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Novel Ferroelectric Fluids

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While there is no fundamental reason that fluids should not be ferroelectric, the only known ferroelectric fluids are chiral smectic-C liquid crystals. In this paper we argue that a variety of nonchiral layered (smectic) phases composed of properly designed oligomeric or polymeric molecules will also be ferroelectric. These ferroelectric fluids, and the solids formed by quenching them, should be of fundamental and practical interest. The nature of these phases, the design of the relevant molecules, and the experimental techniques for identifying the phases are discussed qualitatively.

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A variety of small molecules (mesogens),[1,2] block copolymers,[3,4] and polymers made up of mesogens[5,6] form liquid-crystalline phases. However, only the chiral smectic-C phase[7] (Sm-C^*) has been observed to have ferroelectric ordering. In fact, even this phase can be rigorously considered to be ferroelectric only in two dimensions because the direction of the polarization varies helically through the sample in three dimensions. Many mesogens have symmetries consistent with the formation of a ferroelectric phase and nonzero dipole moments, so that there is no fundamental reason that ferroelectric phases should not exist. Ferroelectric phases are not the lowest-free-energy phases of known mesogens presumably because the intermolecular forces are too weak to align the mesogens parallel to each other, or tend to align the mesogens antiparallel to each other. In this Letter, we argue that certain nonchiral oligomers of mesogens, certain polymers composed of mesogens, and a variety of nonchiral block copolymers should form layered smectic (Sm) phases in which there is no mirror symmetry about the layer normal: a phase with $C_{\infty v}$ (∞mm) point symmetry which otherwise resembles the smectic-A, or a phase with C_{1h} (m) point symmetry, having no symmetry at all in a plane which includes the layer normal and a director, and otherwise resembling the Sm-C. We propose for these ferroelectric, or polar, phases the names Sm-A_p and Sm-C_p. The difference between the Sm-A_p and the Sm-C_p phases is the same as that between the Sm-A and the Sm-C phases, i.e., the mesogens are tilted with respect to the layer normal in the Sm-C but not in the Sm-A.

The essential idea is to form a layered phase with three or more different types of layers. If there are three or more different parts to a molecule which are sufficiently incompatible chemically and/or sterically, and if there is sufficient lateral attraction between identical segments of adjacent molecules, then segregation into three or more different types of layers is expected. If three essentially different layers ($\alpha\beta\gamma$) form and these layers occur in the same order throughout the system, e.g., in the order $\alpha\beta\gamma\alpha\beta\gamma$ rather than $\alpha\beta\gamma\gamma\beta\alpha$, the phase will have the properties described above. Once distinctly different layers are formed even rather weak forces will result in a definite interlayer ordering as the layers interact as a whole so that the total energy difference between the ferroelectric $\alpha\beta\gamma\alpha\beta\gamma$ and the antiferroelectric $\alpha\beta\gamma\gamma\beta\alpha$ configuration is proportional to the area of the domain. In addition, for the Sm-C_p to have long-range polarization perpendicular to the layer normal, the tilt of the mesogens in identical layers, e.g., in each β layer, must be in the same direction.

These phases are different from the Sm-C^* phases in that the formation of the liquid crystalline phase, e.g., the Sm-A, does not *of itself* imply the existence of a polarization; additional chemical and steric forces leading to the proper sequence of layers are required. These phases are also different from the Sm-C^* phase in that the polarization is expected to lie along a relatively well-defined axis of the mesogens, as well as a well-defined axis relative to the layer normal or other macroscopic directions in the liquid crystal, so that synthesis of phases with tailored polarizations should be possible. These phases have in common with the Sm-C^* the fact that their symmetry is lower than that required in principle for ferroelectricity—translational symmetry is broken—; and that their ferroelectric behavior is caused by the interactions which result from the lower symmetry layered phase.

A number of different classes of molecules (mesogens) form layered phases with two different types of layers or other microstructures. These include (a) rigid-rod moieties, e.g., biphenyl, with flexible aliphatic tails, e.g., $(CH_2)_n$, on either side of the rod, (b) rigid-rod moieties connected to a flexible moiety and a polar moiety, e.g., $C{\equiv}N$, (c) flexible aliphatic chains connected to polar or acidic moieties, e.g., COOH, (d) flexible aliphatic chains connected to flexible polar chains, e.g., $(C_2H_4O)_n$, and (e) block copolymers composed of two or more incompatible polymers. These mesogens form layered phases because their different moieties are incompatible with each other. Each type of segment can be made with various lengths and a variety of chemical structures, so that not all segments of the same type are compatible. For example, certain pairs of molecules of type (a) are incompatible in the Sm-A phase.[8] It is also known[9] that there are transitions between Sm-A phases which change the structure of the layering, e.g., the Sm-A_1 to Sm-A_2 transition, which sometimes occurs in molecules of type (b). In fact, it seems reasonable to interpret the formation of the Sm-A_2 as a transition to a phase with three different types of layers (flexible, rigid, polar) in the antiferroelectric ($\alpha\beta\gamma\gamma\beta\alpha$) ordering.

It is also known that liquid-crystalline phases are formed when certain identical mesogens are bonded together head to tail with flexible spacers, forming "main chain" polymeric liquid crystals.[5] Considering the very different chemical structures which lead to smectic mesophases, and thus the very different physical and chemical properties of the mesogens, we may expect that by bonding of distinct mesogens together molecules can be constructed which result in a microstructure of three different types of layers. For example, consider a trimer $\alpha\beta\gamma$ made up of three distinct rigid smectogens connected by aliphatic spacers. If α, β, and γ differ significantly in their sizes or intermolecular interactions, three different types of layers will form. This line of reasoning can be extended to smectic phases with more than three different types of layers, such as a molecule consisting of two distinctly different rigid portions with similar flexible tails, e.g., aliphatic chains, connected by a flexible polar spacer, e.g., a polyether, which is also distinctly different from both the rigid moieties and the flexible tails. Such molecules may form four different types of layers, two different types of rigid-moiety layers and two different types of flexible-moiety layers. In addition, steric considerations imply that even compatible flexible spacers will form different layers if there is a sufficiently large difference in their lengths.

It is important to note that for ferroelectricity the α, β, and γ monomers must not only be different, but must also be so different that they form three distinctly different layers. For example, the trimer $\alpha\alpha\gamma$, in which the first and second monomers are compatible or identical, is not expected to form ferroelectric phases since the layer ordering $\alpha\alpha\gamma\alpha\alpha\gamma$ can be achieved with the γ monomer bonded to either the α on the left or the α on the right, resulting in no net dipole moment. It is also important to note that $\alpha\beta\gamma$ layer ordering implies that the dipoles on the different molecules in the same layers are side by side and parallel. This configuration of dipoles is unfavorable and so the layer incompatibility must dominate this term. However, this unfavorable dipole interaction need not be large if the dipoles are small or if the dipoles are in flexible polar portions of the molecules.

It is therefore expected that the first of the conditions for a Sm-A_p, the formation of three or more different types of ordered layers, should be realized in certain oligomers. We now consider the factors which distinguish between the ferroelectric $\alpha\beta\gamma\alpha\beta\gamma$ and antiferroelectric $\alpha\beta\gamma\gamma\beta\alpha$ configurations. First, it can be shown that, provided the dipoles are in separate, nonoverlapping layers, the Coulombic interactions favor the ferroelectric $\alpha\beta\gamma\alpha\beta\gamma$ ordering, which allows a reduction in the internal electric fields of the system relative to those in antiferroelectric orderings, given that the external field is constant. However, it is important to note that this decrease in the energy is essentially due to the interlayer dipole-dipole interactions. The intralayer dipole-dipole interactions are expected to be much stronger than the interlayer dipole-dipole interactions, because in long, rod-like smectogenic molecules the interlayer spacing is expected to be larger than the intralayer spacing. In addition, the intralayer chemical interactions must dominate the intralayer dipole interactions. Finally, the interlayer dipole interactions must dominate the interlayer chemical interactions for the electrical energy to imply the ferroelectric ordering. It follows that, for this to be an effective mechanism, the interlayer chemical interactions must be much smaller than the intralayer chemical interactions. However, the (short range) interlayer chemical interactions can be made very small if α and γ have similar or identical long, flexible tail groups.

Alternatively, chemical differences between α and γ would favor one of the two orderings and may suffice, in certain circumstances, for the formation of ferroelectrics. The ferroelectric ordering requires that the ends of the entire molecule be compatible, unlike molecules of type (b) whose ends are polar and aliphatic, and thus incompatible. For example, if the two ends (of α and γ) are different, but both are polar, then there will be appreciable short-range interactions between the ends on adjacent molecules. Depending on the details of the structure, this will favor either the ferroelectric or antiferroelectric ordering.

Chemical differences imply, for example, that the ferroelectric sequence will occur in a block copolymer consisting of long segments of four different types of monomers, α', β, γ, and α''. Suppose that all four polymer blocks are incompatible with each other in pairs, as is the usual case, except for α' and α'' which are compatible, as is the case,[4] for example, with polyvinylacetate and polymethylacrylate. Suppose that the polymer blocks are connected in the order $\alpha'\beta\gamma\alpha''$. Then, provided that the polymers are sufficiently long, it is expected that the incompatibility will dominate the entropic mixing[3,4] and the observed phase will have three distinct regions consisting largely of the β, γ, and a mixture of the α' and α'' portions. Provided that the blocks all have roughly the same radius of gyration, roughly the same total volume, and all of the polymers are liquid at the temperatures of interest, it is expected that these regions will form layers in the order $\bar{\alpha}\beta\gamma\bar{\alpha}\beta\gamma$ where $\bar{\alpha}$ indicates the mixed phase of α' and α''. However, this phase will have a very small spontaneous polarization unless at least one of these block copolymers, for example β, is composed of monomers with dipole moments, a majority of which are in the same direction along the chain contour, for example, pointing from the end bonded to the α polymer towards the γ polymer, or there are widely separated charges along the contour of the polymer. If this is the case, the dipolar energy will grow roughly linearly with the length of the polymers so that it is not clear that the polymer incompatibility, which grows linearly with the length of the polymers, will dominate even for long polymers. However, the dipolar energy can be made arbitrarily small either by decreasing the fraction of the monomers with dipoles in this direction along the polymer, or by using an unequal mixture of two different copolymers in which the dipoles along the β chain point in opposite directions. Of course, this also decreases the polarization.

There are a variety of other ways to favor the $\alpha\beta\gamma\alpha\beta\gamma$ configuration. For example addition of the dimers $\gamma\alpha$, $\alpha\beta$, and $\beta\gamma$, or the dimer $\gamma\alpha$ and the monomer β, to the trimer $\alpha\beta\gamma$ will favor the ferroelectric configuration as these dimers will fit more easily and in more places in the ferroelectric configuration than in the antiferroelectric configuration. This idea seems particularly attractive if the β monomers are larger than the α and γ monomers in the sense that the number of monomers per smectic layer per unit area is smaller in the respective monomeric smectic phases. In this case it is probably sufficient to add only the $\gamma\alpha$ dimer which will (1) favor the ferroelectric ordering and (2) increase the areas of the α and γ layers and so increase the possibility of forming these layers together with, but distinct from, the β layers. Other molecules, e.g., other n-mers like the hexamer $\alpha\beta\gamma\alpha\beta\gamma$, consisting of monomers in the ferroelectric order will also favor the ferroelectric ordering of trimers. Larger molecules, such as $\alpha\beta\gamma\alpha\beta\gamma$ or the polymer $(\alpha\beta\gamma)_n$, will favor the ferroelectric ordering as pure phases, as will Y-shaped oligomers with two identical legs, which are persuaded to stack with the unique leg of one Y between the identical legs of the Y above by a combination of steric and chemical interactions.

In addition to the microscopic considerations for the formation of ferroelectric phases, the macroscopic behavior must be considered since, in principle, the direction of the molecules may vary over distances which are large compared to the molecular size (as in the chiral smectic-C's[7]) thereby leading to different, possibly nonferroelectric phases. This behavior can be studied by examination of a Ginzburg-Landau expansion for the free energy in powers of the order parameter as has been done extensively for nonpolar liquid crystals.[1,2] We will not give a complete discussion of such expansions for the phases proposed in this paper, but only comment on two qualitative differences between the polar and nonpolar phases.

In nonpolar nonchiral phases the free energy typically (at low order) is of the form

$$\int d^3x\{c[\partial\psi(x)]^2+r\psi^2+u\psi^4\},$$

where ψ is the order parameter as a function of the position $\mathbf{x}$ and ∂ indicates a spatial derivative. There may also be terms of the form ψ^3 and/or couplings to other fields. In polar phases, two additional types of terms are possible. First, it is expected that in polar systems spatial variations in the order parameter (e.g., the polarization) will result in charge densities. Therefore there will be long-range Coulomb interactions in the free energy of the form

$$\int d^3x\, d^3x'\, a^2[\partial\psi(\mathbf{x})][\partial'\psi(\mathbf{x}')]\exp(-\kappa|\mathbf{x}-\mathbf{x}'|)/|\mathbf{x}-\mathbf{x}'|,$$

where κ is the inverse Debye-Hückel screening length. If we ignore edge effects, this term always favors a uniform, ferroelectric state. Edge effects, in some circumstances, imply that the order parameter varies over distance scales comparable to the size of the system. In addition, there is the possibility of terms of the form $w\psi\partial\psi^2$ which are forbidden by inversion in nonpolar nonchiral phases. Such a term has been studied for a simple system.[10,11] It is found both theoretically and experimentally that, in the absence of long-range Coulomb interactions and when a parameter of the form $z = w^2c^{-1}u^{-1}$ is large enough, such a term leads to phases like the blue phases in liquid crystals in which the order parameter varies in space. Thus, is it possible that such modulated, antiferroelectric phases will form in systems which are expected to be ferroelectric from microscopic arguments. This is *not* expected in general, but only when a^2 is sufficiently small or κ is sufficiently large, and z is sufficiently large. We have not estimated z from microscopic parameters.

In the Sm-A_p phase, the only polarization allowed by the symmetry is along the layer normal. In the Sm-C_p phase, the polarization can be anywhere in the plane including the layer normal and the C director. These phases can be distinguished experimentally from the Sm-A and Sm-C phases by being placed in an electric field with a component along the polarization, e.g., parallel to the layer normal. If the field is then reversed, the ferroelectric polarization will reverse, resulting in turbidity and current flow through the sample. The nonferroelectric or antiferroelectric phases, in which the free energy depends only on the magnitude and direction but not the sign of the electric field, will not be affected by the reversal of the electric field. The ferroelectric phases are also pyroelectric so that a temperature change results in current flow in the directions along which there are polarizations, e.g., the layer normal.

In searching for such ferroelectrics, it may be useful to be able to detect the formation of nonferroelectric phases with different types of layers, e.g., the antiferroelectric $\alpha\beta\gamma\gamma\beta\alpha$ phase or the nonferroelectric $(\alpha\beta)\gamma(\alpha\beta)\gamma$ phase.

The parentheses indicate that the α and β layers are mixed randomly but the γ layer is not. Unfortunately, such phases are harder to distinguish from ordinary smectics than the ferroelectrics. However, the distinction can be made, in principle, either through studies of miscibility[12] with the monomeric Sm-A's, or by x-ray scattering.

These phases would have practical applications. Solid phases, made by rapid quenching of these ferroelectric liquids, may have desirable mechanical and electrical properties, such as plasticity and a well-defined, hard-to-change polarization. For such applications it may be that long, polymeric molecules are superior.

It may be possible to use these fluids in displays or other devices which require rapid change of a liquid crystal's properties. For this purpose the Sm-C_p seems superior to the Sm-A_p. In particular, the Sm-A_p is optically uniaxial, the two electrically different states accessible by reversing the layer normal having identical optical and other tensor properties. In addition, switching between these states requires reordering of the layers and is therefore probably slow. However, the Sm-C_p is optically biaxial and reversal of the electrical field in the plane of the layers will result in a rotation of the C director. This does not require rearrangement of the layers and results in an optically different state. For these purposes small molecules such as dimers or trimers are probably superior, as they are likely to have larger mobilities and thus faster switching rates.

In summary, we have argued that, with careful molecular design, systems which are substantially more symmetric than an ordinary crystal, but still less symmetric than a translationally invariant liquid, will be ferroelectric. Some general considerations in a method for the design of molecules which would form such phases have been discussed.

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[12] Miscibility studies must be interpreted with care, since although phases with different symmetries are immiscible, phases with the same symmetry may also be immiscible; see e.g., Ref. 2, p. 279. However, if an oligomer is mixed with one of its constituents (e.g., $\alpha\beta\gamma$ with α, where α, β, and γ are all the same broad type of mesogen), immiscibility in the absence of layer ordering seems unlikely.