PIEZOELECTRICITY AND THE STRUCTURE OF FERROELECTRIC SMECTIC C* LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS

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Abstract: We discuss the local and global symmetry of chiral smectic C side-chain polymers. We argue on the basis of simple Ginzburg-Landau expansions that in polymeric systems the local symmetry can be C_1 (compared to the conventional C_2 symmetry), which gives globally (i.e. if averaged over many helical pitches) a C_∞ symmetry (compared to the conventional D_∞ symmetry). As a consequence ferroelectricity (or antiferroelectricity) has a non-vanishing component along the layer normal, thus allowing longitudinal piezoelectric and pyroelectric effects.

INTRODUCTION

Conventionally the structure of low molecular weight smectic C^* liquid crystals is described as a tilted layer structure, where the preferred direction (the director $\hat{\mathbf{n}}$) rotates conic helically when going from one layer to the next, with $\hat{\mathbf{n}}$ keeping a fixed oblique tilt angle with the helix axis, which is parallel to the layer normal[1]. This picture is obtained from a Ginzburg-Landau functional using a two-dimensional order parameter[2] (tilt angle and tilt direction) and the D_∞ symmetry for the molecules (i.e. $\hat{\mathbf{n}}$ to $-\hat{\mathbf{n}}$ symmetry). Due to the lack of inversion symmetry a contribution to the energy linear in the twist becomes possible, which leads to the conic helical structure with C_2 symmetry for every layer locally. This implies the existence of a polar direction in every layer (the polarization), which is perpendicular to both, the helical axis and the director. This polar direction is a local two-fold rotational symmetry axis, spiraling (untilted) about the helix axis. In a coarse grained description, averaged over many pitch lengths, the symmetry is D_∞, with the helical axis as preferred direction, and the polar axis (the polarization) is averaged out. The existence of the two-fold local rotational symmetry axis shows that the heli-

cal axis cannot be a polar axis. This implies that there is no ferroelectricity (or antiferroelectricity) along the helical axis (the layer normal) and no longitudinal piezoelectric effect.

Recently the existence of a piezoelectric effect has been demonstrated experimentally[3] in elastomeric smectic C* liquid crystals. This was paralleled by the experimental discovery of longitudinal piezoelectricity in cholesteric elastomers[4,5], where a compression along the helical axis results in a static voltage parallel to the helical axis. It is obvious that the conventional D_2 local (or D_∞ global) symmetry of cholesteric liquid crystals is incompatible[6] with the observed longitudinal piezoelectric effect. The explanation in ref. 7 assumes that there is an anisotropy in the plane perpendicular to the helical axis. This is in contradiction with the experimental results and therefore the analysis of ref.7 is inapplicable. Thus, at least some polymeric and elastomeric cholesteric liquid crystal systems must have unconventional structures, some possibilities of which are discussed in ref. 6.

In this communication we will argue that polymeric or elastomeric chiral smectic C* systems may also show unconventional structures of lower symmetry than usual. As a result piezo-, pyro- and ferro- (or antiferro-) electricity along the layer normal is possible in such structures. In the following we discuss two different unconventional structures and their origin due to the global or local orientation of the polymeric backbone.

CONFORMATIONAL ANISOTROPY

Liquid crystalline (side-chain) polymers are known, experimentally[8,9] as well as theoretically[10], to exhibit anisotropic backbone configurations in their nematic state. This is due to the nematic ordering of the side-chains, which by steric and other interactions reduces anisotropically the volume the polymeric backbones can explore entropically. It seems natural to assume that this conformational anisotropy is still present (or rather even more pronounced) in the smectic C* phase. Thus we are left with three preferred directions, assuming that the helical axis remains parallel to the layer normal: The director $\hat{\mathbf{n}}$, spiraling conic helically around the layer normal (or helix axis) $\hat{\mathbf{p}}$, and the conformational anisotropy axis $\hat{\mathbf{l}}$. If accidentally $\hat{\mathbf{l}}$ is parallel to $\hat{\mathbf{p}}$, then this is a conventional smectic C* structure, i.e. of local C_2 symmetry with the symmetry axis (the polar axis or polarization) within the smectic plane (perpendicular to $\hat{\mathbf{p}}$). However, there is no reason why the angle between $\hat{\mathbf{n}}$ and $\hat{\mathbf{l}}$ should everywhere be equal to the tilt angle and we therefore expect in general, $\hat{\mathbf{p}} \neq \hat{\mathbf{l}}$, to be the generic case. Then the local symmetry is C_1 almost everywhere, i.e. except for the planes, where $\hat{\mathbf{n}}$, $\hat{\mathbf{l}}$, and $\hat{\mathbf{p}}$ are coplanar. This implies a longitudinal component (parallel to $\hat{\mathbf{p}}$) of the polarization changing sign at the planes of coplanarity, thus describing antiferroelectricity. With the conic

helical director

$$\hat{\mathbf{n}} = (\hat{\mathbf{e}}_x \cos q_0 z + \hat{\mathbf{e}}_y \sin q_0 z) \sin \theta + \hat{\mathbf{e}}_z \cos \theta, \tag{1}$$

where $2\pi/q_0$ is the pitch and θ the tilt angle, and with $\hat{\mathbf{l}} = (\hat{\mathbf{e}}_x \cos \phi_l + \hat{\mathbf{e}}_y \sin \phi_l) \sin \theta_l + \hat{\mathbf{e}}_z \cos \theta_l$, where θ_l is the angle between $\hat{\mathbf{l}}$ and $\hat{\mathbf{p}} = \hat{\mathbf{e}}_z$ and ϕ_l is the (constant) azimuthal angle of the projection of $\hat{\mathbf{l}}$ onto the (arbitrary) frame $\hat{\mathbf{e}}_x$ and $\hat{\mathbf{e}}_y$, we can construct a helix independent polar vector $(\hat{\mathbf{n}} \times \hat{\mathbf{l}}) \times (\hat{\mathbf{p}} \times \hat{\mathbf{l}})$ which has the longitudinal component

$$\frac{1}{2} \sin \theta \, \sin 2\theta_l \, \sin(q_0 z - \phi_l) \equiv P_z \tag{2}$$

showing the (longitudinal) antiferroelectric behaviour described before eq.(1). If $\hat{\mathbf{l}}$ is parallel ($\theta_l = 0$) or perpendicular ($\theta_l = \pi/2$) to $\hat{\mathbf{p}}$, there is no such longitudinal component.

If a conic helical structure is unwound by the presence of a wall, e.g. via the planar boundary condition $\hat{\mathbf{n}} \perp \hat{\mathbf{e}}_x$ at $x = 0$, two favourable domains ($\pm$) with $\hat{\mathbf{n}} = \pm \hat{\mathbf{e}}_y \sin \theta + \hat{\mathbf{e}}_z \cos \theta$ emerge. For conventional structures the two domains are energetically equivalent, but with opposite polarization $\mathbf{P}_\pm = \mp P_0 \hat{\mathbf{e}}_x$, while taking into account the longitudinal vector (2) the polarizations of the two domains

$$\mathbf{P}_\pm = \mp(\tilde{P}_0 \hat{\mathbf{e}}_x + P_z \hat{\mathbf{e}}_z) \tag{3}$$

are not perpendicular to the wall but still opposite in direction and equal in amount.

LOCAL OBLIQUE BACKBONE ORDER

In the preceding section we have discussed the possible influence of the global anisotropy of the backbone conformation on the liquid crystalline structure. Now we want to investigate the influence of the backbone on a local scale. Here we assume that the local interaction between side-chains and backbone segments are dominant and lead to a preferred relative angle between the orientation of the side-chains and the backbone segments to which the former are attached. This relative angle, ψ, is often found to be near $\pi/2$, although its precise value is not important for the following discussion.

In a smectic A liquid crystalline side-chain polymer a relative angle ψ near $\pi/2$ allows the backbone segments to lie predominantly in the planes perpendicular to the layer normal and to keep complete orientational randomness of the backbone segments in these planes. In a tilted smectic phase however, a fixed relative angle ψ forces the backbone segments, either to lie in the layer planes but with rather restricted orientational freedom within the layers, or to be also tilted out of the layers. The former situation is rather unlikely, since it contradicts the entropic

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constraints for the polymer chains to have predominantly random orientation and it is incompatible with the fact that the backbone segments are connected in the form of a chain. In the latter case an additional preferred direction (out of the layer planes) exists due to tilt of the backbone segments. Describing a possible backbone segment order by an orientational order parameter $M_{ij} = M(\hat{m}_i \hat{m}_j - (1/3)\delta_{ij})$, the order and orientation of the backbone segments in a smectic C* phase (with the layers kept fixed) are governed by a Ginzburg-Landau functional in terms of M_{ij} and its gradients. It contains e.g. terms linear in $\nabla_i M_{jk}$ due to the existence of the nematic order parameter Q_{ij}, which describes the side-chain order. For simplicity we will take the relative angle ψ to be exactly $\pi/2$ everywhere, i.e. $\hat{\mathbf{m}}$ is perpendicular to $\hat{\mathbf{n}}$ (1)

$$
\begin{aligned}
\hat{\mathbf{m}} = - & \left[(\hat{\mathbf{e}}_x \cos q_0 z + \hat{\mathbf{e}}_y \sin q_0 z) \cos \theta - \hat{\mathbf{e}}_z \sin \theta \right] \cos \chi \\
& + (\hat{\mathbf{e}}_x \sin q_0 z - \hat{\mathbf{e}}_y \cos q_0 z) \sin \chi
\end{aligned}
\tag{4}
$$

where the (still undetermined) tilt angle of $\hat{\mathbf{m}}$, θ_m, (i.e. the angle between $\hat{\mathbf{m}}$ and $\hat{\mathbf{p}}$) is related to the angle χ by $\cos \theta_m = \sin \theta \cos \chi$. The Ginzburg-Landau free energy can then be written as

$$
\begin{aligned}
f_m = M(D_1 \cos^2 \theta_m + q_0[E_1 + E_2 \cos^2 \theta_m] + q_0^2[F_1 + F_2 \cos^2 \theta_m]) \\
+ M^2(D_2 + q_0^2[G_1 + G_2 \cos^2 \theta_m + G_3 \cos^4 \theta_m])
\end{aligned}
\tag{5}
$$

Minimizing eq.(5) with respect to the tilt order parameter M reveals that M is always non-vanishing. This leads to $f_m = \cos^2 \theta_m(-\tilde{\alpha} + \tilde{\beta} \cos^2 \theta_m + \tilde{\gamma} \cos^4 \theta_m)$, which is then minimized with respect to θ_m. As a result there is a finite tilt, i.e. $0 < \theta_m < \pi/2$ the actual value depending on the Ginzburg-Landau coefficients in eq. (5) (the case $\theta_m = \pi/2$ has been excluded before for physical reasons and similarly the case $\theta_m = 0$ is unphysical).

Clearly a biaxial conic helical structure with $\hat{\mathbf{m}}$ und $\hat{\mathbf{n}}$ given by (4) and (1), respectively, has C$_1$ symmetry locally and C$_\infty$ symmetry globally when averaged over many pitch lengths[11] (except for the special case when $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$, and $\hat{\mathbf{p}}$ are coplanar). It exhibits a polar vector with a longitudinal (i.e. parallel to $\hat{\mathbf{p}}$) component

$$
(\hat{\mathbf{n}} \times \hat{\mathbf{m}}) \times (\hat{\mathbf{p}} \times \hat{\mathbf{m}}) \mid_z = \hat{m}_z[\hat{\mathbf{m}} \cdot (\hat{\mathbf{n}} \times \hat{\mathbf{p}})] = \cos \theta_m \cos \theta_{n \times m} \equiv P_z
\tag{6}
$$

with $\theta_{n \times m}$ the tilt angle of the vector $\hat{\mathbf{n}} \times \hat{\mathbf{m}}$. This longitudinal component of the polarization is constant everywhere and thus of truely ferroelectric nature. In an unwound situation, where e.g. the director is planar to a wall ($x = 0$), the total polarization of the two possible domains $\mathbf{P}_\pm = \mp P_0 \hat{\mathbf{e}}_x + P_z \hat{\mathbf{e}}_z$ is no longer perpendicular to the wall nor are the two domains equivalent. In addition there

is a longitudinal piezoelectric effect as discussed in the Introduction in contrast to the conventional smectic C* structures.

SUMMARY

In the preceding two sections we have discussed the possible structural differences between polymeric and low-molecular-weight smectic C* liquid crystals. First we looked at the influence of a global, conformational ordering of the backbone chain on the symmetry of the system, while in the second part we focused on the impact of the local ordering of backbone segments. In nature one can expect both effects to occur and it will depend on the specific system which one will be more important. The point we want to stress is that the presence of the backbone chain generically leads to structural differences between polymeric and low-molecular-weight systems, where the former are generally of lower symmetry than the latter. One implication of this difference is the existence of a polar vector along the layer normal (or the helix axis) in many cases leading to longitudinal ferro- or antiferroelectricity and longitudinal piezoelectricity in polymeric systems.

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