

# Cholesteric liquid crystal polymers containing coordinated copper(II) in the main chain

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## Abstract

New main chain cholesteric liquid crystal copolymers having coordinated copper(II) atoms in the main chain have been prepared, together with some related model compounds. The (*S*)-(+)1-amino-2-propylhexanoate group, directly bound to the metal ion, was used as the chiral centre. Phase behaviour and optical properties of polymers appear to be influenced by the molar amount of the chiral component and by the nature and molar proportion of the flexible segments of the backbone chain. Reflection spectra, including the visible frequency range, recorded for film samples in the planar texture clearly show a dependence of the cholesteric pitch on these structural parameters. Mixtures of structurally related chiral and non-chiral low molecular weight mesogens show cholesteric behaviour even with very low contents of the chiral component. For chiral-rich mixtures, liquid crystalline polymorphism involving a non-birefringent phase has been detected. © 2000 Elsevier Science Ltd. All rights reserved.

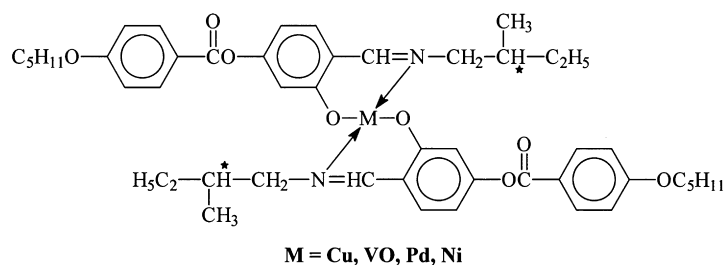
**Keywords:** Polymers; Metallomesogens; Cholesteric

## 1. Introduction

The interest raised by cholesteric polymers is essentially connected to the peculiar optical properties of the cholesteric phase and to their possible applications (such as non-absorbing optical filters, circular polarisers or colour optical

chain [2–5]. As to the chiral metallomesogens, most of the attention has been attracted by low molar mass compounds exhibiting a smectic C\* phase in view of possible applications in fast switching electro-optical devices [6].

Recently, Galyametdinov and Pizuk [7] described the properties of the following compounds:



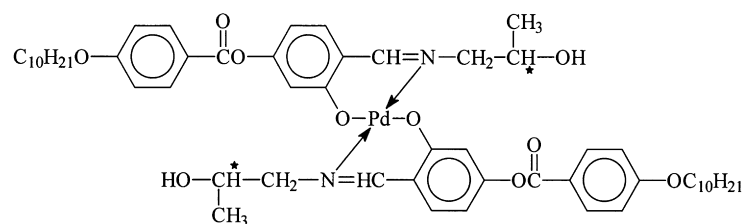
memory devices) stemming from the possibility to couple optical and structural modulations. Many articles have been published concerning totally organic cholesteric polymers having the chiral mesogenic groups either as a side chain pendant [1] (most of them), or as constituents of the main

which seem to exhibit cholesteric mesophases with such a small pitch that even a very dilute mixture with a commercial nematic liquid crystal may be set into coloured cholesteric textures (the planar or Grandjean texture). We know, furthermore, that the following compound, having a

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very similar formula:



produces a coloured cholesteric phase, although at high temperature (melting temperature,  $T_m = 198^\circ\text{C}$ ; isotropisation temperature,  $T_i = 226^\circ\text{C}$  [8]). On this ground, we have undertaken the synthesis and the characterisation of the phase properties both of low molecular weight and polymeric compounds having the following formulas based on the same structural core (Scheme 1).

The latter compounds are, to our knowledge, the first examples of chiral metallomesogenic polymers. The metal-organic core selected allows for excellent yields in the use of the chiral agent, which characterises the route followed in the preparation of these complexes. The chiral agent (*S*)-(+)-1-amino-2-propanol was preferred, as the starting point, to (*S*)-(–)-2-methylbutylamine because of its lower cost, its greater rotatory power, higher purity and chemical versatility.

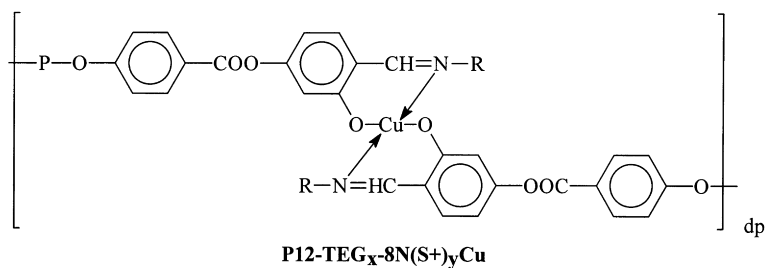
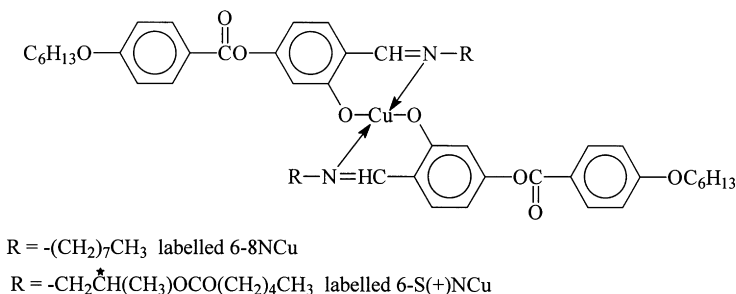
We shall also describe the phase behaviour of mixtures of structurally related low molecular weight chiral and non-

chiral compounds, which were prepared in order to explore the possibility of obtaining coloured cholesteric phases, grasping some reference point for the choice of the chiral component fractions to be included in the copolymers formulation.

## 2. Experimental

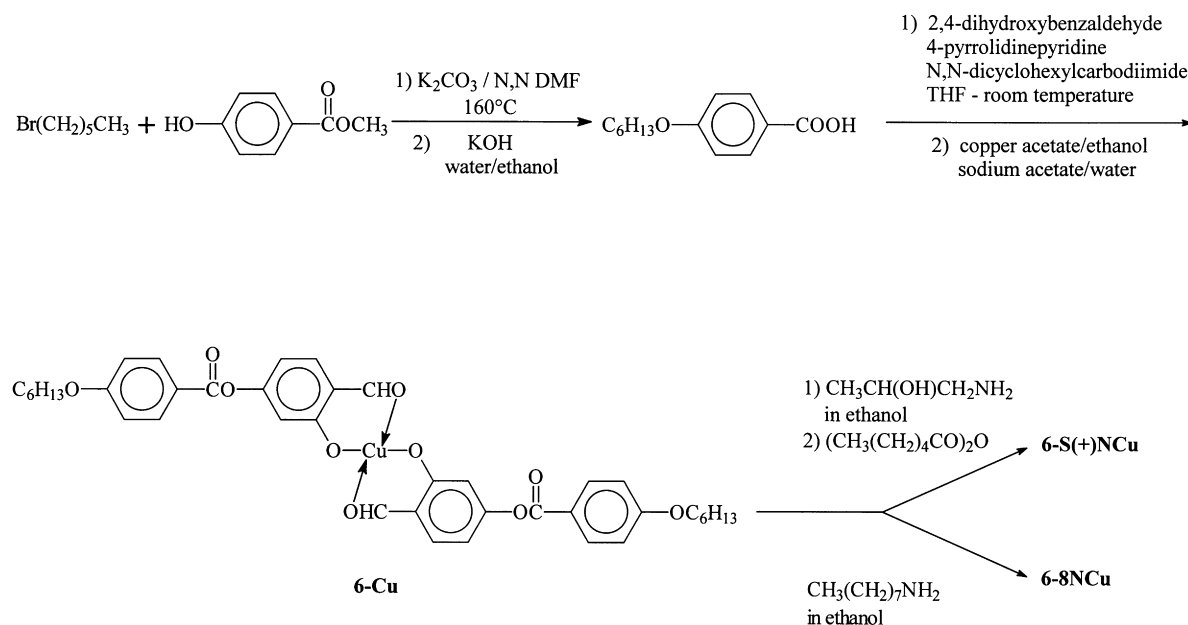
### 2.1. Synthesis of model compounds and their mixtures

The chemical synthesis of the copper-containing low molecular mass complexes is shown in Scheme 2. Compounds 6-Cu and 6-8NCu were obtained according to a procedure described elsewhere [9] with slight changes. 6.55 g of 4-hexyloxybenzoic acid, 4.9 g of 2,4-dihydroxybenzaldehyde and 0.33 g of 4-pyrrolidinopyridine were dissolved in 35 ml of dry tetrahydrofuran; then a solution



R =  $-(\text{CH}_2)_7\text{CH}_3$  labelled 8N and/or  $-\text{CH}_2\overset{\star}{\text{C}}\text{H}(\text{CH}_3)\text{OCO}(\text{CH}_2)_4\text{CH}_3$  labelled (S<sup>+</sup>)  
 P =  $-(\text{CH}_2)_{12}$ - labelled P12 or  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$  labelled TEG  
 x and y = molar percent

Scheme 1.



Scheme 2.

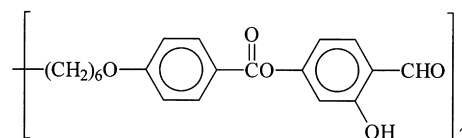
of 6.7 g of N,N-dicyclohexylcarbodiimide in 11 ml of tetrahydrofuran was added drop by drop. The reaction went on for 2 h at room temperature. After filtering off the solid, a solution of 6.48 g of monohydrate copper acetate in 135 ml of absolute ethanol was added. The complex was finally precipitated by addition of a solution of 4.84 g sodium acetate in 30 ml water and adding more water up to a total volume of 300 ml. It was filtered and washed with ethanol; then it was dissolved in 100 ml of chloroform and, after a new filtration, ethanol was added up to a total volume of 400 ml. After boiling, the complex was obtained by crystallisation in a cold water bath and finally separated by filtration (yield 37%). To obtain the chiral complex 6-S(+)-NCu, 1.0 g of complex 6-Cu was dissolved in 20 ml warm dry chloroform, then 0.206 g of S(+)-1-amino-2-propanol were added heating to boiling. After 2 min, 2.0 ml of caproic anhydride were added to the solution leaving it boiling for an additional 10 min. Finally, 40 ml of ethanol were added and the precipitated complex was filtered and washed with ethanol (yield 88%).

Binary mixtures were prepared dissolving the appropriate quantities of 6-S(+)-NCu and 6-8NCu in dichloromethane. Fairly homogenous mixtures were obtained by solvent evaporation while grinding.

## 2.2. Synthesis of polymers

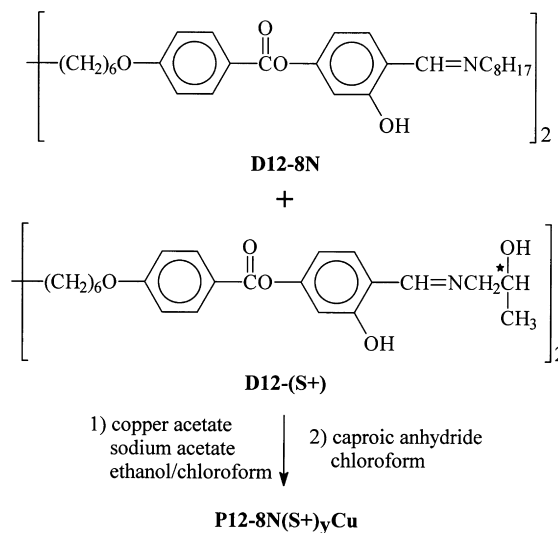
The first family of liquid-crystalline copolymers (P12-8N(S+)<sub>y</sub>Cu) was obtained following the procedure shown in Scheme 3.

Dialdehyde A12G, having formula:

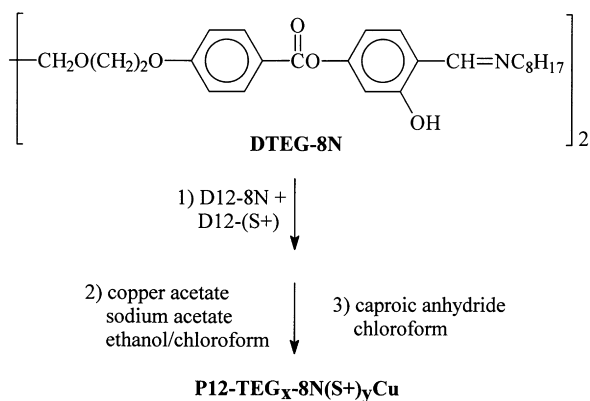


was prepared by hydrolysis of the diimine D12-8N according to a procedure already described [10] but including significant changes.

3.0 g of diimine D12-8N were dissolved in 300 ml ethanol. The clear solution was then heated after sequential addition of 120 ml dilute HCl (1:10) and 180 ml water.



Scheme 3.



Scheme 4.

The product was filtered and washed three times with ethanol and water (1:1) (yield 95%). Purification was obtained by crystallisation from tetrahydrofuran and ethyl acetate solution (1:5). Finally, by dissolving 2.857 g of A12G in 100 ml of hot tetrahydrofuran and by adding 0.7 g of S(+)-1-amino-2-propanol and absolute ethanol up to a total volume of 300 ml, a yellow precipitate of D12-(S+) was obtained (yield 77%).

The preparation of P12-8N(S+)<sub>17.0</sub>Cu will be described in some detail. 1.5 g of D12-8N and 0.265 g of D12-(S+) were dissolved in 90 ml chloroform; then a solution containing 0.398 g of monohydrate copper acetate in 30 ml absolute ethanol was added. This solution was slowly added to 1.3 g sodium acetate dissolved in 120 ml of ethanol to precipitate the copolymer. The dry polymer was dissolved in 90 ml of warm dry chloroform, and 0.5 ml caproic anhydride were added. The solution was left boiling for 10 min before pouring it into 400 ml ethanol containing 1.5 g

sodium acetate to precipitate the final product. The latter procedure was repeated to improve purity. Finally, the precipitated polymer was washed twice with boiling ethanol. (yield 82%). A similar procedure was followed to prepare the second family of liquid-crystalline copolymers P12-TEG<sub>x</sub>-8N(S+)<sub>y</sub>Cu (Scheme 4). The synthesis of DTEG-8N was performed according to a procedure already described [11].

### 2.3. Characterisation

Transition temperatures and enthalpies were measured using a Perkin–Elmer DSC-7 differential scanning calorimeter with a temperature scanning rate of 10°C min<sup>-1</sup>. All samples were examined under dry nitrogen atmosphere. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> solution) were obtained by using a 200 MHz Varian XL or 270 MHz Bruker spectrometer. Mesophase textures were studied with on a Zeiss Axioskop polarised optical microscope equipped with a Mettler FP5 temperature controlled micro-furnace. X-ray diffraction patterns were recorded by the photographic method, using a flat-film camera and Ni-filtered CuKα radiation. Vapour-pressure osmometry (Knauer apparatus) of chloroform solutions at 37.00°C was utilised to measure the average molecular weights. The inherent viscosities of the polymer solutions were measured in chloroform at 25.00°C at a concentration of 0.500 g dl<sup>-1</sup> using an Ubbelohde viscometer. Quantitative analysis of the copper content, as CuO, for some copolymers gave the following results: P12-8N(S+)<sub>17.0</sub>Cu: 8.12% (calc.), 8.08% (found); P12-8N(S+)<sub>18.7</sub>Cu: 8.12% (calc.), 8.10% (found); P12-TEG<sub>80.9</sub>-8N(S+)<sub>10.2</sub>Cu: 8.50% (calc.), 8.52% (found) and PTEG-8NCu 10.02% (calc.), 10.00% (found).

Polymer films in the planar texture, about 0.10 mm thick,

Table 1

Thermodynamic data of mixtures of 6-8NCu with 6-(S+)NCu.  $T_{m1} - T_{m2}$  = melting interval;  $T_{int}$  = transition temperature from the cholesteric phase to the intermediate non-birefringent phase;  $T_i$  = transition temperature from the intermediate non-birefringent phase to the isotropic liquid;  $\Delta H_{int}$  = transition enthalpy from the cholesteric phase to the intermediate non-birefringent phase, measured in the cooling run;  $\Delta H_i$  = transition enthalpy from the intermediate non-birefringent phase to the isotropic liquid, measured in the cooling run

6-S(+ )NCu (mol%)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$T_{int}$ (°C)	$\Delta H_{int}$ (J g <sup>-1</sup> )	$T_i$ (°C)	$\Delta H_i$ (J g <sup>-1</sup> )
0		117			154.0	2.3
4.7	98	115			152.0	2.2
6.0	97	115			151.5	2.1
7.1	96	114			151.0	2.0
9.2	99	112			150.5	2.0
13.6	99	111			148.5	1.9
13.9	98	114			149.0	1.9
18.8	94	109			146.5	1.8 <sup>a</sup>
27.9	96	107	141.5		143.0	1.6 <sup>a</sup>
28.1	90	112	141.0		142.5	1.6 <sup>a</sup>
43.0	89	108	133.0	0.14	137.0	0.83
58.4	91	113	125.5	0.16	131.0	0.56
73.6		120	118.0	0.18	125.0	0.49
93.8	118	127	110.0	0.22	117.0	0.45
100		131	107.0	0.23	107.0	0.38

<sup>a</sup> Unresolved transition.

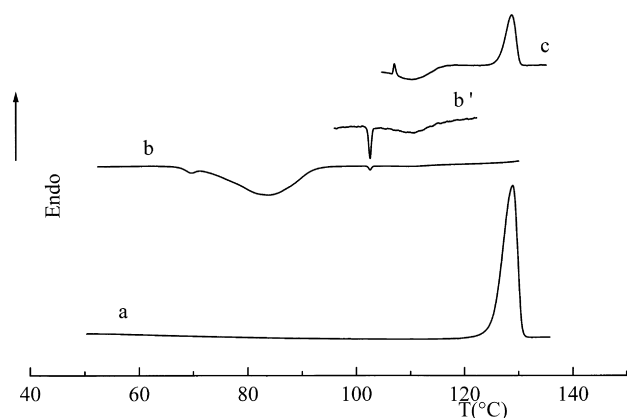


Fig. 1. 6-(S+)NCu: DSC curves: (a) first heating run; (b) first cooling run; (b') same as b, enthalpy scale reduced to 1/10; and (c) heating run following b'.

were obtained bringing the molten polymers to temperatures just below  $T_i$ , followed by quenching to room temperature.

Normal incidence reflectivity spectra on such polymer samples were recorded at room temperature using a Jasco V-570 UV–Vis–NIR apparatus in the range of 250–1000 nm. The spectra were corrected for the intrinsic reflectivity of the non-cholesteric polymer (P12-8NCu) and reflectivity data were reported as ratios to this polymer.

### 3. Results and discussion

Among the intermediates prepared, only diimine D12-S(+) is a new compound. For this compound, polarising microscopy and DSC analysis indicate the occurrence of a solid phase polymorphism for the solution-crystallised substance. At the second heating run, only one solid phase is evidenced with  $T_m = 148^\circ\text{C}$  and  $\Delta H_m = 61 \text{ J g}^{-1}$ . The compound shows also a LC phase having  $T_i = 169^\circ\text{C}$  and  $\Delta H_i = 9.1 \text{ J g}^{-1}$ . The mesophase is cholesteric with an oily

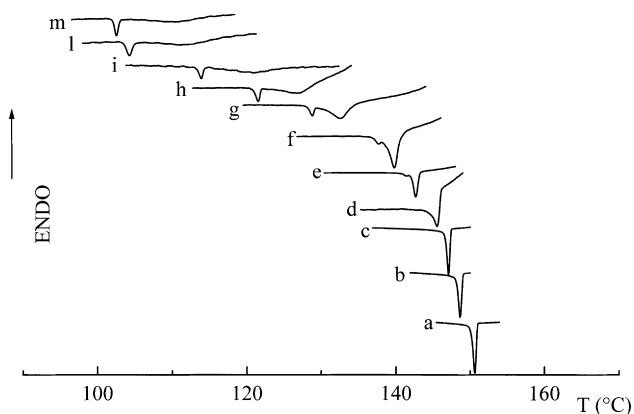


Fig. 2. DSC behaviour of mixtures 6-8NCu/6-(S+)NCu; cooling run. Composition as mol% of the chiral complex: (a) 0%; (b) 4.7%; (c) 9.2%; (d) 13.6%; (e) 18.8%; (f) 27.9%; (g) 43.0%; (h) 58.4%; (i) 73.6%; (l) 97.8%; and (m) 100%.

Table 2  
Thermodynamic data for polymers P12-TEG<sub>x</sub>-8N(S+)<sub>y</sub>Cu

X (mol%)	Y (mol%)	$T_i$ ( $^\circ\text{C}$ )	$\Delta H_i$ ( $\text{J g}^{-1}$ )	$\eta_{\text{inh}}$ ( $\text{dl g}^{-1}$ ) <sup>a</sup>
0	11.4	200	4.6	0.498
0	14.2	198	4.7	0.437
0	17.0	199	4.8	0.524
0	18.7	196	4.4	0.494
31.3	12.3	192	4.5	0.371
31.3	16.7	192	4.3	0.395
51.5	11.0	186	4.0	0.243
80.9	5.4	175	3.1	0.078
80.9	10.2	177	3.0	0.091
80.9	11.9	176	3.0	0.140
TEG	8.7	167	2.2	0.082

<sup>a</sup> Measured at concentration  $0.500 \text{ g dl}^{-1}$ .

streak texture. The assigned formula is confirmed by the  $^1\text{H}$  NMR spectrum.

#### 3.1. Model compounds

Table 1 shows the thermodynamic data concerning the phase transitions for the binary mixtures. The data regarding complex 6-8NCu, included for a comparison, have been already reported [9]. This complex exhibits an enantiotropic nematic mesophase, while compound 6-S(+)NCu shows a monotropic cholesteric mesophase with a fan texture. DSC curves are reported in Fig. 1. Melting occurs at  $127^\circ\text{C}$  (curve a). On cooling (curve b), a monotropic transition to the anisotropic liquid takes place. On the subsequent heating run (curve c), the reverse transition at  $107^\circ\text{C}$  is followed by a wide crystallisation exotherm. On observing the cooling curve with a more extended enthalpy scale (curve b') it

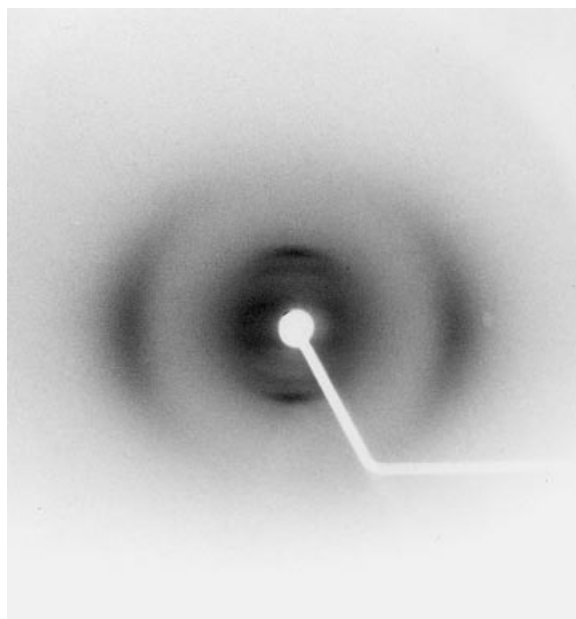


Fig. 3. X-ray diffraction pattern of P12-S(+)NCu polymer fibre recorded on a flat film camera,  $\text{CuK}\alpha$ .

appears that the transition to the liquid crystal phase is preceded by a broad exothermic signal. To this thermal behaviour, which might involve the formation of a blue phase with a very small lattice constant, corresponds no optical effect observable by the polarising microscope. This behaviour is a characteristic of all mixtures containing at least 18.8 mol% of the chiral component. The temperature range involved is  $\sim 7^\circ\text{C}$  in the 98% mixture and progressively diminishes down to  $\sim 1.5^\circ\text{C}$  in the 18.8% mixture, as shown in Fig. 2 that reports DSC cooling curves. The phenomenon involving the two liquid phase transitions outlined above takes place unequivocally in an enantiotropic way. Galyametdinov and Pyzuk observed analogous behaviour on similar copper containing compounds as previously mentioned in Ref. [7]. Mixtures in the  $\sim 5$ –10% composition range give coloured samples in the planar texture. For example, mixtures with 4.7 and 9.2% of 6-S(+ )NCu show, respectively, red and blue colour, at temperatures between  $\sim 115$  and  $150^\circ\text{C}$ . For higher contents of the chiral component, samples in the planar cholesteric texture are transparent.

### 3.2. Cholesteric liquid-crystalline polymers and copolymers

On the basis of these results two families of copolymers named (P12-8N(S + )<sub>y</sub>Cu) and (P12-TEG<sub>x</sub>-8N(S + )<sub>y</sub>Cu) were prepared. In the latter, dodecamethylene groups that constitute the flexible segments are randomly substituted with triethylene glycolic (TEG) groups, which allow a greater mobility of the macromolecular chains. The behaviour of these copolymers was studied by varying the molar fraction of the chiral component in order to investigate the relationship between the composition and the flexibility of the chain and the capability of self-organisation of the mesophase into a coloured planar texture.

Homopolymer P12-8NCu is a nematogenic polymer. It melts at  $182^\circ\text{C}$  and becomes isotropic at  $196^\circ\text{C}$  ( $\Delta H_i = 5.43 \text{ kJ mol}^{-1}$ ). The nematic phase can be preserved at room temperature for a long time by quenching [12]. Homopolymer P12-S(+ )NCu is formed as a non-

crystalline material that shows isotropisation at  $163^\circ\text{C}$  ( $\Delta H_i = 2.2 \text{ J g}^{-1}$ ). The mesophase is probably cholesteric with a very short pitch. In fact, a film sample appears pseudo-isotropic and transparent at the polarising microscope as expected for a planar texture with a pitch outside the visible range. The DSC behaviour, however, reveals the isotropisation transition, similarly to that of the as prepared polymer.

The X-ray diffraction pattern recorded at room temperature for a fibrous sample of P12-S(+ )NCu (Fig. 3) is indicative of a substantially oriented mesomorphic structure. It is characterised by an equatorially polarised diffuse halo centred at  $\sin(\Theta/\lambda) = 0.113 \text{ \AA}^{-1}$  and by a rather sharp meridian Bragg diffraction corresponding to a lattice distance of 9.3 Å. This value is very close to one fourth of the length of the monomer unit in its extended conformation as calculated from structural data concerning a closely related low molecular weight compound, 6-2NCu [13]. The authors have no hypothesis on a possible chain packing (possibly involving intercalation) leading to such a short meridian periodicity. A set of four weak and rather diffuse non-meridian diffractions, symmetrically related at  $\sin(\Theta/\lambda) = 0.044 \text{ \AA}^{-1}$ , is also observable indicating 3D short-scale structural correlation. On the other side of the composition range, no meridian Bragg diffraction was observed in the diffraction pattern of a fibrous sample of P12-8NCu except for a fairly intense “four spot pattern” at  $\sin(\Theta/\lambda) = 0.028 \text{ \AA}^{-1}$  [12].

Table 2 gives the thermodynamic data and the inherent viscosities concerning copolymers of both the families. The thermal behaviour of the first class of copolymers is rather uniform; seemingly the isotropisation temperature decreases with increasing content of the chiral component. However, this influence does not appear to be so drastic to overwhelm or compensate some opposite effect due to a difference in molecular weight. Isotropisation enthalpies lie between 4.8 and  $5.6 \text{ J g}^{-1}$ , near to that measured for homopolymer P12-8NCu. Most of them show no crystallinity and, even after the cooling of the isotropic melts, they do not crystallise, giving rise to LC samples frozen at

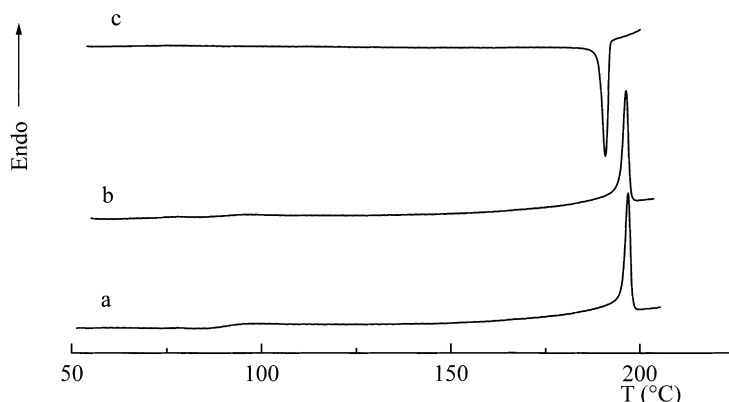


Fig. 4. DSC curves of P12-8N(S + )<sub>17.0</sub>Cu: (a) first heating run; (b) second heating run; and (c) first cooling run.

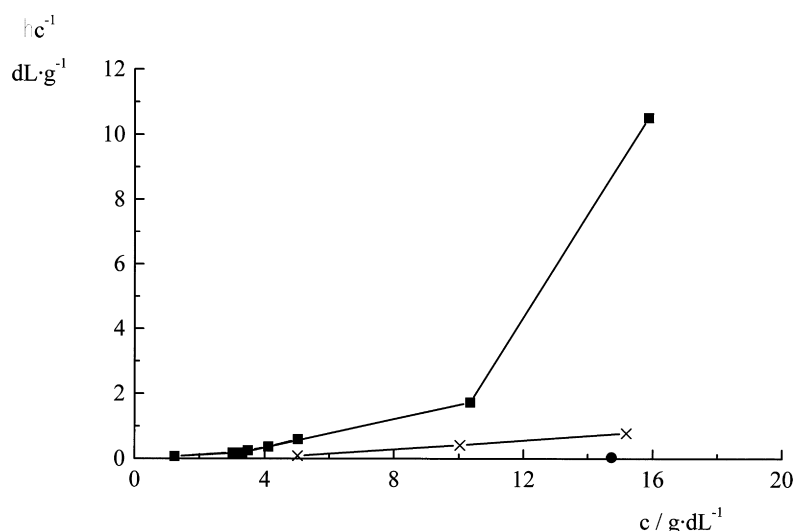


Fig. 5. Specific viscosity/concentration ratios vs. concentration: (■) P12-8N(S+)<sub>17.0</sub>Cu; (◆) P12-TEG<sub>80.9</sub>-8N(S+)<sub>10.2</sub>Cu; and (●) low molar mass mixture with 13.9% 6-(S+)<sub>NCu</sub>.

room temperature. As an example, Fig. 4 shows the DSC curves of P12-8N(S+)<sub>17.0</sub>Cu. Fig. 5 shows, for this copolymer, the specific viscosity/concentration ratios vs. concentration as measured in chloroform at 25.0°C. Solutions more concentrated than ~8 mg ml<sup>-1</sup> have an oily consistence and their viscosity has a sharp increase. This feature did not allow to properly measure the molecular weights by vapour pressure osmometry. In Fig. 5 the viscosity of a TEG-containing copolymer and of a mixture of the two model compounds (in equal ratio to the composition of the first copolymer) are also represented.

Reflection spectra of some chiral polymers in the planar texture have been recorded as described in Section 2. They are reported in Fig. 6 in a normalised form as ratios to the reflectivity values of P12-8NCu. The pitch of the mesophases is almost invariant with temperature. Two features are clearly detectable: (i) for polymers that differ only for a different molar proportion of the chiral component (curves a, d, and b, e) the reflection band is shifted to shorter  $\lambda_{\max}$  with increasing content of the chiral component; and (ii) for polymers containing comparable amounts of the chiral component (curves b, c and d),  $\lambda_{\max}$  is shifted to lower values with increasing molar content of TEG segments. Feature (i) is consistent with numerous observations concerning side chain cholesteric polymers [14]. It has also been reported for cholesteric main chain organic polymers [15]. Feature (ii) is most likely connected to a modification of the helical pitch caused by replacing an increasing fraction of methylenic spacers with the oxyethylenic ones. The quantitative relevance of this effect is so high (e.g.  $\lambda_{\max}(\text{P12-8N(S+)}_{11.4})/\lambda_{\max}(\text{P12-TEG}_{51.5}\text{-8N(S+)}_{11.0}) = 0.86$ ) that it is quite unlikely that it might be merely related to the difference of refractive index.

The thermodynamic data and the inherent viscosities concerning copolymers of the second family are reported

in Table 2. Fig. 7 shows the DSC behaviour of P12-TEG<sub>80.9</sub>-8NS(+)<sub>10.2</sub>Cu as an example. On increasing the content of TEG groups in the copolymers, both viscosity and isotropisation temperature decrease. The inherent viscosity diminishes down to 0.082 dl g<sup>-1</sup> for PTEG-8N(S+)<sub>8.7</sub>Cu, which does not contain dodecamethylene segments. This

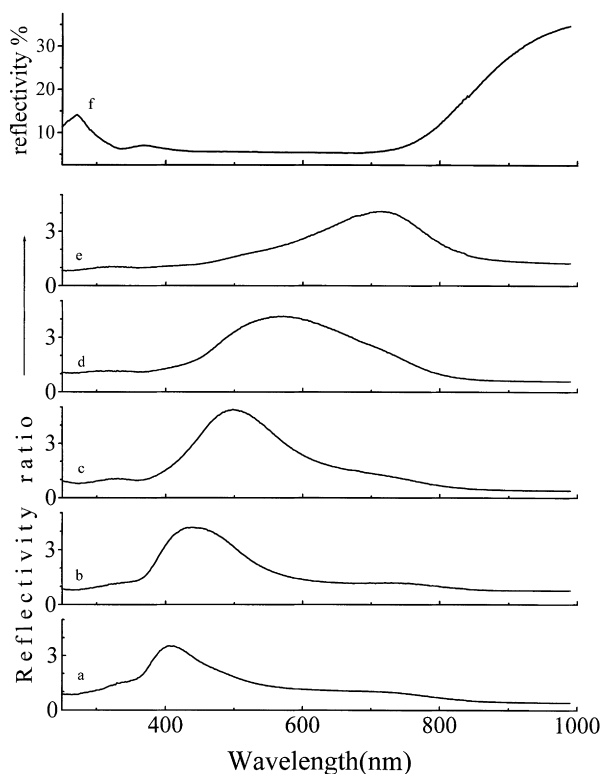


Fig. 6. Relative reflectivity spectra of P12-TEG<sub>x</sub>-8NS(+)<sub>y</sub>Cu: (a)  $x = 0$ ,  $y = 17.0$ ; (b)  $x = 80.9$ ,  $y = 10.2$ ; (c)  $x = 51.5$ ,  $y = 11.0$ ; (d)  $x = 0$ ,  $y = 11.4$ ; and (e)  $x = 80.9$ ,  $y = 5.4$ . Curve (f) reflectivity (%) spectrum of P12-8NCu, taken as the reference sample.

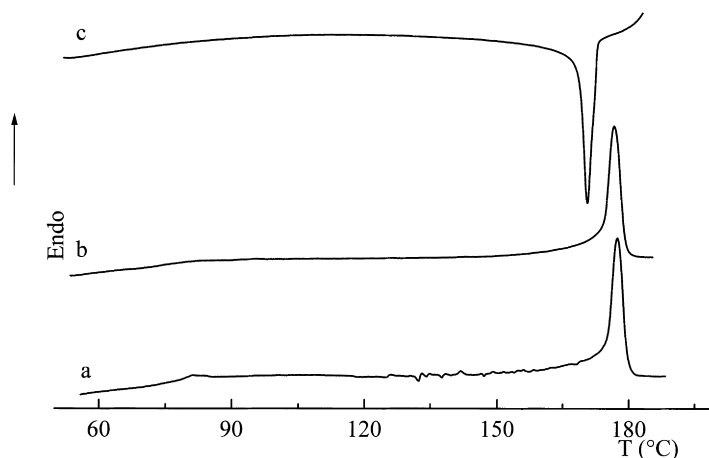


Fig. 7. DSC curves for polymer P12-TEG<sub>80.9</sub>-8N(S + )<sub>10.2</sub>Cu: (a) first heating run; (b) second heating run; and (c) first cooling run.

feature is consistent with the data concerning polymers with  $x = 0$ . The lower viscosity allowed to measure the molecular weight by vapour pressure osmometry with the following results: P12-TEG<sub>31.3</sub>-8N(S + )<sub>16.7</sub>Cu:  $M_n = 11.600 \pm 500 \text{ g mol}^{-1}$ ; P12-TEG<sub>80.9</sub>-8N(S + )<sub>10.2</sub>Cu:  $M_n = 14.800 \pm 500 \text{ g mol}^{-1}$ ; and P12-TEG<sub>80.9</sub>-8N(S + )<sub>11.9</sub>Cu:  $M_n = 13.500 \pm 500 \text{ g mol}^{-1}$ .

Copolymers are not crystalline and exhibit an anisotropic phase. As observed for the P12 family, the effect of an increasing content of chiral component on the isotropisation temperature does not show up clearly. The mesophase exhibited by these copolymers is cholesteric, as confirmed by optical observation and by selective reflection of the light. In this case the content of chiral component of the polymers showing light reflection in planar films ranges from ~5 to ~17%, significantly less than for those containing dodecamethylene groups only. As expected the higher mobility of the polymer backbone affects the self-organisation in the Grandjean texture.

#### 4. Conclusion

We have shown that the (S)-(+)-1-amino-2-propylhexanoate chiral group is very effective in promoting the formation of a low pitch cholesteric phase both in low molecular weight mixtures of metallomesogens and in structurally related copolymers. About 5 mol% of chiral mesogen is sufficient to produce a red reflecting coloured phase in a low molecular weight mixture, rising to about 10% for a copolymer having a much higher melt viscosity. It is noteworthy that an effective chiral component content of 1/2% is sufficient to have cholesteric coloured polymeric samples. Presumably, the homopolymer containing 100% of chiral mesogen shows a chiral phase with a pitch outside

the visible band. For chiral-rich low molecular weight mixtures, the DSC behaviour suggests the existence of a non-birefringent liquid crystal phase at temperatures intermediate between the cholesteric and the isotropic phase.

#### Acknowledgements

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