Liquid-Crystalline Behavior of Polymeric Organometallic Complexes of Copper(II)

Ugo Caruso, Antonio Roviello, and Augusto Sirigu*

Dipartimento di Chimica, Università di Napoli Via Mezzocannone, 4 80134 Napoli, Italy

Received June 12, 1990; Revised Manuscript Received October 25, 1990

ABSTRACT: The synthesis and the partial characterization of the phase behavior of a homologous set of polymers of 4,4′-[1,12-dodecanediylbis(oxy)]bis(benzoic acid) with bis[*N*-[[2,4-dihydroxyphenyl]methylene]-alkylamino]copper(II) is reported. Polymers that differ by the number n (4–13) of carbon atoms in the alkylamino groups exhibit monotropic liquid-crystalline behavior. Calorimetric analysis, polarizing microscopy, and dynamic viscosity measurements indicate the occurrence of nematic mesomorphism for all polymers. With $n > 9$, an additional mesophase of presumably smectic structure forms on cooling the molten polymer and is detectable at room temperature by X-ray diffraction.

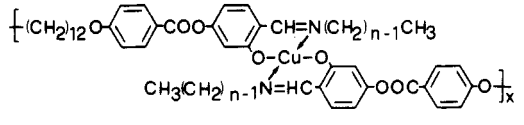
Introduction

The liquid-crystalline behavior of organometallic compounds is attracting increasing attention. This is mostly directed to low molecular weight compounds and is suggested by the opportunities that metal complexation offers for the design of new potentially mesogenic molecular structures, although some interest on the physical properties of ordered arrays of molecules involving short metal to metal distances is also active. To our knowledge, only a few examples of organometallic polymers having liquid crystalline properties are available.[1-4] Yet, to the reasons that have been just outlined, which make organometallic mesogens worth of attention, a further one may be added that is peculiar to polymers, namely, the possibility of obtaining a mechanically self-sustained material having liquid-crystalline structure at room temperature.

In this article the synthesis and the mesomorphic behavior is described for a set of organometallic polymers whose monomer unit is characterized by the presence of a square–planar coordinated Cu(II) atom. The mesogenic potential of the basic chemical structure has been previously investigated by us on a considerable number of low molecular weight analogues.[5,6]

Experimental Section

Polymers of 4,4′-[1,12-dodecanediylbis(oxy)]bis(benzoic acid) (**3**) with bis[*N*-[[2,4-dihydroxyphenyl]methylene]alkylamino]-copper(II) (**2**), hereinafter indicated by the symbol P12-*n*NCu, where n is the number of carbon atoms in the alkylamino chains,



P12-nNCu

were synthesized as summarized in Scheme I. A detailed description of the procedure is reported for polymer P12-8NCu taken as an example. In steps a and b, 6.6 g of *n*-octylamine (Ega, 99.6%) is added to a solution of 7.0 g of 2,4-dihydroxybenzaldehyde (Janssen, 98%) in 200 mL of boiling absolute ethanol. To this solution is added 20 mL of a water solution containing 5 g of sodium acetate and 100 mL of a boiling ethanol solution containing 5.1 g of copper acetate (Carlo Erba, 99%). The reaction mixture is kept boiling for ~5 min and is then cooled. Crystalline **2** (75% yield) precipitates. A second crystallization is performed from ethanol solution. **2** undergoes a solid-phase transition at 398 K and melts with decomposition at 411 K. Table I reports some data relevant for the thermal characterization as well as quantitative copper content (as CuO)

Scheme I

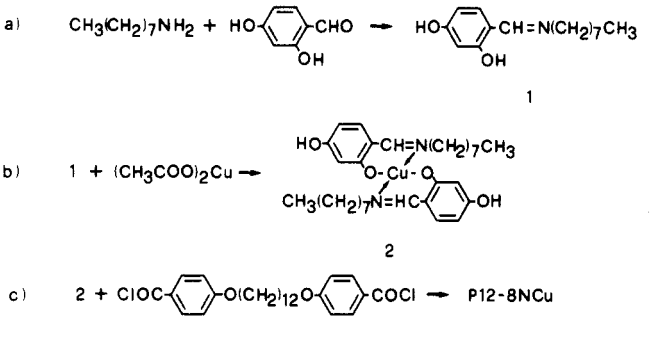


Table I
Characterization of Copper(II) Complexes 2[a]

n	$T(k-k)$	T_m	% CuO calc	% CuO found
4	386, 461	488	17.75	17.41
5	403	430	16.71	16.32
6	383	425	15.78	15.54
7	387	425	14.95	14.73
8	398	411	14.20	14.27
9	378	405	13.52	13.47
10	398, 404	416	12.90	12.71
11	396	409	12.34	12.23
12	381, 392	409	11.83	11.60
13	366, 395	407	11.35	11.21

[a] n, number of carbon atoms in the alkanamine group; $T(k-k)$/K = solid-phase transition; T_m/K melting followed by decomposition. Temperatures (K) are taken at the maximum of transition endotherm.

for the entire set of homologues. With minor modifications, the forementioned procedure had been utilized and tested for the synthesis of **2** containing methylamino ($n = 1$) groups.[5]. In step c, polymerization was performed by interfacial reaction. For a typical preparation, 50 mL of a chloroform solution containing 1.131 31 g of **3**, previously prepared by standard methods, is added under vigorous stirring to 100 mL of an alkaline aqueous solution containing **2** (1.324 71 g), 0.701 g of KOH (less alkaline conditions may also be utilized without significant changes in the final results) and 0.727 g of tetrabutylammonium hydrogen sulfate as interfacial agent. After a 10-min reaction, 150 mL of chloroform is added and the chloroformic phase separated. Water-soluble residues are washed away with repeated treatment with water. The chloroform solution is dried on Na_2SO_4 and added to 800 mL of *n*-hexane. P12-8NCu precipitates as a green solid, which is repeatedly washed with boiling ethanol (final yield >70%). The results of a quantitative analysis of the copper content, as CuO, for all polymers are reported in Table II.

Polymers are soluble in chloroform (solubility increases with n). Vapor pressure osmometry at 37.00 °C (Knauer apparatus)

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Table II
Quantitative Copper Content (as CuO) in Polymers[a]

	% CuO			% CuO	
n	calc	found	n	calc	found
4	9.31	9.26	9	8.00	7.90
5	9.01	8.96	10	7.78	7.88
6	8.73	8.82	11	7.57	7.65
7	8.47	8.45	12	7.37	7.39
8	8.23	8.15	13	7.19	7.23

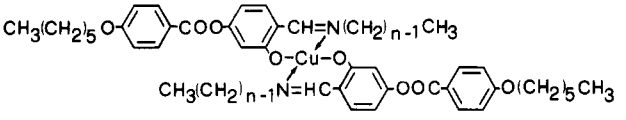
[a] n, number of carbon atoms in the alkanamine group.

of chloroform solutions was utilized to measure molecular weights. For most polymers, M_n was found to exceed the highest significant value measurable with the apparatus (~24 000). Lower values were measured for P12-5NCu (16 000) and P12-7NCu (10 500).

The phase behavior was examined by differential scanning calorimetry utilizing a Perkin-Elmer DSC-2 apparatus. Samples were examined under a dry nitrogen atmosphere with a temperature scanning rate of 10 K/min. Temperature-controlled polarizing microscopy (Leitz microscope, Mettler FP5 microfurnace) was also utilized, in particular for the analysis of the texture of the liquid-crystalline phase. X-ray diffraction patterns (Cu Kα radiation) were recorded at room temperature, utilizing a photographic flat-film camera. Dynamic viscosity measurements were performed on a Rheometrics Recap 2 dynamic rheometer with an oscillatory frequency of 8 Hz at decreasing temperatures (10 K/min cooling rate) starting from the isotropic liquid phase.

Results and Discussion

Polymers P12-*n*NCu pertain to the class of "segmented-chain" or "semiflexible" liquid-crystalline polymers whose structure is characterized by an alternate sequence of rigid and flexible portions. The structural definition of the monomeric unit and, as a consequence, the choice of a low molecular weight model for it cannot be done in a single way. However, as far as the analysis of the liquid-crystal properties is concerned, a suitable model must contain the rigid segment unaltered and possibly preserve an even distribution of the flexible one at both ends. In our specific case, we shall take as reference compounds of formula



which are homologous to those reported in ref 5 and have been prepared according to procedures described therein.[6] All exhibit enantiotropic nematogenic behavior with melting temperatures (for solution-crystallized samples) ranging from 423 (n = 4) to 403 K (n = 13) and isotropization temperatures ranging from 449 (n = 4) to 409 K (n = 13).

The thermal stability interval of the mesophase(s) (i.e., the temperature interval between melting and isotropization) is usually larger for polymers than for their low molecular weight "monomeric" analogues. This is not entirely true for polymers P12-*n*NCu, which also exhibit mesomorphic behavior of nematic character. Isotropization temperatures [measured at the maximum of the transition endotherm in a DSC heating run, which is started immediately after the previous cooling run of the anisotropic liquid has been stopped before crystallization occurs] decrease with increasing n (Table III) and are constantly higher than for the stoichiometrically corresponding low molecular weight analogues. However, mesomorphism is monotropic in all cases. The enantiotropic behavior exhibited by polymers with n = 7–10 is fictitious. In fact, melting temperatures reported in Table III refer to samples

Table III
Thermodynamic Data Concerning Polymers[a]

n	T_m	T_m(fiber)	T_i	ΔH_i
4	530	531	498	5.67
5	499	503	498	5.64
6	503	510	485	5.50
7	474	482	483	5.91
8	455		469	5.43
9	457	468	467	5.85
10	443	460	459	5.83
11	467	467	459	6.15
12	467	468	449	
13	464		445	

[a] T_m/K, melting temperature of as-prepared polymers; T_m(fiber)/K, melting temperture of fibrous samples; T_i/K isotropization temperture. ΔH_i/kJ mol^{-1}, molar isotropization enthalpy. Temperatures (K) measured at the maximum of the transition endotherm.

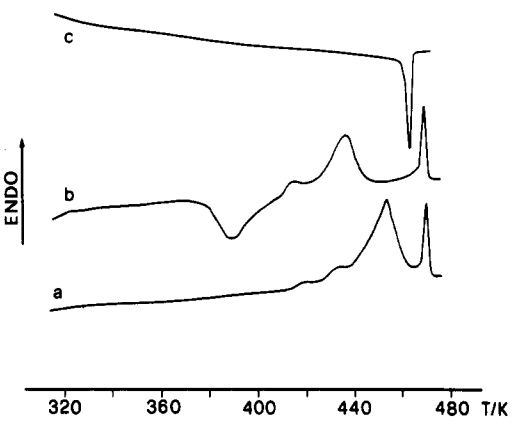


Figure 1. Polymer P12-8NCu. DSC curves: (a) first heating run; (b) second heating run; (c) first cooling run.

with no previous thermal treatment. They may be brought to exceed isotropization temperature by moderate annealing.

The decrease of isotropization temperature with increasing n is expected. The presence of bulky substituents at the mesogenic core also has a similar effect in organic polymers and is presumably related to a negative influence on the lateral packing of the polymer chains.[7-9] The parallel slightly decreasing trend of the isotropization enthalpy apparently confirms that the lateral aliphatic chains play a moderately negative role, if any, on the local ordering of the nematic phase.

Yet, other evidence suggests that lateral chains have a relevant influence on the occurrence of smectic mesomorphism. Before discussing that, it is necessary to point out why the liquid-crystal phase, which eventually isotropizes, has been qualified as nematic.

Figure 1 reports DSC curves for P12-8NCu taken as an example of the behavior of polymers characterized by $n \leq 9$.

Samples that have not undergone any previous thermal treatment have moderate crystallinity; melting and successive isotropization is recorded by curve a. A remarkable feature is the reduced width of the isotropization endotherm with respect to most unfractionated organic polymers of comparable molecular weight. The transition from the isotropic liquid to the liquid-crystalline phase takes place with a moderate supercooling (curve c). Annealing or slow cooling of the liquid-crystalline phase produces crystallization. Because of that, no X-ray diffraction pattern of the mesophase could be recorded at high temperature. However, no crystallization occurs at the cooling rate of the DSC scan (10 K/min) and the liquid-crystalline phase is preserved at room temperature.

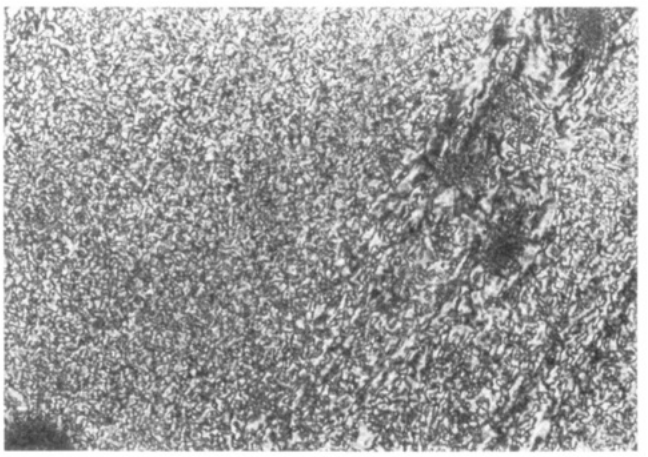


Figure 2. Polymer P12-8NCu. Schlieren texture preserved at room temperature. Crossed polarizers.

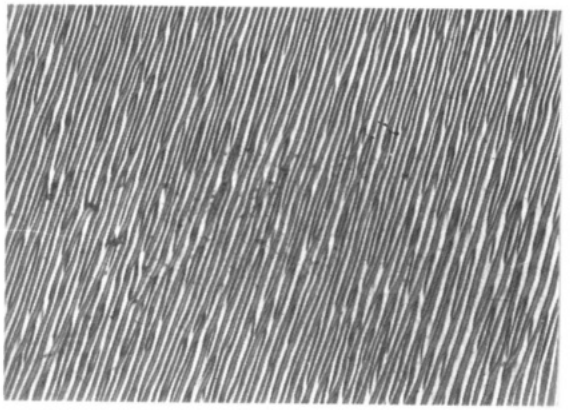


Figure 3. Polymer P12-7NCu. Band structure from a sample sheared in the nematic phase and quenched to room temperature. Crossed polarizers.

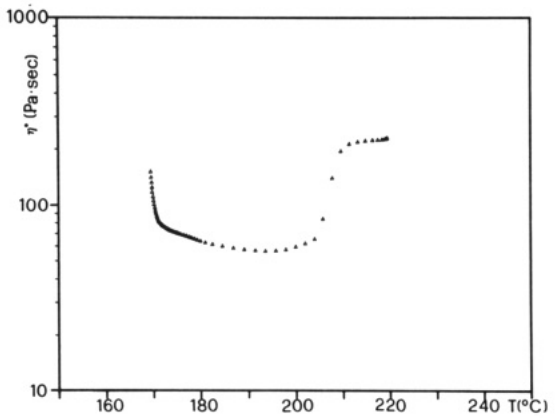


Figure 4. Polymer P12-7NCu. Melt viscosity as a function of temperature.

Coherently with that, during the successive heating run (curve b) some premelting crystallization takes place. The texture of the liquid-crystalline phase is a very dense schlieren pattern, which may be preserved without any significant modification down to room temperature (Figure 2). Shearing the liquid-crystal phase produces a well-formed band structure, which also can be quenched at room temperature. Figure 3 shows a band structure concerning polymer P12-7NCu at room temperature.

The measurement of the shear viscosity at decreasing temperatures (Figure 4 concerns polymer P12-7NCu) shows that the transition from the isotropic liquid to the liquid-crystal phase involves a dramatic decrease of viscosity.

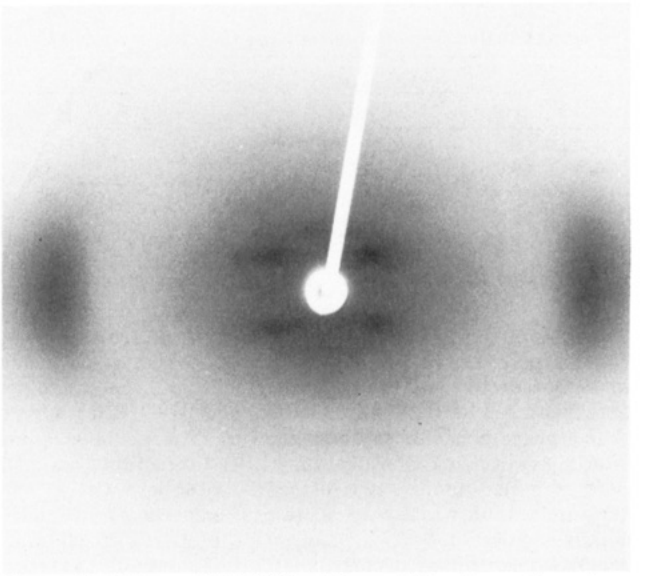


Figure 5. Polymer P12-8NCu. X-ray diffraction pattern from a fibrous sample. Nematic phase quenched at room temperature.

Extrusion of polymer melts to fibers produces a remarkable macroscopic orientation. Figure 5 shows the X-ray diffraction pattern of a fiber of P12-8NCu recorded at room temperature. It is characterized by an equatorial halo at $\sin\theta/\lambda = 0.1151$ A^{-1} and by a set of rather diffuse diffractions at lower angles, which is essentially characterized by an intense four-spot pattern at $\sin\theta/\lambda = 0.0280$ A^{-1}. A totally correspondent spectrum, apart from the absence of any evidence of macroscopic orientation, is afforded by an unoriented sample that has undergone melting and successive rapid cooling to room temperature.

The diffraction spectrum is indicative of a noncrystalline structure and we take it as representative of the liquid-crystal phase that forms at ~465 K. Coherently with that, the DSC cooling curve (curve c of Figure 1) lacks in any exothermic signal that might correspond to the crystallization or to the transition to another mesophase.

In conclusion, the schlieren texture, the band structure formation, the decrease of viscosity at the transition from the isotropic liquid to the mesophase, and the X-ray diffraction pattern are in favor of the nematic structure of the liquid-crystal phase. The four-spot pattern that characterizes the low-angle portion of the diffraction spectrum suggests the cybotactic nature of the phase as defined by De Vries[10] for low molecular weight nematogens.

This conclusion holds for polymers with $n < 10$, which behave very much like P12-8NCu. The fiber X-ray diffraction patterns are also qualitatively analogous but for the low-angle diffractions, which become more and more diffuse as n decreases.

As to polymers with $n > 9$, their behavior shows some analogies with that of the lower homologues as well as some sharp differences.

The most significant analogies are the band structure formation when the liquid-crystal phase is subjected to mechanical shear and the decrease of viscosity measured at the transition from the isotropic liquid to the mesophase (shown in Figure 6 for P12-10NCu). These features, together with the absence of any apparent discontinuity in the set of the thermodynamic data concerning isotropization, favor the conclusion that the liquid-crystal phase is nematic for all polymers.

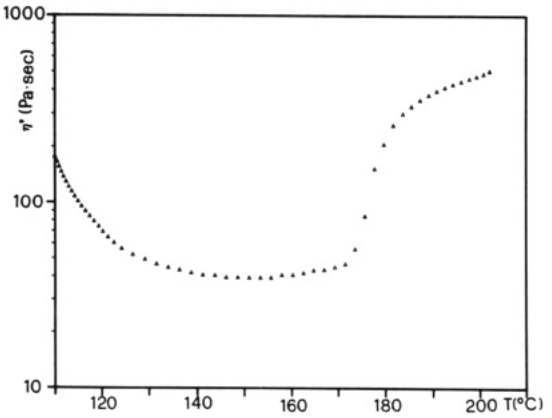


Figure 6. Polymer P12-10NCu. Melt viscosity as a function of temperature.

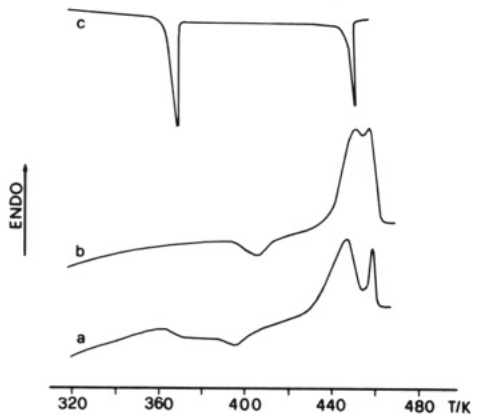


Figure 7. Polymer P12-10NCu. DSC curves: (a) first heating run; (b) second heating run; (c) first cooling run.

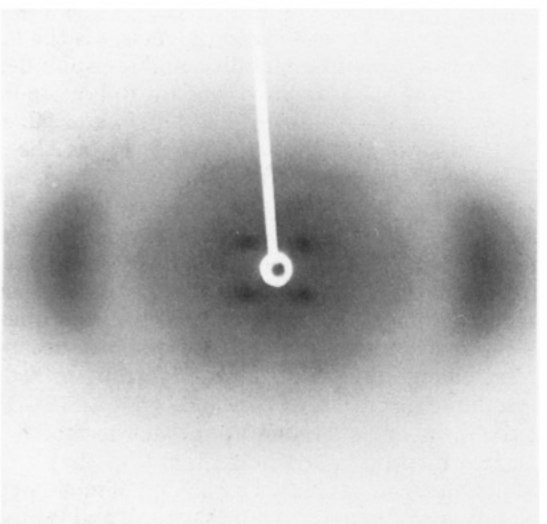


Figure 8. Polymer P12-10NCu. X-ray diffraction pattern from a fiber extruded in the nematic phase and quenched at room temperature.

As far as differences are concerned, P12-10NCu offers the best example for a discussion.

Figure 7 shows the DSC behavior of that polymer. Curve c shows, in addition to the exothermic signal of the isotropic–nematic transition, a second exotherm at ~370 K, which indicates the transition of the nematic liquid to the phase observable at room temperature.

The X-ray diffraction spectrum of that phase, as recorded for a fibrous sample at room temperature, is shown in Figure 8. A diffraction pattern coherent with this but lacking of any evidence of macroscopic orientation

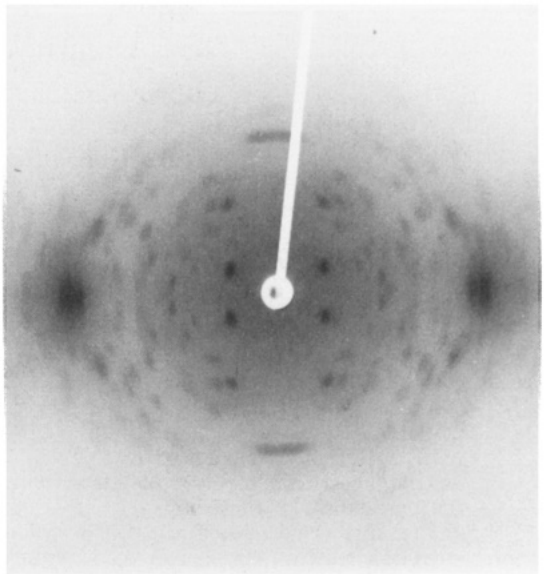


Figure 9. Polymer P12-10NCu. X-ray diffraction pattern recorded at room temperature from a fiber sample previously annealed at 445 K.

(e.g., a single diffraction ring replaces the four-spot pattern) is obtained from an unoriented sample. The four-spot pattern at low angle is pretty sharp and corresponds to a Bragg distance of 22.3 Å. However, this is no indication of crystalline structure. On the contrary, the equatorial diffuse halo centered at $\sin\theta/\lambda = 0.1151$ Å^{-1} excludes that hypothesis. A diffraction pattern that is unequivocally indicative of a crystalline structure is obtained from a fibrous sample after annealing. Figure 9 concerns a sample that has been annealed at 445 K. The spectrum was recorded at room temperature.

The diffraction pattern of the noncrystalline phase is compatible with a tilted smectic structure with rather loose lateral packing. Further investigation is needed to decide whether a smectic C or F or some other phase is involved.

The behavior of polymer P12-11NCu is quite similar to that described for P12-10NCu. For polymers with $n > 11$, anisotropization and crystallization take place at very close temperatures and the corresponding DSC endotherms are not resolved. For this reason, no isotropization enthalpy could be measured and no evidence of smectic mesomorphism was detected.

Acknowledgment. Research was supported by Ministero della Pubblica Istruzione. We are grateful to Prof. M. Acierno and Dr. E. Amendola for making dynamic viscosity measurements possible.

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