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Molecular correlations in a ferroelectric liquid crystal

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Measurement of the molecular correlation length of the ferroelectric liquid crystal *S*-2-methylbutyl-4-*n*-decanoyloxybiphenyl-4′-carboxylate (2M4DBC) has been obtained from field-dependent pyroelectric studies. The liquid-crystal behavior can be described in terms of a dynamically fluctuating mixture of two conformers having polarizations of opposite sense. The relative density of these species can be altered with an electric field, thereby allowing measurement of the effective dipole moment and correlation volume of the molecular clusters.

Smectic-*c*-phase liquid crystals are fluids in which the molecules are arranged in layers with the molecular axes tilted with respect to the layer planes. The structure is stabilized by relatively short-range steric interactions between neighboring molecules in the planes. When the smectic-*c*-phase contains chiral molecules, the interaction results in alignment of the dipoles associated with the environments about the chiral centers resulting in a spontaneous polarization P_s.[1]

The sense and magnitude of P_s depends on the magnitudes of the dipole moments at or in the environment of the chiral center, the position of the chiral center in the molecule, the tilt angle of the molecules with respect to the normal to the smectic layers, and the degree to which rotation of the molecules is hindered by the steric interaction with its neighbors.

Little is known about the molecular correlations which result in the macroscopic polarization in ferroelectric liquid crystals. In this paper we investigate the magnitude of the correlation volume by studying the electric field dependence of the pyroelectric coefficient of the ferroelectric liquid crystal *S*-2-methylbutyl-4-*n*-decanoyloxybiphenyl-4′-carboxylate (2M4DBC).

Recent studies[2] of this ester have shown that the temperature dependence of the polarization showed most unusual behavior which cannot be described by a simple Landau theory. However, the behavior could be interpreted by assuming that two different species, thought to be conformers of the constituent molecules, contribute to the polarization with opposite signs. The temperature dependence of P_s now contains an additional factor arising from the thermal activation of the molecules from one conformer to the other over an energy barrier of magnitude E_a. The total polarization can now be written

$$P = N_1\mu_1 + N_2\mu_2 , \tag{1}$$

where $N_2/N_1 = e^{-\Delta E_a/kT}$ and μ_1, μ_2 are the time-averaged dipole moments of the individual conformers of density N_1 and N_2 projected along the polar axis. Since the total molecular density $N_t = N_1 + N_2$ then

$$P = N_t[\mu_1(1+e^{-\Delta E_a/kT})^{-1} + \mu_2(1+e^{+\Delta E_a/kT})^{-1}] . \tag{2}$$

This expression reduces to that in Ref. 2 for large values of ΔE_a.

The model accounts for the observed behavior remarkably well if the temperature dependences of μ_1 and μ_2 are described by[3,4]

$$\mu_1 \propto \mu_2 \propto (T_C - T)^{\alpha} \text{ with } \alpha \sim 0.5 , \tag{3}$$

where the same Curie temperature T_c was assumed for both molecular species.

Within this model, the liquid crystal consists of an inhomogeneous, dynamically fluctuating mixture of at least two interconvertible conformers, the relative density of which changes with temperature. Rotational conformational changes about the carbon-carbon bond adjacent to the chiral carbon atom are expected to affect the molecular packing in the liquid-crystal state. Because of this steric interaction of neighboring molecules, a correlation length can be associated with the fluctuations.

Application of an electric field along the polar axis should significantly alter the equilibrium densities of the two conformers because of the interaction of the correlated dipolar clusters with the external field. Since electric fields can only be applied parallel to P_s (antiparallel fields merely reverse the sign of P_s), the density of the conformer with a dipole moment parallel to the applied field E is enhanced relative to that with a dipole moment antiparallel to E. Thus measurements of the field dependence of P_s or dP_s/dT will provide a measure of the dipole interaction energy $\Delta E_d = \mu_{\text{eff}}E$, where μ_{eff} is the effective dipole moment associated with the antiparallel clusters, i.e.,

$$P(E) = N_t[\mu_1'(1+e^{-(\Delta E_a+\Delta E_d)/kT})^{-1} + \mu_2'(1+e^{(\Delta E_a+\Delta E_d)/kT})^{-1}](T_C - T)^{\alpha} , \tag{4}$$

where μ_1' and μ_2' are now temperature independent.

Temperature-dependent pyroelectric measurements were made using the dynamic technique described previously.[5] A liquid-crystal cell was fabricated with two parallel glass plates 9 μm apart coated with indium tin oxide (ITO) on the inside surfaces of the cell. The cell was filled with the thin layer of liquid-crystal material and fields up to 7×10^4 V/cm were applied across the indium tin oxide electrodes. Since the cell thickness (9 μm) was greater than the helical pitch length of the smectic liquid crystal, a voltage of at least 9 V was needed to unwind the helix. For voltages below 9 V (fields below 10^4 V/cm), the observed pyroelectric signal decreased due to spatial averaging of the polarization throughout the cell thickness owing to the helical structure. All measurements were made with bias voltages greater than 9 V since this eliminated any contributions to the pyroelectric effect from a temperature dependence of the helical pitch length.

Experimental data are shown in Fig. 1. The pyroelectric signal was found to reverse signs twice for all values of the applied electric field. This is consistent with earlier measurements of the polarization. The sign change just above room temperature is due to a sign reversal of P_s while the sign change at temperatures between 40 °C and 50 °C, depending on the applied field, is due to the fact that P_s goes through a maximum value at this temperature. A pronounced feature of the data is the fact that for increasing values of applied field, the zero crossing of the pyroelectric coefficient at a temperature T_z between 40 °C and 50 °C decreases in temperature. No shift of the phase-transition temperature T_C at 56.7 °C was observed. Above T_C small pyroelectric signals were observed in the nonpolar smectic-*A* phase and isotropic phase due to a field-induced polarization.

A reasonable fit of the zero-field polarization and pyroelectric data could be obtained with a relatively wide range of activation energies ΔE_a, and a corresponding variation of μ_1' and μ_2'. However, by differentiating Eq. (4) and fitting the field-dependent pyroelectric data of Fig. 1 the range of parameters was narrowed considerably. To limit the number of fitting parameters α was fixed at the Landau value of 0.5. A value of $N_T = 1.34\times10^{21}$ cm^{-3} was calculated from the molecular weight and density of the liquid crystal. With this approach we find

$$\mu_1' = 0.025 \pm 0.006D\ ,$$

$$\mu_2' = -0.21 \pm 0.04D\ ,$$

$$\Delta E_a = 0.055 \pm 0.015\ \text{eV}\ ,$$

$$\mu_{\text{eff}} = 35 \pm 9D\ .$$

The negative sign of μ_2' indicates antiparallel orientation to the applied electric field. The theoretical fit to the data of Fig. 1 is shown in Fig. 2. Considering the simplicity of the model, agreement is good over a wide temperature range. The deterioration of the fit at temperatures close to the phase transition is presumably related to the assumption of temperature independence of ΔE_d, μ_1', and μ_2', or even to the assumption of a simple two component system. Furthermore, the measured pyroelectric coefficient does not diverge at T_C as expected from Landau theory as previously noted in smectic liquid crystals.[5] The parameters listed above all fall within reasonable expectations. The gauche conformer is expected to have a larger time-averaged dipole moment μ_2 both because of the larger dipole moment at (and near) the chiral center as well as increased damping of the rotational motion compared with the all trans conformer.

From the ratio of the cluster moment μ_{eff} and the time averaged, molecular moment $\mu_2 = \mu_2'(T-T_c)^{1/2}$, the number of correlated molecules is found to be approximately 53 ± 12 molecules at a temperature 10 °C below the Curie temperature. The shape anisotropy of the correlation volume cannot be obtained from this procedure. If, however, correlations within the smectic layers are dominant (as might be anticipated in this phase) then the correlation length in the plane is 37 ± 10 Å. For isotropic three-dimensional correlations, the correlation length is about 20 ± 6 Å. These values are in good agreement with the correlation length of about 25 Å obtained from x-ray linewidth studies in the smectic-*c* phase of another liquid crystal.[6] Since the dipolar alignment in these liquid crys-

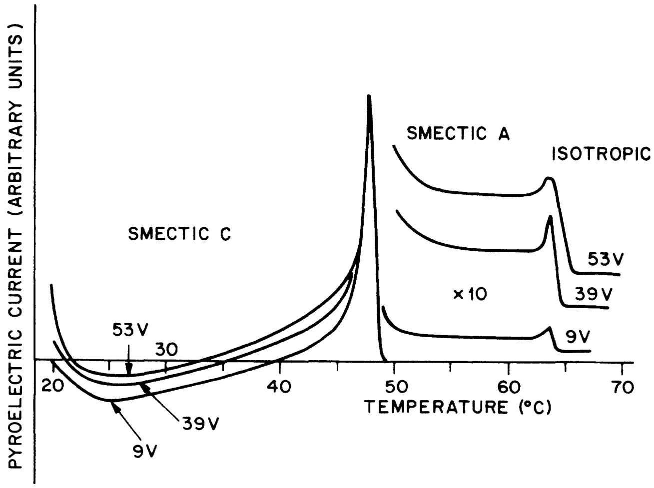

FIG. 1. Temperature dependence and bias-voltage dependence of the pyroelectric current of the smectic liquid-crystal *S*-2-methylbutyl-4-*n*-decanoyloxybiphenyl-4′-carboxylate (2M4-DBC) in a 9-μm thick cell. [9 V bias $=10^4$ V/cm; 39 V bias $=4.3\times10^4$ V/cm; 59 V bias $=6.5\times10^4$ V/cm.]

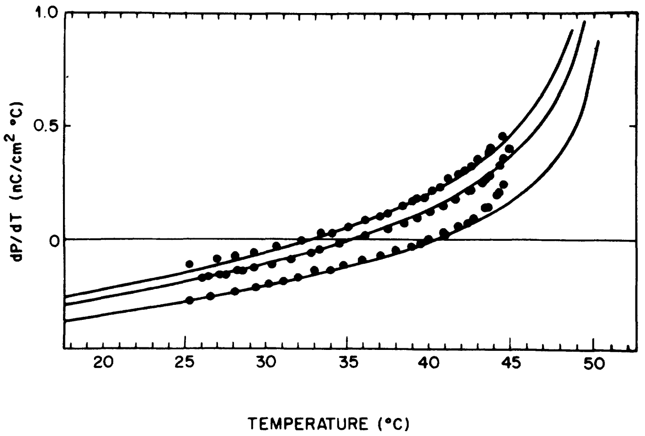

FIG. 2. Comparison of the field-dependent pyroelectric data with theory (see text). Solid lines were calculated from Eq. (4), points are experimental values.

tals is a consequence of molecular alignment, it would be expected that the positional correlation length obtained from x rays is equivalent to the dipolar correlation length obtained from this study. Field-dependent pyroelectric measurements thus provide a measure of the correlation of neighboring molecules due to steric interactions, in a situation where two or more constituent molecular species contribute to the polarization with opposite sense. In this work we find that isolated individual molecular conformations are energetically unfavorable but that dynamically fluctuating domains of several correlated conformer units exist, having dimensions of a few tens of molecules. In this respect, such liquid-crystal systems resemble conventional (crystalline) mixed ferroelectrics which have composition fluctuations on a microdomain scale. In the liquid crystals, however, the phase transition is not broadened by the disorder since the disorder is not frozen into a lattice but can diffuse freely and reach equilibrium with respect to the other degrees of freedom. Under such situations, a sharp phase transition may be expected.[7]

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