DabNH_2)_3]^{2+}$
E	6–8	2.24	0.017	$[Cu(H_2O)_2(LysNH_2)_4]^{2+}$
	5–9	2.23	0.018	$[Cu(H_2O)_2(OrnNH_2)_4]^{2+}$
	5–6	2.24	0.019	$[Cu(H_2O)_2(DabNH_2)_4]^{2+}$
F	8–9	2.22	0.018	$[Cu(H_2O)_2(LysNH_2)_3(RCONR)]^{+}$
	8–10	2.21	0.019	$[Cu(H_2O)_2(OrnNH_2)_3(RCONR)]^{+}$
	5–7	2.22	0.020	$[Cu(H_2O)_2(DabNH_2)_3(RCONR)]^{+}$
G	>9	2.16	0.021	$[Cu(H_2O)_2(LysNH_2)_2(RCONR)_2]$
	>9	2.17	0.021	$[Cu(H_2O)_2(OrnNH_2)_2(RCONR)_2]$
	>5	2.18	0.021	$[Cu(H_2O)_2(DabNH_2)_2(RCONR)_2]$
H	>12	2.27	0.019	$[Cu(OH)_4]^{2-}$

[a] 30:1 amino acid residue:Cu(II).

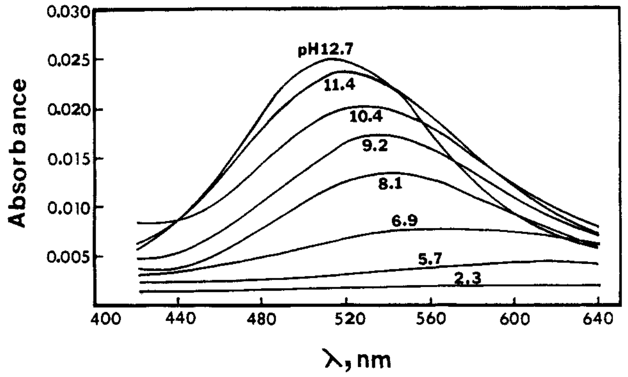

Figure 3. Representative absorption spectra of 30:1 Orn:Cu at 300 K. [Dab] = 0.005 M.

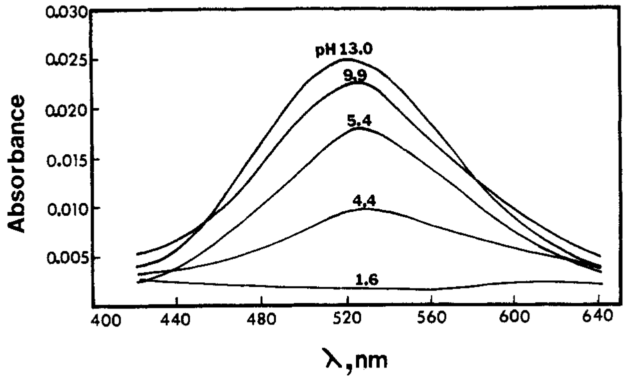

Figure 4. Representative absorption spectra of 30:1 Dab:Cu at 300 K. [Dab] = 0.005 M.

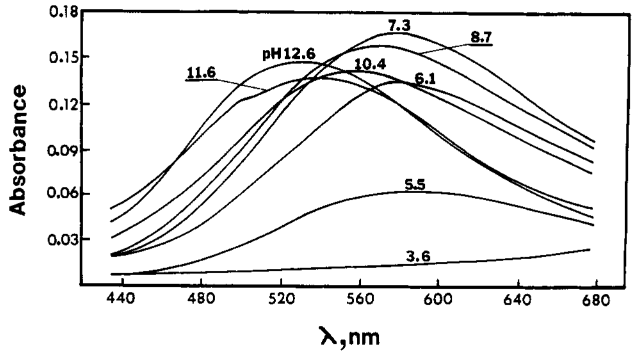

Figure 5. Representative absorption spectra of 4:1 Dab:Cu at 300 K. [Dab] = 0.005 M.

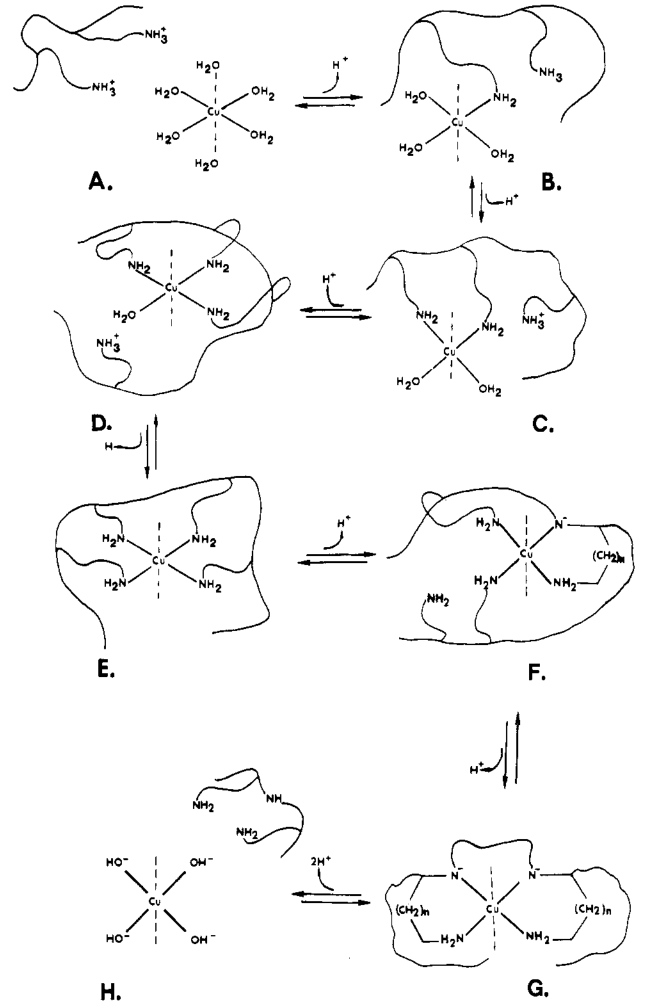

Figure 6. Diagrammatic representation of structures proposed on the basis of EPR parameters. Refer to Table I for details.

scopic results lead to the conclusion that as the pH increases, the ligand field about the Cu(II) increases in strength, causing a decrease in $g_{\|}$ and in the wavelength of the d–d transition. The EPR data show that this is due to replacement of water molecules first by amine nitrogen atoms and then by deprotonated peptide nitrogen atoms. Structures assigned to the species are indicated in Figure 6. As discussed previously,[16] the axial ligands are probably water molecules, although this has not been definitely established. The wavelength of the copper d–d band maximum has been correlated with the nature of the copper ligands by the equation[19]

$$\lambda_{\max}\ (\text{nm}) = 1000/[0.494N(\text{deprotonated peptide}) + 0.460N(\text{amino}) + 0.294N(\text{water or carboxyl})]$$

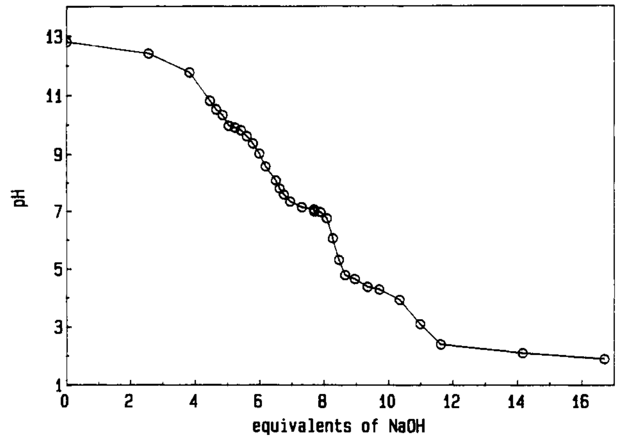

Figure 7. Potentiometric titration of a 4:1 Dab:Cu solution, initially at pH 13, with acid [Dab] = 0.005 M.

where N represents the number of axial ligands of each type. This equation predicts wavelengths of 850, 745, 663, 597, 543, 534, and 524 nm, respectively, for species A–G. For species G, the observed d–d band maxima are 517 nm for Cu(Dab)_n and 530 nm for Cu(PLO)_n, in good agreement with this prediction. Band positions cannot be accurately determined for species B–F because of band overlap from different species, but the energy of the band maximum and the intensity of the band do steadily decrease as the pH is lowered, as expected. Species with absorption bands below 560 nm result in deep violet-blue colors, sometimes thought to be characteristic of deprotonated peptide coordination to Cu(II).[8,19] However, species E also has a band near 540 nm, indicating that the violet color should not be used as an indication of coordination of deprotonated peptide nitrogens. Although species with this characteristic exist only at pH >8 for $(\text{Lys})_n$ and $(\text{Orn})_n$, for $(\text{Dab})_n$ such species are stable at a pH as low as 5.

Potentiometric titrations are commonly used to investigate Cu(II) binding to homopoly(amino acids). Published results for $(\text{Lys})_n$, $(\text{Orn})_n$, and $(\text{Dab})_n$ are not all in agreement because of slow attainment of equilibrium in some experiments.[4,6,8–11] To help explain our spectroscopic data and to be sure that kinetic effects were eliminated, we have therefore duplicated some of these titrations. As we observed with $(\text{Lys})_n$, binding of Cu(II) to $(\text{Orn})_n$ and $(\text{Dab})_n$ is very slow unless the pH is first raised to at least 11. Although the same species are ultimately observed, no matter how the final pH is attained, equilibrium can take up to several days to be established when copper is added to solutions of the polymers at pH <11. Therefore all titrations were carried out by adding standard acid solutions to solutions initially at pH 13. Even so, some considerable time is required to ensure that equilibrium has been reached after each addition of acid. A typical titration curve is shown in Figure 7 for Cu(Dab)_n with a 4:1 Dab:copper ratio. This curve extends over a wider pH range than previous studies.[8,9] The pH profiles are affected by the amino acid:copper ratio, but all reveal four inflection points, which we attribute to the following basic processes:

$$2\text{H}^+ + \text{Cu(OH)}_4{}^{2-} \rightarrow [\text{Cu(RCONR}^-)_2(\text{NH}_2)_2]$$

$$2\text{H}^+ + [\text{Cu(RCONR}^-)_2(\text{NH}_2)_2] \rightarrow [\text{Cu(RNH}_2)_4]^{2+}$$

$$2\text{H}^+ + [\text{Cu(RNH}_2)_4]^{2+} \rightarrow [\text{Cu(RNH}_2)_2(\text{H}_2\text{O})]^{2+} + 2\text{RNH}_3{}^+$$

$$2\text{H}^+ + [\text{Cu(RNH}_2)_2(\text{H}_2\text{O})_2]^{2+} \rightarrow [\text{Cu(H}_2\text{O})_4]^{2+} + 2\text{RNH}_3{}^+$$

These are consistent with our EPR data. Although others have reported coordination of three or four deprotonated peptide nitrogen atoms to Cu(II) at very high pH,[19] we did not observe any such species. Instead, we observed some formation of $Cu(OH)_4^{2-}$, particularly at high Cu:residue ratios.

The effects of changing the amino acid:copper ratio were also studied. Ratios were varied between 4:1 and 30:1. This caused minor shifts in equilibria, most noticeably with $Cu(Dab)_n$, for which species F is observed at pH as high as 9 for the lower amino acid ratio but only to about pH 6 for the higher amino acid ratio. This causes spectral differences between solutions of different amino acid:Cu ratios (Figures 4 and 5). Below a 15:1 ratio, copper hydroxide precipitation occurs between pH 8 and pH 11 (the exact range depending on the ratio) for $(Orn)_n$ and $(Lys)_n$ [3,5,6], but not for $(Dab)_n$ systems. The fact that $(Dab)_n$ gave no copper hydroxide indicates that coordination of Cu(II) to $(Dab)_n$ is much stronger than to $(Orn)_n$ at pH >7. To avoid precipitation of the copper hydroxide and to enable comparisons between the three systems under comparable conditions, comparative data are given for 30:1 ratios.

Although we have not studied the effect in detail, we have noticed that the ionic strength of the solution also affects the formation of the copper compounds, especially between pH 8 and pH 10. Increasing the ionic strength of the solution increases the amount of $Cu(OH)_2$ precipitating from solution between pH 8 and pH 11. We attribute this to greater charge neutralization at higher ionic strengths, which increases the stability of the free polymer and decreases the copper binding.

The Cu(II) complexes of $(Orn)_n$ have very similar EPR parameters to the $Cu(Lys)_n$ system, and absorption maxima are also similar. The fact that similar species are present at similar pH in the two systems shows that formation constants are of similar magnitude. Experimental similarities between the two systems have been noted before.[8,9,11] Some of the EPR parameters for the $Cu(Dab)_n$ system, while similar, are consistently slightly different from the other two systems. Because the uncertainty in these parameters is rather large, we have not attempted to interpret this in terms of basic electronic parameters. The difference is, however, also consistent with a slight difference in the absorption maxima for the three systems and suggests that Dab coordinates slightly more strongly to the copper, even when coordination is through the amine nitrogen only. This is not due to differences in basicity, since the γ-amine of Dab is a slightly weaker base than the the δ or ϵ-amines of Orn and Lys, as indicated by the pK_a values of the amino acids.[24]

The major difference among the three polymer systems is that $Cu(Dab)_n$ shows a significantly different pH dependence of the species populations. The equilibrium constants for the $Cu(Dab)_n$ system are substantially different from those for $Cu(Lys)_n$ and $Cu(Orn)_n$ above pH 6, with the result that only species present in any significant amount between pH 6 and 12 has the copper bound to two deprotonated peptide nitrogens and two amine nitrogens. The particular stability of the $Cu(Dab)_n$ system can only be explained in terms of a chelate effect, due to the formation of six-membered rings that stabilize the coordination of the deprotonated peptide. In $Cu(Orn)_n$ and $Cu(Lys)_n$ the ring size would be 7 and 8, respectively, which imparts negligible entropy of stabilization to the complex. This in turn indicates that the coordinated amine and deprotonated peptide are from the same amino acid residue in $(Dab)_n$, even when Dab:Cu ratios are quite high. Phan et al.[11] have suggested that adjacent peptide nitrogens are bound to Cu(II) at high pH in $Cu(Orn)_n$. However, since adjacent peptide nitrogens would coordinate equally well in all three polymers, our results indicate that this coordination mode is not important. Deprotonated peptides have been found to bind to Cu(II) in other systems at pH 5, although most such ligands were not polymeric and involved ligation of chain terminus groups.[20-23] In most of these structures, more than two adjacent ligands bind to the Cu(II), giving extra entropic contributions to stability.

Many studies implicate coordination of carbonyl groups at pH <7, although in general there is little clear evidence for this because there are few experimental techniques that can give unambiguous results for aqueous solutions. Carbonyl coordination has been shown to occur in the solid state.[19,21,25] We attempted FTIR studies of our solutions to try to resolve the question of whether the C=O coordinates to copper in preference to water at pH <7 but could not observe shifts in amide bands, such as would be expected to occur on coordination of the C=O to copper. Similarly proton NMR experiments could not detect the peptide hydrogen attached to the nitrogen, whose chemical shift should also be affected by coordination of the peptide carbonyl oxygen. The only selective broadening by Cu(II) we observed was for the γ-protons of Dab and the δ-protons of Orn, as expected for coordination of the amine nitrogen. We thus find no evidence for carbonyl coordination, although we cannot discount it.

Acknowledgment. This work was supported in part by The Kroc Foundation.

Registry No. Poly(L-lysine) hydrochloride (homopolymer), 25988-63-0; poly(L-lysine) hydrobromide (SRU), 26588-20-5; poly(L-ornithine) hydrobromide (homopolymer), 27378-49-0; poly(L-ornithine) hydrobromide (SRU), 27380-46-7; poly(L-2,4-diaminobutyric acid) hydrobromide (homopolymer), 108416-07-5; poly(L-2,4-diaminobutyric acid) hydrobromide (SRU), 108434-32-8; copper(II) perchlorate, 13770-18-8.

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Structure and Morphology of Ethylene–Vinyl Chloride Copolymers

M. A. Gomez,[†] A. E. Tonelli,* A. J. Lovinger, F. C. Schilling, M. H. Cozine,[‡] and D. D. Davis

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received October 27, 1988; Revised Manuscript Received May 2, 1989

ABSTRACT: A series of ethylene–vinyl chloride copolymers with a sequence distribution toward the alternating side of random and a wide range of comonomer content (up to 37.3 mol % vinyl chloride) have been examined in the solid state by diffraction and microscopic techniques and high-resolution ^{13}C NMR spectroscopy. Significant expansion of the unit cell in the *a* dimension, observed as the amount of chlorine in the copolymer increases, indicates a significant incorporation of the Cl substituents inside the crystal. X-ray diffraction also shows progressive intermolecular disorder with increasing vinyl chloride content, resulting in a change in the packing of chains from orthorhombic to pseudohexagonal. Differences in the chemical shifts of crystalline and amorphous CH(Cl) resonances, together with differences in their mobilities (T_1's) as observed by solid-state ^{13}C NMR spectroscopy, cooroborate the incorporation of Cl inside the crystal. Comparison of quantitative ^{13}C NMR spectra at temperatures above and below the melting point indicates that at least 20% of the Cl's reside inside the crystal. The irregular distribution of chlorine in our copolymers also affects their morphology. Electron microscopy showed the lamellar characteristics to progressively depart from those of polyethylene, although the preferred growth direction and the molecular chain axis tilt within the crystals are preserved for the copolymers with up to 2.4 mol % Cl content. For higher Cl contents, the crystals become increasingly more disordered and defective but retain an essentially lamellar character for copolymers with up to 21.2 mol % Cl.

Introduction

One of the most important and controversial aspects in the study of copolymer crystallization is the incorporation of branches or sidechains into the crystal. A large body of work has been devoted to this topic, especially for ethylene copolymers.[1-10] While some theories[1,11] consider the side chains and branches to be totally excluded from the crystals during the crystallization process, experimental results seem to indicate that they are at least partially incorporated in some cases.[2-5] In their kinetic theory of copolymer crystallization, Helfand and Lauritzen[7] have removed the assumption that only one of the two comonomer units constituting a copolymer is permitted to enter the crystal. They found that the composition of comonomer units in the crystal increasingly departs from their equilibrium composition as the rate of crystallization is increased by lowering the crystallization temperature. We will discuss their result in relation to the observations made here on crystalline ethylene–vinyl chloride copolymers.

In the case of ethylene copolymers, it seems to be generally accepted that methyl groups are easily incorporated into the crystal,[3,8,12,13] but there are different points of view in relation to other longer and bulkier branches.[3,5,12] Experimentally, the expansion of the unit cell as determined by X-ray diffraction has been considered as proof of the incorporation of the branches, although it has been pointed out that other factors can also account for this expansion.[12,14] The extent to which the branches are accommodated has been reported to depend upon the side-chain length and crystallization conditions. Baker and Mandelkern[3] studied several ethylene copolymers and found that methyl groups expand the crystal lattice while larger branches do not. However, other workers[2,5,15] concluded that longer branches, up to ten carbons in length, could be incorporated in the crystal lattice as evidenced by X-ray diffraction.

Supporting experimental evidence comes from the dependence of the melting behavior of copolymers on their comonomer composition. It has been concluded that methyl groups not only enter the crystal lattice in a significant proportion, but they do so as part of an equilibrium process,[12,13] resulting in significantly higher melting temperatures than ethylene copolymers with longer alkyl-type side chains. Branches larger than methyl groups were found[12] to be excluded from the crystal and their melting behavior to be very dependent on overall comonomer concentration and distribution but independent of the chemical nature of the side chain.[12]

Apparently many factors affect the incorporation of these branches into the crystalline lattice. However, even more important is the establishment of their distribution between amorphous, interfacial, and crystalline phases and the characterization of the degree of disorder introduced into the crystal by their incorporation. Several studies have dealt with this topic employing mainly small-angle X-ray and neutron scattering[9,16,17] and recently solid-state ^{13}C NMR.[18-21]

In previous work,[22-24] we have studied and characterized by different techniques a series of ethylene–vinyl chloride (E–V) copolymers. These copolymers were obtained by reductive dechlorination of poly(vinyl chloride), and they have a "random"-like comonomer sequence distribution. Because they are all obtained from the same parent compound, each copolymer is of the same average chain length and polydispersity; the major distinguishing characteristic among them is their chlorine content. Moreover, the van

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[†] Permanent address: Instituto de Ciéncia y Tecnología de Polimeros, Juan de la Cierva 3, 28006 Madrid, Spain. Work done while at AT&T Bell Labs.

[‡] Permanent address: Department of Chemistry, Yale University, New Haven, Connecticut. Work done while at AT&T Bell Labs.

0024-9297/89/2222-4441$01.50/0