

Synthesis and characterization of a novel liquid crystalline side chain metallopolymer

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SUMMARY: The synthesis of a novel kind of form-retaining liquid crystalline crosslinked metallopolymer is reported. Copper(II) is complexed by Schiff's base units as part of a mesogenic side chain polymer. This leads to remarkable antiferromagnetic exchange interactions between the copper centers that are not present in related monomeric model compounds. IR spectroscopic investigations in the region 4000–200 cm⁻¹, X-ray diffractometry and temperature dependent magnetic susceptibility measurements were carried out to elucidate the structure of this new material. The observed considerably strong antiferromagnetic coupling is assumed to be due to the interactions between the copper centers through oxygen bridges in the polymeric matrix.

Introduction

The magnetic behaviour of metal containing polymers with chelating units situated in the main or the side chain has received increased attention during the last years¹. In some cases, the attachment of paramagnetic cores to a polymer leads to drastic deviations from the Curie-Weiss law magnetic behaviour². This has not been observed in analogous monomer compounds, demonstrating the leading influence of the polymeric conformation. On the other hand, no systematic investigation has been reported clarifying this phenomenon that involves the structure of the polymer. Nevertheless, a fundamental work devoted to this problem was presented in ref.³

The number of reports on crosslinked liquid crystalline (LC) polymers with paramagnetic units is still very limited. Hanabusa et al.⁴ reported on a polyacrylate β -diketonate containing copper as the first example of a metal containing LC side chain polymer. The full characterization of such systems is usually very difficult due to problems of solubility. Also the synthesis of highly crosslinked materials deals with nonsoluble products that can include trapped inorganic impurities which have not reacted. As a final result these impurities increase the conductivity and can change the properties of the system.

Our strategy of preparing LC metallopolymer implies the use of high experience on preparation of Schiff's base complexes with long enough side chain alkyl substituent looking to reach liquid crystallinity, remarkable magnetic properties and a good solubility. Those kinds of material are also promising in the field of optics. The possible

inclusion of rare earth elements in a polymeric matrix may lead to optical active devices⁵. These compounds could be interesting for modern applications, e.g., for polymer optical amplifiers⁶.

Here we present the synthesis and structural characterization of a novel side chain liquid crystalline methacrylate metallopolymer that offers the capability to complex different metal ions for magnetic and nonlinear optical investigations. The magnetic behaviour of those LC polymers has been already published^{7,8} and will not be discussed here in detail.

Experimental part

Materials and methods

The commercial reactants were available from Aldrich and E. Merck Co. The investigated compounds were characterized by ¹H NMR spectroscopy using a 300 MHz spectrometer (WM 300, Bruker) and elemental analysis (Perkin Elmer 240 B). The characterization of both complexed polymer fractions was carried out with the soluble part of the reaction mixture using toluene or tetrahydrofuran as solvent. The molecular weight \bar{M}_w and the polydispersity index for the polymers, \bar{M}_w/\bar{M}_n , were determined by gel permeation chromatography (GPC) (Waters 510 microflow pump, Waters RI 410 detector) using poly(methyl methacrylate) (PMMA) standards (ultrastyrigel columns, tetrahydrofuran as eluent at a rate 1 ml/min).

The phase transition temperatures were determined using a differential scanning calorimeter (Perkin Elmer DSC-2C) with an accuracy of ± 0.1 K. A polarizing microscope (Leitz

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Orthoplan Pol) supported with a heating stage (Mettler Hotstation FP82) and a S-VHS video system (Sony, Panasonic) allowed the observation of the phase transitions and the mesomorphic textures.

The infrared spectra in the region 200–4000 cm^{-1} were obtained using a Perkin Elmer 580B IR spectrophotometer with a Perkin Elmer circulatory Air Dryer CD3. A complex similar to the metallopolymers under investigation, bis[4-(6-hydroxyhexyloxy)-*N*-(4-octyloxyphenyl)-salicylaldiminato]-copper(II), was used as a model for the IR and magnetic characterizations. With this monomer, a tablet of polyethylene (spectroscopically graded, Aldrich Co.) for the region 200 to 700 cm^{-1} and a tablet of KBr (700 to 4000 cm^{-1}) were prepared. The IR spectrum for polymer without metal was registered on melted films. The metallopolymers were measured using films obtained by slow evaporation of their toluene solutions.

X-ray measurements were carried out with $\text{CuK}\alpha$ radiation using photo method and X-ray diffractometry. The monomer was measured in 1 mm glass capillaries (Lindemann), whereas the metallopolymer films were placed between lamellar foils and held in a copper block. The photoplates were performed by a flat camera. In case of monomer **3** (see Fig. 1), a permanent magnet of 0.8 T was used for the alignment of the mesophase. Oriented films for polymer without metal were prepared using shear aligning technique. The polymer was placed between glass plates and heated to a temperature close to the transition into isotropic liquid. Then, to provide a shear, the cover glass was repeatedly (and circularly) moved relative to the substrate. After quenching to room temperature the oriented textures with smectic planes parallel to the film surface were memorized. The exact data analysis along meridional direction for aligned compounds was performed by focusing a horizontal two-circle X-ray diffractometer (STOE STADI 2) with a linear position sensitive detector (STOE mini PSD) for the data collection. By means of a differential temperature stabilizer near the location of the sample, the accuracy of temperature control was better than ± 0.1 K during the measurements. A detailed description of X-ray set-up and oven device has been already presented in ref.^{9,10}

Synthesis

6-[3-Hydroxy-4-(4-octadecyloxyphenyliminomethyl)phenoxy]hexyl methacrylate (**3**): 3 g of **1** and 2 g of 4-octyloxyaniline (**2**) dissolved in 50 ml of ethanol were refluxed with a catalytic amount of hydroquinone (HQ) for 2 h. After two recrystallization procedures from methanol, pale yellow plates of **3** were obtained with 70 % yield.

$^1\text{H NMR}$ (CDCl_3): $\delta = 13.95$ (s, 1H, Arom.-OH); 8.50 (s, 1H, CH=N); 7.22 (m, 3H, Arom.-CH=N; Arom.-OC₈H₁₇); 6.92 (d, 2H, Arom.-OC₈H₁₇); 6.45 (m, 2H, Arom.-CH=N); 6.10 (s, 1H, *trans* H₂C=C); 5.56 (s, 1H, *cis* H₂C=C); 4.16 (t, 2H, CO₂-CH₂); 3.98 (m, 4H, CH₂-O); 1.95 (s, 3H, CH₃); 1.29–1.83 (m, 20H, -CH₂); 0.89 (t, 3H, -CH₂-CH₃). $J_{\text{O}, \text{OCH}_{17}}$: 8.8 Hz.

Poly[6-[3-hydroxy-4-(4-octadecyloxyphenyliminomethyl)phenoxy]hexyl methacrylate] (**4**): 2 g of monomer **3** in 15 ml of toluene was radically polymerized for 72 h at 60 °C in a

sealed vial degassed with nitrogen, using 2 mg of *a,a'*-azoisobutyronitrile (AIBN) as initiator. Subsequent precipitations of the swollen polymer with methanol from concentrated toluene solutions gave the yellow polymer in 76% yield. The polydispersity index, \bar{M}_w/\bar{M}_n and the weight-average molar mass (\bar{M}_w) determined by GPC were 2.1 and 81 500, respectively (see Tab. 1), with a degree of polymerization of ≈ 160 .

$^1\text{H NMR}$ (CDCl_3): $\delta = 13.88$ (s, 1H, Arom.-OH); 8.33 (s, 1H, CH=N); 7.12 (m, 3H, Arom.-CH=N; Arom.-OC₈H₁₇); 6.81 (d, 2H, Arom.-OC₈H₁₇); 6.38 (m, 2H, Arom.-CH=N); 3.85 (m, 6H, -H₂C-C(CH₃); -CO₂-CH₂, -CH₂-O); 1.27–1.73 (m, 22H, -CH₂-); 0.89 (m, 6H, -CH₃).

IR (film): 2933 (s; C-H Arom.), 2860 (s; C-H Aliph.), 1733 (vs; C=O), 1618 (s; C=N), 1520, 1470 (vs; C=C Arom.), 1290, 1250 (s; C-O), 830 cm^{-1} (vs; C=C Arom.) (see Fig. 2a).

(C₃₁H₄₃NO₅)_n (509)_n Calc. C 73.08 H 8.45 N 2.75
Found C 72.86 H 8.49 N 2.75

Polymer 4/copper(II) complex (5): 0.6 mmol of Polymer **4** dissolved in 10 ml of dioxane was mixed for 3 h at 55 °C with 0.45 mmol of copper acetate (**5a**) or copper chloride (**5b**) also dissolved in 10 ml of dioxane. The reaction mixture was cooled, the precipitate filtrated and washed with portions of methanol. Part of the solid was dissolved in 5 ml of toluene and filtrated. From the toluene solution the metallopolymer **5** is obtained with 30% yield after evaporation of the solvent. The weight-average molar mass (\bar{M}_w) determined by GPC is presented in Tab. 1.

5a:

IR (film): 2933 (s; C-H Arom.), 2870 (s; C-H Aliph.), 1728 (vs; C=O), 1615 (s; C=N), 1595, 1470 (vs; C=C Arom.), 1292, 1248 (s; C-O), 832 (vs; C=C Arom.), 616 (s; Cu-O), 465, 403 cm^{-1} (s; Cu-N) (see Fig. 2b).

(C₆₂H₈₄N₂O₁₀Cu)_n (1079.5)_n Calc. C 68.92 H 7.71 N 2.59
Found C 70.83 H 8.12 N 2.48

5b:

IR (film): 3000 (s; C-H Arom.), 2870 (s; C-H Aliph.), 1720 (vs; C=O), 1620 (s; C=N), 1595, 1465 (vs; C=C Arom.), 1292, 1248 (s; C-O), 832 (vs; C=C Arom.), 616 (s; Cu-O), 465, 403 cm^{-1} (s; Cu-N) (see Fig. 2b).

(C₆₂H₈₄N₂O₁₀Cu)_n (1079.5)_n Calc. C 68.92 H 7.71 N 2.59
Found C 70.16 H 8.25 N 2.49

Results

A) Synthesis

Fig. 1 shows the synthetic route for the preparation of metallopolymers. The synthesis of 6-(4-formyl-3-hydroxyphenoxy)hexyl methacrylate (**1**) has been reported in a separate paper¹¹. Compound **3** was prepared by refluxing **1** and the aniline derivative **2** in ethanol with a trace of hydroquinone. The methacrylate polymer **4** was synthesized by radical polymerization of monomer **3** in toluene

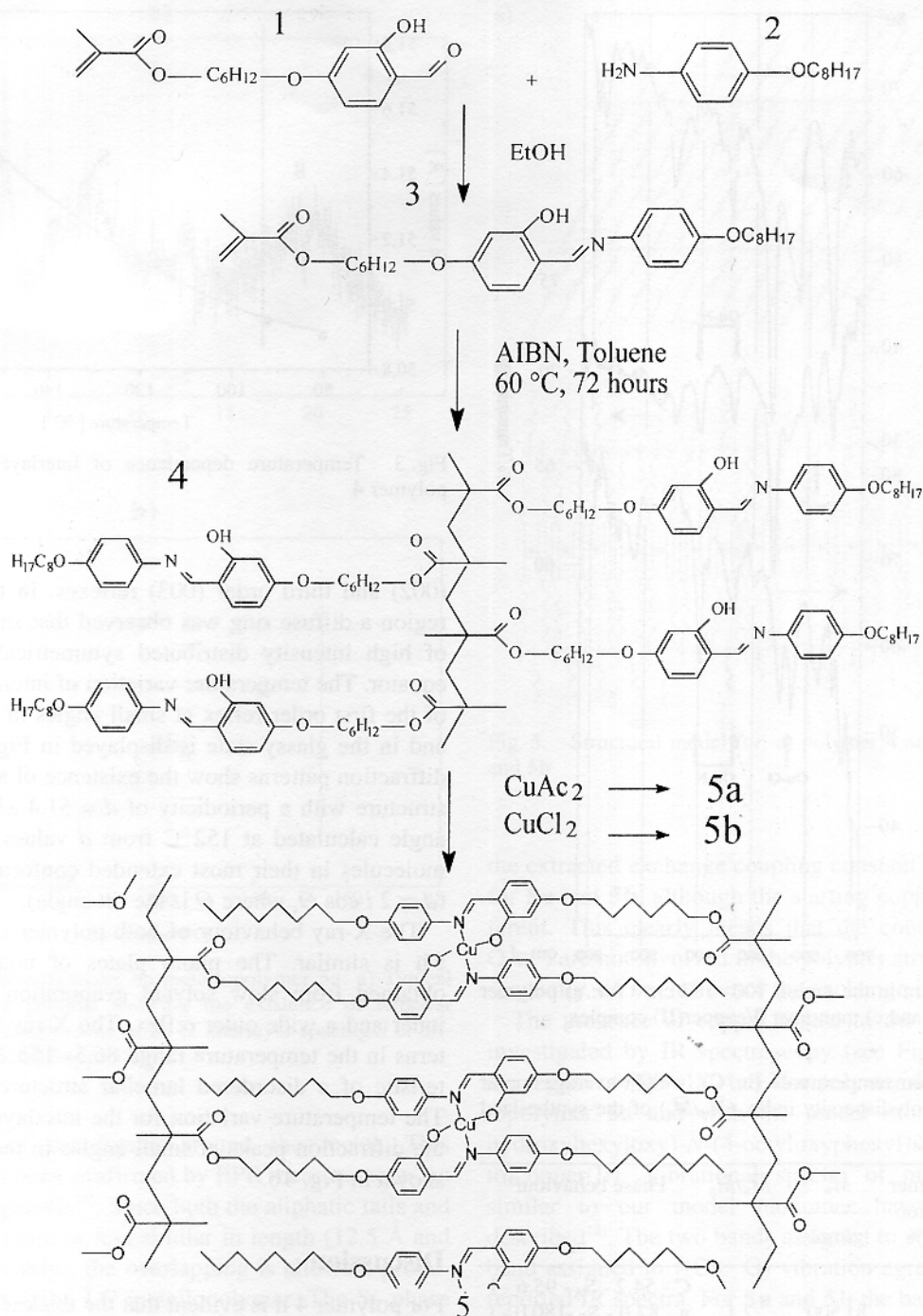


Fig. 1. Reaction scheme for the synthesis of copper-metallopolymers

with AIBN as initiator. The complexation of polymer **4** was carried out according to the procedure already described by Galyametdinov et al.¹²⁾ for related chelated monomers. The IR spectra of polymer **4**, its copper(II) complex **5a** and the copper(II) complex of monomer **3** are displayed in Fig. 2. Bands at 616 (Cu—O) and 465 and 403 cm^{-1} (Cu—N) indicating the complexation with copper(II) are clearly visible for the polymer complex **5a** (Fig. 2b).

B) Mesophase characterization

The phase transition temperatures of the investigated compounds are summarized in Tab. 1. Monomer **3** shows a schlieren texture accompanied with sharper dark lines and fan shaped texture. The X-ray diffraction photographs taken in the range 54.2–95.6 °C identify the smectic A phase, with a corresponding layer spacing of 34 Å.

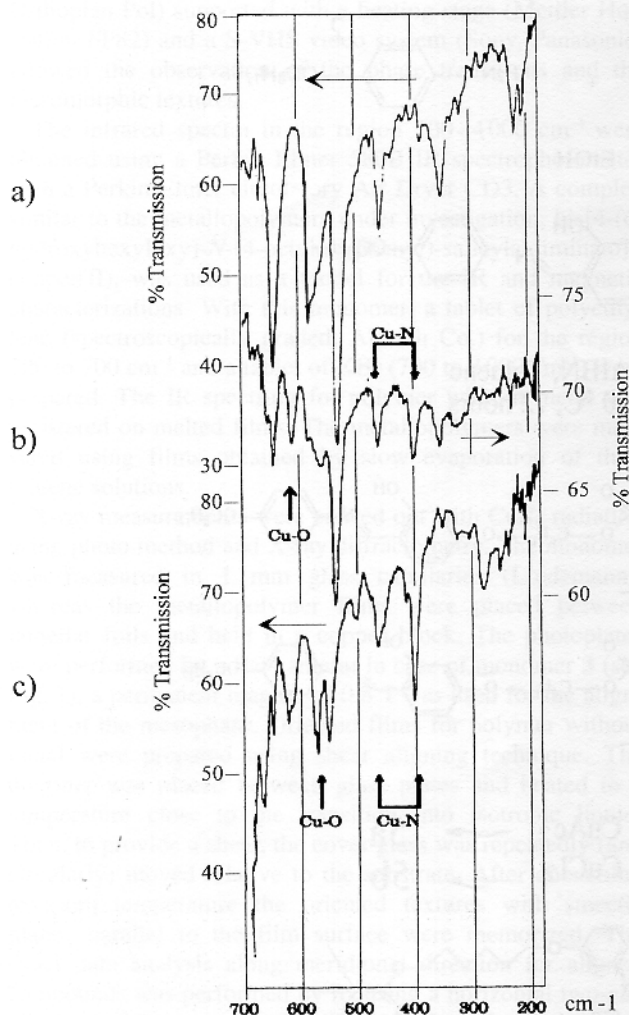


Fig. 2. IR spectra in the region 700–180 cm^{-1} for: a) polymer **4**, b) polymer **5a** and c) monomer **3**/copper(II) complex

Tab. 1. Transition temperatures (in $^{\circ}\text{C}$), weight-average molar mass (\bar{M}_w) and polydispersity index (\bar{M}_w/\bar{M}_n) of the synthesized compounds

Compound	Polymer fraction in %	\bar{M}_w g/mol	\bar{M}_w/\bar{M}_n	Phase behaviour ^{a)}
Monomer 3				C - 54.2 - S _A - 95.6 - I
Polymer 4		81 500	2.1	g - 82.0 - S _C - 180.0 - I
Polymer 5a	79.4	20 700	1.2	g - 86.5 - S _A - 153.2 - I
Polymer 5b	97.0	17 800	1.3	g - 76.4 - S _A - 184.1 - I

^{a)} C: crystalline, g: glassy state, S_A, S_C: smectic A or C phase, I: isotropic.

The calculated length l of the monomer in its most extended conformation assuming standard bond lengths, angles and van der Waals radii is 33.7 Å.

X-ray patterns carried out on oriented films of polymer **4** show the existence of 3 inner sharp peaks corresponding to the first order reflex (001) followed by the second

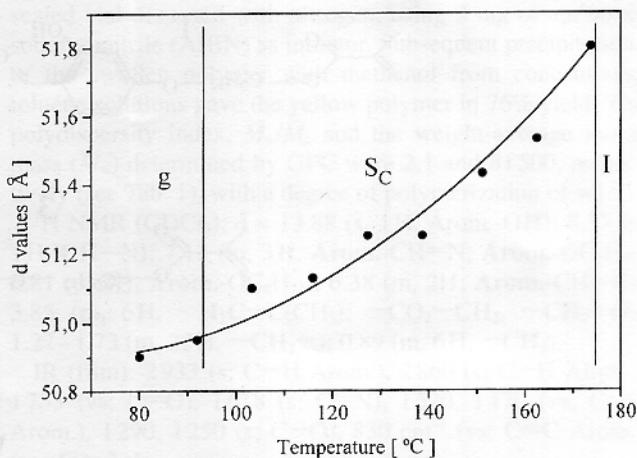


Fig. 3. Temperature dependence of interlayer spacing d for polymer **4**

(002) and third order (003) reflexes. In the wide angle region a diffuse ring was observed that shows four spots of high intensity distributed symmetrically around the equator. The temperature variation of interlayer spacing d of the first order reflex at small angles in the mesophase and in the glassy state is displayed in Fig. 3. The X-ray diffraction patterns show the existence of a tilted lamellar structure with a periodicity of $d = 51.4 \pm 0.3$ Å. The tilt angle calculated at 152 $^{\circ}\text{C}$ from d values assuming two molecules in their most extended conformation is 40.3° ($d \approx 2l \cos \theta$, where θ is the tilt angle).

The X-ray behaviour of both polymer samples **5a** and **5b** is similar. The photo plates of nonoriented films obtained from slow solvent evaporation show a sharp inner and a wide outer reflex. The X-ray diffraction patterns in the temperature range 86.5–153.2 $^{\circ}\text{C}$ are characteristic of a disordered lamellar structure (see Fig. 4a). The temperature variation for the interlayer spacing d of the diffraction peaks at small angles in the mesophase is shown in Fig. 4b.

Discussion

For polymer **4** it is evident that the thickness d is approximately 1.52 times the length l of the side chain at 140 $^{\circ}\text{C}$. These results and the observed X-ray data agree with the formation of a smectic C₂ phase. The proposed structure model for the mesophase of the methacrylate polymer is shown in Fig. 5a. A detailed description of the mesomorphic behaviour of polymer **4** is given in ref.¹³⁾

For both samples of the metallopolymer **5**, the backbone density is modulated with a period $d \approx l$. This result is reasonable considering the complexation process, where two ligands must be antiparallel for the binding through the metal center (Fig. 5b). This is quite a usual situation where the complexation way goes to a *trans*

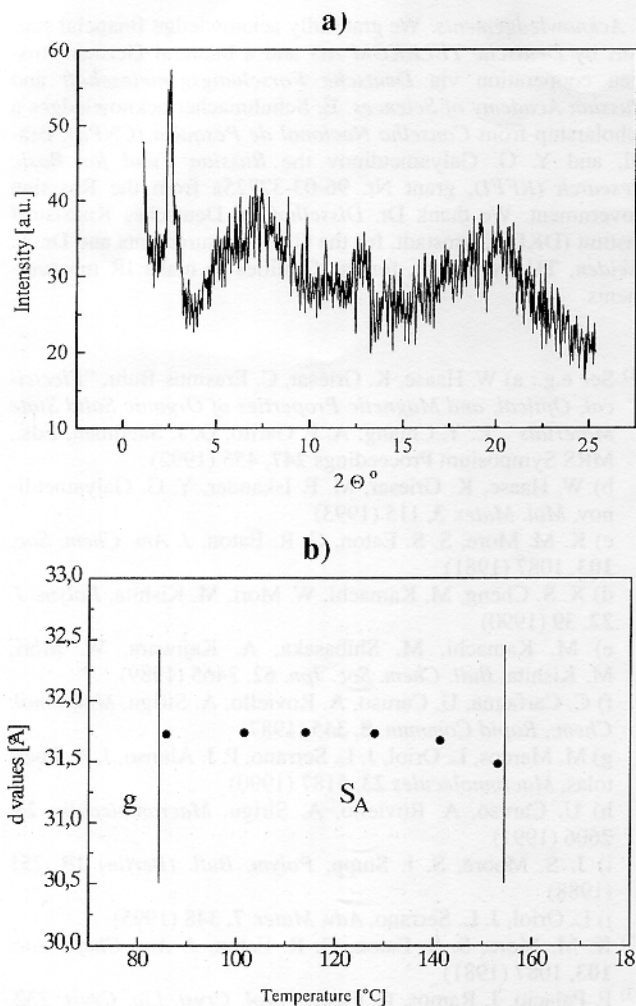


Fig. 4. X-ray investigations on metallopolymer **5a**: a) Typical X-ray diffraction patterns showing the existence of lamellar structure. b) Temperature variation of interlayer spacing d of diffraction peaks at small angles

configuration of the ligand around the metal. This mechanism has been confirmed by EPR measurements on monomer compounds¹¹). Since both the aliphatic tails and the spacer are more or less similar in length (12.5 Å and 10.2 Å, respectively), the overlapping is allowed, producing a form-retaining LC metallopolymer. The S_C phase present in the linear polymer **4** goes to an interdigitated structure necessary for the complexation process. This results in a crosslinked material observed directly in the products isolated from the reaction media.

Two different synthetic routes were followed to elucidate the influence of counterions in the synthesis of the metallopolymer **5** from polymer **4** and their possible inclusion into the final structure. The IR spectrum in the region of 4000 to 200 cm^{-1} of the crosslinked polymer **5a** correlates completely with the spectrum of polymer **5b**. This evidence is confirmed by the results of magnetic investigations⁷) and elemental analysis. The magnitude of

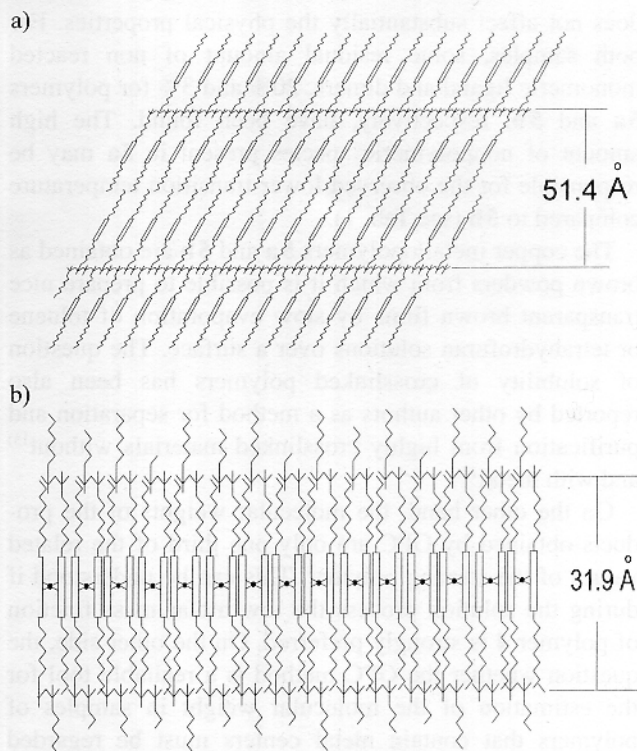


Fig. 5. Structural model for: a) polymer **4** and b) polymers **5a** and **5b**

the extracted exchange coupling constant J is comparable for **5a** and **5b**, although the starting copper salts are different. This clearly means that the counterions (Cl^- or OAc^-) are not involved in the polymer structure and, consequently, do not influence the exchange interactions.

The presence of copper linked to the polymer **4** was investigated by IR spectroscopy (see Fig. 2) comparing the region of 700–180 cm^{-1} for polymer **4** with the metallopolymer **5a** and with the model monomer bis[4-(6-hydroxyhexyloxy)- N -(4-octyloxyphenyl)salicylaldimino]copper(II). Vibrational spectra of metal complexes similar to our model monomer have already been described¹⁴). The two bands assigned to $\nu(\text{Cu}-\text{N})$ and the band assigned to $\nu(\text{Cu}-\text{O})$ vibration agree well with the reported IR spectra. For **5a** and **5b** the band vibration for $\text{Cu}-\text{O}$ present in the monomer model at 557 cm^{-1} is shifted to higher energy (616 cm^{-1}), which can be related with an axial interaction of copper ions with oxygen atoms of neighbouring molecules.

For the metallopolymers **5**, the glass transition temperature T_g is observed at lower temperatures than for the linear polymer **4** due to the softening effect of the crosslinking process¹⁵). The crosslinking process needs to be regarded over the 80% of yield considering the elemental analysis data of both samples **5a** and **5b** and the observed values of the effective magnetic moments⁷). The samples show a slight difference in the weight distribution that

does not affect substantially the physical properties. For both samples, some residual amount of non reacted monomeric ligand and dimers, 20% and 3% for polymers **5a** and **5b**, respectively, have been found. The high amount of nonpolymeric species present in **5a** may be responsible for the observed lower transition temperature compared to **5b** (see Tab. 1).

The copper metallopolymers **5a** and **5b** are obtained as brown powders from which it is possible to prepare nice transparent brown films by slow evaporation of toluene or tetrahydrofuran solutions over a surface. The question of solubility of crosslinked polymers has been also reported by other authors as a method for separation and purification from highly crosslinked materials without¹⁵ and with metal¹⁶.

On the other hand, the molecular weights of the products obtained by GPC are only one third of the related values of the starting polymer. This can be understood if during the solution process the low molar mass fraction of polymer **4** is strongly preferred. On the other side, the question whether the GPC method is a reliable tool for the estimation of the molecular weight in samples of polymers that contain metal centers must be regarded carefully. Guo et al.¹⁷ reported about differences in the estimation of the molecular weight for Ni-containing polymers using GPC and the absolute viscosimetry method. Such differences can be attributed to the high polarity introduced by the metal centers that can drastically change the retention time of the samples in the GPC columns due to stronger interactions. In our case it can be the reason for the observed lower molar mass of the metallopolymers **5**. The determination of the molecular weight of the polymers by osmotic methods or viscosity measurements are in progress.

As already discussed^{7,8}, most of the spin centers are involved in a chain structure-motive, leading to 1-D-Heisenberg antiferromagnetic behaviour. However, such kind of 1-D magnetic arrangement is not completely realized throughout the material, since our work-up procedure leads to the presence of some of monomeric copper ions which obey a Curie-Weiss behaviour, and dimeric copper ions which can be described by the isotropic Heisenberg exchange operator.

Due to the 1-D chain structure, each copper atom must exhibit a five- or six-fold coordination due to the presence of axial interactions via oxygen with the neighbouring copper centers. But this 1-D chain structure is realized only in isolated domains which are randomly distributed over the layer in the smectic A phase. The question whether such magnetic ordering could be realized in crystalline smectic phases, e.g. S_{Bcryst} , is currently an object of strong interest. Magnetic investigations of the highly crosslinked nonsoluble part of the polymer does not show any antiferromagnetic behaviour.

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