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Metastable states in antiferroelectric liquid crystalline mixtures

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We report on the observation of relaxation phenomena with extremely long relaxation times, amounting to several hours. These effects take place in some liquid crystal mixtures exhibiting ferroelectric and antiferroelectric dipole order. The observed phenomena are connected with the transformation from the supercooled ferroelectric state to another, metastable state. This transition may be described using a Debye type relaxation formula. At low temperatures, a second slow transition takes place: from the metastable intermediate state to the antiferroelectric phase. This transition is characterized by unidimensional growth of the antiferroelectric domains with a constant velocity. Close to the lower temperature limit of existence of the ferroelectric phase, a direct transition from the ferroelectric to the antiferroelectric phase takes place. This transition is described by an Avrami model, hence it is governed by the creation and growth of nuclei of the antiferroelectric phase.

1. Introduction

The phase transitions occurring in antiferroelectric liquid crystals are of a quite complicated nature. It is a result of the frustration between synclinic and anticlinic interlayer interactions, equivalent to the frustration between ferroelectric (F) and antiferroelectric (AF) polar order. In ferroelectric liquid crystals the chiral molecules are on average tilted in the same direction (synclinic arrangement), thus producing a spontaneous polarization, directed in (almost) the same direction in each smectic layer. In antiferroelectric liquid crystals on the other hand, the tilt direction in adjacent smectic layers is opposite (the arrangement of molecules is anticlinic) and the polarization of each pair of smectic layers is (almost) cancelled. Additionally, many intermediate structures are possible. Besides different phases, numerous subphases can also be distinguished [1]. This results in a very complicated picture of phases and phase transitions in materials called antiferroelectric although they have many other phases, among them ferroelectric. Some order was brought by the concept called the clock model [2, 3]. In this model, various phases and subphases differ only by the distribution of the tilt direction. However, the number and kind of phases depends on many external parameters: sample history, surface interactions, external fields, etc. [4, 5]. In some cases, new phases appear as a result of mixing. The antiferroelectric phase may even appear in a mixture whose components do not possess this phase in their pure state. Such mixtures were made several years ago by Dąbrowski *et al.* [6]. Some of these mixtures are the subject of investigations reported in this paper.

2. Experimental

We studied several mixtures exhibiting a mixing induced antiferroelectric phase [6, 7]. The properties of these mixtures were quite similar, therefore we present here results on an example of the binary mixture composed of substances with acronyms D7, D9 (figure 1). We call this mixture 7N9/*m*, where *m* denotes the molar fraction of the compound D7.

Neither of the substances D7, D9 possesses the antiferroelectric phase, but after mixing the antiferroelectric phase emerges over a broad concentration range [6, 7]. The temperature range of the antiferroelectric phase depends on the direction of the temperature changes [8]. The region in the phase diagram placed between the ferroelectric smectic C* and antiferroelectric smectic C_a^* phases is the region of thermal hysteresis. The effect of hysteresis can be best investigated by a dielectric method, because of the considerable differences in the electric permittivities of the ferroelectric and antiferroelectric phases. The dielectric measurements were performed using a computer controlled Hewlett-Packard HP4192A impedance analyser.

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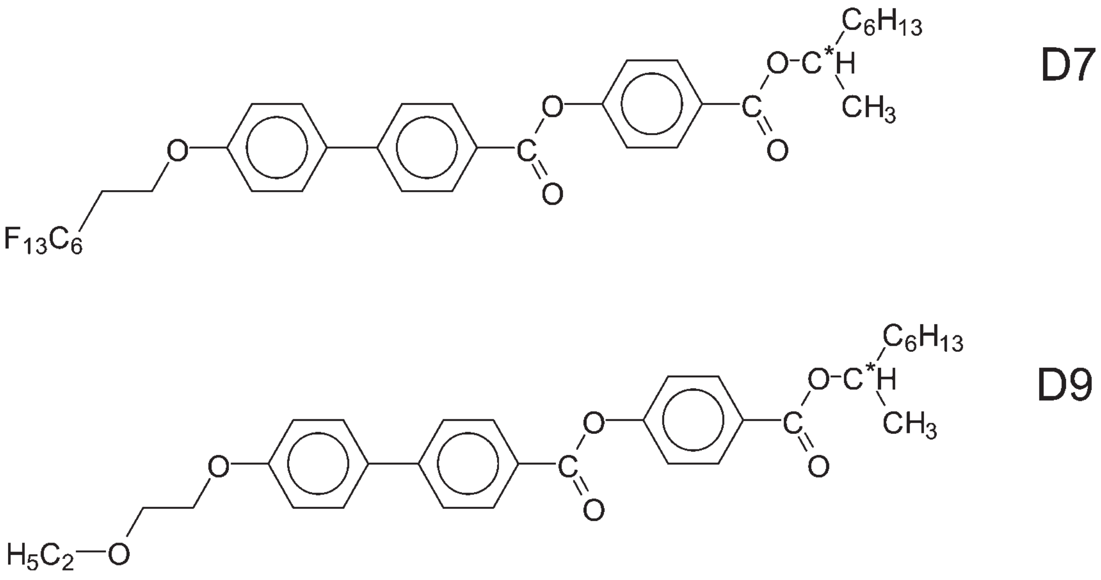


Figure 1. Chemical formulae of the components of the mixture 7N9/*m*.

3. Results and discussion

The temperature of transition from the AF to F phase in mixture 7N9/0.75 is more than 20°C higher than the transition in the opposite direction (see figure 2). We observed a similar hysteresis for other compositions of the mixture, for some pure substances and for various binary and ternary systems. This observation indicates that the free energy of the ferroelectric and antiferroelectric phases are nearly the same. Thermal hysteresis is the next factor in making the complex description of phases and phase transitions.

In the hysteresis region, V-shaped, thresholdless switching has been observed [6–8]. It occurs in a certain range of temperature and frequency of the external electric field. However, in this paper we focus attention on the hysteresis phenomenon. This effect has been reported several times [8–11] but without systematic investigation.

During our investigations, we noticed that the temperature range of the hysteresis depends on the rate of temperature change. This phenomenon is demonstrated in figure 2. It is evident that the range of thermal hysteresis is broader when the cooling rate is higher. While the transition from the antiferroelectric to the ferroelectric phase (AF → F) observed on heating is practically independent of the heating rate, the transition in the opposite direction does depend on the cooling rate. These observations suggest that the electric permittivity is time-dependent. Indeed, such dependence can be observed under isothermal conditions (figure 3).

Figure 3 presents the changes in electric permittivity of mixtures composed of the substances D7 and D9. The permittivity was registered after cooling the mixtures from the ferroelectric phase and holding at temperatures indicated in the figure. The permittivity continuously decreases with time and does not reach a constant value even after many hours.

The observed changes indicate the phase transition from the polar ferroelectric phase to a phase of lower polarity. Figure 2 suggests that this phase is the antiferroelectric smectic C_a^* phase. This supposition is supported by the texture observation in polarized light. In the ferroelectric phase, the whole sample has a dark colour, like the background in figure 4.

During cooling, bright lines of the antiferroelectric phase appear. They grow parallel to the smectic planes, the growth rate decreasing with time. Probably, line growth stops when it meets a defect or impurity particle. At every moment, we observe a coexistence of ferroelectric and antiferroelectric phases. The growth of antiferroelectric areas causes the lowering of the electric permittivity, therefore the electric permittivity ε can serve as a measure of the relative amount of both coexisting phases. If we denote the permittivity of the old (ferroelectric) phase ε_1 and the permittivity of the new metastable phase ε_2, then the volume fraction of the new phase is:

$$V_2 = \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 - \varepsilon_2}. \qquad (1)$$

Using this method, we are able to determine the composition of coexisting phases and to follow the transformation of the metastable ferroelectric phase into another phase. This method is easier and more

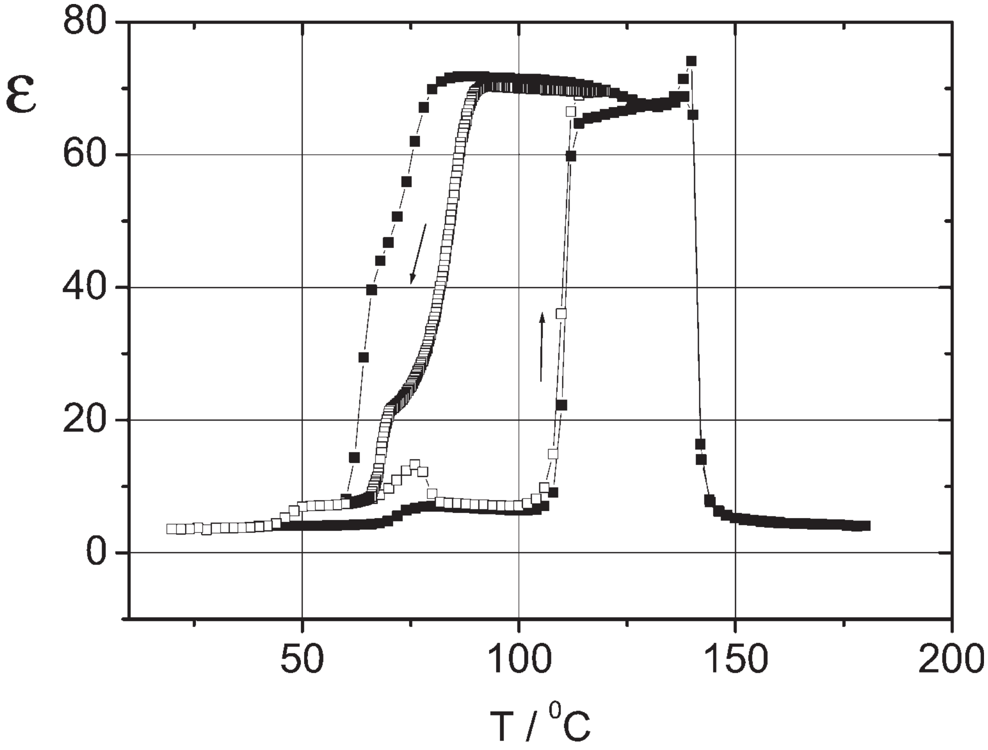


Figure 2. Temperature dependence of the electric permittivity of mixture 7N9/0.75 measured during heating and cooling cycles with different rates of temperature change: 1 K min^{-1} (full symbols) and 0.05 K min^{-1} (open symbols). Thickness of the sample is 5 µm, frequency of the measuring field is 440 Hz.

accurate than the usual photographic or calorimetric methods [12, 13]. It becomes possible to describe the kinetics of the transformation in a quantitative way. The dielectric method allows us to measure not only the growth of existing domains of the new phase (as can be done in the photographic method), but also the creation and growth of new nuclei.

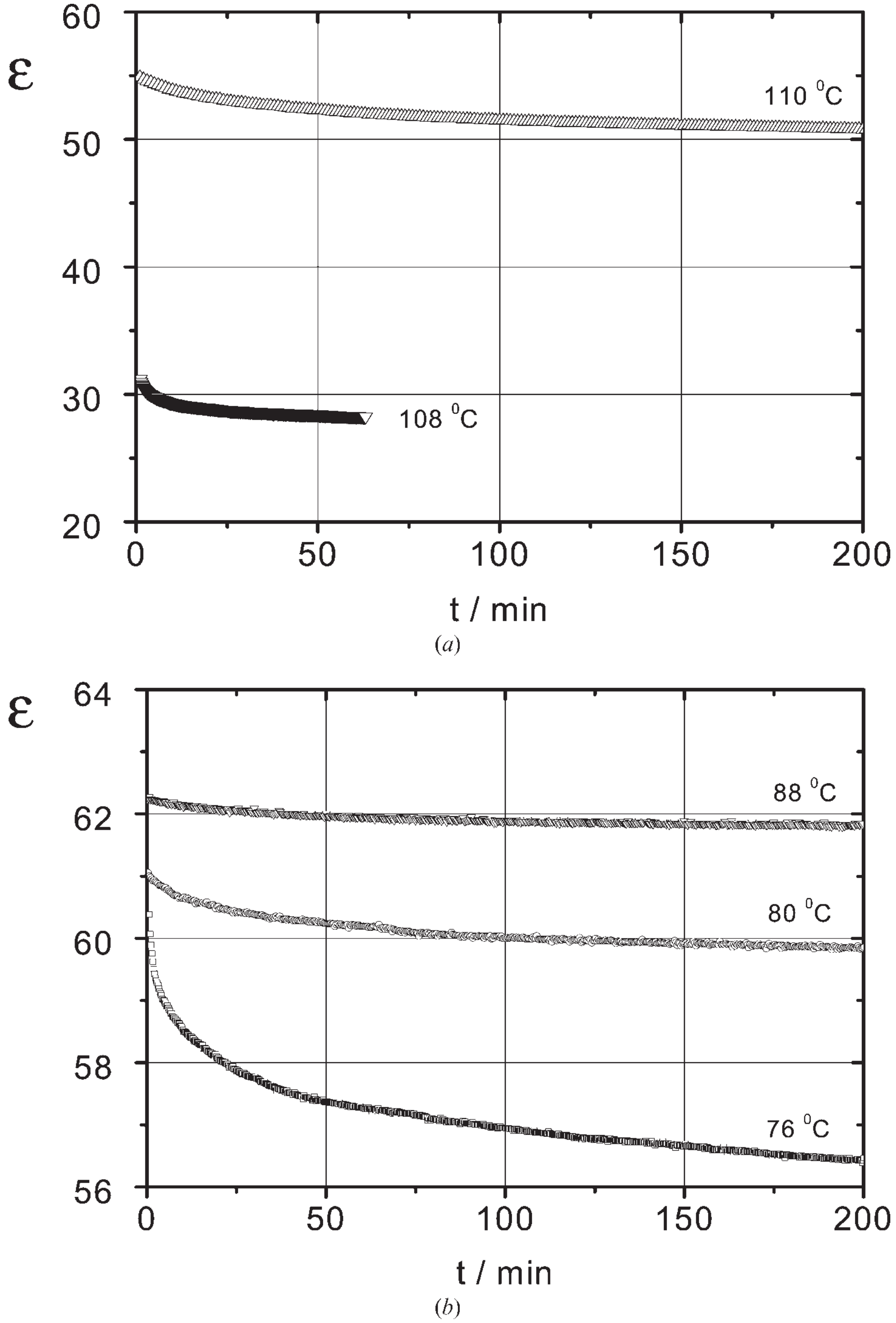
The kinetics of phase transition is usually described using the Avrami model [14]. It is assumed in this model that the isothermal transition of the metastable supercooled phase **1** is governed by the creation and growth of nuclei of the new, stable phase **2**. Then, the temporal changes of the volume fraction of the new phase V_2 are described by

$$V_2 = 1 - \exp\left[-(kt)^d\right] \qquad (2)$$

where k and d are constants and t denotes time. The constant k is a measure of the transition rate and d is responsible for the dimensionality of the transition process. As figure 5 indicates, our experimental data fit well to the Avrami equation. Similar results were obtained for many other mixtures at various temperatures.

Thus, it appears that the Avrami model describes well the transformation of the ferroelectric phase into the antiferroelectric phase. The starting and final values of permittivity, ε_1 and ε_2 in equation (1), have reasonable values, however the d-constant is very low. The value d-1 describes the dimensionality of the process. In our case, the dimensionality would have the value about −0.8. Such a low value, and negative, makes no physical sense. We obtained similar results for other temperatures and compositions. Low values of the d-constant are often interpreted as the result of diffusion in highly viscous materials [12]. In that case the d-constant should be reduced to one half. In our case, the reduction is much greater. Besides, in the case of diffusion the transition process should not be isokinetic [15]. We have observed no clear temperature dependence of the d-constant and do not consider that diffusion can explain our observations. The agreement of our results with the Avrami theory is purely formal and we must search for another explanation of the observed phenomena.

Another theory often used for the description of phase transformation kinetics, is the Bray theory [16]. This describes the changes in dimensions of grains of the new phase during the recrystallization process. As the grain dimensions have no influence on the electric permittivity (at least for macroscopic grains), this theory is not applicable in our case. A phenomenon



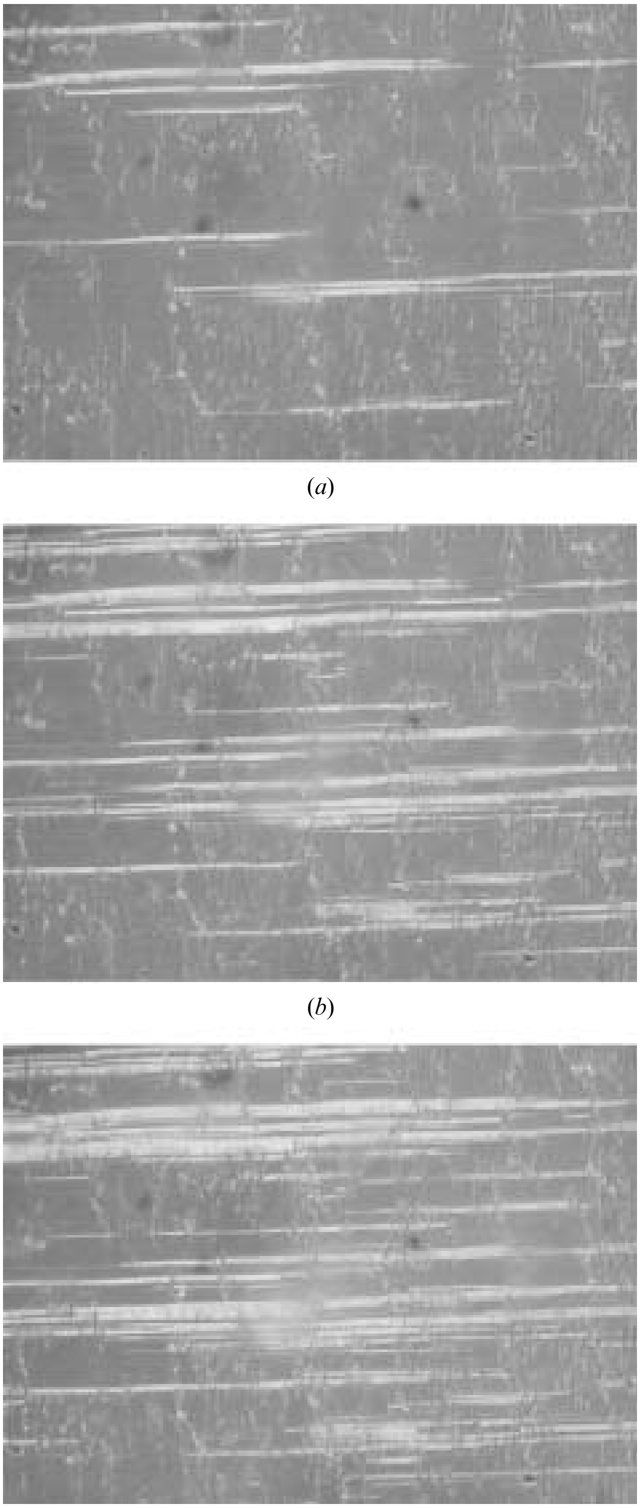
(*a*)

(*b*)

Figure 3. Isothermal changes of electric permittivity in the mixture 7N9/*m*, with different molar fractions of the substance D7: $m = (a)$ 0.55, (*b*) 0.75.

similar to that presented in this paper, observed by Wang *et al*. [17], was explained in terms of a non-linear diffusion equation. However, that phenomenon must be of a rather different nature, as its characteristic time is four orders of magnitude shorter than the time registered in our experiment.

As we see, models usually applied for the description of phase transition kinetics are not useful in the case of the transition from the supercooled ferroelectric state. Hence, we must look for another process capable of explaining our observation. We notice that the permittivity is a decreasing function of time, which



(*a*)

(*b*)

(*c*)

Figure 4. Textures of thin (5 μm) sample of the mixture 7N9/0.55 in the intermediate state. The sample was cooled from the ferroelectric phase to 110°C. The pictures were taken after: (*a*) 5 min, (*b*) 1 h and (*c*) 1 day. The long side of the picture corresponds to 570 μm. The bright antiferroelectric areas are growing at the expense of the dark ferroelectric areas.

tends to a value higher than the permittivity of the antiferroelectric phase. One can then suspect that after lowering the temperature the system tends to a new equilibrium state, characterized by electric permittivity ε_2. Presumably, the rate of change of ε depends on the distance from this new equilibrium level. We assume that this rate is proportional to the deviation from this equilibrium state:

$$\frac{d\varepsilon}{dt} = -\frac{1}{\tau}(\varepsilon - \varepsilon_2). \tag{3}$$

The solution to this differential equation has the shape of a typical relaxation dependence:

$$\varepsilon = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2)\exp\left(-\frac{t}{\tau}\right) \tag{4}$$

where τ is the relaxation time. The fitting of experimental data to this equation is also quite good (except for a few points at the beginning of the experiment, see figure 6). The linear dependence in the logarithmic scale is also fulfilled, as expected. This time, however, the physical model corresponding to the equation is relevant to the experimental situation. Therefore, we think that this theoretical model is correct. Possible doubts can be removed on inspecting the texture changes (see figure 4).

The deviation of experimental points from the theoretical curve at the start of the experiment indicates that there exists another, rather faster relaxation process. Taking into account this possibility, we obtain excellent agreement of the experimental data with equation (5) rewritten for two relaxation times τ_1 and τ_2 and for two equilibrium levels of permittivity ε_2 and ε_3:

$$\varepsilon = \varepsilon_2 + (\varepsilon_1 - \varepsilon_3)\exp\left(-\frac{t}{\tau_1}\right) + (\varepsilon_3 - \varepsilon_2)\exp\left(-\frac{t}{\tau_2}\right). \tag{5}$$

What are these two relaxation processes? Microscopic observations performed simultaneously with the registration of permittivity showed that the process, with a relaxation time of several minutes, is associated with changes in the sample alignment. Immediately after changing the temperature (or removing the external electric field), the alignment of molecules in the sample alters. This modification is mainly associated with changes in the tilt angle and the tilt plane. This process causes changes of the twist angle distribution (in the twisted director configuration) and in the number and type of defects.

More interesting is the second, slower process with a relaxation time of order of one hour. As microscopic observation confirmed, this process consists in the transition from a supercooled, metastable ferroelectric state to a different state. The final value of the electric permittivity is quite high. In this example, it amounts

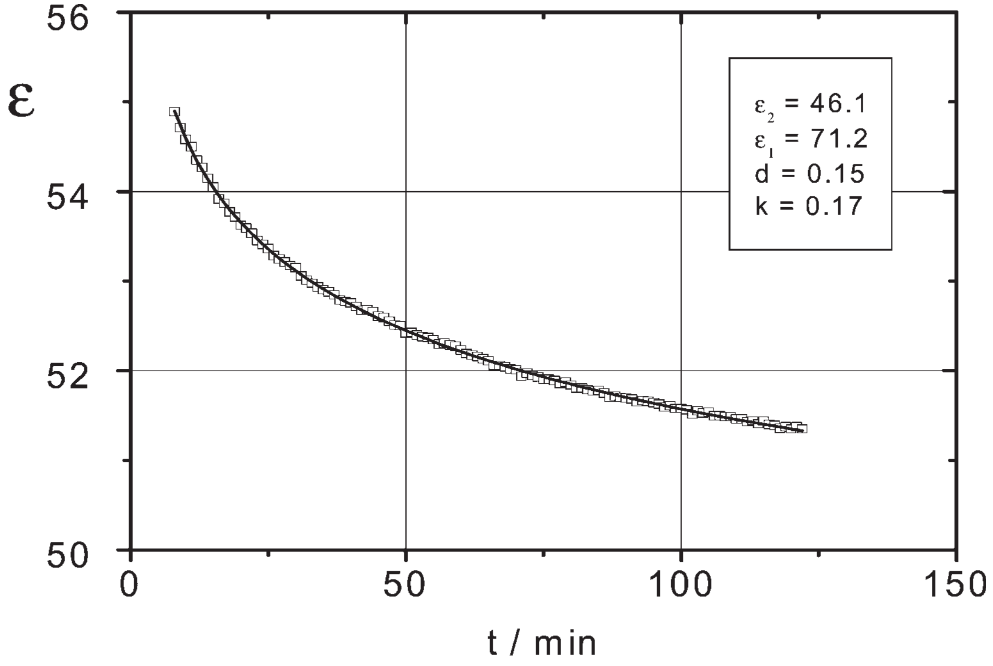


Figure 5. Fitting of the experimental results obtained for mixture 7N9/0.55 to the Avrami theory. The fitting parameters are displayed in the figure; temperature 110°C.

to about 50, much higher than the value characteristic for an antiferroelectric phase (≈8). We can thus conclude that the final state in the discussed process is an intermediate state, not the antiferroelectric state. In this intermediate state both phases—ferroelectric and antiferroelectric—coexist in equilibrium. The fractions of each phase are functions of temperature. Using appropriate thermal treatment of the sample makes it possible to adjust the value of the electric permittivity at an arbitrary level between the values for

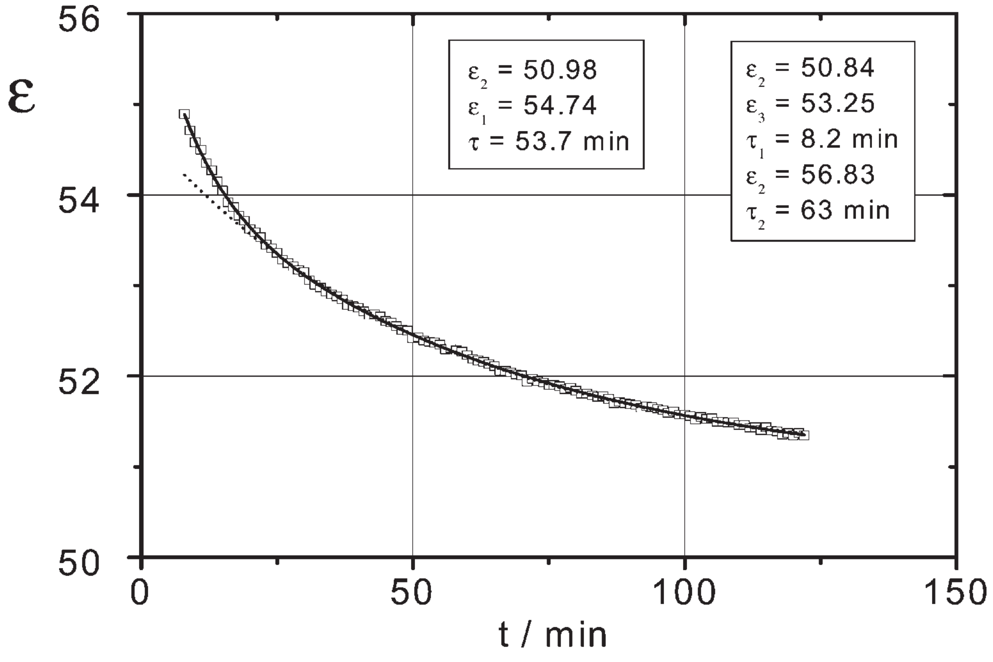


Figure 6. Fitting of the experimental results (the same data as in figure 5) to the relaxation form: with one relaxation time (dotted curve) and two relaxation times (solid curve). The fitting parameters are displayed in the figure.

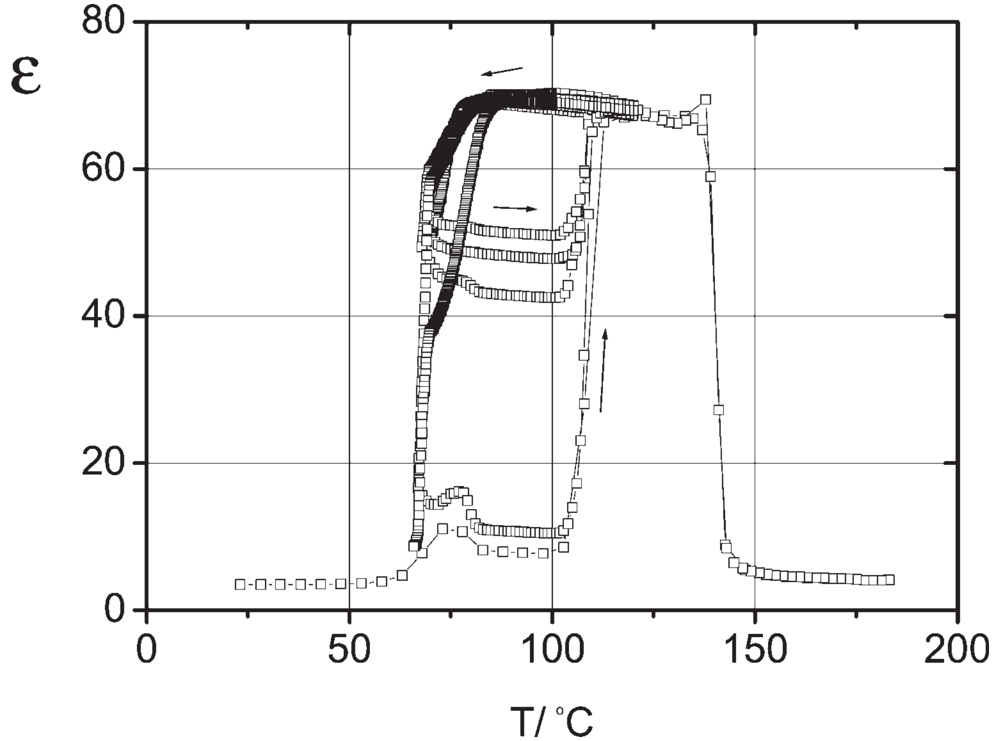


Figure 7. Tuning of the electric permittivity of the mixture 7N9/0.75.

the ferroelectric and antiferroelectric phases (see figure 7). This feature might be of some practical importance.

Intermediate values of permittivity are often interpreted as a mark of existence of the ferrielectric phase. The term 'ferrielectric' is commonly used to describe a phase that exhibits a partial compensation of the spontaneous polarization on a *microscopic* scale, on a distance comparable to the crystallographic lattice

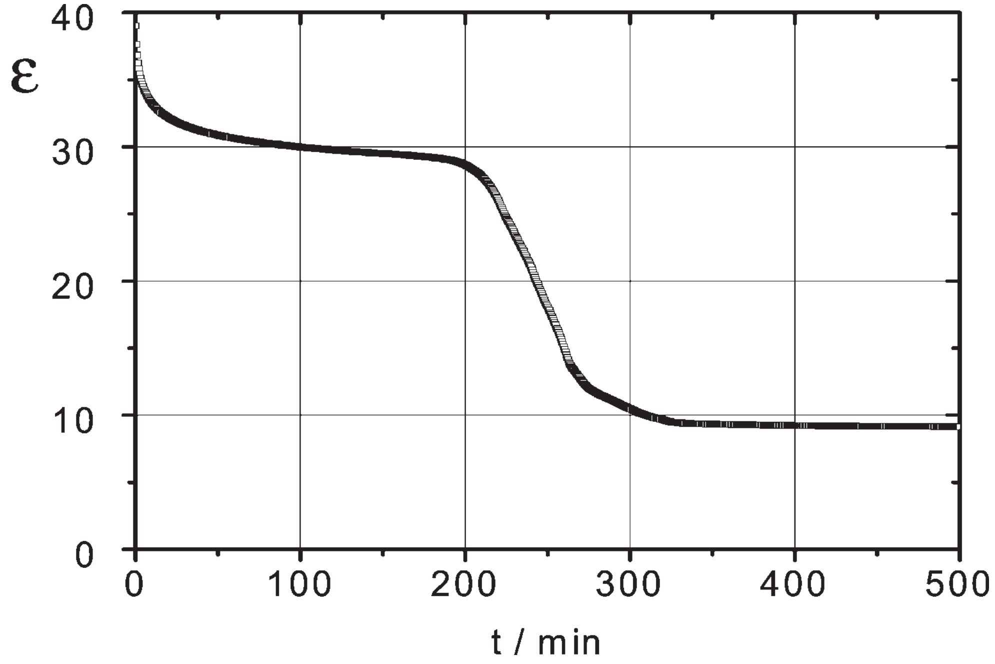


Figure 8. Isothermal transition at 74°C of the mixture 7N9/0.75 from the supercooled ferroelectric phase to the metastable intermediate state (up to about 150 min) and from the intermediate state to the stable antiferroelectric phase.

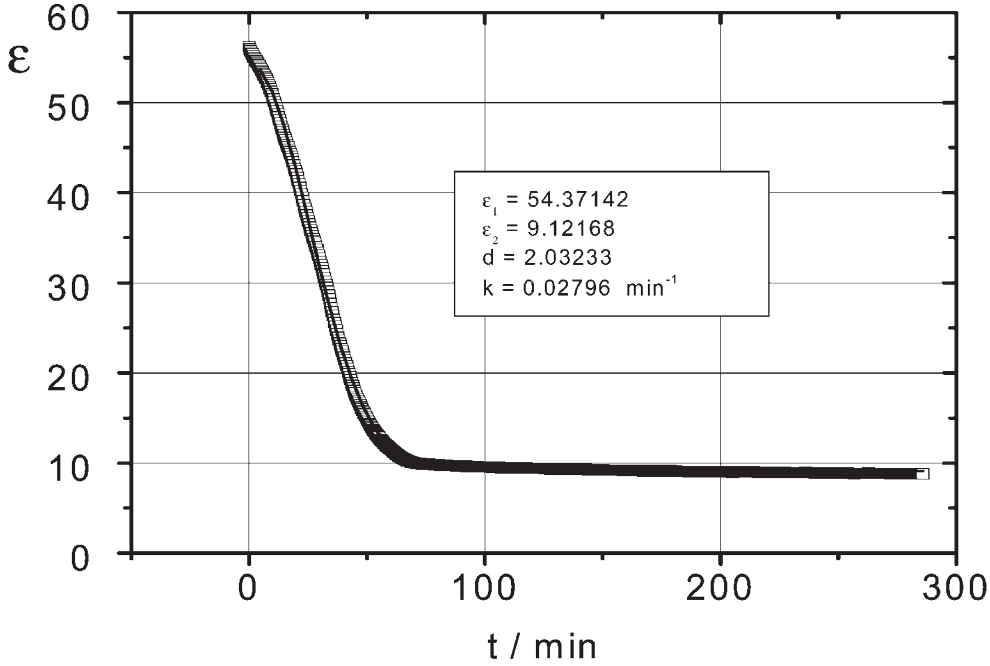


Figure 9. Isothermal transition at 72°C of the mixture 7N9/0.75 from the supercooled ferroelectric phase to the antiferroelectric phase. Squares represent experimental data; the solid line; the result of fitting to the Avrami equation using parameters indicated in the figure.

constant. This may occur because of the existence of two sublattices with different polarization [5]. In our experiments we deal with coexisting *macroscopic* domains (of dimensions of many μm, see figure 4) of both the ferroelectric and the antiferroelectric phase. Such a mixture cannot be treated as the ferrielectric phase. A similar coexistence has already been observed by Lagerwall *et al.* [9], who stated that this mixed state is thermodynamically stable. We also have observed this state for many days. However, quantitative studies performed using the sensitive dielectric method proved that the stability of this state is limited, the sample spontaneously transforming to the antiferroelectric phase (see figure 8).

This transition lasts about one hour and takes place mostly near to the lower limit of the hysteresis range. The transition is characterized by a linear decrease of the electric permittivity, i.e. it occurs with a constant velocity. In polarized light one observes a sudden appearance of new antiferroelectric domains growing along the smectic layers. It is not clear why the volume of the antiferroelectric phase suddenly increases after a long period of stability. In a supercooled sample, the nuclei of the new stable phase are created continuously, but they also continuously vanish. A stable growth of germs can take place only when their dimensions exceed a critical value [14]. The unexpected growth of antiferroelectric domains starts probably after the dimensions of nuclei have exceeded a critical value. The problem remains unsolved, why the new nuclei of an antiferroelectric phase appear avalanche-like after a long time of stability. Most likely, this is a result of either a fluctuation or an accidental mechanical shock.

Thus, the intermediate state is metastable; the probability of transition from the intermediate state to the antiferroelectric phase increases on lowering the temperature. This time, however, the final state is the stable, antiferroelectric phase. The proof for this statement is the value of the permittivity $\varepsilon \approx 8$. The transition from the intermediate state to the antiferroelectric state cannot be described using a relaxation form, equations (4) or (5). It is obvious from figure 8 that the curve $\varepsilon(t)$ does not have an exponential shape. A considerable part of the curve is approximately linear, indicating a unidimensional growth with constant rate.

At low temperatures, close to the lower limit of existence of the supercooled ferroelectric phase, we observed a direct transition from the ferroelectric state to the antiferroelectric phase, without the intermediate state (see figure 9). This direct transition is described by the Avrami equation. The value of the d parameter (close to 2, see figure 9) indicates that the transition is governed by the creation and unidimensional growth of antiferroelectric nuclei.

4. Conclusions

Thermal hysteresis, relaxation phenomena and phase coexistence demonstrate that the free energy of both the ferroelectric and the antiferroelectric phase is almost the same for the system under study. In this situation, any small perturbation like surface action, impurity, defect or external field can decide which phase occurs under given conditions. However, it is by no means a proof of weak interactions between smectic layers, as it is often assumed in the literature [18, 19]. We consider that the interactions are strong but twice degenerated. The two energy minima at synclinic and anticlinic order are separated by a high energy barrier; this barrier is the cause of the extremely slow kinetics of the phase transition observed in our experiments.

The transformation of the supercooled metastable ferroelectric state into a stable antiferroelectric phase might occur in two different ways. Close to the upper limit of the hysteresis range, an indirect transition occurs, via an intermediate state. This intermediate state is quite stable, and may persist for many days. The transition to the intermediate state is of relaxation type, i.e. it is driven by thermally activated random jumps of molecules over the energy barrier separating the synclinic and anticlinic states. The intermediate metastable state is characterized by the value of the electric permittivity, typical for a ferrielectric phase, and which may be tuned by proper selection of temperature. The intermediate state, however, does not represent the ferrielectric phase but a mixture of macroscopic ferroelectric and antiferroelectric domains. The transition from the ferroelectric phase to the intermediate state is characterized by a relaxation process with a very long relaxation time. At lower temperatures the intermediate state becomes less stable and may transform to the antiferroelectric phase; this transformation occurs through the movement of the border between the ferroelectric and antiferroelectric phases with a constant velocity.

Close to the lower limit of the hysteresis range direct transition from the supercooled ferroelectric phase to the antiferroelectric phase occurs. This transition is described by the Avrami equation, thus it is governed by the creation and unidimensional growth of antiferroelectric nuclei.

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