

TRUE FERROELECTRICITY IN CHIRAL SMECTIC POLYMERIC LIQUID CRYSTALS

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Abstract. – Side-chain liquid crystalline polymers differ from their low molecular weight counterparts not only *quantitatively* with respect to the macroscopic properties, but can show even *qualitative* differences in symmetry and structure. We discuss theoretically chiral smectic side-chain polymers, which can exhibit true ferroelectricity due to the polymeric backbone, while low molecular weight systems are known to be helielectric in fluid phases. We give two scenarios of large and small scale orientational order of the backbone, respectively, and discuss a number of experimental implications.

1. Introduction

Liquid crystalline side-chain polymers [1] are hybrid systems combining liquid crystal properties due to the mesogenic side-chains with the polymeric behaviour of long chain molecules. The latter aspects make these systems very interesting for certain applications, e.g. concerning their high viscosity (or rather visco-elasticity) and durability [2]. On the other hand, the mesogenic side-chains show qualitatively similar behaviour as their low molecular weight counterparts, e.g. concerning their dielectric response over a large frequency range [3]. It is therefore appropriate in many situations to describe such systems macroscopically by a combination of the variables of the two subsystems and derive the coupled dynamical equations for all of them. In addition, there is a class of relevant macroscopic variables that does not exist in either of the two isolated subsystems, but only in the combined system. In the nematic phase we mention as an example the relative rotation of the side-chains with respect to the backbone segments to which they are attached, – a variable, which is neither defined in isotropic polymers nor in low molecular weight nematics, but influences considerably the macroscopic properties of side-chain systems [4].

This procedure of combining the two subsystems is based on the assumption that the symmetries (and broken symmetries) of a given liquid crystal phase are the same whether the phase is formed by a low molecular weight or by a polymeric material. However, this assumption need not be true in all cases. If the backbone orders orientationally, this additional order can interfere with the liquid crystalline order of the side-chains to yield an overall different (and lower) symmetry for the combined system compared to the liquid crystalline system alone. Hints for such a case can be found in weakly biaxial side-chain nematics [5], where the mesogenic units can no longer rotate freely about their long axis, since they are attached to the backbone via the flexible spacers in an umbilical fashion

(side-on side-chain polymers). A rather striking evidence for the symmetry reduction in polymeric systems is provided by the existence of a *longitudinal* piezoelectric effect in certain side-chain cholesteric liquid crystal elastomers [6], which must be absent in low molecular weight cholesteric phases of the conventional symmetry [7]. There is also experimental evidence that the same phenomenon occurs in chiral smectic side-chain polymers [8].

In the following we investigate theoretically, using simple arguments of the Ginzburg-Landau type, how the symmetry of a polymeric chiral smectic phase can be lower than that of a low molecular weight C^* phase due to either an orientational ordering of the backbone conformation (section 2) or due to a local oblique ordering of backbone segments (section 3). We expect most of our results to be applicable as well to elastomeric (permanently cross-linked) systems. We will show that due to the reduced symmetry in polymeric chiral smectic phases the electric polarization has a ferroelectric (or antiferroelectric) component, while in low molecular weight systems the symmetry of the C^* phase only allows helielectricity [9] (i.e. the polarization spirals about a direction, which is perpendicular to the polarization itself). Thus, in polymeric systems conic helical polarizations (i.e. the spiraling polarization makes an angle less than 90 degree with the helical axis), ferroelectric and even more complicated structures are possible.

All these liquid crystal phases are 'improper' ferroelectrics etc.[10, 11], since the phase transitions from states without a polarization to states with any kind of spontaneous polarization (or between states of different types of polarization) are not driven by the formation of ordered patches of molecular electric moments, but by structural changes of the mean orientation of the molecules. E.g. the phase transition from a smectic A to a C^* phase (in low molecular weight materials) is governed by the occurrence of a tilt angle

(the molecules start to be tilted in the mean with respect to the normal of the smectic layers), which lowers the symmetry and allows the formation of a (helical) polarization as a secondary effect. Accordingly, in the polymeric case the existence of a ferroelectric component is a consequence of the additional backbone ordering (and not the origin of the latter). This absence of 'proper' ferroelectricity etc. in liquid crystalline and polymeric liquid crystalline structures appears to be a result of the fluidity, which allows an easy reorientation and compensation of electrical moments on the molecular level.

In low molecular weight smectic C* phases averaging over many pitch lengths of the helix reduces the mean polarization to almost zero. Thus, electrooptic devices using chiral smectic phases are obtained by unwinding the helical structure using surface effects, which makes such devices rather complicated in detail and requires thin samples. The existence of a spontaneous ferroelectric component in polymeric systems would make helix unwinding unnecessary and large bulk domains could be achieved. Since the switching times are still quite short in polymeric systems and given their enhanced mechanical stability such systems may be a good alternative to low molecular weight systems for a number of applications.

2. Conformational Anisotropy

Low molecular weight smectic C* phases show several preferred directions, the normal of the smectic layers \mathbf{k} ($\mathbf{k} = \hat{\mathbf{e}}_z$), which is identical to the helical axis and the director \mathbf{n} ($\mathbf{n} = [\hat{\mathbf{e}}_x \cos q_0 z + \hat{\mathbf{e}}_y \sin q_0 z] \sin \theta + \hat{\mathbf{e}}_z \cos \theta$), which spirals conic helically about the helical axis and which has a fixed angle (the tilt angle θ) with \mathbf{k} . Since the structure of the liquid crystalline phase is invariant under the combined transformation $\mathbf{k} \rightarrow -\mathbf{k}$ and $\mathbf{n} \rightarrow -\mathbf{n}$, the direction $\mathbf{k} \times \mathbf{n}$ is the only polar axis in the system and, thus, the direction of the

polarization \mathbf{P}_0 . The latter also spirals helically about \mathbf{k} , but is by symmetry completely confined within the layers, i.e. it is always perpendicular to \mathbf{k} . As mentioned above this helix has to be unwound by external fields or surfaces in order to get a macroscopic net polarization.

In nematic liquid crystalline side-chain polymers the backbone configuration is not isotropic [12-14], but shows an anisotropy axis (\mathbf{l}). It is very likely that such an anisotropy prevails in the more complicated phases as e.g. in chiral smectic phases. There, however, already several preferred directions exist and it is not obvious, how the additional direction \mathbf{l} ($\mathbf{l} = \hat{\mathbf{e}}_x \sin \theta_l + \hat{\mathbf{e}}_z \cos \theta_l$), orients itself with respect to the liquid crystalline directions \mathbf{k} , \mathbf{n} or \mathbf{P}_0 [15]. A simple Ginzburg-Landau type ansatz for the free energy density f

$$f = \frac{a}{2}(\mathbf{l} \cdot \mathbf{k})^2 + \frac{b}{2}(\mathbf{l} \cdot \mathbf{n})^2 + \frac{1}{2}K_{ijkl}(\nabla_j n_i)(\nabla_l n_k) + K_2 q_0 \mathbf{n} \cdot \text{curl} \mathbf{n} \quad (1)$$

reveals after minimization that \mathbf{l} is constant in space (i.e. not spiraling) and can either be parallel to \mathbf{k} , or oblique to it (fixed angle θ_l between \mathbf{k} and \mathbf{l}), or perpendicular ($\theta_l = \pi/2$) depending on the values of the (unknown) parameters a and b . The tensor K_{ijkl} is the orientation elastic tensor depending generally on \mathbf{n} , \mathbf{k} and \mathbf{l} and containing the Frank constants (e.g. K_2), while q_0 is the helical wave vector [16]. In the first case ($\mathbf{k} \parallel \mathbf{l}$) the symmetry of the total system is the same (C_2) as that of a low molecular weight smectic C^* phase, i.e. no ferroelectricity (only helielectricity) and no longitudinal piezoelectric effect is possible. In the other two cases the symmetry of the polymeric system is different (C_1) from that of ordinary low molecular weight systems. The lack of any symmetry axis in this case allows polar directions, which have also longitudinal (i.e. parallel to \mathbf{k}) and non-spiraling components. This general scenario is true except for the very special layers, where \mathbf{k} , \mathbf{l} , and \mathbf{n} are accidentally coplanar. Here the C_1 symmetry degenerates into C_2

(with the 2-axis perpendicular to \mathbf{k}) and no longitudinal component of the polarization is possible [17]. These special layers repeat every half pitch leading to an antiferroelectric structure of the longitudinal component. The general structure of the polarization is more complicated and can be described by the following possible contributions:

$$\mathbf{P}_0 = \mathbf{k} \times \mathbf{n} = \sin \theta (-\mathbf{e}_x \sin q_0 z + \mathbf{e}_y \cos q_0 z) \quad (2a)$$

$$\mathbf{P}_1 = (\mathbf{n} \times \mathbf{l}) \times (\mathbf{k} \times \mathbf{l}) = \sin q_0 z \sin \theta \sin \theta_l (\mathbf{e}_x \sin \theta_l + \mathbf{e}_z \cos \theta_l) \quad (2b)$$

$$\mathbf{P}_2 = (\mathbf{l} \times \mathbf{k})(\mathbf{n} \cdot \mathbf{l}) = -\mathbf{e}_y \sin \theta_l (\cos \theta \cos \theta_l + \sin \theta \sin \theta_l \cos q_0 z) \quad (2c)$$

$$\mathbf{P}_3 = (\mathbf{l} \cdot \mathbf{n})(l_i \vec{\nabla} n_i) = -q_0 \mathbf{e}_z \sin q_0 z \sin \theta \sin \theta_l (\cos \theta \cos \theta_l + \sin \theta \sin \theta_l \cos q_0 z) \quad (2d)$$

where \mathbf{k} is along the z -axis and \mathbf{l} is in the $x - z$ plane. The angles θ and θ_l are the tilt angles of \mathbf{n} and \mathbf{l} with respect to the layer normal \mathbf{k} and q_0 is the helical wave vector. The first contribution (2a) is the usual helical in-plane polarization that vanishes after averaging over many pitch lengths. The second one (2b) contains (for $\theta_l \neq \pi/2$) an out-of-plane (i.e. longitudinal) antiferroelectric polarization that changes sign every half pitch. The third one (2c) shows a non-helical in-plane part that does not vanish by averaging over many pitch lengths and thus, denotes a true ferroelectric contribution (perpendicular to both, \mathbf{l} and \mathbf{k}). The last one (2d) is helix induced, i.e. it is proportional to the helical wave vector and vanishes upon unwinding, it is longitudinal and antiferroelectric (a superposition of wavelength modulations of a pitch and a half pitch, respectively). There are other contributions (e.g. $(\mathbf{l} \times \mathbf{n})(\mathbf{p} \cdot \mathbf{l})$ etc.), which however are not independent from the terms already kept.

The total polarization is then the sum $\mathbf{P} = P_0 \mathbf{P}_0 + P_1 \mathbf{P}_1 + P_2 \mathbf{P}_2 + P_3 \mathbf{P}_3$, where the relative weight factors, P_i , of the various contributions are material dependent and for $i = 1, 2, 3$ also S_l dependent, with S_l the strength of the orientational backbone order. Here

P_0 is the saturation polarization of usual low molecular weight smectic C* phases [18]. If the helix is destroyed by a surface perpendicular to the smectic layers (bookshelf geometry), which forces \mathbf{n} to lie within the surface, there are two states possible differing in their polarization, which are used in applications to switch between them. In low molecular weight systems the two states have opposite polarizations perpendicular to the surface. In polymeric systems the polarization of the two unwound states depends on the surface conditions for \mathbf{l} . If \mathbf{l} also lies within the surface, the polarizations are still orthogonal to the surface, but unequal in length, while for \mathbf{l} perpendicular to the surface, the polarizations of the two states are neither orthogonal to the surface, nor antiparallel to themselves, nor equal in length. However, we would like to emphasize that, as discussed above, helix unwinding is unnecessary in polymeric systems to obtain a ferroelectric polarization .

3. Local Oblique Backbone Order

In Sec. 2 we have discussed the influence of a possible global anisotropy of the backbone conformation on the overall symmetry of a polymeric chiral smectic phase. Now we want to investigate the implications of the presence of the backbone on a local scale. This will become relevant, if the local interaction between side-chains and backbone segments is strong and leads 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 untilted smectic A phases the backbone lies predominantly in the layers keeping complete orientational randomness of its segments within these layers. This is still possible, if there is a fixed relative angle ψ of order $\pi/2$. However, for tilted smectic phases (angle $\theta \neq 0$ between \mathbf{n} and \mathbf{k}) such a fixed relative angle forces the backbone segments

to be also tilted out of the smectic planes, since otherwise the orientational freedom of the backbone segments would be completely destroyed, which is incompatible with the entropic behaviour of the chain and with the fact that the backbone segments are connected in the form of a chain. In addition, the orientation of the backbone segments is not completely random, but shows a preferred direction. This is demonstrated by using a Ginzburg-Landau free energy expansion for an orientational backbone segment order parameter $M_{ij} = M(m_i m_j - (1/3)\delta_{ij})$, where M denotes the strength of this order and \mathbf{m} the preferred direction,

$$f = a Q_{ij} M_{ij} + b M_{ij} M_{ij} + c Q_{ij} M_{ik} M_{jk} + d Q_{ij} Q_{kl} M_{ik} M_{jl} + f_g \quad (3)$$

Here Q_{ij} is the nematic order parameter of the side-chains, which is assumed to be unchanged by the existence of M_{ij} , i.e. $Q_{ij} = S(n_i n_j - (1/3)\delta_{ij})$ with the director \mathbf{n} of the conic helical form. The (very many) terms containing gradients (of M_{ij} as well as Q_{ij}) are abbreviated by f_g . Due to the existence of the nematic side-chain order there are various contributions to (3), which are linear in M_{ij} . Thus, minimizing (3) with respect to M always gives a non-zero value for M . Taking $\psi = \pi/2$ for definiteness the preferred direction \mathbf{m} still has one degree of freedom, the angle χ denoting the orientation of \mathbf{m} in the plane perpendicular to \mathbf{n} . It is related to the tilt angle of \mathbf{m} , θ_m , by $\sin \theta \cos \chi = \cos \theta_m$ ($\mathbf{m} = -[(\hat{\mathbf{e}}_x \cos q_0 z + \hat{\mathbf{e}}_y \sin q_0 z) \cos \theta - \hat{\mathbf{e}}_z \sin \theta] \cos \chi + (\hat{\mathbf{e}}_x \sin q_0 z - \hat{\mathbf{e}}_y \cos q_0 z) \sin \chi$). Further minimizing eq. (3) with respect to χ gives a finite tilt depending on the Ginzburg-Landau parameters [19]. Of course, due to their entropic behaviour the backbone segments are only weakly oriented.

Clearly the biaxial conic helical structure of \mathbf{n} and \mathbf{m} is of C_1 symmetry except for the limiting case, where \mathbf{n} , \mathbf{m} and \mathbf{k} are coplanar ($\theta_m + \theta = \pi/2$). Thus, the following

contributions to the polarization are possible $\mathbf{P} = P_0\mathbf{P}_0 + P_4\mathbf{P}_4 + P_5\mathbf{P}_5$ with

$$\mathbf{P}_0 = \mathbf{k} \times \mathbf{n} = \sin \theta (-\mathbf{e}_x \sin q_0 z + \mathbf{e}_y \cos q_0 z) \quad (4a)$$

$$\mathbf{P}_4 = \sin \theta \cos \theta \sin \chi \cos \chi (\mathbf{e}_x \cos q_0 z + \mathbf{e}_y \sin q_0 z) \quad (4b)$$

$$\mathbf{P}_5 = \mathbf{e}_z \sin^2 \theta \sin \chi \cos \chi \quad (4c)$$

where \mathbf{P}_4 and \mathbf{P}_5 result from expressions like $(\mathbf{n} \times \mathbf{m}) \times (\mathbf{k} \times \mathbf{m})$, $(\mathbf{k} \cdot \mathbf{m})(\mathbf{m} \times \mathbf{n})$, $(\mathbf{k} \cdot \mathbf{m})(m_i \vec{\nabla} n_i)$ or $(\mathbf{m} \cdot \vec{\nabla})\mathbf{m} \times (\mathbf{n} \cdot \vec{\nabla})\mathbf{n}$. Obviously the in-plane polarization is no longer perpendicular to \mathbf{n} (due to \mathbf{P}_4), but is still helical, i.e. vanishes by averaging over many pitch lengths. In addition, there is a non helical (ferroelectric) contribution along the layer normal \mathbf{k} . If the helix is unwound by a surface, the polarizations of the two different possible states are neither orthogonal to that surface, nor are they antiparallel to each other nor of equal absolute value.

4. Summary

In the preceding two sections we have discussed the possible structural differences between polymeric and low molecular weight chiral smectic liquid crystals. First we looked at the change of the symmetry of the system due to a global, conformational ordering of the backbone chains, while in the second part we focused on the impact of the local ordering of backbone segments. In nature one can expect that both effects occur together and that they are thus mixed. The point we want to stress is that the presence of the backbone chain can lead to qualitative 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 non-helical contributions to the polarization, i.e. to true ferroelectricity. This in turn leads to a more complicated hydrodynamics of such systems [20, 21] including e.g. longitudinal piezoelectricity.

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- 15 The energy, which fixes the tilt angle θ between \mathbf{k} and \mathbf{n} , is assumed to be much larger than the energies in (1); hence θ is not affected by \mathbf{l} .
- 16 The helix of \mathbf{n} is slightly distorted due to the presence of \mathbf{l} ; this effect will be neglected below.
- 17 Since the pitch and the thickness of the smectic layers are incommensurate, there is no layer, where the three directions are coplanar exactly. However, since the pitch is so much larger than the smectic layer thickness, coplanarity is almost fulfilled in a few layers every half pitch.
- 18 In principle one has to discriminate even in low molecular weight systems between the absolute value of the in-plane polarization in the helical and in the unwound state, since the additional contribution $(\mathbf{n} \cdot \vec{\nabla})\mathbf{n}$ to \mathbf{P}_0 vanishes in the latter, but not in the former state.
- 19 Explicitly one finds $\pi/2 \geq \theta_m \geq \pi/2 - \theta$ with θ the tilt angle of \mathbf{n} .
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