

ARTICLES

Role of Hydrophobicity on Structure of Polymer–Metal Complexes

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Metal complexation of a series of polymeric gels, with different degrees of ionization, prepared from acrylic acid and acryloyl amino acid monomers ($\text{CH}_2=\text{CHCONH}(\text{CH}_2)_n\text{COOH}$, where $n = 4, 6$ and 8), were investigated. The binding of Cu(II) ions to the gels was studied by means of swelling, quantitative determination of the amount of “bound” or complexed Cu(II), and EPR spectroscopy of Cu(II) complexes. Both the amount of Cu(II) and the structure of polymer–Cu(II) complex were influenced by the length of the pendent chain, i.e., “hydrophobicity” of the polymer gels. The metal uptake by the gels increases with increasing “hydrophobicity”. Two types of polymer–Cu(II) complexes (monomer and dimer, respectively) were identified by EPR spectroscopy, their concentrations were found to be a function of hydrophilic–hydrophobic balance of the polymer gels.

Introduction

Metal complexation is a process by which certain inorganic metal ions coordinate with organic functional groups through ionic bonds, coordination bonds, and ion dipole interactions to form organometallic hybrids having many interesting properties and applications. Metal complexation with polymers is used in wastewater treatment for selective removal of toxic metal ions^{1–4} and to improve the thermal properties of polymers.^{5–7} An important application of polymer–metal complexes is in the area of catalysis. Catalytically active organic polymers can be obtained through the coordination of certain transition metal ions with functional groups on the polymers.^{8,9} Recently, metal-complexed stimuli responsive polymer gels have been used to produce smart catalysts, which combine the advantages of homogeneous catalysis such as high activity and high selectivity with those of heterogeneous catalysis such as long life and easy separation.^{10–12} The catalytic function of polymer–metal complex depends on the structure of the complexes. In this paper we investigate the role of “hydrophobicity” of polymer gels on the structure of the metal-gel complexes.

The effect of mono-, di-, and polyvalent metal ions on the swelling behavior of gels has been investigated earlier.^{13–16} The observed decrease in swelling capacity of polyelectrolyte gels in the presence of mono- and divalent alkaline earth metal ions is mainly due to the screening effect. However, the decrease in swelling of gels in the presence of multivalent transition metal ions is mainly due to complexation of the ions with the polymer network, which increases its apparent cross-link density.¹⁷ Transition metal ions also affect the volume transition temper-

ature of thermoreversible gels by subtly modifying the hydrophobic–hydrophilic balance.^{1,18}

The hydrophilic and hydrophobic interactions in the gel also influence the metal uptake by the gel. Lehto et al.¹⁹ found an enhancement of metal uptake in *N*-isopropylacrylamide copolymer gels containing ionic comonomers over that of the homopolymer gel. Sasaki et al.²⁰ showed that the binding efficiency of Ca^{2+} to polyelectrolyte gels increased with an increase in the hydrophobicity of the gels.

There are very few reports on the understanding of the influence of hydrophobic and hydrophilic interactions on the structure of the polymer–metal complexes. Kruczala et al.²¹ reported two type of monomeric Cu(II)–poly(acrylic acid)s in which Cu^{2+} was complexed with one or two carboxylic acid groups on the polymer chains. El-Sonbati et al.²² reported the formation of binuclear Cu(II) complexes with poly(5-vinylsali-cylenedene-2-aminopyridine). Schlick et al.²³ reported the formation of Cu(II)–Cu(II) dimer in Nafion membranes. In this paper we investigate specifically the influence of hydrophobic interactions in a series of acrylic acid and acryloyl amino acid gels on the structure of gel–Cu(II) complexes. Our goal is to design potential organometallic hybrids with varying nuclearity. Examples of such hybrids include protein-supported copper complexes, which are well-known catalysts for biological functions.²⁴ The present study, therefore, would hopefully provide insight into designing new polymeric catalysts based on the understanding of the effect of molecular interactions on the structure of the polymer–metal complex.

Experimental Section

Materials. Acrylic acid (AAc) and 8-aminocaprylic acid were obtained from Aldrich Co. *N,N'*-methylenebis(acrylamide) (Bis-Am, cross-linking agent), ammonium persulfate (APS, initiator), *N,N,N',N'*-tetramethylethylenediamine (TEMED, accelerator),

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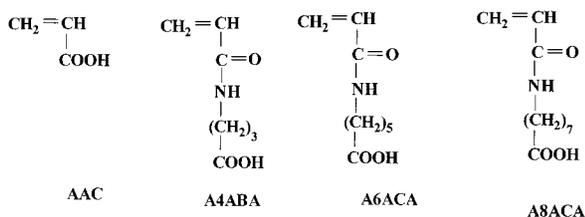


Figure 1. Structures of the monomers used in the preparation of the gels.

thionyl chloride, copper chloride (CuCl_2), and sodium hydroxide (NaOH) were all procured from S. D. Fine Chemicals, India. 4-Aminobutyric acid and 6-aminocaproic acid were obtained from SRL, India.

Synthesis of Acryloyl Chloride. Acryloyl chloride was synthesized by reacting acrylic acid with thionyl chloride.²⁵ To a mixture of 40.1 mL of acrylic acid (0.6 M) along with 3 mL of dimethylformamide and 5 g hydroquinone was added dropwise 46 mL of freshly distilled thionyl chloride, over a period of 3 h. After complete addition of thionyl chloride, the reaction mixture was maintained at 333 K for 6 h with continuous stirring. Pure acryloyl chloride was distilled out at 343 K. Polymerization of the acryloyl chloride was prevented by adding hydroquinone.

Synthesis of Monomers. The hydrophobic monomers were synthesized by reacting the respective amino acids with acryloyl chloride.²⁵ The structures of the monomers are shown in Figure 1.

Acryloyl-4-aminobutyric acid (A4ABA). A clear solution of 4-aminobutyric acid (10.3 g, 0.1 M) in 80 mL of water containing 4 g of NaOH was prepared, and to this was added dropwise 9 mL (0.1 M) of acryloyl chloride in 9 mL of dichloromethane over a period of 1–2 h at 278–283 K. While adding acryloyl chloride, the pH of the solution was maintained between 7.5 and 7.8. Dichloromethane and unreacted acryloyl chloride were removed by extracting with ethyl acetate. The clear aqueous layer was acidified to pH 5.0–5.5 and extracted with ethyl acetate. The product in the ethyl acetate layer was dried using anhydrous sodium sulfate and concentrated. The concentrate was precipitated in petroleum ether. It was further purified by dissolving in ethyl acetate and reprecipitating in petroleum ether.

Other acryloyl-derivatized amino acids such as acryloyl-6-aminocaproic acid (A6ACA) and acryloyl-8-aminocaprylic acid (A8ACA) were synthesized by reacting acryloyl chloride with respective amino acids as described above.

Synthesis of Gels. AAC, A4ABA, A6ACA, and A8ACA homopolymer gels were synthesized by free radical polymerization of the respective monomers in water using Bis-Am as cross-linker and APS as an initiator in the presence of TEMED as an accelerator. To a well-stirred aqueous solution of 1 mol of monomer, 10 mol % of cross-linking agent, and 40 mg of initiator was added 50 μL accelerator. Nitrogen gas was continuously bubbled through the solution. The homogeneous solution so obtained was poured into glass test tubes and sealed. Polymerization was carried out at 333 K for 24 h. After polymerization the gel rods were taken out of the tubes and immersed in water for 72 h to remove the unreacted reactants. Fresh water was added frequently during washing. The washed gels were dried in an oven at 323 K to constant weight. The pH of this gel (hereafter referred to as “un-ionized gel”) was 2.6. The “un-ionized” gel is the acid form of the gel, which means that carboxyl groups exist in non-ionized “–COOH” state. The “partially ionized” and “completely ionized” gels were

prepared by adjusting the pH of the reactants with aqueous NaOH to 7.6 and 12.1, respectively. In the “partially ionized” gels some of the carboxyl groups exist in their salt form, i.e., $-\text{COO}^-\text{Na}^+$ state. However, in the “fully ionized” gel most of the carboxyl groups are in their salt form. This was verified by using excess NaOH to ensure complete ionization of the carboxyl groups and then measuring the swelling capacity of the gel. Ionization increases the swelling capacity of the gel due to the electrostatic repulsion between the charges on the network. After complete ionization of all the carboxyl groups in the gel, the swelling capacity of the gel remains unchanged. The un-ionized gels were opaque, the partially ionized gels were translucent, and the completely ionized gels were transparent.

Complexation of Gels with Metal Ions. The complexation of the gels with Cu(II) ions was carried out by the batch equilibrium method. Dried gels were placed in CuCl_2 solution and allowed to equilibrate for 72 h. Metal uptake was investigated using a Shimadzu UV-420 UV–visible spectrophotometer. The concentrations of the metal ions before and after complexation were estimated following the intensity of the d–d band at 810 nm. For spectrophotometric estimation, standard solutions of CuCl_2 of different concentrations were prepared and their absorbance was measured to plot a calibration curve. The concentration of copper uptake by the gels was estimated using this calibration curve and the copper content in gels is listed in Table 1.

Swelling Ratio Measurements. Dried gels of known weights were immersed in CuCl_2 solutions (0.1 M) as well as in pure water for 72 h until equilibrium swelling was achieved. Swelling ratios of the gels were measured gravimetrically. The swelling ratio (Q) was defined as the weight of the solvent uptake per unit mass of the dried polymer.

$$Q = \frac{\text{weight of the equilibrated gel}}{\text{weight of the dried gel } (W_d)}$$

EPR Studies. EPR spectra of the complexed gels were recorded in the temperature range 77–298 K by using a Bruker EMX spectrometer operating at X and Q-band frequencies. A field modulation of 100 kHz was used. The microwave frequency was calibrated with a frequency counter fixed in the microwave bridge Bruker ER 041 XG-D and the magnetic field was calibrated using a Bruker ER 035 M NMR Gaussmeter. Spectral editing and simulations were done by using the Bruker WINEPR and Simfonia software packages.

Results and Discussion

When a weakly cross-linked gel is immersed in an aqueous solution of CuCl_2 (0.1 M), the Cu(II) ions bind to the polymeric network and the gel attains a collapsed state, as indicated by the swelling behavior tabulated in Table 1. The gel that is equilibrated with the salt solution of the metal ion contains, in general, two types of metal ions, those complexed with the polymer chain and those simply osmotically absorbed along with the solvent (water) in the gel matrix. The metal ions absorbed by the polymer network can be estimated by assuming that the concentration of metal ions outside the solution is equal to the concentration of metal ions inside the gel.¹⁴ We have calculated the amount of metal ions that are complexed with the polymeric network by subtracting the absorbed quantity of metal ions from the total metal uptake. The amount of metal ions absorbed into the polymer network was calculated using the following equation.

TABLE 1: Swelling Behavior of Polyacid Gels in Water and CuCl₂ Solutions

gel	swelling ratio in water ^a (g/g)	swelling ratio in CuCl ₂ ^a (g/g)	amt of Cu(II) complexed (g mol/g)	% COOH groups complexed ^b	monomeric species ^c	dimeric species ^c
AAc(H)	4.4	2.3	1.2×10^{-4}	1.6	<i>d</i>	<i>d</i>
AAc(Na/H)	16.3	4.9	1.7×10^{-3}	24	<i>d</i>	
AAc(Na)	24.8	4.8	1.3×10^{-2}	26	<i>d</i>	
A4ABA(H)	1.1	1.0	5.0×10^{-5}	1.6	<i>d</i>	<i>d</i>
A4ABA(Na/H)	24.9	1.1	9.3×10^{-4}	28	<i>d</i>	<i>d</i>
A4ABA(Na)	98.8	1.0	9.9×10^{-4}	30	<i>d</i>	
A6ACA(H)	1.0	1.0	5.4×10^{-5}	1.8	<i>d</i>	<i>d</i>
A6ACA(Na/H)	147.0	1.9	2.4×10^{-4}	32	<i>d</i>	
A6ACA(Na)	230.0	1.0	9.8×10^{-4}	36	<i>d</i>	<i>d</i>
A8ACA(Na)		1.0	9.8×10^{-4}	40	<i>d</i>	<i>d</i>

^a Swelling measurements made 4 h after immersion in salt solution. ^b % complexation = 100(gram moles of metal ion complexed)/gram moles of COO⁻ on dry gel. ^c EPR studies. ^d Present.

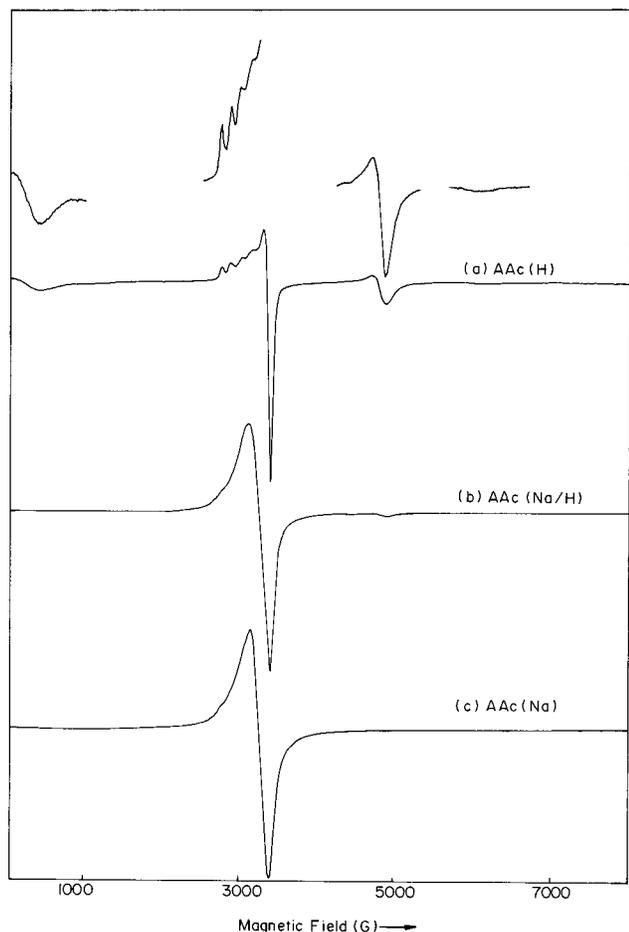


Figure 2. EPR spectra of Cu(II)-AAc gels as a function of degree of ionization at 298 K.

$$AD = C_0 V_1 \quad (1)$$

where AD is the moles of metal ions absorbed, C_0 is the concentration of the metal solution outside the gel, and V_1 is the amount of water picked up by gel. V_1 can be estimated from the swelling capacities reported in Table 1. In all gel systems it was observed that a very small amount of metal ions was absorbed by the polymer network while most of the metal ions were coordinated with or “adsorbed” on the chains. Evidently, the gels collapse in the presence of the metal ions, which serve additional “cross-links” through interchain complexation. The swelling ratio of the acid form of the gels (i.e., un-ionized gels) in pure water decreased with the alkyl chain length, as shown in Table 1. This is expected since the linear polymers having longer alkyl side chains are more hydrophobic and hence absorb

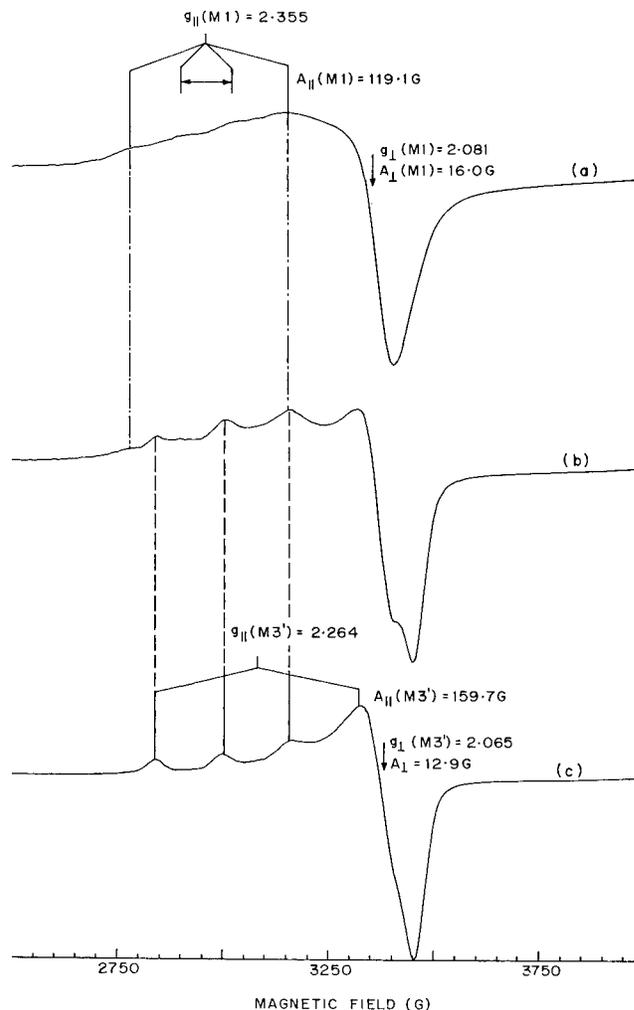


Figure 3. EPR spectra of monomeric Cu(II) species in A6ACA gels as a function of degree of ionization at 298 K.

less water. However, the salt form of the gels (i.e., ionized gels) showed a reverse trend in that the swelling ratio increased with the alkyl chain length. This seemingly anomalous swelling behavior of the salt form of gels could be possibly due to two reasons: The first reason pertains to the cross-link density of the gels.²⁶ Since we do not have direct control over the cross-link density during polymerization, it is possible that gels with longer alkyl side chains happen to have lower cross-link density and hence swell more. The other possible reason could be that the longer flexible side chains place the ionic charges at a finite distance away from the main chain, because of which the polymer chains are forced to adopt a more “open” configuration

TABLE 2: EPR Spin Hamiltonian Parameters of Cu(II) Complexed Polymer Gel

gel	species	g_{\parallel}	g_{\perp}	g_{av}	A_{\parallel} (G)	A_{\perp} (G)
AAc(H)	M1	2.356	2.076		128.8	<i>a</i>
AAc(Na/H)	M2			2.119		
	M3	2.325	2.082		150.5	
AAc(Na)	M2'			2.133		
A4ABA(H)	M1	2.360	2.088		125.2	<i>a</i>
A4ABA(Na/H)	M1	2.358	2.085		119.8	<i>a</i>
A4ABA(Na)	M3	2.328	2.083		150.2	<i>a</i>
A6ACA(H)	M1	2.367	2.082		119.1	16.0
	M3'	2.264	2.071		159.7	12.9
A6ACA(Na/H)	M3'	2.264	2.065		159.7	12.9
A6ACA(Na)	M1	2.355	2.081		119.1	16.0
A8ACA(Na)	M1	2.352	2.081		120.1	<i>a</i>

^a Hyperfine features not resolved.

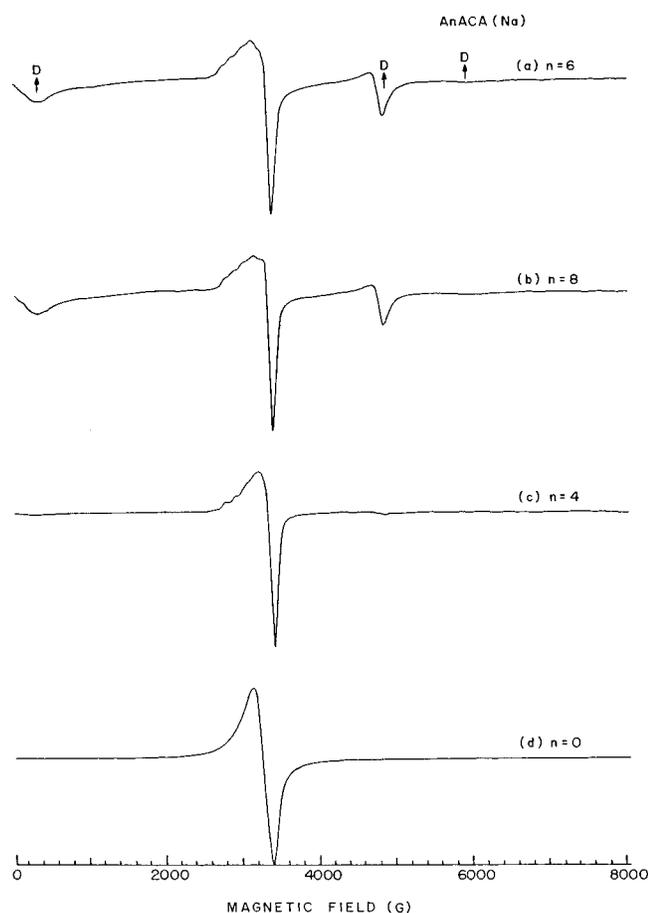


Figure 4. EPR spectra at 298 K showing the effect of hydrophobic alkyl chain length on Cu(II) species in the completely ionized Cu(II) complexed AAc, A4ABA, A6ACA, and A8ACA gels.

in order to overcome the electrostatic repulsion; hence the higher swelling capacity.

The percentage of carboxyl group involved in complexation is defined as follows:

$$\% \text{ COOH group in complexation} = 100 \times \frac{\text{gram moles of metal ion complexed}}{\text{gram moles of COO}^- \text{ on dry gel}}$$

Our experimental data in Table 1 indicate that as the alkyl chain length of the gel increases, the percentage of COOH groups involved in complexation increases. These findings are similar to those of Sasaki et al.²⁰ who observed that the binding

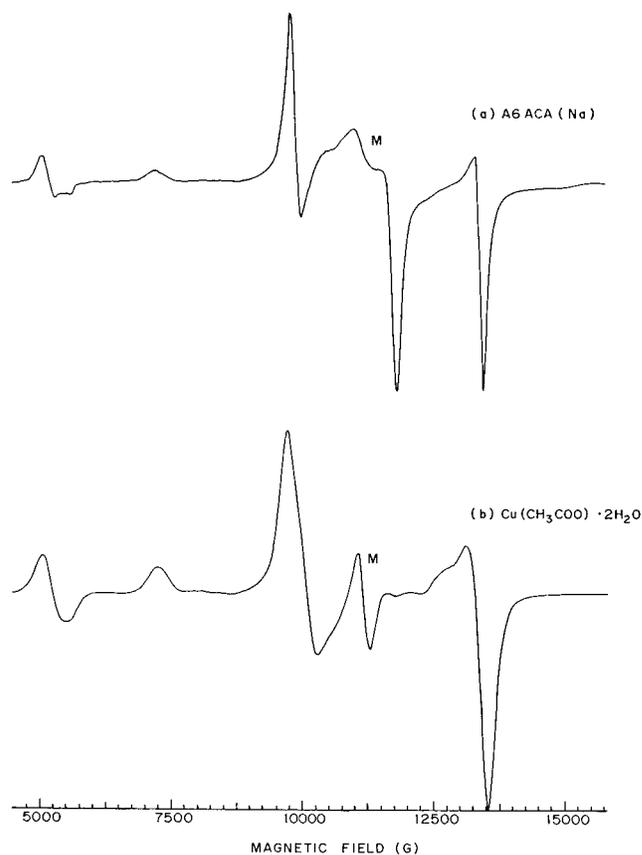


Figure 5. EPR spectra at Q-band frequency of (a) A6ACA gel and (b) dimeric copper acetate monohydrate at 298 K.

of Ca^{2+} to the polymer gel increased with the “hydrophobicity” of the gel. This was attributed to the cooperative effect of hydrophobicity and metal binding. The complexation of the metal ions with the carboxylic groups increases the overall hydrophobicity of the system since the metal-complexed carboxyl groups are not available to the water molecule. We have reported this complexation-induced hydrophobicity and its effect on volume phase transition in our earlier report.¹⁸ This complexation-induced hydrophobicity drives the polymer chains to attain a compact conformation and in turn enhances the metal binding to the polymer chains.

It may also be noted that the percentage of carboxyl groups involved in complexation is low for the un-ionized gels and high for completely ionized gels for the same alkyl chain length. This is simply due to the fact that the ionized carboxyl ions can coordinate with the Cu(II) ions much more effectively than the un-ionized carboxyl group.

We now show that the hydrophobicity also affects the structure of the polymer–metal complex. X-band EPR spectra of the complexed poly(acrylic acid) gels of different degrees of ionization AAc(H), AAc(Na), and AAc(H/Na) at 298 K are shown in Figure 2. In general, two types of Cu(II), dimeric and monomeric, species were detected in the EPR spectra. The signals denoted by D around 230, 4800, and 6075 G correspond to dimeric Cu(II) species, while those denoted by M1/M2 in the region 2690–3600 G are attributed to monomeric species. The nature of the EPR spectrum, i.e., the intensities of the dimer signals and the spectral characteristics of the monomeric species, are dependent on the degree of ionization. The resolved parallel hyperfine features of the monomeric species in AAc(H) correspond to a distorted molecular geometry for Cu(II). Only an averaged signal was observed in the complexed gels of AAc-

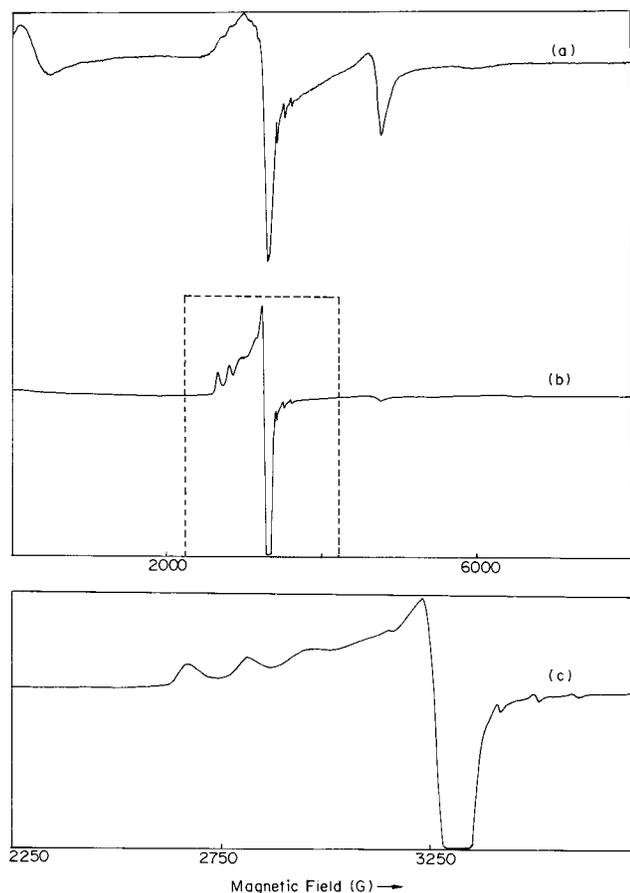


Figure 6. EPR spectra of Cu(II)-complexed A6ACA(Na) gels at (a) 298 K and (b) 80 K and (c) dotted portion of (b) in expanded scale.

(Na) and AAc(H/Na). In other words, the monomeric species in AAc(H) (hereafter referred to as M1) has a geometry different from that in AAc(Na) and AAc(H/Na) (hereafter referred to as M2). The complexed gels of AAc(H/Na) contain a trace amount of yet another monomer species M3.

Figure 3 shows the changes in the nature of the EPR spectrum of the monomer as a function of ionization for A6ACA. The monomeric species (M3') in A6ACA(Na/H) is characterized by $g_{\parallel} = 2.264$, $g_{\perp} = 2.065$, $A_{\parallel} = 159.7$ G, and $A_{\perp} = 12.9$ G, while that in A6ACA(Na) (M1) is characterized by $g_{\parallel} = 2.355$, $g_{\perp} = 2.081$, $A_{\parallel} = 119.1$ G, and $A_{\perp} = 16.0$ G. The gel A6ACA(H)

contained both types of the monomeric species (M1 and M3'). Hence, the EPR spectra reveal that the structure of the Cu(II)-complexed gel changes with the degree of ionization.

The spin Hamiltonian parameters for the monomeric species are listed in Table 2. It is apparent that three types of monomeric Cu(II) species are formed, one exhibiting an average signal (M2; $g_{av} = 2.119$) and the other two, M1 and M3/M3', having distorted molecular geometry.

The length of the pendent chain has a pronounced effect on the nature of the copper(II) species. Figure 4 reveals this effect on the EPR spectra of the fully ionized gels as a function of alkyl chain length. As the alkyl chain length increases, larger quantities of copper are seen to be present in the dimeric form (D). The intensity of the dimer signals in the fully ionized gels increases with the chain length in the order

AAc(Na) \ll A4ABA(Na) \ll

A8ACA(Na) $<$ A6ACA(Na)

The gel A6ACA (Na) appears to have an optimal alkyl chain length to form the maximum amount of dimer species (D).

The spectrum of the dimer species at X-band ($\nu = 9.75$ GHz) corresponds to axial symmetry, in which zero field splitting is larger than the microwave quantum ($h\nu$). It is interesting to note from the Q-band ($\nu \approx 35$ GHz) spectra that the dimer spectrum (Figure 5a) matches well with that of dimeric copper acetate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ complex (Figure 5b) wherein four acetate groups bind two Cu(II) ions to form a dimeric copper complex. This observation clearly indicates that on complexation four strands of the polymer rearrange to form the Cu–Cu dimer species in the polymer gel. Variable temperature studies on A6ACA(Na) in the range 77–298 K indicated that the intensity of dimer signals decreased, as shown in Figure 6, and the monomeric signals were better resolved and more intense at lower temperatures. This is in agreement with the antiferromagnetic coupling between the two copper(II) ions of the dimeric species. Tentative structures of different Cu(II) complexed gels are proposed in Figure 7. The spin Hamiltonian parameters, especially $g_{\parallel} = 2.264$ and $A_{\parallel} = 159.7$ G, suggest a distorted geometry around copper with oxygens or amide nitrogen as the coordinating ligands. However, studies with poly(acrylamide) and poly(*N*-isopropylacrylamide) gels did not reveal any complexation with Cu(II) ions, indicating that the amide nitrogen is most probably not involved in complexation.

The formation of dimer species is also dependent on the

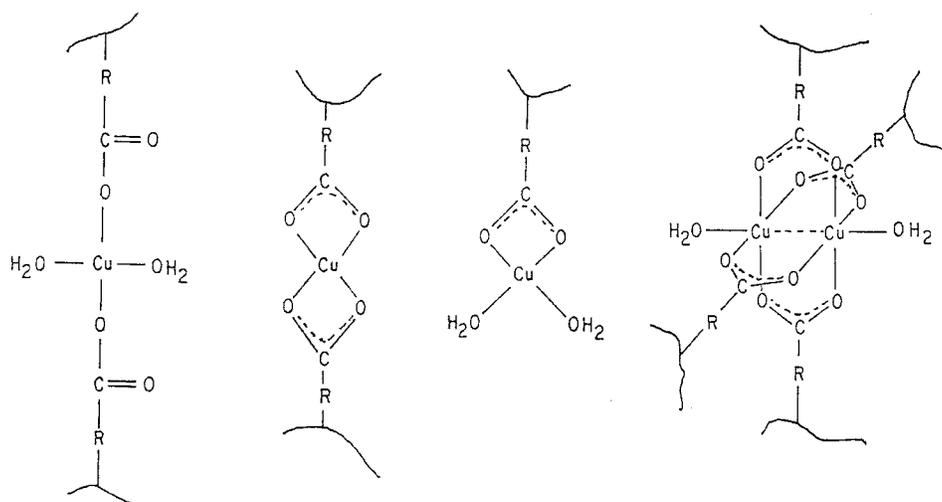


Figure 7. Structures of monomeric and dimeric Cu(II) species in metal ion complexed gels.

degree of ionization. In the case of acrylic acid gels, as shown in Figure 2, the dimer species is relatively more abundant in AAc(H) compared to that in gels AAc(H/Na) and AAc(Na). Cu(II) in AAc(Na) is present mostly as a monomeric species. Thus, as hydrophobicity decreases, the tendency to form dimeric species also decreases. In the case of hydrophobic A4ABA gels, the dimeric Cu(II) species was observed in the un-ionized as well as in the partially ionized gels. Further, in the case of more hydrophobic A6ACA gels the dimeric Cu(II) species was found even in the completely ionized forms. These observations clearly suggest that an "optimum hydrophobicity" (i.e., a balance of hydrophilic and hydrophobic interactions) of the polymeric gel is required to form dimeric species with Cu(II) ions. The data in Table 1 show that swelling does not determine the structure of the Cu(II) complexes. For example, both the acid as well as the salt forms of the Cu(II)-complexed A6ACA gels showed dimers irrespective of their swelling behavior. Moreover, we have also observed that A6ACA gels of two different cross-link densities, viz., 10% and 30%, showed identical EPR spectra consistent with identical structures of Cu(II) complexes, although their swelling capacities in water were 230 and 60 g/g, respectively. Thus, we conclude that the structure of the complex is not determined by the cross-link density but is certainly influenced by the hydrophobic–hydrophilic balance of the polymer.

Conclusions

We have investigated the effect of alkyl chain length on metal complexation using a series of homopolymer gels having different alkyl chain lengths varying from zero to seven. The nature of the Cu(II) complexes and the number of COOH groups involved in complexation were strongly dependent on alkyl chain length or hydrophobicity of the gel. The EPR analysis showed two types of complexes, dimeric and monomeric. The present work gives an insight into the role of the hydrophobic–hydrophilic balance on the molecular structure of the Cu(II) complexed polyacids. It is known that encapsulation of copper acetate in zeolite cavities enhances the catalytic activity.²⁷ Here we present another innovative way of encapsulating metal complexes within the polymer matrix. In principle, by this method one should be able to design new catalysts for enhanced catalytic activities. These gels could also find applications in water purification, wherein the ability of the gels to form complexes with the divalent metal ions, such as Pb(II), could be used effectively.

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