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Short Communication

Highly oriented fibres of copper laurate obtained by melt-spinning of its columnar mesophase

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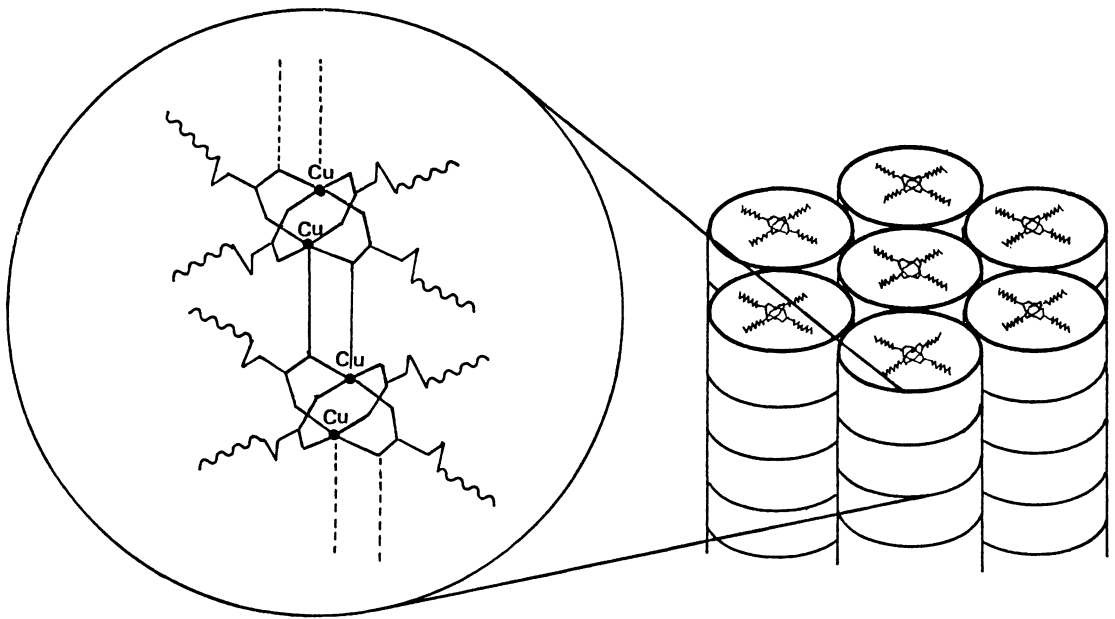
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Résumé.— Le laurate de cuivre peut être obtenu sous forme de fibres par extrusion à chaud de sa mésophase colonnaire thermotrope. L'examen de ces fibres par microscopie électronique à balayage et par diffraction des rayons X révèle un très haut degré d'orientation du laurate cuivrique à l'état cristallin et dans la mésophase.

Abstract.— Copper laurate was processed into oriented fibres by melt spinning of its thermotropic columnar mesophase ; examination by scanning electron microscopy and X-ray diffraction shows a high degree of orientation of the spun fibres in the solid state as well as in the columnar mesophase.

There is considerable current interest in the design of metal-containing molecular materials with specific properties such as electrical conductivity or ferromagnetism [1]. Liquid crystalline behaviour would be an added bonus to the desired properties, as it would possibly provide ease of processing and macroscopic orientation. The search for efficient methods of alignment of nematic liquid crystals was highlighted by Janning's discovery in 1972 that a very thin film of silicon monoxide deposited onto a surface at an oblique angle resulted in uniform, permanent, and reproducible orientation of

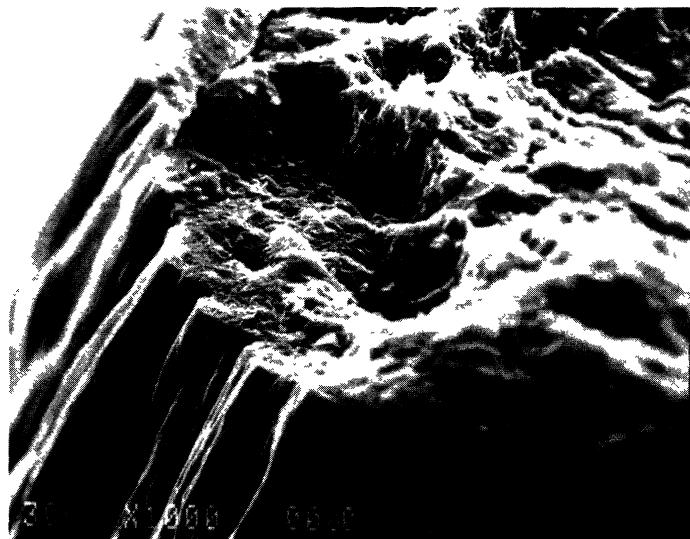
the mesogen on the surface [2]. This process has become very popular with liquid crystal display manufacturers, and it is widely used in the industry. The alignment of columnar liquid crystals, on the other hand, has been a challenging research area since the discovery of discotic mesogens [3]. Several alignment techniques including use of a magnetic field [4], various surface treatments [5], slow flow through a capillary [6], or stretching of the mesophase [7] have resulted in limited degrees of alignment. A process employing a mechanically operated pin which draws a strand from a reservoir cup of the mesogen at a desired temperature in the columnar phase has recently been shown to give highly oriented fibres [8]. In this communication, we report that upon melt-spinning, the columnar mesophase of copper laurate [9] (Scheme I) easily affords oriented solid fibres, which upon heating result in columnar liquid-crystalline fibres of high anisotropic order.



Scheme I.

About 2 g of microcrystalline, powdered copper laurate (dicopper tetrakis(dodecanoate)) were put inside the heating cylinder of a manually operated rod-spinning apparatus (Davenport Melt Indexer 3). The extrusion temperature, 120°C, was 13°C above the transition to the columnar mesophase. The spinneret diameter was 0.3 mm. The length of the spun fibres was limited to 10-20 cm by the poor mechanical properties of the solid material. Figure 1a displays a scanning electron microscope photograph of a copper laurate fibre coated with platinum-gold by vacuum deposition. Evidence of an anisotropic inner structure is provided by the surface corrugation, parallel to the fibre axis. This is indicative of greater radial than longitudinal shrink-

age of a melted core sheathed in a clotted plastic skin as the fibre cools away from the spinneret. The observed anisotropic thermal contraction is fully consistent with the previously reported thermal evolution of the intercolumnar distance [9], nearly constant value of the intracolumnar stacking period [10], and sharp increase in molar volume upon the transition to the columnar mesophase [10]. On the other hand, slower extrusion rates can result in the formation of a central hole when the thicker skin resists corrugation, as shown in figure 1b. Finally, the microfibrillar structure seen in the fibre core (Fig. 1a) suggests the presence of columnar microdomains parallel to the spinning direction.

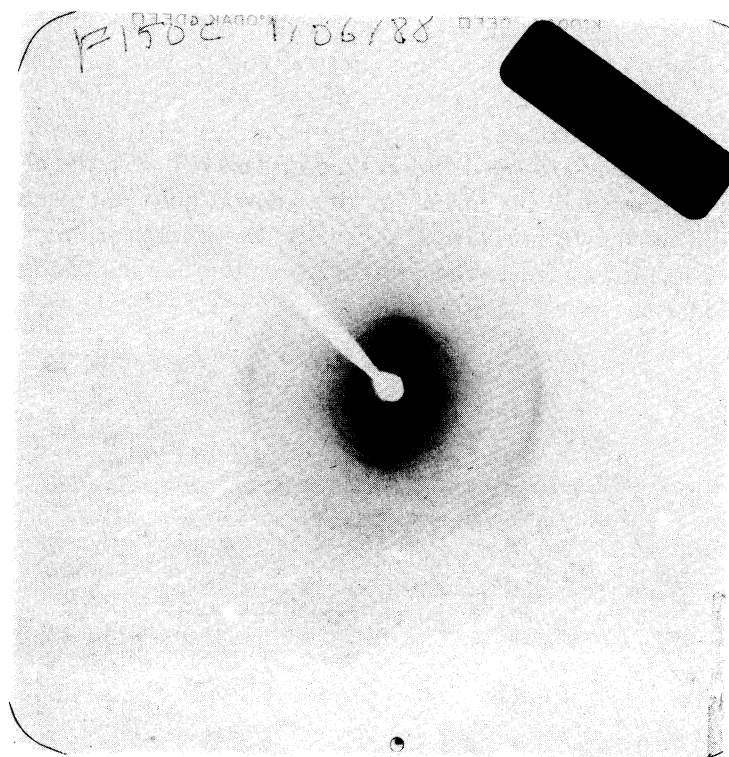


(a)

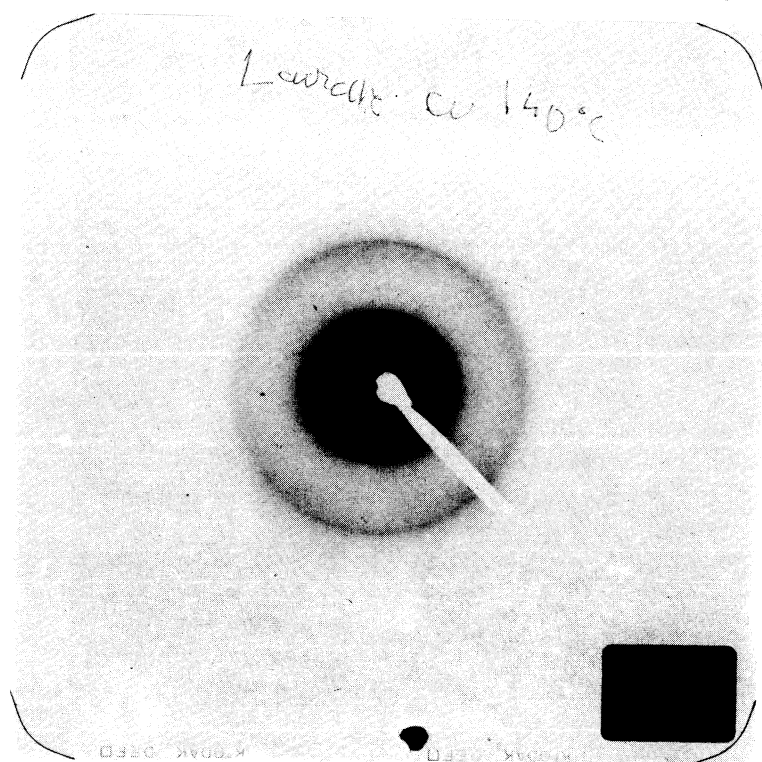


(b)

Fig. 1.— Scanning electron microscope photographs of melt-spun copper laurate fibres. Anisotropic contraction upon cooling is indicated by the corrugated surface (a) and the central hole (b). A microfibrillar structure is seen on the fracture surface (a).



(a)



(b)

Fig. 2.— X-ray diffraction diagrams of the columnar mesophase of copper laurate at 150°C :
(a) melt-spun fibre ; the fibre axis is approximately horizontal and perpendicular to the beam ;
(b) unoriented sample.

X-ray diffraction patterns were taken at various temperatures for copper laurate fibres placed in 0.5 mm Lindemann capillaries, and they were recorded photographically with a flat-plate camera parallel to the fibre axis. The beam from a rotating anode (Elliott GX20) was perpendicular to the spinning direction. Figure 2a shows a typical pattern obtained at 150°C in the columnar mesophase ; the corresponding pattern obtained for an unoriented sample is shown for comparison in figure 2b. The localization of diffracted intensity maxima in limited lobes in figures 2a indicates that the sample is oriented.

Examination of the small-angle equatorial region shows sharp Bragg reflection arcs with reciprocal spacings in the ratios $1 : 3^{1/2} : 4^{1/2} : 7^{1/2}$. The high degree of orientation is apparent from the low extent of arcing of the reflections. The pattern is characteristic of a two-dimensional hexagonal array of columns that are parallel to the spinning direction. On the other hand, the rather narrow reflection observed at wide Bragg angle in the meridional plane corresponds to the 4.7 Å stacking period of the binuclear copper cores along the column axes. A diffuse isotropic band partially overlapping the latter reflection corresponds to the stacking of the disordered aliphatic chains of the complex [11]. Finally, the half-height width of the meridional reflection indicates a coherence length of approximately 120 Å ; this corresponds to a stack of about 25 binuclear diffracting units, i.e. a medium-range crystalline order within the columns of the mesophase. This result is in agreement with our recent study of the analogous copper stearate complex by copper K edge EXAFS, which indicates that a high degree of order of the polar cores is retained in the columnar mesophase [12].

The X-ray pattern shown in figure 3a is that of an "as-made" copper laurate fibre at room temperature. Numerous reflections are seen in the equatorial plane ; these can be shown to belong to two different patterns. one pattern is derived from a two-dimensional hexagonal array, almost identical to that of the columnar mesophase (Fig. 2a) ; apparently, the columnar structure is quenched in the solid phase as the spun fibre quickly cools away from the spinneret. The other pattern exhibits a series of regularly spaced reflections with a period corresponding to that of the lamellar crystalline phase of copper laurate [9] ; the corresponding distribution of diffracted intensity about the equatorial plane reflects preferential orientation of the crystal sheets parallel to the spinning direction. This is consistent with a crystal growth from an oriented mesophase. Interestingly, annealing the "as-made" fiber at 100°C (7°C below the phase transition) for 24 h results in disappearance of the quenched hexagonal phase and improvement of the crystalline order and orientation of the lamellar solid phase (Fig. 3b).

These results demonstrate that the melt-spinning technique is an easy and reliable method for the alignment of the thermotropic columnar mesophase of a mesogenic transition metal complex. The degree of orientation may not be as high as that obtained by some of the previously described techniques [7,8], but a significant improvement of the present method is its simplicity and the ease of obtention of large amounts (grams !) of oriented samples. The ability to obtain oriented fibres over macroscopic distances is likely to bring significant progress for the processing and physicochemical investigation of columnar molecular materials.

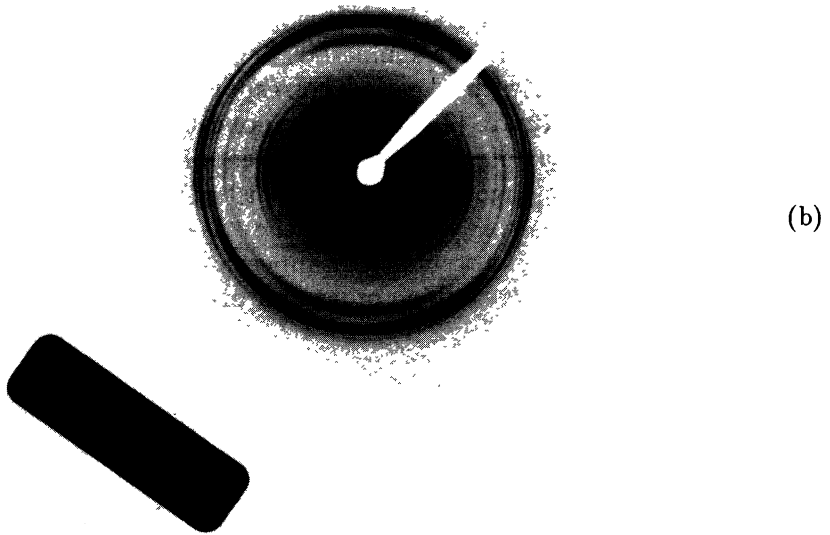
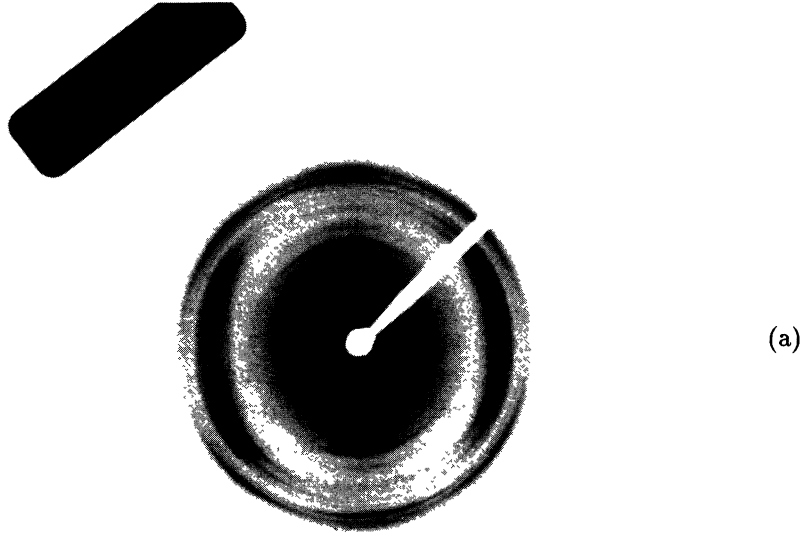


Fig. 3.— X-ray diffraction diagrams of copper laurate fibres at room temperature : (a) “as-made” fibre ; (b) after annealing at 100°C for 24 h.

Acknowledgments.

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