Structural Studies of Copper(II)-Chelated Polymers Derived from Hydroxy-Functionalized Liquid Crystalline Homo- and Copolyazomethines

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ABSTRACT: Different hydroxy-functionalized polyazomethines have been modified by complexation using paramagnetic copper(II) ions. The molar percentage of copper introduced into the polymeric chains is determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The introduction of the metal might give rise to cross-linking or bending of the polymeric chains depending on the structure of the modified repeating units. The influence of the copper content on thermal and mesogenic behavior has been studied by DSC, TG, and optical microscopy. The EPR measurements of this new type of metal-coordinated polymer provide significant structural information about the metal-containing polymers and the pristine polyazomethines. The study of the metal-containing copolymers derived from ethylenediamine and aromatic diamines has given evidence of the selective copper insertion into repeating units derived from ethylenediamine. An alternating order in the structure of the copolyazomethines, which could not be studied by any other technique, can be drawn from the EPR spectra.

Introduction

Metal-containing mesogenic polymers have received increasing attention in recent years because of the interesting properties which may result from the presence of metals in ordered fluid phases.[1,2] Furthermore, metal insertion has often been reported to modify electronic properties like the increase of the conductivity[3] or to enhance nonlinear optical properties.[4] Three general strategies allow us to obtain this type of material:[5] (i) Metal complexes which have functional groups on their periphery which can lead to polymers. (ii) Polymer formation through coordination reactions using a ligand which can be attached simultaneously to two metal atoms or ions. (iii) Coordination of a metal ion to a preformed polymer containing chelating groups.

Recently, we have described some metal-containing polymers showing a paramagnetic nematic mesophase which have been obtained using the first approach.[6,7] These materials are easily processable as fibers and exhibit interesting structural and physical properties.[8] In this paper we describe a new type of magnetic material which is based on polymeric Schiff-base complexes and can be obtained by the third approach. For the work we selected polyazomethines as the preformed organic polymers. These polymers allow us to obtain thermally stable films or fibers which exhibit good mechanical properties and, very often, exhibit thermotropic and lyotropic liquid crystallinity.[9] In a recent paper we reported the synthesis and characterization of a new series of hydroxy-functionalized liquid crystal polyazomethines.[10] The hydroxyl groups are introduced in the ortho position of the azomethine group and lead to the formation of strong chelation rings with the nitrogen atom by means of hydrogen bonds. The chelation rings afford an exceptionally good position to capture some transition metals by complexation.[11]

The complexation with different transition metal ions with magnetic properties is possible. For the present work copper(II) was selected because our previous experience with metallomesogenic copper derivatives makes a comparative study possible.[12] Copper(II) salicylaldimine complexes have a square-planar configuration and consequently a structure which is suitable for mesogenic behavior. Moreover, Cu(II) is a paramagnetic entity and its EPR spectrum is easily measured at moderately high temperatures. This spectrum is strongly dependent on the copper neighborhood and makes Cu(II) an excellent probe to investigate the site where the metal is incorporated into the polyazomethine chain. On the other hand, since the Cu(II) EPR spectrum is greatly affected by the metal–metal short distance exchange interaction as well as the long distance dipole–dipole interaction, the study of these parameters for Cu(II) EPR spectra provides information about the microstructure of the materials.

The present work was first approached by selecting three hydroxy-functionalized polyazomethines (Figure 1): two homopolymers derived from ethylenediamine (coded as ED) and 1,5-naphthalenediamine (coded as NP), respectively, and a copolymer derived from ethylenediamine and 1,5-naphthalenediamine (coded as CEN).

These polymers were chosen because of the difference in the structure of the central core of the repeating unit. The introduction of transition metals might produce two different effects. First, the metal ion can be coordinated to two different repeating units (Figure 2a). In this case repeating units act as bidentate ligands and an interchain coordination takes place preferably, giving a cross-linked material. Second, bending of the polymeric chain is made possible by complexation of the metal ion with a tetradentate repeating unit (Figure 2b). This intrachain coordination can only take place in the case of the ethylenediamine derivative repeating units due to the rigid structure of *N*-arylsalicylaldimine ligands. Polymer ED is not mesogenic but both NP and CEN polymers exhibit nematic behavior in a wide range of temperatures (92 and 82 °C, respectively).

In order to prove the conclusions obtained with the three above mentioned polyazomethines, two further polymers were modified: a homopolyazomethine derived from 1,4-phenylenediamine (PH) and the corresponding copolymer-(1:1) derived from ethylenediamine and 1,4-phenylene-

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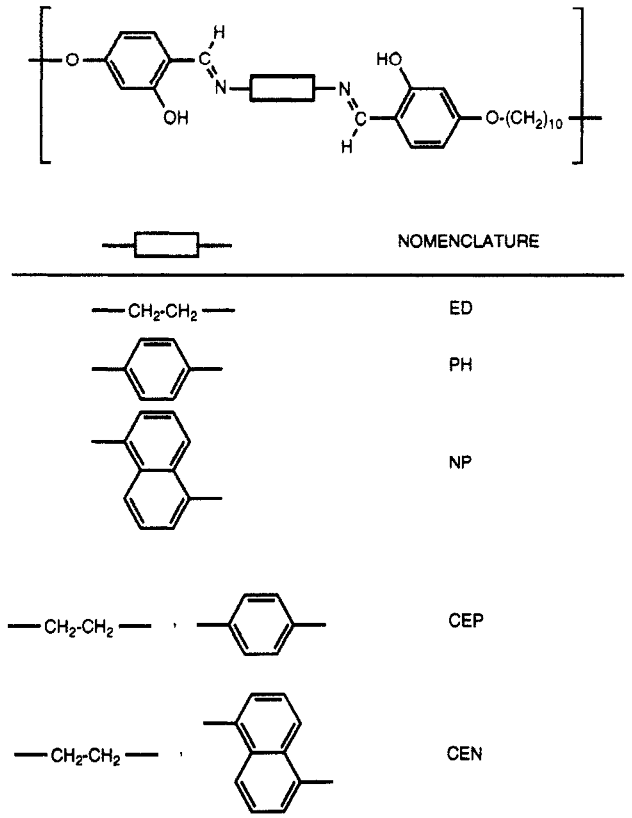

Figure 1. Schematic representation and nomenclature of the hydroxy-functionalized homo- and copolyazomethines.

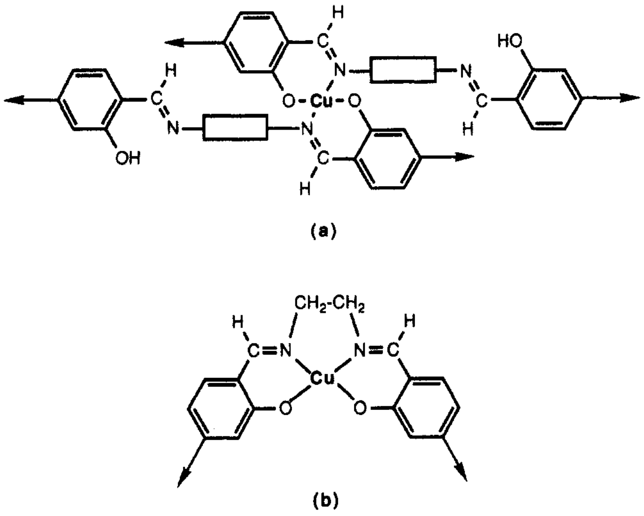

Figure 2. Structural modifications produced by the introduction of Cu(II) ions: (a) cross-linking due to interchain coordination; (b) bending due to intrachain coordination of the tetradentate repeating unit.

diamine (CEP) (see Figure 1). The results obtained have been included in the tables and figures given in the text.

Copper-complexed polyazomethines have been represented with a code derived from the pristine polyazomethine: ED-Cu-*x*, PH-Cu-*x*, NP-Cu-*x*, CEP-Cu-*x*, and CEN-Cu-*x*, where *x* represents the mole percentage of complexed repeating units based on the initial calculations of synthesis.

Experimental Section

Materials. Polyazomethines (EC, NP, PH, CEN, and CEP) were synthesized as previously described[10] from a complex dialdehyde (1,10-bis((4-formyl-3-hydroxyphenyl)oxy)decane) and commercial diamines previously purified.

ED: IR (KBr, cm^{-1}) 1625 (C=N). Anal. Calcd: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.80; H, 8.27; N, 6.06. η_{inh}: >0.84 (due to the degradation).

NP: IR (KBr, cm^{-1}) 1628 (C=N). Anal. Calcd: C, 76.09; H, 6.76; N, 5.22. Found: C, 75.43; H, 6.76; N, 4.53. η_{inh}: 0.32.

PH: IR (KBr, cm^{-1}) 1616 (C=N). Anal. Calcd: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.42; H, 7.49; N, 5.44. η_{inh}: 0.41.

CEN: IR (KBr, cm^{-1}) 1628 (C=N). Anal. Calcd: C, 73.89; H, 7.23; N, 5.75. Found: C, 73.64; H, 7.46; N, 5.44. η_{inh}: 0.59.

CEP: IR (KBr, cm^{-1}) 1625 (C=N). Anal. Calcd: C, 72.70; H, 7.41; N, 6.06. Found: C, 73.26; H, 8.20; N, 5.80. η_{inh}: 0.32.

The proportion of different repeating units in the copolymers was determined by ^{1}H NMR as a function of the signals corresponding to the proton of the azomethine groups. The proportion found corresponds approximately to the feed composition. In the case of CEN the proportion of ED:NP units was 1.1:1. In the case of CEP the ratio ED:PH was 1:1.

Complexation of the Hydroxy-Functionalized Polyazomethines. Functionalization of the polyazomethines was carried out by addition of a copper(II) acetate solution to a suspension of the corresponding pristine polyazomethine in 1,4-dioxane. The solvent was previously passed through a column of alumina and distilled. A description of the procedure is reported for polymer NP-Cu-10 taken as an example.

Polyazomethine NP (186.4 mg) was suspended in 20 mL of freshly destilled 1,4-dioxane under reflux and magnetic stirring. $(AcO_2Cu)_2 \cdot 2H_2O$ (7.9 mg) in 10 mL of hot 1,4-dioxane was added dropwise for 15 min. The suspension was stirred for 2 h under reflux. After cooling, the reaction mixture was filtered and the powdery solid was washed with 1,4-dioxane, hot water, and methanol. The polymer was dried under vacuum over P_2O_5 for 24 h at 80 °C.

Techniques. Elemental analysis was carried out with a Perkin-Elmer 240C microanalyzer and IR spectra were measured from KBr pellets on a Perkin-Elmer FTIR 1600. The copper content was determined by inductively coupled plasma atomic emission spectroscopy using a Perkin-Elmer P-40 spectrometer.

The inherent viscosities of polyazomethines were measured at a concentration of 0.5 g/dL in methanesulfonic acid at 40 °C using a Cannon-Fenske viscosimeter.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks. Both transition temperatures and enthalpy changes were determined using indium and tin as calibration standards.

The mesogenic behavior was confirmed by optical microscopy using a Nikon polarizing microscope fitted with a Mettler FP-82 hot stage and a Mettler FP-80 control unit.

Thermogravimetric analysis was performed with a Perkin-Elmer TGS-2 equipped with a System 4 microprocesor controller using powdered samples which were heated at 10 °C/min under nitrogen atmosphere.

Table 1 collects characterization data for the metal-chelated polyazomethines. Table 2, collects the thermal properties and mesogenic behavior of the pristine polyazomethines and the metal-chelated polymeric derivatives.

EPR measurements were taken at room temperature (RT) with a Bruker ESP-380 spectrometer working in the X-band. The powdered samples were measured introducing them in a standard EPR quartz tube (707-SQ from Wilmad).

Results and Discussion

Synthesis of the Copper-Chelated Polyazomethines. Normally, insertion of transition metal ions into polymeric Schiff-base ligands has been carried out by addition of a solution of the corresponding metal salts to a solution of the polymer.[11] In the same way, reported examples of metal complexation of main-chain liquid crystalline polymers are obtained in polymeric solutions.[13,14] In our case, due to the insolubility of these hydroxy-functionalized polyazomethines in common organic solvents, the complexation was performed by the addition of several molar ratios of copper(II) to a suspension of the polymer in hot 1,4-dioxane. In all cases, a percentage of around 50% of

Table 1. Characterization Data for Copper(II) Complexed Polyazomethines

polymer	% Cu[a]			ν(C=N, st), cm^{-1}
	calcd	found	introduced	
ED-Cu-5	5.09	2.58	51	1627
ED-Cu-10	12.68	7.03	55	1627
ED-Cu-20	16.60	9.56	58	1624
ED-Cu-30	30.16	17.81	59	1627
NP-Cu-5	6.13	3.48	58	1628, 1635
NP-Cu-10	11.77	7.54	64	1628
NP-Cu-20	22.03	15.49	70	1628, 1635
NP-Cu-30	32.85	22.75	69	1626, 1636
PH-Cu-5	5.10	2.92	57	1608
PH-Cu-10	10.79	6.37	59	1610
PH-Cu-20	19.61	10.03	51	1613
PH-Cu-30	29.50	18.19	62	1608
CEN-Cu-5	5.32	2.21	42	1626
CEN-Cu-10	13.70	6.22	45	1627
CEN-Cu-20	21.40	11.50	54	1627
CEN-Cu-30	31.74	17.46	55	1628, 1635
CEP-Cu-5	5.00	2.78	56	1623
CEP-Cu-10	10.19	6.40	63	1623
CEP-Cu-20	21.30	13.23	62	1626, 1620
CEP-Cu-30	31.60	19.26	61	1626, 1619

[a] % mol of repeating units complexed with copper(II) ions: % calculated obtained from the copper(II) used in the chemical modification of polyazomethines; % found by ICP-AES; % introduced corresponds to the percentage of copper(II) ions inserted into the polymeric chains compared with the % calculated (found/calculated) × 100).

Table 2. Thermal Characterization of Polymers[a]

polymer	T_m (°C)	T_i (°C)	mesogenic properties	TGA (°C)
ED	195			338
ED-Cu-5	180			318
ED-Cu-10	186			315
ED-Cu-20	181			316
ED-Cu-30	161			315
NP	216	308	nematic	374
NP-Cu-5	185	dec	nematic	365
NP-Cu-10	192	dec	nematic	360
NP-Cu-20	179	dec	hazy melt[b]	360
NP-Cu-30	182	dec		333
CEN	184	260[c]	nematic	335
CEN-Cu-5	169	260[c] (dec)	nematic	340
CENCu-10	168	260[c] (dec)	nematic	345
CEN-Cu-20	168	270[c] (dec)	nematic	342
CEN-Cu-30	169	dec	hazy melt[b]	352

[a] The transition temperatures were read at the second heating (scan rate = 10 °C/min). [b] A highly viscous state was observed but not clearly identified as the nematic mesophase. [c] Optical data.

that expected was determined by AES (see Table 1). In the complexation process a large number of factors play a part, namely growth of the grain, partial solubility of the polymers, the degree of polymerization, etc. For this reason we did not make a comparative study of the copper content in the different types of polymers. These results suggest that the present polyazomethines can easily be modified with other transition metal ions.

Complexation can easily be observed by a change of the color of the original polymer. This effect is particularly marked for ED which has a slightly yellow color that changes to green when copper(II) ions are inserted. However, the IR spectra of the complexes showed no significant changes. This could be due to the low copper content in the polymeric complexes.

Mesogenic and Thermal Properties of Copper-Chelated Polyazomethines. Thermal data and mesogenic properties of the copper-containing polyazomethines are collected in Table 2. Data corresponding to PH-Cu-*x* and CEP-Cu-*x* have not been collected because these polymers decompose before melting at temperatures near 300 °C, the same as the original polymers.[10]

The introduction of copper into the polymeric chains increases the melt viscosity and makes the identification of the mesophase by optical microscopy difficult. In some cases, an elastic behavior of the sample is observed under mechanical stress.

For the copper-modified polyazomethines derived from ethylenediamine (ED-Cu-*x*) a small decrease in the melting temperature is observed when compared with the starting polymer. These metal-chelated polyazomethines do not show mesogenic properties, as was expected from the nonmesogenic polyazomethine ED. A hazy melt above 161 °C was observed by optical microscopy for ED-Cu-30.

For copper-modified polyazomethines derived from 1,5-naphthalenediamine (NP-Cu-*x*) a progressive disappearance of the mesophase was observed as the metal content increased. Therefore, in the case of NP-Cu-20 it is not possible to be sure whether it still has some mesogenic properties. Above 200 °C (which corresponds to the end of the transition with a peak maximum to 179 °C) a softening of the sample was observed by optical microscopy. The sample exhibited a rubberlike behavior under mechanical stress. In the case of NP-Cu-30 no melting or softening was detected. On carrying out DSC measurements, an endothermic transition was observed in all NP-Cu-*x* samples about 180–210 °C (melting region of NP). Furthermore, the introduction of metal ions into the polymeric chain preserved the crystallization of the nematic on cooling the melt, even in NP-Cu-5. This behavior may be due to the decrease in mobility of mesogenic groups in the neighborhood of metal cross-links. On the other hand no clearing temperatures were determined due to the decomposition of the samples.

The same effect of copper(II) content on the mesogenic properties can be observed for CEN-Cu-*x*. A slight decrease in T_m was observed in the case of the pristine polymer. However, T_m was not modified by the copper content. A larger amount of copper(II) can be introduced into the copolyazomethine CEN than into NP without loss of a clearly identified mesophase. Only with CEN-Cu-30 does the nematic behavior start to be uncertain.

Generally, the copper modified polymers showed thermal instability on DSC when heated at temperatures above 260 °C, even though thermal decomposition in thermogravimetric analysis appears at temperatures higher than 300 °C. Decomposition involving metal complexes without weight loss can justify this behavior.

EPR Measurements. The EPR results of ED-Cu-*x*, NP-Cu-*x*, and CEN-Cu-*x* samples have been measured at room temperature. The traces corresponding to $x = 5$ are plotted in Figure 3. It can be seen that the spectra of ED-Cu-5 and CEN-Cu-5 samples closely coincide whereas they show some marked differences when compared to the spectrum of the NP samples.

All the traces show a *perpendicular* feature at their high field region ($g \approx 2.07$) without a resolved hyperfine (hf) structure. The *parallel* features at the low field side show hf structure. At least the two lowest field lines are clearly resolved. These spectra are associated with Cu^{2+} ions in a nearly axial environment with the following values for the Hamiltonian spin parameters: $g_\parallel = 2.22 \pm 0.01$, $g_\perp = 2.07 \pm 0.01$, and $A_\parallel = 520 \pm 5$ MHz in the case of NP-Cu-5 and $g_\parallel = 2.19 \pm 0.01$, $g_\perp = 2.08 \pm 0.01$, and $A_\parallel = 595 \pm 5$ MHz for ED-Cu-5 and CEN-Cu-5.

In spite of the fact that copper has two naturally occurring isotopes (^{63}Cu in 69.2% and ^{65}Cu in 30.8%) with a very close nuclear *g* factor ($^{63}g_N = 1.484$ and $^{65}g_N = 1.588$;

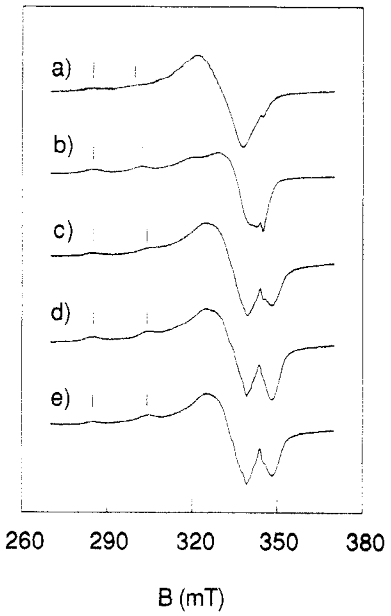

Figure 3. EPR spectra measured at room temperature of PH-Cu-5 (a), NP-Cu-5 (b), ED-Cu-5 (c), CEN-Cu-5 (d), and CEP-Cu-5 (e). The position of the two lowest field hyperfine components of the parallel signal are indicated.

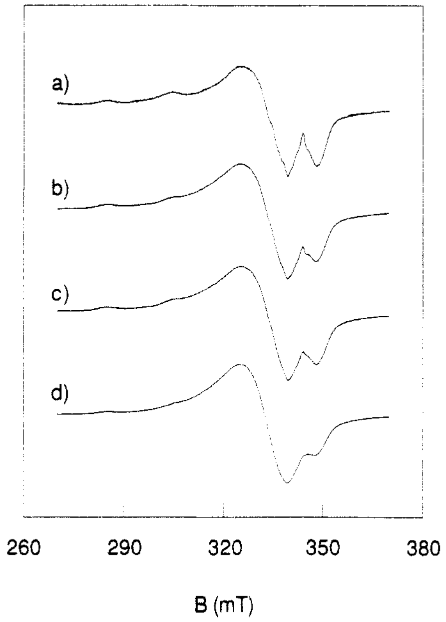

Figure 4. Room temperature EPR spectra of CEN-Cu-x: (a) $x = 5$; (b) $x = 10$; (c) $x = 20$; (d) $x = 30$.

$^{63}g_N/^{65}g_N = 0.935$) the hyperfine lines of both species are not resolved in the spectra. Thus, the formerly given values for the hyperfine coupling constants correspond to the average value.

When the copper concentration is varied, the spectra are basically the same except for an increase in the line width as the metal content increases. This behavior is due to the dipolar–dipolar interaction. Figure 4 displays the EPR spectra of CEN-Cu-x corresponding to the different values of the copper content.

The evolution of the parallel g factor and the splitting between the two lowest field parallel lines are given as a function of the actual copper content (% found) in Figure 5 and Table 3. These results show the similarity between ED-Cu-x and CEN-Cu-x which remains as the copper content changes.

The only difference between the ED-Cu-x and CEN-Cu-x samples is the lower line width, mainly in the *perpendicular* contribution of the CEN-Cu-x spectra in comparison with ED-Cu-x (see Figure 3).

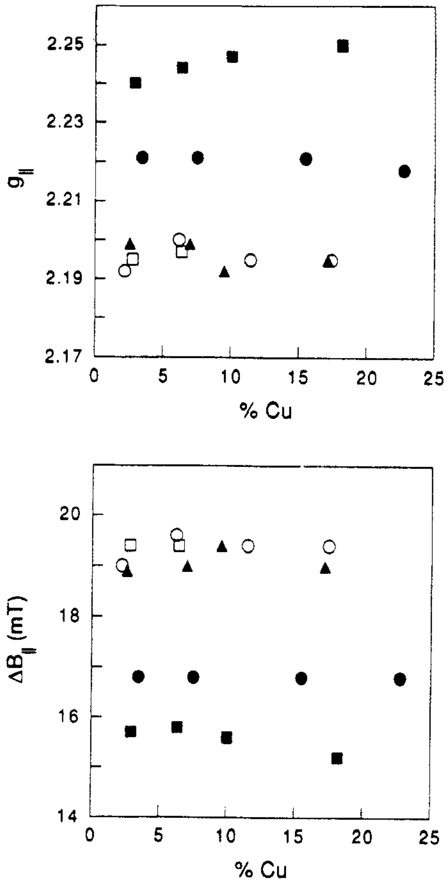

Figure 5. $g_\parallel$ (upper) and splitting between the two lowest field hf lines (lower) as a function of copper content: (■) PH-Cu-x; (●) NP-Cu-x; (▲) ED-Cu-x; (□) CEN-Cu-x; (○) CEP-Cu-x.

Table 3. Parallel g Factor ($g_\parallel$) and Hyperfine Constant $A_\parallel$ (MHz) from the Cu(II) EPR Spectra in the Diverse Samples[a]

sample	% Cu found	$g_\parallel$	$A_\parallel$
ED-Cu-5	2.58	2.20	581
ED-Cu-10	7.03	2.20	585
ED-Cu-20	9.56	2.19	584
ED-Cu-30	17.81	2.19	595
NP-Cu-5	3.48	2.22	521
NP-Cu-10	7.54	2.22	521
NP-Cu-20	15.49	2.22	521
NP-Cu-30	22.75	2.22	521
PH-Cu-5	2.92	2.24	494
PH-Cu-10	6.37	2.24	495
PH-Cu-20	10.03	2.25	491
PH-Cu-30	18.19	2.25	480
CEP-Cu-5	2.78	2.19	596
CEP-Cu-10	6.40	2.20	603
CEP-Cu-20	13.23	*b*	*b*
CEP-Cu-30	19.26	*b*	*b*
CEN-Cu-5	2.21	2.19	600
CEN-Cu-10	6.22	2.20	603
CEN-Cu-20	11.50	2.19	595
CEN-Cu-30	17.46	2.19	595

[a] The accuracies are ±0.01 for g factors and 5 MHz for hyperfine constants. [b] The data cannot be measured with accuracy because of the broadness of the corresponding signals in the EPR spectra.

Copper Environment. With regard to the EPR spectra of powdered samples, the observed differences might arise from the different possibilities for incorporation of the metal into the polymeric chains. In the case of NP-Cu-x, due to the rigidity of the 1,5-naphthylene group of the mesogenic unit only cross-linking can occur. However, for ED-Cu-x the assignation of the Cu(II) spectra to an interchain (repeating units as bidentate ligands, Figure 2a) or intrachain (repeating units as tetradentate ligands, Figure 2b) coordination is not easy at first sight. Nevertheless, the differences observed for the copper $g_{\parallel}$ factor as well as the $A_{\parallel}$ constant of the NP-Cu-*x* compared to those of ED-Cu-*x* and CEN-Cu-*x* samples suggest a stronger modification of the neighborhood of the metal than that provided by the only modification of the central part of the repeating unit. This indicates that in the case of ED-Cu-*x* polymers the metal is coordinated to a tetradentate repeating unit (see Figure 2b). This is also supported by the values of the Hamiltonian spin parameters for ED-Cu-*x* compared to those reported by Ellis et al.[15] for *N,N'*-ethylenebis(salicylidenaminato)copper(II): $g_{\parallel} = 2.180 \pm 0.003$, $g_{\perp} = 2.050 \pm 0.002$, and $A_{\parallel} = 576 \pm 6$ MHz (these values depend on the solvent). For this compound the neighborhoods of the copper(II) ion are the same as in ED-Cu-*x* assuming that an intrachain position is occupied by the metal.

A comparison of the spectra of CEN-Cu-*x* samples with those of the homopolymers means that in the case of the copolymer the metal is coordinated only at the sites corresponding to ethylenediamine derivative repeating units giving the same structural modifications (intrachain chelate).

Structure of the Copolymer CEN. A study in depth of the structure of the copolymer CEN raises a question about the type of copolymer obtained. A mixture of homopolymers could be the result of the polymerization process. At this point, EPR studies may supply useful structural data. Due to the fact that in the copolymerization copper ions only react with ED units, the spectrum of the mixture should coincide with that of the ED homopolymer corresponding to a metal concentration of twice the nominal value (only half of the units in the copolymer correspond to ED units). The narrower lines of CEN-Cu-*x* EPR spectra compared with those of ED-Cu-*x* (with similar copper content) rule out the possibility of a mixture. Similar arguments exclude the possibility of a block copolymer.

In the case of a true copolymer another question arises: how the ED and NP units are distributed along the copolymer chain. This point might be studied by introducing the probability p_a that an alternating sequence ED–NP occurs. Values of p_a close to 0 would correspond to the formation of blocks (–NP–NP– or –ED–ED–), while values of p_a close to 1 would indicate a well-ordered alternating polymer (–NP–ED–NP–ED–). Random distribution would give values of p_a close to 0.5.

In depth discussion of this issue is outside the scope of this paper, but the differences in the line width of the spectra of ED-Cu-*x* and CEN-Cu-*x* samples suggest a distribution of the ED and NP units in which alternation is more likely than a simple random distribution (where the sequences –ED–NP–, –ED–ED–, and –NP–NP– are equally probable). In the last case, the distribution of the magnetic ion around a particular copper ion should be the same as in the case of the ED-Cu-*x* homopolymer (half the random sites with a double probability of occupation).

A simple model based on a linear chain with sites which can be randomly occupied by the magnetic ion could illustrate this point. The contribution of the magnetic dipoles in the linear chain to the line width is proportional to the variance of the r^{-3} distribution $\sigma(\sum r^{-3})$, where r is the distance between two copper atoms in the chain.[16] A Monte Carlo procedure was used to calculate the variance. Chains with 20 units are built, and the ED and NP unit distributions on each of them are obtained in the following way. The distance between adjacent units is taken as a constant, and the origin is occupied by an ED unit. While the n site unit is obtained from the $(n - 1)$ site unit by comparison of a random number in the (0, 1) interval with the alternation probability (p_a), the occupation of each ED site by a copper(II) ion is randomly obtained according to the copper content values. In both random choices, random number generation using the code given under the name RAN1 in ref 17 has been used.

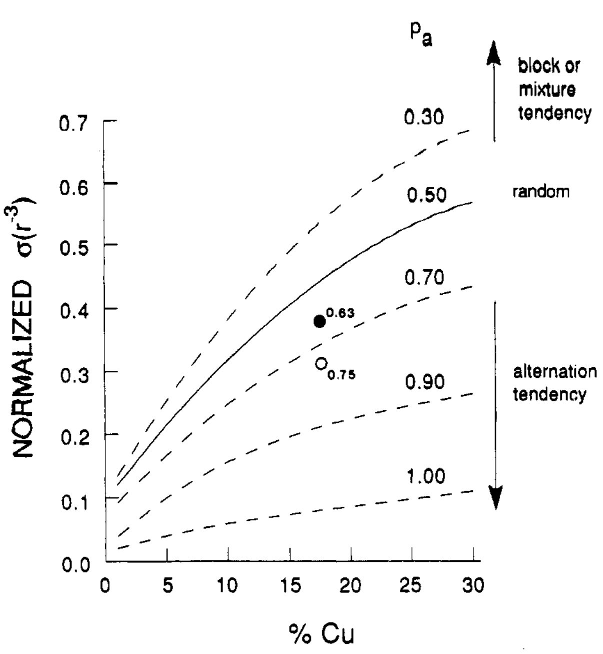

Figure 6. $\sigma(\sum r^{-3})$ as a function of the copper content for different values of the alternation probability p_a: (●) alternation probability, p_a, of CEN-Cu-30 (% Cu found = 17.46) if w_{inter} is not considered; (○) alternation probability of CEN-Cu-30 if both intra- and interchain contributions were the same (see text).

The evolution of $\sigma(\sum r^{-3})$ as a function of the copper content for different values of the alternation probability, p_a, calculated with this model is shown in Figure 6. In this plot, the solid line corresponds to a value of $p_a = 0.5$, which coincides with the evolution of $\sigma(\sum r^{-3})$ for the ED homopolymer. The value of the half-width experimentally measured from the EPR spectra for the CEN copolymer is about 85% of the value measured for the ED homopolymer. As an example, in the case of the CEN copolymer containing 17.46% copper (copper content found for CEN-Cu-30, as can be seen from Table 1) a value of $p_a = 0.63$ is obtained (see Figure 6). However, the fact that in the half-width values two contributions are involved needs to be taken into account. These are the interchain and the intrachain interactions. It can be reasonably assumed that the interchain contribution is the same in both the homo- and copolymer; however, it cannot be experimentally determined. For this reason the above estimated value of p_a ($p_a = 0.63$) is the lowest possible value of p_a if the interchain contribution is not considered. For instance, in the example previously discussed, if both intra- and interchain contributions were the same, the calculated value of the intrachain interaction in CEN-Cu-30 would be about 70% of the intrachain contribution in the ED homopolymer.[18] This value corresponds to $p_a = 0.75$ (shown in Figure 6). In spite of the crudeness of our model these results clearly indicate that the organization of ED and NP moieties in the CEN copolymers is closer to an alternation than to a random distribution.

Check of the Results. As can be seen from Figures 3 and 5 and also from Table 3, the data obtained for PH-

Cu-x and CEP-Cu-x bear out all the results discussed so far. The line widths of the EPR spectra show in both cases a strong dependence on the copper content. While the PH-Cu-x samples show different spectra but close to those of NP-Cu-x, indicating a cross-linked structure, the CEP-Cu-x spectra coincide with those of ED-Cu-x and CEN-Cu-x. Consequently, it seems clear that copper ions react only with tetradentate ED units, giving an intrachain complexation. As was pointed out for CEN-Cu-x, narrower spectral lines on the EPR were observed compared with those of ED-Cu-x with a similar copper content. As a consequence a predominant alternating structure can be proposed for CEP.

The values higher than 0.5 of alternating probability p_a can be explained by taking into account the difference in reactivity of ethylenediamine and aromatic diamines during polymerization.

This type of step-growth polymer was prepared *via* addition–elimination reaction between the dialdehyde and different diamines. The difference in the reactivity of the diamines is related to their nucleophilic power and is generally in the same order as their basicity, although basicity is thermodynamically controlled and nucleophilicity is kinetically controlled.[19] Thus it is possible to establish an approximate order of nucleophilicity using K_b values. Aromatic amines are much weaker bases than their aliphatic analogues:[20] K_b(ethylenediamine) = 5.15×10^{-4} and K_b(p-phenylenediamine) = 1.45×10^{-8}. Assuming that the K_b for 1,5-naphthalenediamine is of the same order as that for 1,4-phenylenediamine, we can observe that the aliphatic diamine has a K_b value 10^4–10^5 higher than those for aromatic diamines. In other words, aliphatic diamines are more powerful nucleophiles.

For this reason, it can be assumed that ethylenediamine is consumed in the first steps of the polymerization, giving predominantly a trimer with carbonyl groups as end groups (dialdehyde–ethylenediamine–dialdehyde). The polymerization continues by reaction of the trimer with the aromatic diamines, giving a polymer with a predominantly alternating structure.

Conclusions

Copper(II) ions can be introduced into hydroxy-functionalized polyazomethines with salicylaldimine-derived repeating units. Depending on the structure of this repeating unit, the metal gives rise to cross-linking (NP-Cu-x and PH-Cu-x) or bending (ED-Cu-x, CEN-Cu-x, and CEP-Cu-x) of the polymeric chains.

The thermal and mesogenic properties of the pristine polymers are disturbed by the metal. In general, transition temperatures slightly decrease and an elastic behavior appears when the metal content increases. Nevertheless, mesogenic behavior can be clearly observed for low metal contents.

On the other hand, EPR measurements of these samples provide valuable information about the copper affinity of the different repeating units during the complexation process and microstructural information about the original polymers. The EPR spectra of Cu(II) introduced in the ED, NP, and PH homopolymers allow us to distinguish between the interchain cross-linking site and the tetradentate intrachain site for the foreign ion. While the former situation takes place in the aromatic diamine polymers (NP and PH), the latter occurs in the case of the ED homopolymer.

Apart from this, a comparison of the EPR spectra measured in the copolymers with the homopolymers indicates that Cu(II) occupies in copolymers a tetradentate intrachain site, forming the same chelate as in the ED homopolymer (ED-Cu-x). No evidence for cross-linking has been found.

An analysis of the line-width evolution as a function of the copper content provides useful information about the structure of the copolymers. A tendency to alternate the repeating units has been observed. This result is interpreted as being due to different reactivities of the ethylenediamine and aromatic diamines used in the polymerization.

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