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PRELIMINARY COMMUNICATION

Untwisting of the helical superstructure in the cholesteric and chiral smectic C* phases of cross-linked liquid-crystalline polymers by strain

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It is possible to untwist reversibly the helical superstructure of elastomers with cholesteric and chiral smectic C* phases by using strain. In that way a cholesteric structure can be transformed into a nematic structure and a chiral smectic C* into a smectic C structure. The latter case is especially interesting because a structure without a macroscopic polarization (chiral smectic C*) is transformed into one with a macroscopic polarization (smectic C like arrangement).

Slightly cross-linked liquid-crystalline networks with elastic properties (elastomers) have been prepared from different types of liquid-crystalline polymers [1–3]. In these cross-linked elastomers the liquid crystal phase can be well oriented by small mechanical strains [2–5] and this orientation is reversible [6]. It is interesting therefore to see if it is also possible to untwist the helical superstructure in elastomers with cholesteric and chiral smectic C* phases by stretching the sample. Such a transformation from a cholesteric structure into a nematic structure or from a chiral smectic C* into a smectic C structure is well known from low molar mass liquid crystals. It can be caused by strong electric or magnetic fields and by surface forces [7, 8] as well as in flow fields [9, 10]. If stretching a cholesteric elastomer would reversibly transform a structure with a selective reflection (cholesteric) into one without a selective reflection (nematic), then this elastomer should act like a device that transforms a mechanical signal (the strain) into an optical signal (see figure 1 (*a*), (*b*)). If stretching an elastomer with a chiral smectic C* phase would reversibly transform a structure without a macroscopic polarization (chiral smectic C*) into one with a macroscopic polarization (smectic C like arrangement), then this elastomer should act like a piezo element, which transforms a mechanical signal into an electrical response (see figure 1 (*c*), (*d*)).

Only a few examples of liquid-crystalline elastomers with chiral constituents have been described so far [1, 11], and none of them showed a chiral smectic C* phase. By variation of the cross-linkable copolymers of [11], we have prepared a series of new chiral liquid-crystalline polymers [6, 12] and cross-linked liquid-crystalline elastomers [13]. Both the uncross-linked polymers and the cross-linked elastomers show chiral smectic C*, smectic A and cholesteric phases. One of these elastomers, the synthesis of which is given later, was used to investigate the orientability of chiral liquid crystal phases by strain.

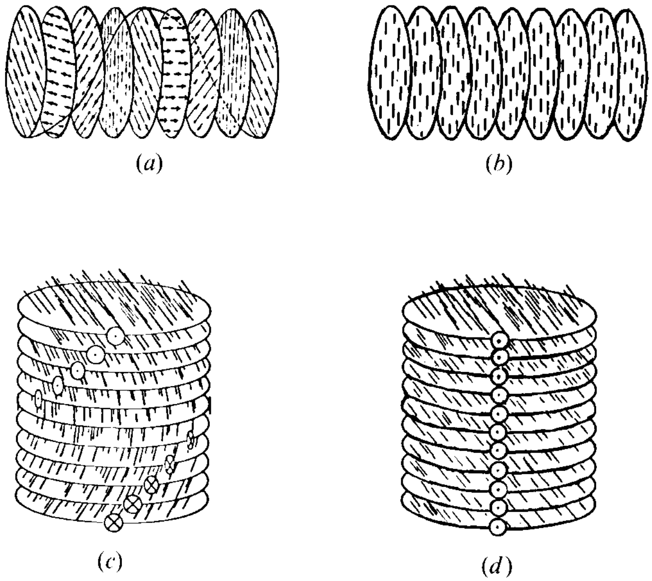
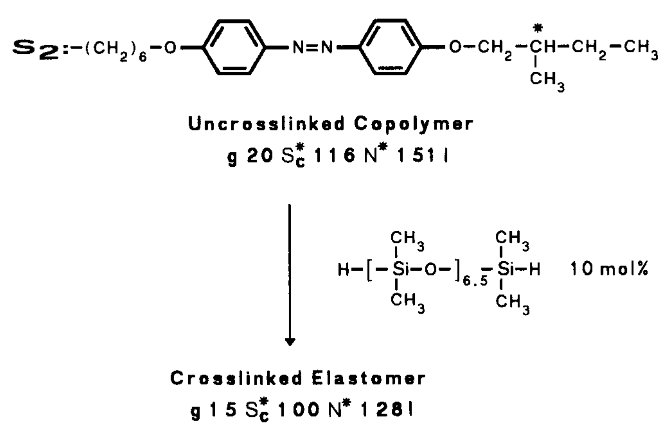


Figure 1. Twisted and untwisted states of cholesteric and chiral smectic C* phases. Cholesteric phase: (*a*) helical superstructure (ground state), selective reflection; (*b*) nematic arrangement, no selective reflection. Chiral smectic C* phase: (*c*) helical superstructure (ground state), no macroscopic polarization; (*d*) smectic C like arrangement, macroscopic polarization.



Scheme.

The uncross-linked copolymer was prepared by melt copolycondensation in analogy to procedures described elsewhere [11, 12], using chiral diethyl 6-(4-(2-methylbutyloxy)phenylazophenoxy) hexylmalonate [11] with a $[\alpha]_D^{20} = 7{\cdot}5$ (CH_2Cl_2) as one of the comonomers (diesters). The phase assignment was achieved by D.S.C. measurements, by polarizing microscopy and by X-ray scattering (see figure 2). In the chiral smectic C* phase a lined texture [14] is observed (the estimated pitch of the helix is 7 μm at 115°C). In the cholesteric phase a texture with oily streaks or a polygonal texture [14] is observed (the estimated pitch of the helix is 3 μm at 117°C).

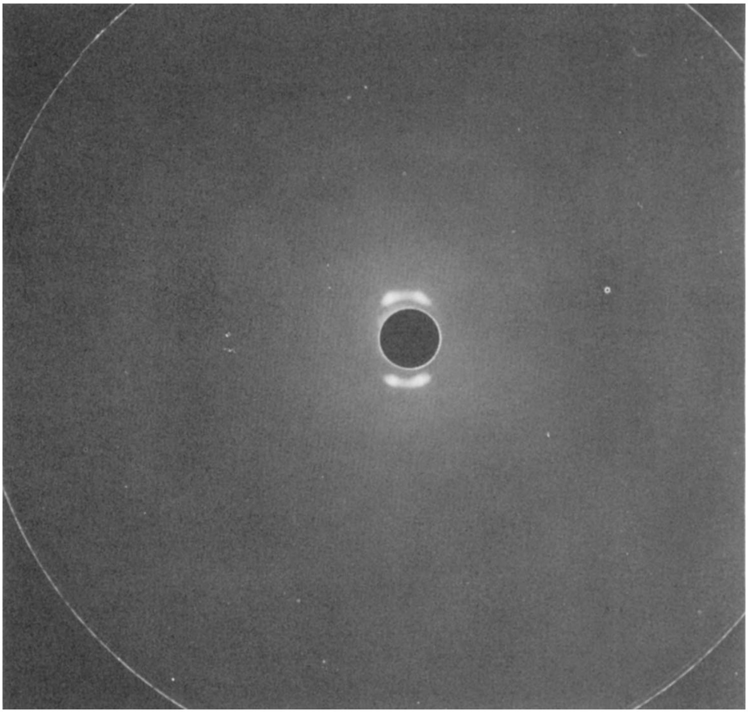


Figure 2. Fibre pattern of the uncross-linked copolymer at room temperature (fibre axis vertical); wide angle reflection: 4·5 Å, small angle reflection: 26 Å.

The cross-linked elastomer was prepared by reaction of some of the olefinic double bonds of the copolymer with the Si–H groups of the oligo (dimethylsiloxane) [2, 11]. Pieces of the elastomer (roughly 5 × 2 × 0·5 mm) no longer show typical textures because of the high viscosity of this soft solid. However they did show an X-ray pattern typical of cholesteric (cf. figure 3) and chiral smectic C* phases (cf. figure 4). Since the selective reflection of the cholesteric phase did not occur in the visible region, X-ray measurements were used to follow the strain induced orientation [5]. For this purpose pieces of the elastomer were fixed to a heatable sample holder, which allowed the sample to be stretched during the X-ray measurements (a flat-plate camera with Ni filtered Cu K_α radiation).

Small strains (30–100 per cent) were not sufficient to obtain an oriented X-ray pattern in the cholesteric phase. This is different from the behaviour of elastomers from non-chiral polymers [2–6], which can be well oriented by strains of this magnitude. However it is typical for a cholesteric structure, in which the molecules have different orientations in space, even if the helix axis is oriented (see figure 1 (*a*)).

However for higher strains (> 150 per cent), oriented X-ray patterns could be obtained (see figure 3). They show a wide angle reflection (lateral packing) that is centred at the equator and diffuse lines in the small angle region at the meridian (cybotactic groups or the one dimensional lattice of the polymer chains). These fibre patterns do not change during rotation of the sample around the fibre axis. They are typical of nematic phases and prove that all the mesogenic groups tend to be oriented parallel to the fibre axis (see figure 1 (*b*)). This means that the helical superstructure of the cholesteric phase has been untwisted by using strain. On removing the strain an unoriented X-ray pattern is restored [6].

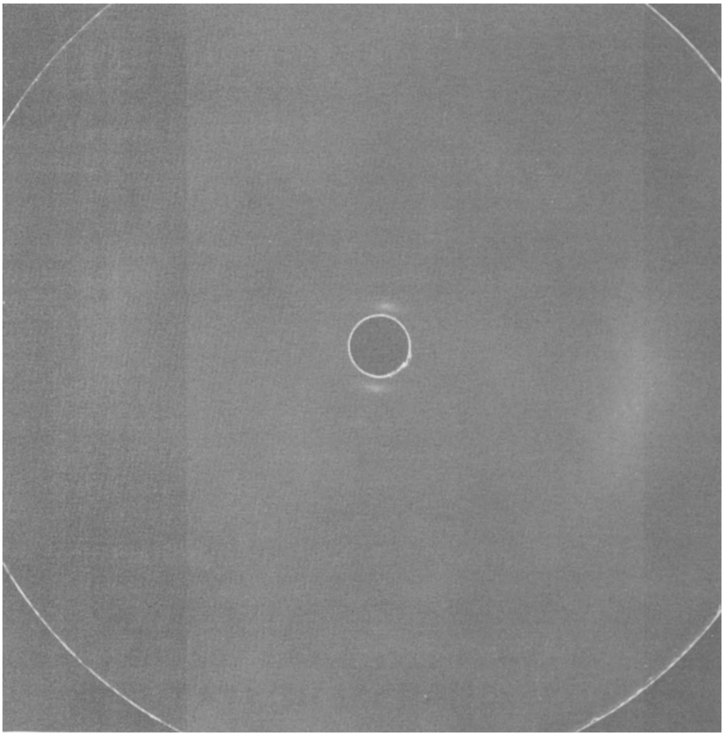
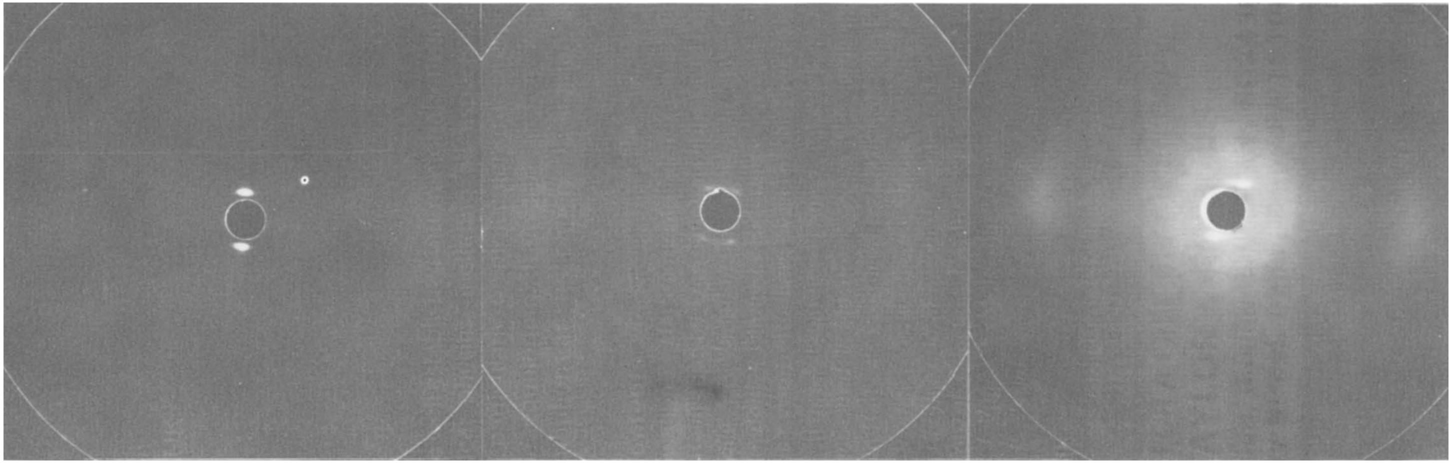


Figure 3. Fibre pattern of the cross-linked elastomer at 107°C in the cholesteric phase (fibre–film distance: 100 mm); a strain of 300 per cent was applied in the vertical direction. The wide angle reflection corresponds to 4·5 Å and the small angle reflection corresponds to 27 Å.

In the chiral smectic C* phase, an oriented X-ray pattern could be obtained, even for small strains (50–300 per cent, see figure 4 (*a*)). They are typical of a chiral smectic C* structure as presented in figure 1 (*c*), the smectic layers being perpendicular to the fibre axis. In this arrangement the tilt angle of the director causes only a broader angular distribution of the wide angle reflections, compared to smectic A phases [15]. In order to investigate the sample at much higher strain rates, we stretched the sample in the chiral smectic C* phase and afterwards cooled it to room temperature (glass transition temperature). Thereby the orientation of the liquid crystal phase was frozen



(*a*) (*b*) (*c*)

Figure 4. Fibre pattern of the cross-linked elastomer in the chiral smectic C* phase (fibre–film distance: 100 mm). (*a*) A strain of 300 per cent was applied at 90°C in the vertical direction. (*b*) and (*c*) Strains of more than 400 per cent were applied in the vertical direction. The measurements were performed at room temperature. The wide angle reflections correspond to 4·4 Å and the small angle reflections correspond to 26–27 Å.

in and could be investigated without tearing the sample. The X-ray patterns thus obtained are presented in figure 4 (*b*), (*c*). They correspond to the smectic C like arrangement of figure 1 (*d*). All the mesogenic groups tend to be oriented parallel to the fibre axis. This is most notable from the wide angle reflection in figure 4 (*c*), which is very well centred at the equator. The smectic layers are tilted with respect to the fibre axis. Thus the helical superstructure has been untwisted by using strain. On removing the strain, fibre patterns as shown in figure 4 (*a*) are reformed, by restoring the helical superstructure of the chiral smectic C* phase. A transition between the structures corresponding to the X-ray pattern displayed in figure 4 (*a*), (*c*) is especially interesting in this context. The structure corresponding to figure 4 (*a*) (figure 1 (*c*)) should have no macroscopic polarization, but the structure corresponding to figure 4 (*c*) (figure 1 (*d*)) should.

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