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Metallomesogenic Homopolymers. 1. Synthesis and Influence of Metalloorganic Structure on Mesogenic Behavior

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ABSTRACT: Different series of new liquid crystalline homopolymers containing paramagnetic units of copper(II) salicylaldiminates have been synthesized. Interfacial polycondensation of hydroxy-functionalized copper(II) complexes is shown to be the most suitable way of obtaining these polymers. In general, the polymers exhibit good thermal stability. Depending on the structure of the metalloorganic core and the length of the flexible spacer, some of the polymers proved to be mesogenic. The presence of enantiotropic and monotropic nematic phases in the *N*-alkyl polymers is related to the length of the *n*-alkylamine lateral group. *N*-Aryl polymers display nematic behavior at high transition temperatures.

Introduction

Over the past few years there has been increasing interest in metal-containing liquid crystals (metallomesogens).[1] However, little is known about liquid crystal metal-containing polymers.[2–16] Research into these polymers is important for several reasons. First, metal complexes exhibit a variety of geometries not to be found in organic compounds. Second, new physical properties and potential applications may be derived from the presence of metals in the ordered fluid phases of polymeric materials. For instance, materials with a long-range magnetic order may be obtained from the combination of the molecule's anisotropic paramagnetic susceptibility and the cooperative reorientation of liquid crystals in external fields.[17,18] Lastly, the considerable electronic density of these metal atoms and its high degree of polarizability suggest that these compounds could be nonlinear optical materials.[19]

In this paper we present the synthesis of metallomesogenic homopolymers, with the general structure shown in Figure 1.

Three different general methods for obtaining coordination polymers have been described:[20] (i) preformed metal complexes polymerized through functional groups, where the actual polymer-forming step can be either a condensation or an addition reaction; (ii) coordination of a metal ion by a preformed polymer containing chelating groups; (iii) polymer formation through a coordination reaction using a ligand which can attach itself simultaneously to two metal atoms or ions.

In the present work we use the first method, which permits a ready correlation of the structure of the polymer with its mesogenic properties since the homopolymers contain a repeating unit with one metal ion per unit.

This polymerization method involves an esterification reaction between two different monomers: the first is an acid dichloride bearing a flexible spacer, and the second is a coordination complex with hydroxyl groups on its periphery. Schiff base Cu(II) complexes were chosen as monomers because of their paramagnetic properties and their square-planar configuration. In magnetic fields these units may control the molecular orientation[21] of the polymers.

To the best of our knowledge, these polyesters are the first examples of enantiotropic metal-containing homopolymers.[12–15] We describe here the most suitable way of obtaining the polymers and the influence of structural modifications of the metalloorganic core on mesogenic behavior.

In a previous paper[12] we reported the first results obtained with this type of homopolymer. While we were working on the present article, another paper[15] was published reporting homologous *N*-alkyl derivative polymers with a different flexible spacer.

The homopolymers synthesized are coded as shown in Figure 1. The nomenclature corresponds to the symbols of the monomers involved in the polymer synthesis: [N*n*Cu], [NAR-O*n*-Cu], and [NAR-*n*-Cu] are the dihydroxy-functionalized copper(II) complexes, and [P10], [P2], and [C10] are the acid dichlorides. To simplify matters, we define the polymers derived from [N*n*Cu] as *N*-alkyl derivatives and the polymers derived from [NAR-O*n*-Cu] and [NAR-*n*-Cu] as *N*-aryl derivatives.

Experimental Section

Synthesis of the Monomers. The complete synthetic route to the target polymers is outlined in Scheme I.

The copper-containing monomers (diols B) were synthesized by the Sacconi method[22] as previously described for [N*n*Cu].[12] In the case of [NAR-O*n*-Cu] and [NAR-*n*-Cu] a solution of 10 mmol of the appropriate 4-alkyl- or 4-(alkyloxy)aniline in the minimum volume of ethanol was added slowly to a stirred mixture of 5 mmol of bis(4-hydroxysalicylaldehydato)copper(II) (A) in 20 mL of ethanol. The reaction mixture was refluxed overnight and then concentrated by evaporation to 50% of the initial volume. The complex was precipitated by adding dropwise sodium acetate (0.5 M) and purified by precipitation twice from solutions of acetone with water. The product was dried at 70 °C under vacuum over P_2O_5 for 24 h. 4-Alkylanilines and 4-methoxyaniline were commercially purchased and used without additional purification. 4-(Pentyloxy)- and 4-(decyloxy)aniline were synthesized as previously described.[23]

All the copper-containing monomers, except [N1Cu], were hygroscopic and contain one molecule of crystallization water per molecule of the complex.

Characterization data are collected in Table I.

The aromatic acid dichlorides ([P*n*]) were obtained according to the Griffin method,[24] recrystallized from carbon tetrachloride, and filtered under a nitrogen atmosphere.

Sebacoyl chloride ([C10]) was obtained by the reaction of sebacoyl acid with an excess of thionyl chloride and purified by distillation.

Synthesis of the Polymers. Sodium hydroxide (2 mmol) and 1 mmol of the corresponding copper(II)-containing monomers (B) were dissolved in 25 mL of a water–dioxane mixture with an adequate proportion of the latter to obtain complete solution of the complex. Aliquat 336 (355 mg) as a phase-transfer catalyst in 1 mL of dioxane was added, and the mixture was stirred slowly. A solution of 1 mmol of the acid dichloride in 10 mL of chloroform was added quickly, and the mixture was stirred for 30 min at

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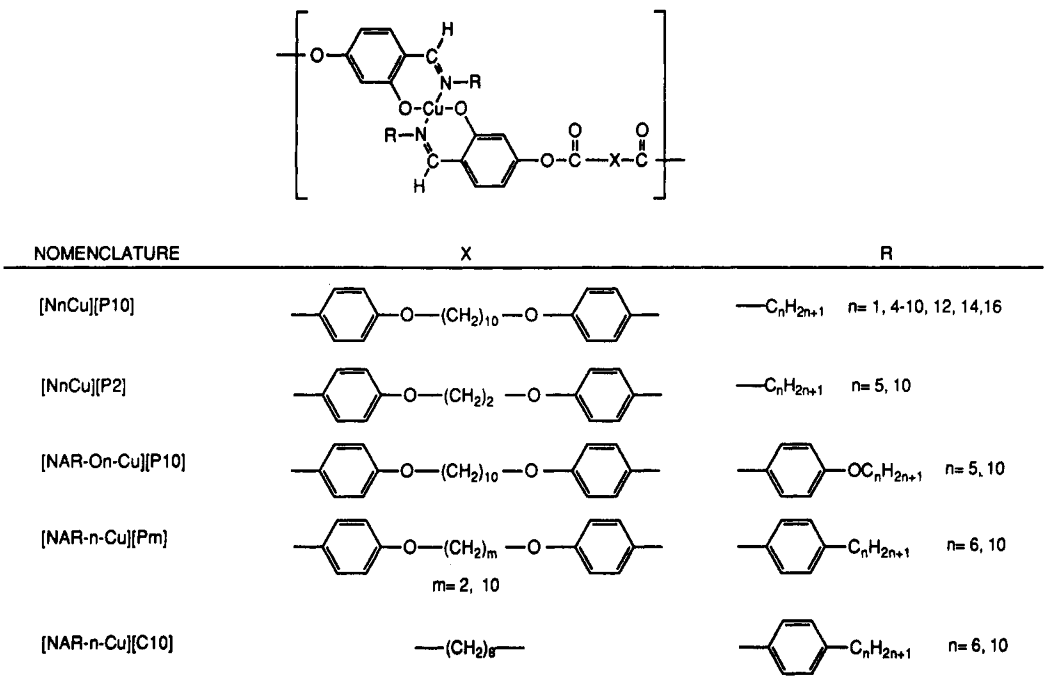
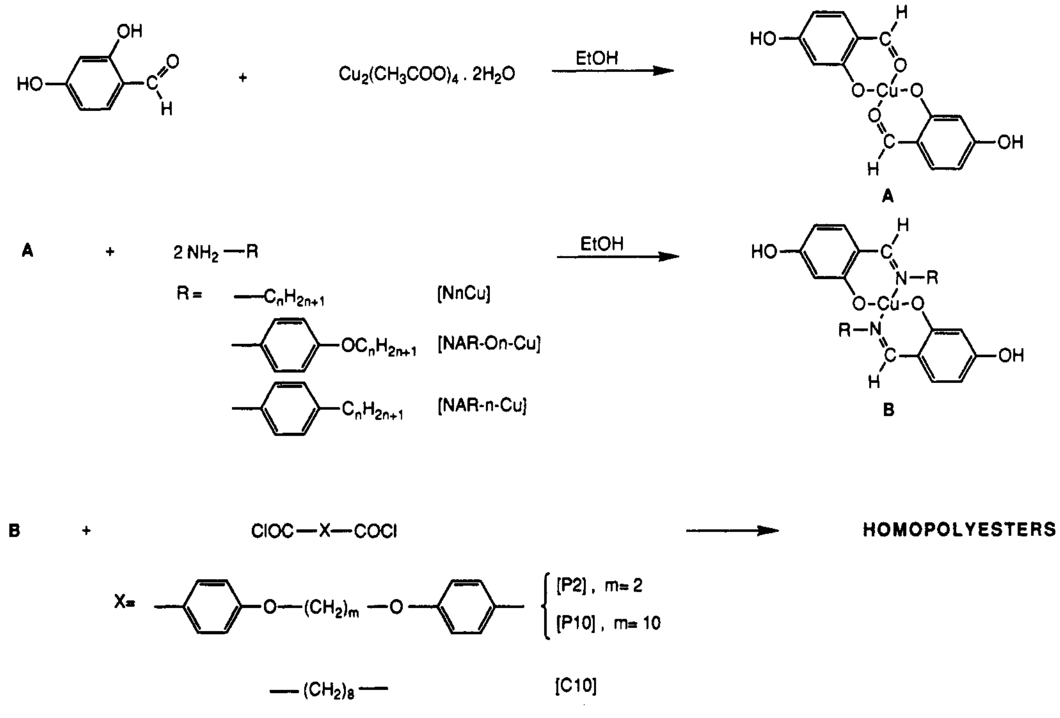


Figure 1. Schematic representation and nomenclature of the synthesized homopolymers.

Scheme I



3600 rpm. The polymer was precipitated by pouring the resulting mixture into 150 mL of methanol, filtered, and washed with water, methanol (twice), and finally acetone. The polymers obtained were dried under vacuum over P_2O_5 at 80 °C for 24 h. Yield, elemental analysis, and solution viscosity of the polymers are collected in Table II.

Techniques. Inherent viscosities were determined with a Cannon-Fenske viscosimeter at a concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane at 50 °C.

Thermogravimetric analysis was performed with a Perkin-Elmer TGS-2 equipped with a System 4 microprocessor controller. Powdered samples (about 7 mg) were heated from 40 to 600 °C at 10 °C/min in nitrogen. At this temperature the atmosphere was changed (nitrogen to air), and the sample was maintained for 20 min and heated again to 750 °C at the same heating rate to complete the oxidation. The copper percentage of the sample was calculated from the inorganic residuum, CuO.

DSC measurements were carried out with a Perkin-Elmer DSC-7 apparatus calibrated with indium (mp 156.6 °C, heat of fusion 28.4 J/g) and tin (mp 321.9 °C, heat of fusion 60.4 J/g). Mesogenic behavior was studied with a Nikon polarizing microscope fitted with a Mettler FP-82 heating stage and an FP-80 control unit. Transition temperatures were read at the maximum of the transition peaks.

Elemental analysis was performed with a Perkin-Elmer 240C microanalyzer. IR spectra were measured from KBr pellets on a Perkin-Elmer FTIR 1600.

Results and Discussion

Polymer Synthesis. Three condensation methods were tested: direct polycondensation using the method described by Higashi et al.,[25] low-temperature solution polycondensation using pyridine as a solvent, and finally interfacial polycondensation. When the first two methods were used, nonmesogenic polymers were obtained in poor yields. These methods are not particularly helpful because

Table I
Characterization Data of Copper-Containing Monomers

monomer	mp (°C)[a]	elemental anal. (calcd) % C	% H	% N	% Cu (calcd)[b]
[N1Cu]	>300 (dec)	53.07 (52.82)	4.43 (4.43)	7.88 (7.70)	17.70 (17.46)
[N4Cu]	176–180	56.85 (56.69)	6.00 (6.49)	6.08 (6.01)	14.12 (13.64)
[N5Cu]	149–151	58.50 (58.34)	7.09 (6.93)	5.44 (5.67)	12.85 (12.86)
[N6Cu]	147–150	60.30 (59.81)	7.31 (7.33)	5.10 (5.37)	12.05 (12.17)
[N7Cu]	146–148	60.84 (61.12)	8.10 (7.69)	4.85 (5.09)	10.80 (11.55)
[N8Cu]	133–136	62.15 (62.32)	7.99 (8.02)	4.77 (4.84)	11.91 (10.99)
[N9Cu]	130–132	63.51 (63.39)	8.60 (8.31)	4.63 (4.62)	10.37 (10.48)
[N10Cu]	110–114	64.37 (64.37)	8.86 (8.58)	4.15 (4.41)	9.10 (10.02)
[N12Cu]	133–135	66.30 (66.10)	9.36 (9.05)	3.97 (4.06)	9.00 (9.20)
[N14Cu]	124–127	68.17 (67.57)	10.21 (9.45)	3.53 (3.75)	8.68 (8.57)
[N16Cu]	126–128	69.20 (68.83)	10.45 (9.79)	3.60 (3.49)	7.38 (7.92)
[NAR-O1-Cu]	>300 (dec)	59.32 (59.40)	4.51 (4.63)	4.88 (4.95)	13.42 (12.52)
[NAR-O5-Cu]	>200 (dec)	63.31 (63.75)	6.45 (6.24)	4.11 (4.13)	8.99 (9.35)
[NAR-O10-Cu]	170–173	68.03 (67.50)	7.95 (7.63)	3.77 (3.42)	7.87 (7.76)
[NAR-6-Cu]	>190 (dec)	67.60 (67.68)	7.10 (6.87)	3.94 (4.15)	10.44 (9.42)
[NAR-10-Cu]	172–174	70.29 (70.24)	8.37 (7.95)	3.69 (3.56)	6.80 (7.73)

[a] Melting point determined by optical microscopy. [b] Determined by TGA of the inorganic residuum at 750 °C in an air atmosphere.

Table II
Characterization Data of Polymers

polymer	yield (%)	elemental anal. (calcd) % C	% H	% N	η_{inh}[a] (dL/g)
[N1Cu][P10]	62	63.11 (64.72)	6.03 (5.70)	3.25 (3.77)	*b*
[N4Cu][P10]	88	66.93 (66.85)	6.94 (6.59)	3.34 (3.39)	0.15
[N5Cu][P10]	89	68.22 (67.47)	7.46 (6.84)	3.41 (3.28)	0.14
[N6Cu][P10]	87	68.43 (68.04)	7.45 (7.08)	3.13 (3.17)	0.16
[N7Cu][P10]	88	70.15 (68.59)	7.95 (7.31)	2.65 (3.08)	0.16
[N8Cu][P10]	83	70.52 (69.09)	8.15 (7.52)	2.43 (2.98)	0.15
[N9Cu][P10]	86	69.75 (69.57)	8.23 (7.71)	2.48 (2.90)	0.15
[N10Cu][P10]	76	69.34 (70.03)	7.89 (7.90)	2.72 (2.82)	0.14
[N12Cu][P10]	87	71.28 (70.86)	8.62 (8.25)	2.50 (2.67)	0.17
[N14Cu][P10]	83	72.48 (71.61)	8.44 (8.56)	2.74 (2.53)	0.15
[N16Cu][P10]	81	72.24 (72.28)	9.76 (8.84)	2.49 (2.41)	0.13
[N5Cu][P2]	91	62.88 (64.72)	5.67 (5.70)	3.48 (3.77)	*b*
[N10Cu][P2]	69	67.42 (68.04)	7.08 (7.08)	2.73 (3.17)	0.14[c]
[NAR-O1-Cu][P10]	93	63.72 (65.21)	5.62 (5.41)	2.56 (2.98)	0.05
[NAR-O5-Cu][P10]	89	67.23 (69.38)	6.76 (6.40)	2.78 (2.70)	0.07
[NAR-O10-Cu][P10]	86	69.09 (71.31)	7.49 (7.35)	2.20 (2.38)	0.06
[NAR-6-Cu][P10]	88	70.76 (71.96)	6.82 (6.82)	2.51 (2.71)	0.05
[NAR-10-Cu][P10]	81	72.76 (73.30)	7.89 (7.56)	2.17 (2.44)	0.05
[NAR-6-Cu][P2]	80	69.18 (70.30)	5.55 (5.90)	2.92 (3.04)	0.11
[NAR-10-Cu][P2]	84	71.67 (71.96)	7.10 (6.82)	3.09 (2.71)	0.11
[NAR-6-Cu][C10]	86	70.62 (70.09)	7.39 (7.11)	3.99 (3.41)	0.08
[NAR-10-Cu][C10]	72	71.91 (71.96)	8.51 (7.98)	2.96 (3.00)	0.08

[a] Concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane at 50 °C. [b] Not soluble. [c] Residuum ≈ 25%.

of the hygroscopic character of the copper-containing monomers and the presence of pyridine, which reacts as a ligand and modifies the structure of the metallomesogen as revealed by elemental analysis and the IR spectra of the polymers obtained. Furthermore, the electron-withdrawing character of the metal complex decreases the reactivity of the phenol groups.[26]

Interfacial polycondensation proved to be a good way of obtaining the target polymers in good yields (Table II). The influence of the different experimental variables was studied to obtain optimum experimental conditions.[27]

The low thermal stability of the monomers made melt polymerization unsuitable.

Polymer Characterization. The polymers are soluble in chlorinated solvents, especially 1,1,2,2-tetrachloroethane. Depolymerization was not detected in solution viscosimetry, and it was possible to precipitate the polymer solutions with acetone as a nonsolvent and obtain fractionated samples of the starting material. The solubility of the polymers depends to a large extent on the structure of the metallomesogenic core and the length of the flexible spacer. *N*-Aryl derivatives are readily soluble, but with *N*-alkyl derivatives the solubility depends on the rigidity of the polymer chain and the length of the *n*-alkylamine group. Consequently, [N1Cu][P10] is not soluble in 1,1,2,2-tetrachloroethane, in spite of its decamethylene flexible spacer. *N*-Alkyl derivatives of [P2] acid dichloride are only slightly soluble.

The electron-withdrawing character of the metal complex led us to expect low degrees of polymerization. In fact, the viscosimetric data (see Table II) point to low molecular weights, especially in the case of the *N*-aryl polymers. The differences observed in solubility and η_{inh} between the *N*-aryl and *N*-alkyl derivatives are due to the different reactivities of the corresponding copper-containing monomers, which may be accounted for by the lower steric hindrance in the *N*-alkyl derivative monomers.

Elemental analysis and IR spectra confirm the structure of the expected repeating unit. End groups were detected (OH, COCl, COOH) in the [N10Cu][P2] and *N*-aryl [P2] and [C10] polymers, which corroborate their low molecular weight.

Thermal Stability. Thermogravimetric and DSC measurements of these polymers were carried out to

Table III
Thermogravimetric Data of Polymers

polymer	TGA[a] (°C)	DTGA[b] (°C)	1% wt loss (°C)	% Cu (calcd)[c]
[N1Cu][P10]	311	360	302	10.44 (8.56)
[N4Cu][P10]	295, 337	305, 380	297	7.67 (7.69)
[N5Cu][P10]	302, 344	306, 378	304	7.98 (7.44)
[N6Cu][P10]	295, 333	300, 373	295	7.65 (7.20)
[N7Cu][P10]	300, 359	309, 405	298	6.34 (6.98)
[N8Cu][P10]	297, 355	305, 405	291	6.77 (6.77)
[N9Cu][P10]	302, 363	310, 412	302	6.73 (6.57)
[N10Cu][P10]	263, 365	290, 410	280	6.64 (6.38)
[N12Cu][P10]	303, 377	311, 430	302	6.25 (6.05)
[N14Cu][P10]	293, 381	307, 431	299	5.87 (5.74)
[N16Cu][P10]	288, 380	309, 450	292	5.55 (5.46)
[N5Cu][P2]	301	309	295	10.68 (11.58)
[N10Cu][P2]	293	370	265	6.68 (7.20)
[NAR-O1-Cu][P10]	321	325, 348, 410	296	10.95 (9.56)
[NAR-O5-Cu][P10]	320	344, 399	314	7.36 (6.12)
[NAR-O10-Cu][P10]	318	310, 345, 420	310	7.61 (5.39)
[NAR-6-Cu][P10]	313	310, 360, 405	305	8.51 (8.24)
[NAR-10-Cu][P10]	326	304, 355, 420	303	6.23 (5.54)
[NAR-6-Cu][P2]	327	340, 393	318	7.01 (6.89)
[NAR-10-Cu][P2]	321	325, 406	320	6.25 (6.14)
[NAR-6-Cu][C10]	273	281, 398, 475	276	7.86 (7.73)
[NAR-10-Cu][C10]	266	281, 383, 430	272	6.87 (6.80)

[a] Onset of the decomposition curve. [b] Derivative thermogravimetric analysis. [c] Determined by TGA of the inorganic residuum at 750 °C in an air atmosphere.

determine their thermal stability. The thermogravimetric data are collected in Table III.

As can be deduced from these data, the synthesized homopolymers generally show good thermal stability in spite of the low thermal stability of the copper complexes used in the synthesis of the polymers. These data also show the influence of the number of aromatic rings in the structure of the repeating unit at the onset of the decomposition curve. *N*-Aryl polymers derived from aromatic acid dichlorides ([P10] and [P2]) are therefore more stable than the [C10] derivatives and the homologous *N*-alkyl polymers. The polymers are generally stable at temperatures lower than 290 °C and show a weight loss of less than 1%. Unlike the corresponding monomers, no evidence of crystallization or coordinated water loss was observed in the case of the polymers.

When the atmosphere was changed during the thermogravimetric analysis at 600 °C (inert to oxidative), strong decomposition took place, leading to the formation of CuO, which allowed us to determine the copper content. Differences between the calculated (from the repeating unit) and found copper percentage on *N*-aryl derivatives may be attributed to their low degrees of polymerization.

DSC Measurements and Mesogenic Behavior. Transition temperatures, thermodynamic data, and the mesophase of the polymers are gathered in Table IV. Thermal data correspond to the first heating scan at a scanning rate of 10 °C/min.

***N*-Alkyl Polymers.** In the series of [N*n*Cu][P10] both enantiotropic (*n* = 5 and 7–9) and monotropic (*n* = 10, 12, and 16) mesogenic behavior were detected. Polymers with *n* = 6 and 10 displayed an enantiotropic nematic mesophase on optical microscopy, but no endotherm corresponding to isotropization was detected in DSC.

Table IV
DSC and Optical Data of Polymers

polymer	phase transitions[a] (°C)	$\Delta H_{N\text{-}I}$[a] (kJ/mru)	$\Delta S_{N\text{-}I}$[a] (J K^{-1} mru^{-1})
[N1Cu][P10]	dec		
[N4Cu][P10]	K 264 dec		
[N5Cu][P10]	K 219 N 237 I	7.0	13.7
[N6Cu][P10]	K 221 I[b]		
[N7Cu][P10]	K 188 N 213 I	8.8	18.1
[N8Cu][P10]	K 174 N 197 I	5.2	11.0
[N9Cu][P10]	K 184 N 196 I	6.5	14.0
[N10Cu][P10]	K 174 I[b]		
[N12Cu][P10]	K 198 (N 166) I	5.3	12.0
[N14Cu][P10]	K 163 (N 147) I	10.6	25.1
[N16Cu][P10]	K 151 (N 142) I	11.0	26.5
[N5Cu][P2]	dec		
[N10Cu][P2]	K 212 dec		
[NAR-O1-Cu][P10]	dec		
[NAR-O5-Cu][P10]	K 289 N dec		
[NAR-O10-Cu][P10]	K 262 N 271 I	4.7	8.6
[NAR-6-Cu][P10]	K 270 N 288 dec		
[NAR-10-Cu][P10]	K 257 N 265 I	4.3	7.9
[NAR-6-Cu][P2]	dec		
[NAR-10-Cu][P2]	K 274 N dec		
[NAR-6-Cu][C10]	dec		
[NAR-10-Cu][C10]	K 151 N 172 I[c]	2.9[c]	6.6[c]

[a] Data corresponding to the first heating at 10 °C/min. [b] Nematic mesophase was observed in optical microscopy. Endotherm was not detected in DSC measurements. [c] Sample annealed at 130 °C for 1 h. Heating rate = 10 °C/min.

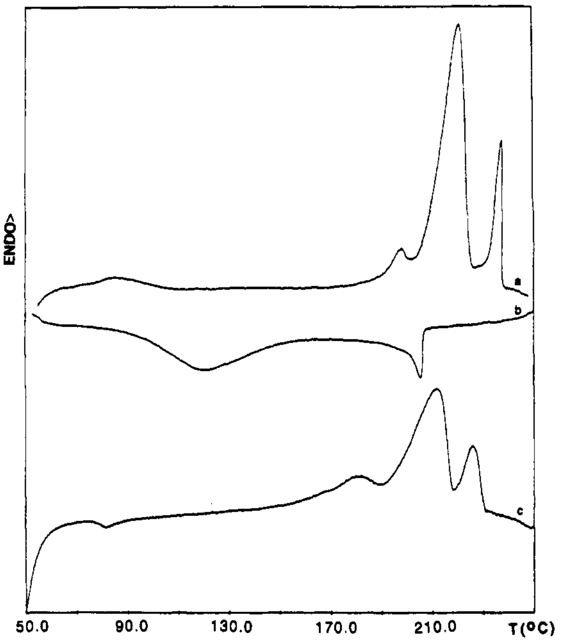


Figure 2. DSC traces of polymer [N5Cu][P10] (scan rate = 10 °C/min): (a) first heating run; (b) first cooling run; (c) second heating run.

In the first heating, enantiotropic behavior was characterized by a broad melting transition followed by isotropic transition (Figures 2 and 3), provided the sample did not decompose (see Table IV). In the cooling run (cooling rate = 10 °C/min) an exothermic peak corresponding to a transition from the isotropic liquid to the liquid crystalline phase (nematic mesophase) takes place with hysteresis in all cases. At lower temperatures a crystallization peak can be observed (Figure 2b), but in some cases the mesophase is preserved at room temperature (nematic glass, Figure 3b). A cold crystallization corresponding to the nematic glass was observed during the second heating scan (Figure 3c).

The isotropization temperature of enantiotropic polymers generally decreases slightly during the second heating, which could be attributed to some chemical instability of the polymers at high temperatures. As a consequence, a narrowing of the nematic range was observed except in the case of [N9Cu][P10]. Samples of enantiotropic polymers annealed prior to melting for 1 h were studied by DSC and optical microscopy. Figure 3d corresponds to the heating run of a sample of [N7Cu][P10] annealed

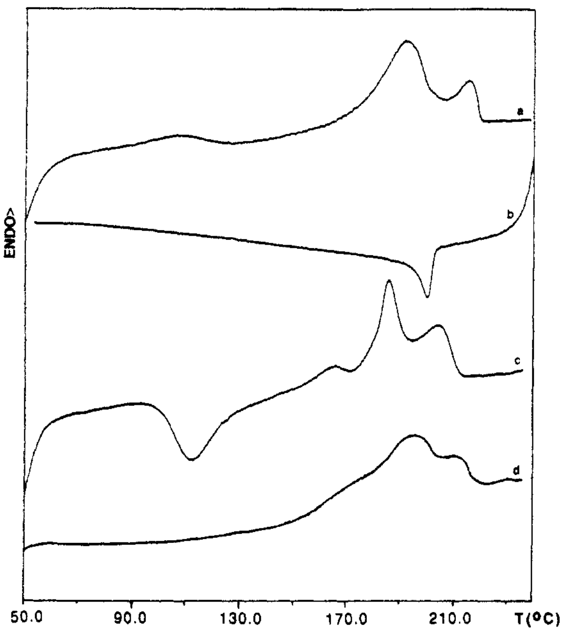


Figure 3. DSC traces of polymer [N7Cu][P10] (scan rate = 10 °C/min): (a) first heating run; (b) first cooling run; (c) second heating run; (d) first heating run of a sample annealed at 150 °C for 1 h.

Table V
Data Characterization of the Glass Transition Region

polymer	T_g (°C)	ΔC_p (J g^{-1} K^{-1})	T_{g1}[a] (°C)	T_{g2}[a] (°C)	$\Delta C_{p1}/\Delta C_{p2}$[a]
[N5Cu][P10]	61	0.36	43	64	0.52
[N7Cu][P10]	55	0.32	41	57	0.75
[N8Cu][P10]	45	0.46	41	57	1.28

[a] Data corresponding to the two separate glass transitions.

at 150 °C (incipient melting) for 1 h. Optical microscopy reveals a nematic mesophase on heating. Unlike the results of Caruso et al.[15] with similar polymers which differ only in the length of the flexible spacer (m = 12), enantiotropic behavior remains unchanged after annealing.

Glass transition steps were not detected in the DSC curves obtained in the previously described experimental conditions. However, samples quenched from the isotropic melt to liquid nitrogen and rerun show a glass transition before cold crystallization. The data are collected in Table V. A variation of T_g according to the length of the lateral N-aliphatic group is observed. Moreover, two separate glass transitions[28-31] appear, as shown in Figure 4. Taking into account the similar values of η_{inh} of the three polymers (with n = 5, 7, and 8) obtained under the experimental conditions, we can assume the polymers have a similar chain length and polydispersity. With this hypothesis, the differences observed in the heat capacity increments corresponding to the two separate glass transition regions (tabulated as $\Delta C_{p1}/\Delta C_{p2}$) indicate a relationship between the very local motions involved in the glass transition regions and n. Bearing in mind the structure of the polymers, the first region (region 1) of the glass transition may be explained by the involvement of the local motions of mobile structural moieties of the N-alkyl lateral groups. The local motions of the rest of the structural mobile moieties are involved in region 2. The length of the N-alkyl lateral group increases when n increases and consequently $\Delta C_{p1}/\Delta C_{p2}$.

In Figure 5 an example of monotropic behavior is shown. This behavior has been previously described in metal-containing liquid crystalline homopolymers.[5]

The mesophase was identified as nematic by the textures observed in optical microscopy (see Figure 6a). Additionally, miscibility studies of some representative polymers of the series with a low molecular weight metallonematogen (bis[N-n-pentyl-4-[[(decyloxy)benzoyl]oxy]salicylaldiminato]copper(II)) showed uninterrupted miscibility.[12]

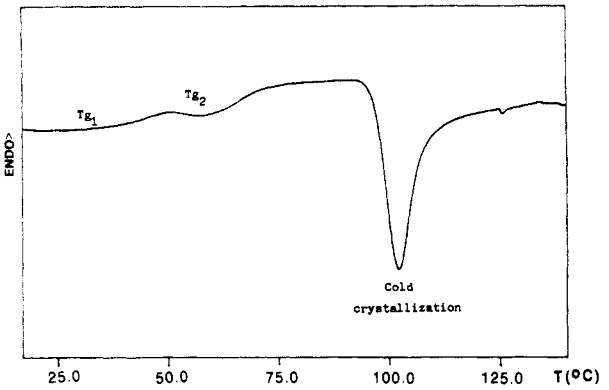


Figure 4. DSC trace in the glass transition region of a sample of polymer [N5Cu][P10] quenched from the isotropic melt: two separate glass transitions, regions 1 (T_{g1}) and 2 (T_{g2}), and cold crystallization. Heating rate = 20 °C/min.

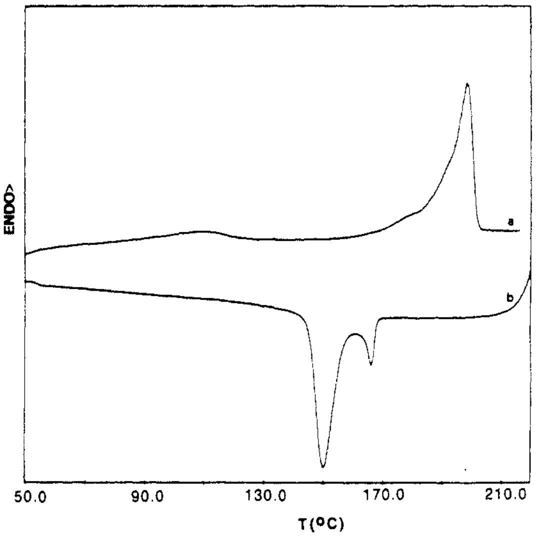


Figure 5. DSC traces of polymer [N12Cu][P10] (scan rate = 10 °C/min): (a) first heating run; (b) first cooling run.

[NnCu][P2] polymer decomposes before or during melting, and mesogenic behavior was not observed.

***N*-Aryl Polymers.** The N-aryl polymers show higher melting temperatures. When thermal decomposition did not take place, mesogenic behavior appeared at high temperatures. DSC measurements were carried out at different heating and cooling rates to avoid decomposition. In polyesters derived from [P10] with long aliphatic chains, reproducible transitions appear from samples cooled from the isotropic melt and run at 40 °C/min. However, the polyesters derived from [P2] and [C10] showed complex thermal behavior, and annealing at a temperature before melting was necessary to study the mesogenic behavior (see Table IV).

The textures observed in N-aryl polymers were not easy to identify because of the decomposition of the samples. However, a marbled texture appeared after mechanical stress at a high temperature, and nematic droplets were observed at the clearing point with singularities with two brushes. These textures indicate the nematic mesophase (Figure 6b).

Thermodynamic Data. In spite of the new metallomesogenic structure, thermodynamic data correspond-

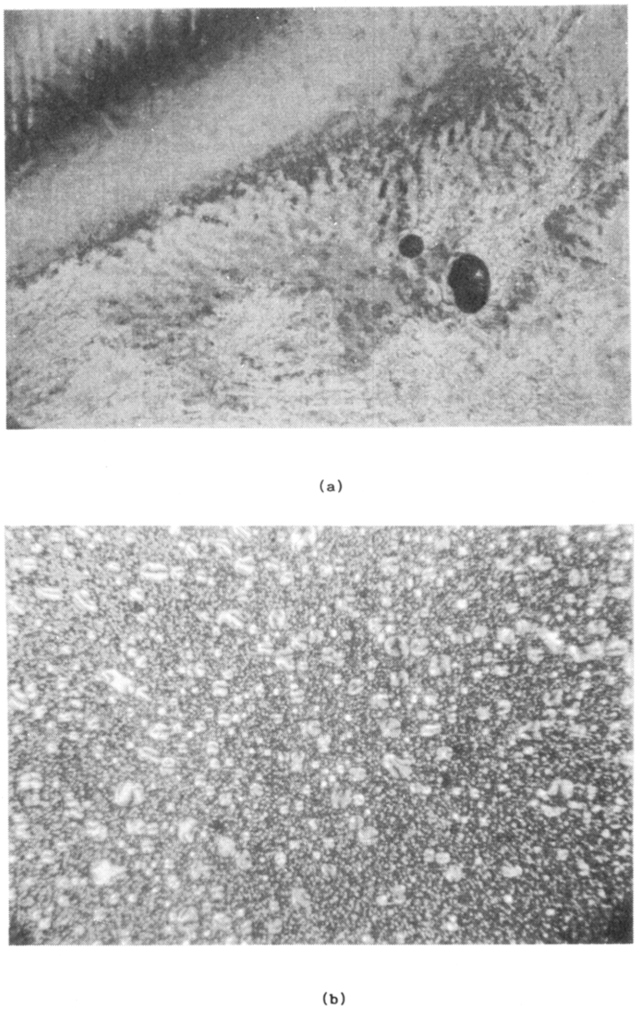


Figure 6. Polarized light micrographs of (a) polymer [N7Cu]-[P10] at 190 °C under mechanical stress (×100) and (b) polymer [NAR-O10-Cu][P10] at 255 °C on cooling (×100). [The magnifications given are original magnifications. The micrographs have been reduced to 55% of their original size for publication purposes.]

ing to ΔH_{N-I} and ΔS_{N-I} (calculated by deconvolution of the curves) are similar to the literature data for semiflexible liquid crystal polymers with an even number of carbon atoms in the flexible spacer.[32] Furthermore, the ΔS_{N-I} of these metallomesogenic polyesters are about 3 or 4 times higher than the values reported for homologous low molecular weight metallomesogens,[33,34] due to the conformational contribution of the flexible spacer briefly reported.[35]

Influence of Structural Modifications on the Metallomesogenic Core. The mesogenic behavior of these homopolyesters is a consequence of the metalloorganic structure of the monomers. The stepped structure of the square-planar complexes of Cu(II)[36] is ideal for obtaining metallomesogens incorporated into a main-chain polymer. The square-planar geometry gives a rodlike shape to the metallomesogenic unit, and the step disrupts the linearity of the polymeric chain. This structure may be compared to a crankshaft monomer. The lateral *N*-alkyl or *N*-aryl chains decrease the high melting temperature expected with this kind of structure because of the hindrance of the lateral packing of the polymeric chains. The transition temperature very much depends on the length of the lateral N substituent, as can be observed in Table IV for the [N*n*Cu][P10] series. Moreover, either an enantiotropic or a monotropic mesophase was obtained according to the length of this lateral *n*-alkylamine group.

The introduction of para-substituted aromatic lateral groups in the metalloorganic core increases rigidity and intermolecular interactions, as can be deduced from the high transition temperatures of *N*-aryl [P10] derivatives ([NAR-O*n*-Cu][P10] and [NAR-*n*-Cu][P10]). Even such a minor modification as the introduction of *p*-alkyloxy ([NAR-O*n*-Cu][P10]) instead of *p*-alkyl ([NAR-*n*-Cu]-[P10]) terminal chains modified T_m. The molecular shape of these metallomesogens is very different from the disk-like shape due to the fact that both the *N*-aryl and benzoyl groups are twisted with respect to the salicylidene moiety.[37]

The polyester with a short flexible spacer ([P2]) showed higher transition temperatures and poorer thermal stability. This can be attributed to the high concentration of metallomesogenic units. In other words, the length of the flexible spacer is a crucial factor for the observation of stable mesophases in metal-containing homopolyesters.

The polyesters derived from sebacoyl chloride showed poor thermal stability.

Conclusions

Interfacial polycondensation is shown to be a suitable method for obtaining mesogenic homopolymers containing Cu(II) complexes. The stepped square-planar structure of these Cu(II) complexes is ideal for obtaining paramagnetic liquid crystals. Structural variations of the repeating unit of the homopolymers allow us to decrease melting points and observe a broad range of mesophase. To obtain polymers with adequate thermal stability, the aromatic acid dichloride which incorporates a long flexible spacer ([P10]) is shown to be the most suitable monomer. Furthermore, *N*-alkyl copper complex monomers display lower transition temperatures than *N*-aryl monomers. These copper complexes may be classified as crankshaft monomers with bulky substituents, briefly reported in the synthesis of organic liquid crystals polymers.

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Registry No. [N1Cu][P10] (copolymer), 130325-90-5; [N4Cu][P10] (copolymer), 142926-90-7; [N5Cu][P10] (copolymer), 130325-94-9; [N6Cu][P10] (copolymer), 142925-59-5; [N7Cu][P10] (copolymer), 142926-91-8; [N8Cu][P10] (copolymer), 142926-92-9; [N9Cu][P10] (copolymer), 142925-60-8; [N10Cu][P10] (copolymer), 130325-98-3; [N12Cu][P10] (copolymer), 142925-61-9; [N14Cu][P10] (copolymer), 142865-87-0; [N16Cu][P10] (copolymer), 142840-71-9; [N5Cu][P2] (copolymer), 142925-62-0; [N10Cu][P2] (copolymer), 142925-63-1; [NAR-O1-Cu][P10] (copolymer), 142840-73-1; [NAR-O5-Cu][P10] (copolymer), 142840-75-3; [NAR-O10-Cu][P10] (copolymer), 142840-77-5; [NAR-6-Cu][P10] (copolymer), 142840-79-7; [NAR-10-Cu][P10] (copolymer), 142840-81-1; [NAR-6-Cu][P2] (copolymer), 142840-82-2; [NAR-10-Cu][P2] (copolymer), 142840-83-3; [NAR-6-Cu][C10] (copolymer), 142840-84-4; [NAR-10-Cu][C10] (copolymer), 142840-85-5; [N1Cu], 130325-89-2; [N4Cu], 133295-30-4; [N5Cu], 130325-93-8; [N6Cu], 133295-31-5; [N7Cu], 133295-32-6; [N8Cu], 133295-33-7; [N9Cu], 133295-42-8; [N10Cu], 130325-97-2; [N12Cu], 133295-35-9; [N14Cu], 142840-86-6; [N16Cu], 142840-70-8; [NAR-O1-Cu], 142840-72-0; [NAR-O5-Cu], 142840-74-2; [NAR-O10-Cu], 142840-76-4; [NAR-6-Cu], 142840-78-6; [NAR-10-Cu], 142840-80-0.