Main chain liquid crystalline polymers with laterally linked organometallic mesogens

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U. CARUSO, A. ROVIELLO, A. SIRIGU* and C. TROISE

Università di Napoli 'Federico II', Dipartimento di Chimica,
Complesso di Monte S. Angelo, Via Cintia 80126 Napoli, Italy

The synthesis and characterization of the phase behaviour of a homologous set of polymers of 1,*m*-diamino-*n*-alkanes with bis[4-(4-alkoxybenzoyloxy)-2-hydroxybenzaldheyde]copper(II) is reported. The structural peculiarity of these polymers, which is indicated in the title, stems from the presence of metal-complexed salicylideneaminato segments connected via the nitrogen atoms. Calorimetric analysis, polarizing optical microscopy, X-ray diffraction and dynamic viscosity measurements indicate the occurrence of nematic mesomorphism for all the polymers—including two structural analogues containing Ni(II) or Pd(II) in place of Cu(II).

1. Introduction

It is well known that the liquid crystalline properties of a polymeric system are related to the chemical and stereochemical features of the constitutive mesogenic segments as well as to the way these segments are connected together, and contribute to define the structural features of the polymer chain [1, 2].

Among the liquid crystals containing metal atoms, a consistent set of information has been collected for low molecular mass [3–8] and related polymers [9–12] containing mesogenic groups based on salicylideneaminato metal complexes. Actually, this complexation form is very effective in allowing property variations related to the chemical nature of the coordinated metal ion, and structural features affecting the overall shape of the mesogenic group, as well as the way these crucial segments are positioned as part of the polymeric structure. Concerning this latter point, two basic structures may be considered for linear polymers, as shown in the following scheme 1.

Mode A implies that the polymeric sequence proceeds through the salicylic groups, while in the other mode B, it proceeds through a …N* M* N* connection. Mode A has been followed in most cases under the assumption that it allows the construction of mesogenic segments whose axis of elongation fits more strictly with the polymer chain direction in the extended conformation. In this case, the structure of the molecular segment connected to the nitrogen atom of the salicylaldiminate group may be restricted to a bare methyl group, reducing the average cross section of the mesogen to a minimum. It is apparent that these polymers comply with the structural scheme most usually followed in the design of organic main chain liquid crystalline polymers bearing the mesogenic groups axially appended along the polymer chain.

Mode B, which obviously requires at least partially different synthetic procedures to be followed, actually does not necessarily imply that drastically different mesogenic structures are to be obtained. We report here
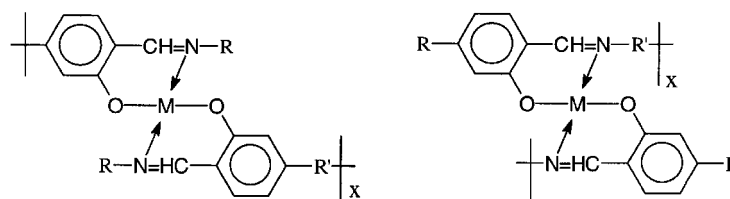
Scheme 1.   mode A   mode B

*Author for correspondence; e-mail: sirigu@chemistry.unina.it

on the synthesis and liquid crystalline properties of a set of mode B polymers represented by formula 1; these are closely analogous to previously reported mesogenic mode A polymers [11] represented by formula 2. The two polymer types share the same basic structure of the mesogenic core to the extent that the same mesogenic group may be taken as axially (mode A) or laterally (mode B) linked along the polymer chain.

2. Experimental

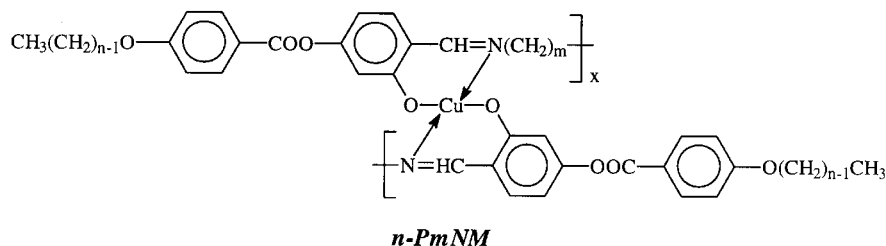All polymers were prepared according to the procedure reported in the scheme 2:

We describe, as an example, the synthesis of 8-P12NCu. 4.02 g of **1**, previously synthesized and purified according to a procedure already reported [6] was dissolved in 100 ml of cold absolute ethanol and interacted with 1.08 g of copper(II) acetate previously dissolved in 50 ml of absolute ethanol. The reaction mixture was kept boiling for 5 min and eventually cooled. Green coloured **2** precipitated out and was purified by crystallization from ethanol/chloroform solution (60:40) (yield 50%). The results (wt %) of quantitative analysis of the copper content for compound **2** ($n = 8$) and its homologues are in accordance with the attributed formulae ($n = 6$: 10.66% calc., 10.91 found; $n = 8$: 9.91% calc., 9.87% found; $n = 10$: 9.26% calc., 9.40% found: $n = 12$: 8.70%

calc., 8.87% found). All the compounds **2** decompose without melting at a temperature higher than 300°C. Both calorimetric and thermogravimetric data are consistent with this behaviour.

Polymerization was performed in solution. 0.98682 g of **2** was dissolved in 25 ml of boiling chloroform and 0.246 g of 1,12-diaminododecane previously dissolved in 25 ml of ethanol was added. The solution was heated at reflux for 10 min. Eventually, it was added to a cold solution of 0.5 g of sodium acetate in 60 ml of ethanol to precipitate the polymer. After filtration, the polymer was washed twice with boiling ethanol (yield 90%). A similar procedure was followed for the synthesis of the copolymers nP10/12NCu utilizing an equimolar proportion of the appropriate α,ω-diaminoalkane.

Nickel- and palladium-containing polymers were prepared according to scheme 3. The synthesis of 8-P12NPd is reported as an example.

1.33775 of **3**, obtained by decomplexation of 8-P12NCu by a standard procedure [10], were dissolved in 20 ml of hot dioxan (~50°C) and added to a solution of 0.567 g of $(C_6H_5CN)_2Cl_2Pd$ previously dissolved in 15 ml of dioxan. The reaction mixture was kept at 50°C for 5 min and then added to a solution of 0.485 g of sodium acetate dissolved in 50 ml of hot ethanol. The brown–yellow precipitate was washed twice with boiling ethanol (yield 80%).

n-PmNM

n= 6, 8, 10, 12; m= 10, 12, 10/12; M= Cu

n= 8; m= 12; M= Ni, Pd

Formula 1.

Pn-mNCu

n= 12; m= 4-13

Formula 2.

$CH_3(CH_2)_7O$—⬡—COO—⬡—CHO + $(CH_3COO)_2Cu$
|
OH

1

$CH_3(CH_2)_7O$—⬡—COO—⬡—CHO
O—Cu—O
OHC—⬡—OOC—⬡—O$(CH_2)_7CH_3$

2

$H_2N(CH_2)_{12}NH_2$
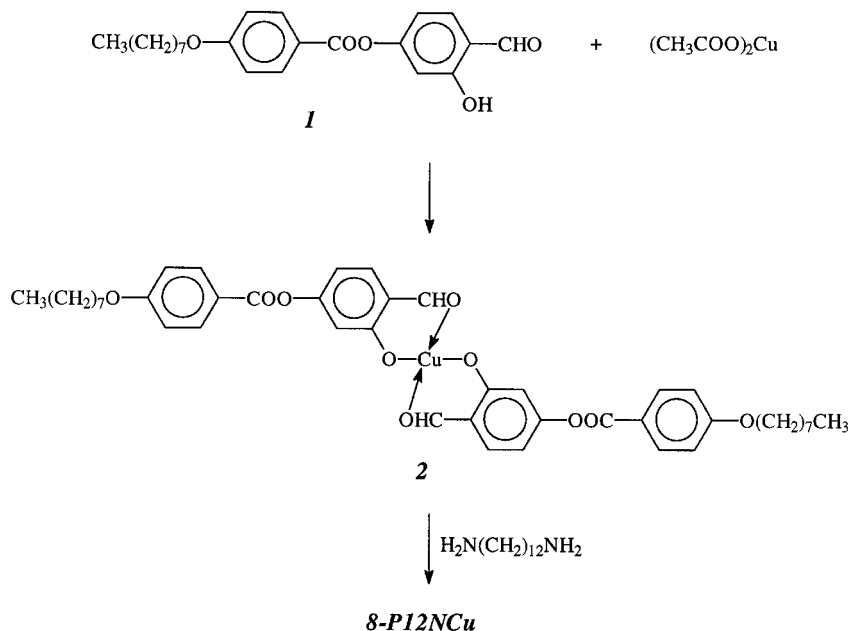
8-P12NCu

Scheme 2.

$\left[CH_3(CH_2)_7O\text{—⬡—COO—⬡—}CH=N(CH_2)_6 \right]_2$
|
OH

3

$(C_5H_6CN)_2Cl_2Pd$

8-P12NPd
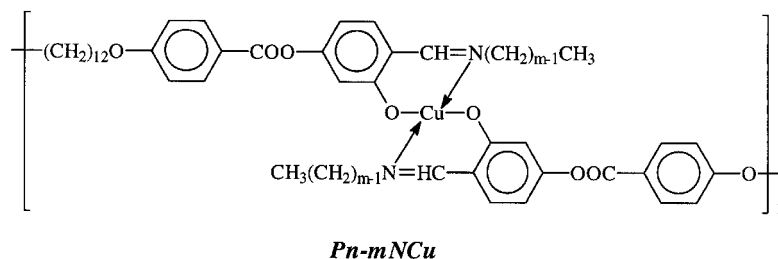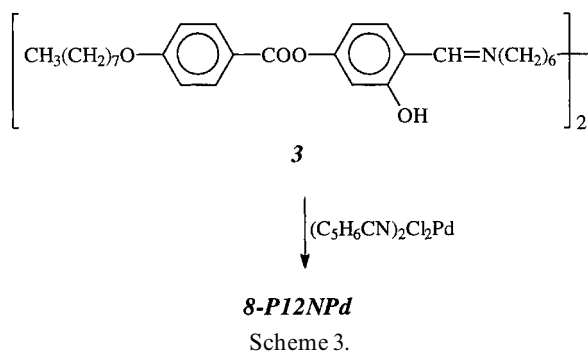
Scheme 3.

For characterization of the phase behaviour, differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) were employed. For the DSC analysis, an indium calibrated Perkin Elmer DSC7 apparatus was utilized. Samples were examined under a dry nitrogen atmosphere with a temperature scanning rate of $10°C\,min^{-1}$. The phase transition temperatures reported in the discussion section were measured at the maxima of the transition endotherms for the polymers, while for low molecular mass compounds they represent onset values. Optical observations were performed with a Zeiss Axioskop polarizing microscope equipped with a Mettler FP5 micro-furnace. XRD patterns were recorded by the photographic method utilizing a flat-film camera and Ni-filtered CuK_α radiation. Dynamic viscosity measurements were performed using a Rheometrics Recap 2 apparatus at an oscillatory frequency of 10 Hz. Measurements were performed for decreasing temperature ($10°C\,min^{-1}$ cooling rate) starting from the isotropic liquid. The intrinsic viscosity of a chloroform solution of the polymers was measured utilizing an Ubbelohde viscometer at 25.0°C. Average molecular mass was measured for polymer 6-P10NCu as a reference by vapour pressure osmometry using a Knauer apparatus. Measurements were made at 37°C on a chloroform solution; the resulting average molecular mass is $5500\,g\,mol^{-1}$. This rather low molecular mass might have some negative influence on the isotropization temperature, but should be high enough to exclude any influence on the nature of the liquid crystalline phase [2]. Chemical structure and purity of all synthesized compounds were checked by ^{1}H NMR spectrometry, performed using a Bruker 250 MHz or a Varian 200 MHz spectrometer.

3. Results and discussion

The table reports thermodynamic data concerning the copper-containing polymers as samples without previous thermal treatment. All the polymers exhibit liquid crystalline behaviour. For some (6-P10NCu and all copolymers *n*-P10/12NCu) the mesomorphic phase shows up in a clearly enantiotropic way. For all the other polymers, with the probable exception of 8-P12NCu, monotropic phases are featured. Figure 1 shows the thermal DSC behaviour of 10-P12NCu taken as an example for this class of polymer. Samples without any previous thermal treatment have moderate crystallinity. The melting transition (curve *a*) overshadows the isotropization which possibly involves the non-crystalline fraction at similar temperatures. The liquid crystalline behaviour shows up on cooling (curve *b*) as the anisotropization transition, as confirmed by POM, followed by crystallization of the considerably supercooled mesophase. The monotropic character of the mesophase is

Table.   Thermodynamic and viscosity data for the polymers.

| n	m	$T_m/°C$[a]	$T_i/°C$[b]	$\Delta H_i/J\,g^{-1}$[c]	$[\eta]_{inh}/dL\,g^{-1}$[d]
6	10	197	237	6.6	0.324
8	10	217	219	5.8	0.257
10	10	201	205	5.2	0.301
12	10	191	194	4.5	0.275
6	10/12	—	231	6.9	0.125
8	10/12	159	212	5.9	0.201
10	10/12	169	199	5.2	0.180
12	10/12	158	187	4.7	0.160
6	12	225	226	6.9	0.355
8	12	185	207	6.2	0.378
10	12	196	193	5.4	0.290
12	12	186	185	4.8	0.305

[a] Melting temperature.
[b] Isotropization temperature.
[c] Isotropization enthalpy.
[d] Intrinsic viscosity.
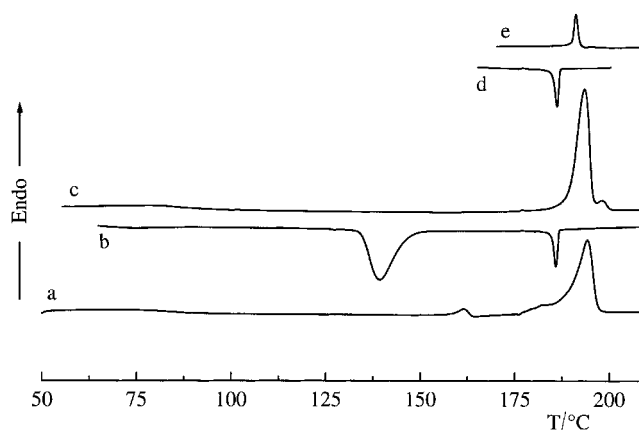
Figure 1.   DSC curves of 10-P12NCu: (*a*) first heating run; (*b*) first cooling run; (*c*) second heating run; (*d*) second cooling run; (*e*) third heating run.

clearly shown by curves *d* and *e*. The mesophase obtained on cooling the isotropic liquid (curve *d*) undergoes sufficient supercooling to allow the reverse heating process to be undertaken before crystallization takes place. Therefore, the isotropization transition may be clearly detected and its temperature properly measured (curve *e*). Most of the T_i and ΔH_i values reported in the table were measured in this way. For other polymers showing a seemingly enantiotropic behaviour (such as *n*-P10NCu; $n > 6$ and 6-P12NCu), annealing at the incipient melting temperature increases the thermal stability of the crystalline phase up to temperatures higher than T_i. Less clear-cut evidence is available for polymer 8-P12NCu. Annealing this polymer at 180°C for 1 h raises the melting temperature to 194°C. However, the possibility cannot be ruled out that prolonged annealing at progressively increasing temperatures might lead to monotropic behaviour.

Various pieces of experimental evidence suggest that the liquid crystalline phase is probably nematic for all the polymers. The texture most commonly observed consists of very minute schlieren. Band structures are developed by shearing the molten polymer in the liquid crystalline phase. Such a morphology quenched to room temperature is shown in figure 2 for polymer 10-P10NCu, taken as an example. Further support for the nematic nature of the mesophase is afforded by the dependence of the melt viscosity on temperature. Figure 3 shows the melt viscosity measured for decreasing temperature for polymer 8-P12NCu. A sharp decrease marks the transition from the isotropic to the liquid crystalline phase. Final evidence is afforded by the XRD patterns of fibrous polymer samples quenched to room temperature. Figure 4 shows such a pattern for polymer 6-P12NCu. It is characterized, as for all the polymers, by an equatorial diffuse halo centred at $(\sin\theta)/\lambda = 0.116\,\text{Å}^{-1}$ and by four rather diffuse diffractions, symmetrically related, centred at $(\sin\theta)/\lambda = 0.052\,\text{Å}^{-1}$. The non-equatorial diffraction
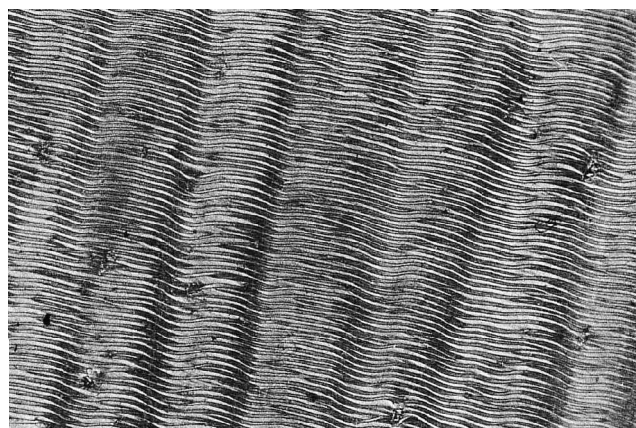

Figure 2.   Polymer 10-P10NCu: band structure for a sample sheared in the nematic phase and quenched to room temperature; crossed polarizers.
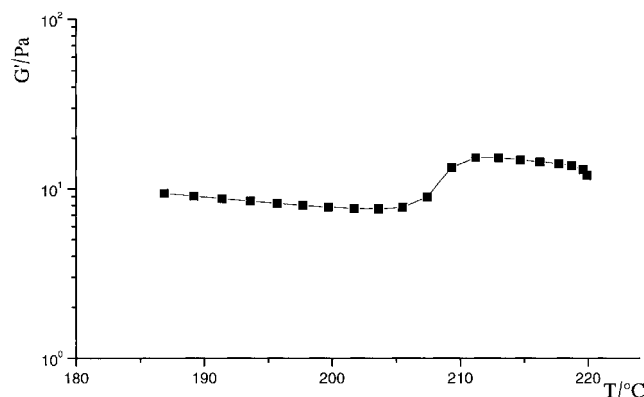

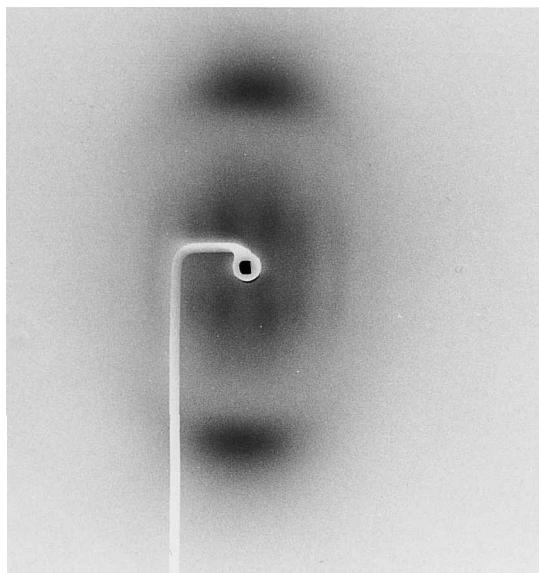Figure 3.   Polymer 8-P12NCu: melt viscosity as a function of temperature.

Figure 4. XRD pattern recorded at room temperature for a quenched fibrous sample of 6-P12NCu.

at low angles, which is observed for all the polymers at angular positions and with a sharpness depending on the parameters *n* and *m*, suggests a cybotactic nature for the nematic phase [13]. They bear no apparent relationship to any set of symmetric diffractions of the crystalline phase obtained by fibre annealing, as shown in figure 5 for 6-P12NCu.

Changing the nature of the coordinated metal ion has no substantial influence on the liquid crystalline properties of the polymers except for a significant increment in
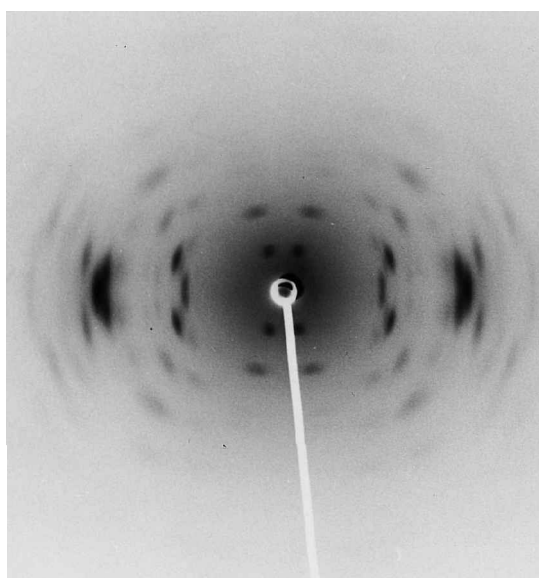

Figure 5. XRD pattern recorded at room temperature for a fibrous sample of 6-P12NCu previously annealed at 200°C.

the thermal stability of the mesophase. Both polymers examined, 8-P12NPd and 8-P12NNi, exhibit nematic mesomorphism with isotropization temperatures significantly higher ($T_m = 185°C$, $T_i = 249°C$, $\Delta H_i = 4.4 \text{ J g}^{-1}$ for 8-P12NPd; T_{kk} (crystal–crystal) $= 143°C$, $T_m = 188°C$, $T_i = 228°C$, $\Delta H_i = 6.0 \text{ J g}^{-1}$ for 8-P12NNi) than that found for the corresponding copper containing polymer. This feature was also observed for different A-mode polymers and for structurally related low molecular mass compounds [6, 12].

Devising a sensible packing model for the liquid crystalline phase is not a straightforward matter. However, some suggestion may be put forward, taking into account the conformational flexibility of the molecular structure. A reference model is shown in figure 6 for a short chain segment in its most extended conformation. It has been obtained by linking through all-*trans*-dodecamethylene segments the mesogenic organometallic cores whose molecular structure has been assumed to be identical to that found in a single crystal XRD study of a low molecular mass analogue [14]. It is quite obvious that no particular significance has to be attached to maintaining the specific conformation (containing two *gauche*-bonds) found for the hexyloxy terminal segments attached to the organometallic group.

The chain model shown in figure 6 corresponds to a rather anisometric flat structure with a chain axis direction far from parallel to the average elongation direction of the organometallic (mesogen) segments. No experimental evidence supports the hypothesis that such a structure (which would suggest the occurrence of extended interdigitation of the mesogenic segments to allow for a reasonable density, and possibly a smectic C type structure for the LC phase) might be present to a substantial extent in the liquid crystalline phase. However, different structural models for chain segments may be obtained by allowing *gauche*-bonds to be formed where required along the dodecamethylene chain segments. Figure 7 shows one such model containing 5 monomer units characterized by the $tg^+ tttg^- tg^+ tg^+ t$ bond conformation sequence. The monomer sequence along the chain axis has a co-axial helical structure. As a result, a rod-like chain segment is formed (its axial ratio is close to 5, for the case shown in figure 7) whose length may be changed in two ways in the liquid crystalline state following thermally induced conformational modifications.

The structural model suggested is entirely compatible with the nematic nature of the liquid crystalline state and with the XRD data recorded for oriented fibrous samples quenched in that state. It might also offer a hint explaining why the thermal stability of the liquid crystalline phase of (mode B) polymers 6-P10NCu ($T_i = 237°C$) and 6-P12NCu ($T_i = 226°C$) is higher than that found
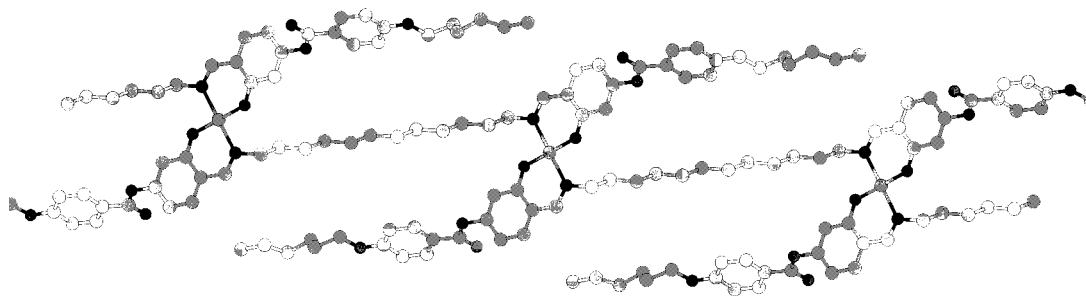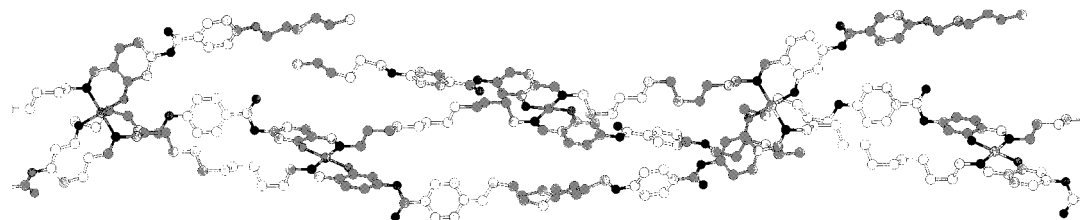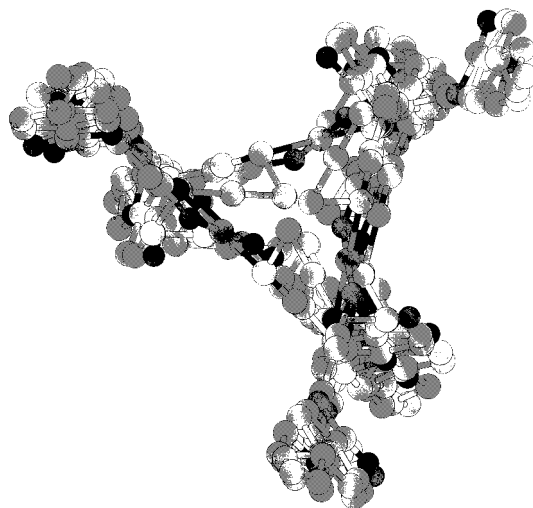
Figure 6. Extended chain model for polymer 6-P12NCu.

(*a*)

(*b*)

Figure 7. Chain model for polymer 6-P12NCu: (*a*) view normal to the chain extension axis; (*b*) enlarged view along the chain extension axis. Conformation of the C12 chain segment: $tg^+ \, tttg^- \, tg^+ \, tg^+ \, t$.

for strictly homologous (mode A) polymers P12-5NCu ($T_i = 225°C$) and P12-6NCu ($T_i = 212°C$) [11]. This feature, which is opposite to that observed for some organic mode A and mode B homologous pairs [15], might be the consequence of the formation of 'mesogenic' rod-like segments longer than a single monomer unit and axially connected along the polymer chain.

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