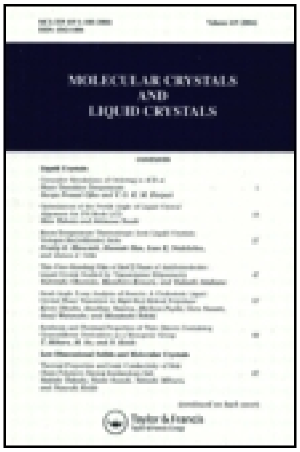

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Growth Kinetics of Cholesteric Spherulites Under Electric Fields

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The growth kinetics of cholesteric spherulites of cholesteryl laurate-cholesteryl caprilate mixture (50 : 50% by weight) is investigated. It is shown that the nucleation is bidimensional and the growth is determined by the orientational relaxation of the molecules near the interface. The same growth mechanism holds when the nucleation was followed under d.c. electric fields; in this case the growth rates were lower.

The electric field effects on growth kinetics can be explained by considering both changes in critical supersaturation and changes in some coefficients associated with dissipative effects during relaxation.

INTRODUCTION

The growth kinetics of crystalline spherulites of organic compounds has been the subject of many experimental and theoretical investigations. However, relatively little has been done in the case of cholesteryl esters or other substances exhibiting mesomorphic behaviour.

The first investigations in this field were concerned with the nucleation and growth of solid spherulites from the mesomorphic phase.[1,2] The growth rates of crystalline spherulites developing either from the smectic or from the cholesteric phases of several cholesteryl esters (cholesteryl myristate, cholesteryl nonanoate or cholesteryl acetate) were determined by Price and Fritzsche.[3] By using the theory of nucleation and growth either for homogeneous or for heterogeneous nucleation it was found that for all these esters the growth kinetics fitted the Avrami equation with $n = 4$, indicating that spherical nuclei were developed from the mesomorphic phase.

As it is known, in some cholesteryl esters, the cholesteric mesophase is nucleated from the blue phase by the intermedium of cholesteric spherulites. These are revealed by optical microscopy under polarized light and exhibit a sharp interface boundary, which is rather regular. This makes possible the observation of their growth kinetics using the same procedure employed for crystalline spherulites.

Jabarin and Stein[4] were the first to undertake such investigations. They have used the small angle light scattering method, the depolarized light transmission technique and the microscopic investigations to determine the growth kinetics of blue phase-cholesteric transition in cholesteryl myristate. They found that the kinetics of transformation fitted the Avrami equation with $n = 3$, which showed that the growth units were disc-shaped. The kinetics was proved to be of first order and diffusion controlled.

Würtz, Klar and Chan[5] investigated the kinetics of phase transitions in cholesteryl nonanoate and cholesteryl decanoate. Their results were in contradiction to those obtained by Jabarin and Stein, as the spherulite growth proved to be not determined by secondary nucleation. The results were explained in terms of another mechanism: the local orientational relaxation of the molecules near the interface was considered[6] and the experimental results were fitted satisfactory by the theoretical curves.

In a previous paper[7] we noticed that when mixtures of cholesteryl laurate-cholesteryl caprilate were cooled down from the isotropic phase in the presence of d.c. electric fields, the nucleation of cholesteric spherulites from the blue phase occurred at much lower temperatures than those needed for the nucleation in the absence of the field. The most striking effect was obtained in case of the mixture 50 : 50% (by weight). One possible explanation of this field-induced supercooling consists in assuming that the d.c. electric fields changed the growth rates of the cholesteris spherulites. In order to prove that, we investigate in this paper the effect of d.c. electric fields on nucleation and growth kinetics of the cholesteric spherulites for the mixture cholesteryl laurate-cholesteryl caprilate 50 : 50% (by weight).

EXPERIMENTAL

Liquid crystal cells with transparent and conductive SnO_2 electrodes were filled by cappillarity with mixtures of cholesteryl laurate-cholesteryl caprilate (50 : 50%, by weight). Then the cells were introduced into a special furnace, provided with transparent windows, which allowed controlled heating and cooling. In order to perform microscopic investigations, the furnace containing the cell was mounted on a polarizing microscope stage (MC-1, IOR). Magnifications of about 150 were used.

The growth kinetics of the cholesteric spherulites nucleated from the turbid blue phase was obtained as follows:

The sample was first heated at a temperature within the isotropic range and then cooled down to a temperature corresponding to the cholesteric range. When the nucleation was started, photomicrographs were taken at different time intervals and in this way the radii of the growing spherulites could be measured as functions of time, the temperature being kept constant (the temperature control was ±0.1°C).

In order to follow the electric field effects on the growth kinetics, the liquid crystal cell was heated at a temperature within the isotropic range at least $\frac{1}{2}$ hour, to reach randomization and to anneal polarization effects, due to electric fields; then, it was rapidly cooled down to the measuring temperature. After the nucleation of several cholesteric spherulites, a definite d.c. field was switched on and the changes in cholesteric radii were recorded using the same procedure mentioned above.

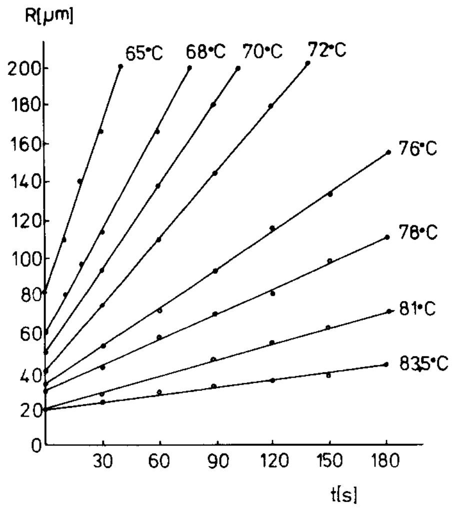

FIGURE 1 The time evolution of the cholesteric spherulite radii obtained at different temperatures.

RESULTS AND DISCUSSION

The growth of the cholesteric spherulites was determined first in the absence of d.c. electric fields; the results obtained at different temperatures (i.e. different supersaturations) are shown in Figure 1. In all cases, the time evolution of the cholesteric spherulite's radius, nucleated from the blue phase, is described by straight lines; this shows that the growth rates are independent on the spherulite size.

These results are similar to those reported by Jabarin and Stein[4] with reference to the growth of cholesteryl myristate spherulites and also to those reported by Würz, Klar and Chan[5] for other cholesteryl esters.

When the growth is watched under different d.c. electric fields, the evolution of the spherulite radii is also a linear function of time. The results obtained at 72°C are given in Figure 2. Similar data were obtained at other temperatures.

This shows that the time evolution of the spherulite radii grown in the presence of d.c. fields is independent on the spherulite size and we may conclude that the growth law is not affected by electric fields.

The growth rates were determined from the slope of the straight lines shown in Figure 1 or Figure 2 and then plotted as functions of temperature. The results are shown in Figure 3. It may be seen that the

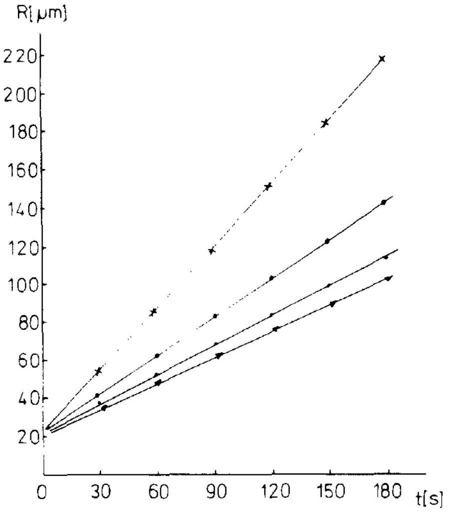

FIGURE 2 The time evolution of the cholesteric radii grown without and under different applied d.c. electric fields at 72°C; cell thickness 30 μm. Applied voltages: × 0 V, ○ 5 V, ● 10 V and ▲ 15 V.

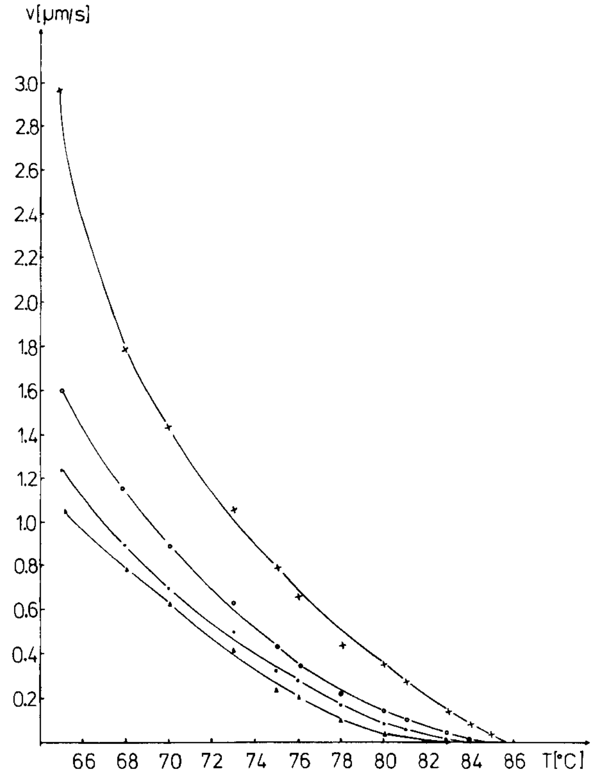

FIGURE 3 The growth rate as a function of temperature and applied electric voltages: × 0 V, ○ 5 V, ● 10 V and ▲ 15 V.

growth rates are decreased by electric fields, the higher the field, the lower the growth rates.

In order to get more information about the growth mechanism we followed the same procedure used by Jabarin and Stein.[4]

By assuming that the cholesteric spherulite growth occurred as a result of a heterogeneous nucleation process, similar to that encountered in polymeric systems, the growth rate $v = dR/dt$ for the two dimensional nucleation is given by:

$$\ln v = \alpha - \beta T_0/(T\Delta T) \tag{1}$$

and the growth rate or the three dimensional cylindrical case nucleation is:

$$\ln v = \alpha - \gamma T_0^2/T(\Delta T)^2 \tag{2}$$

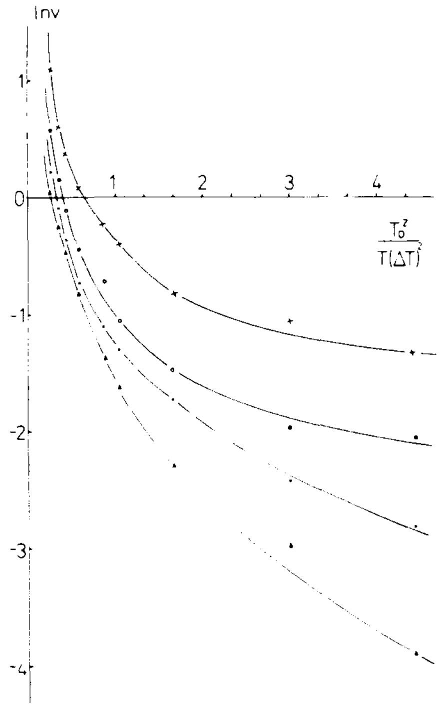

FIGURE 4 The logarithm of the growth rate as a function of $T_0^2/T(\Delta T)^2$ obtained for × 0 V, ○ 5 V, ● 10 V and ▲ 15 V.

Here T_0 is the transition temperature (cholesteric-blue phase), $\Delta T = T - T_0$ the degree of supercooling, α, β and γ constants.

As it is shown in Figure 4, $\ln v$ vs. $T^2/T(\Delta T)^2$ is not fitted by a straight line, in agreement to the result obtained in Ref. 4. This is an indication that the growth nuclei are not tridimensional.

The results obtained for $\ln v$ vs. $T/T(\Delta T)$ are shown in Figure 5.

In the case of cholesteryl myristate, Jabarin and Stein obtained a straight line for a similar dependence and showed that the growth was sustained by a secondary nucleation mechanism.

Our results are in contradiction to those reported by Jabarin and Stein[4] but in qualitatively good agreement to those of Würz, Klar and Chan[5] who assumed that the kinetics of transformation is determined by the orientational relaxation of the molecules in the vicinity of the interface.

In order to get more insight about the growth mechanism, we had to consider the theory of diffusionless kinetics developed by Chan.[6] As

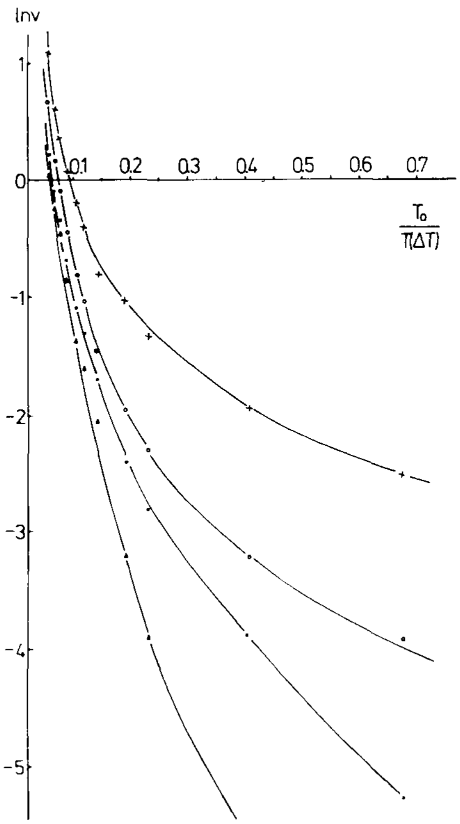

FIGURE 5 The logarithm of the growth rate as a function of $T_0/T\Delta T$ obtained for × 0 V, ○ 5 V, ● 10 V and ▲ 15 V.

shown,[5,6] the asymptotic growth rate is given by:

$$v = (3/\gamma)\left[2\kappa a(T_0 - T^+)\right]^{1/2}\left\{1 - \left[1 - (T_0 - T)/(T_0 - T^+)\right]^{1/2}\right\} \tag{3}$$

where γ is a frictional coefficient associated with dissipative effects during relaxation, κ a coefficient associated with the gradient term that accounts for the interfacial free energy, a a constant originating from the mean field approximation, T^+ the lower critical temperature at which the blue phase becomes absolutely unstable† and T_0 the

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†As the upper critical temperature T_c at which the cholesteric phase becomes unstable cannot be determined accurately, it was assumed that $T_c = T_0$.

temperature at which the two phases may be at equilibrium with each other.

The effects of d.c. fields on the growth rate may be explained first by considering changes in temperatures such as T_0 or T^+. It was proved[7,8] that T_0 is decreased by electric fields and that the dependence $T_0 = T_0(U)$, where U is the voltage applied on the liquid crystal cell, is quadratic in accordance to Helfrich's findings.[9] These changes are shown in Figure 6 (top curve (a)). Similar results were obtained for $T^+ = T^+(U)$; this dependence is also shown in Figure 6 (top curve (b)). We note that the difference $T_0(U) - T^+(U)$ was found to be the same within the range of the applied voltages.

From (3) we get:

$$\gamma v/3(2\kappa a)^{1/2} = f(T, T_0(U), T^+(U)) \qquad (4)$$

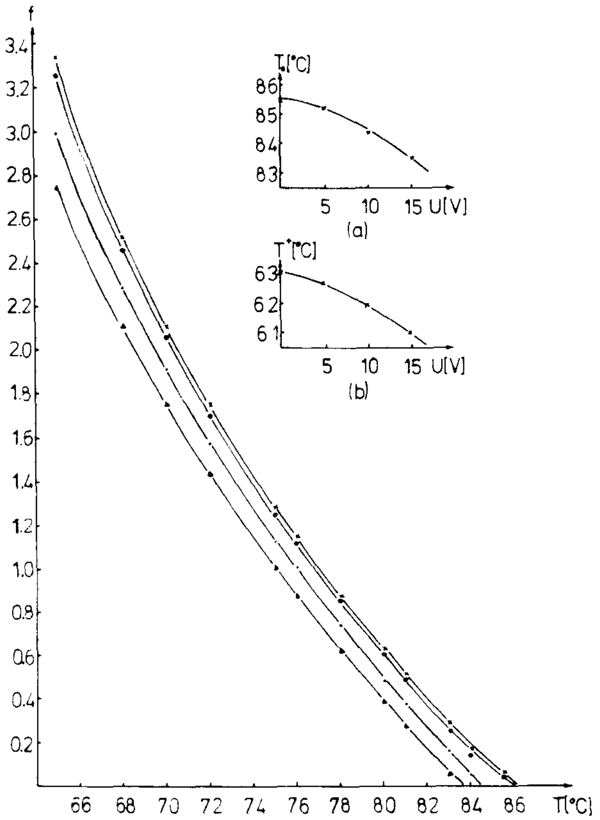

FIGURE 6 The temperature dependence of the function $f = \gamma v/3(2\kappa a)^{1/2}$ calculated for × 0 V, ○ 5 V, ● 10 V and ▲ 15 V. Top curve (a): the dependence $T_0 = T_0(U)$. Top curve (b): the dependence $T^+ = T^+(U)$.

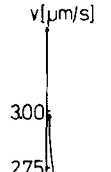

FIGURE 7 The temperature dependence of the growth rate obtained when the liquid crystal cell was subjected to different electric voltages.

where:

$$f = \left[T_0(U) - T^+(U)\right]^{1/2} \times \left\{1 - \left[1 - (T_0(U) - T)/(T_0(U) - T^+(U))\right]^{1/2}\right\} \qquad (5)$$

Hence, by evaluating (5) we may obtain information with reference to the temperature dependence of the growth rate and the electric field effects on it†. These results are shown in Figure 6.

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†We assume first that $\gamma/3(2\pi a)^{1/2}$ is constant.

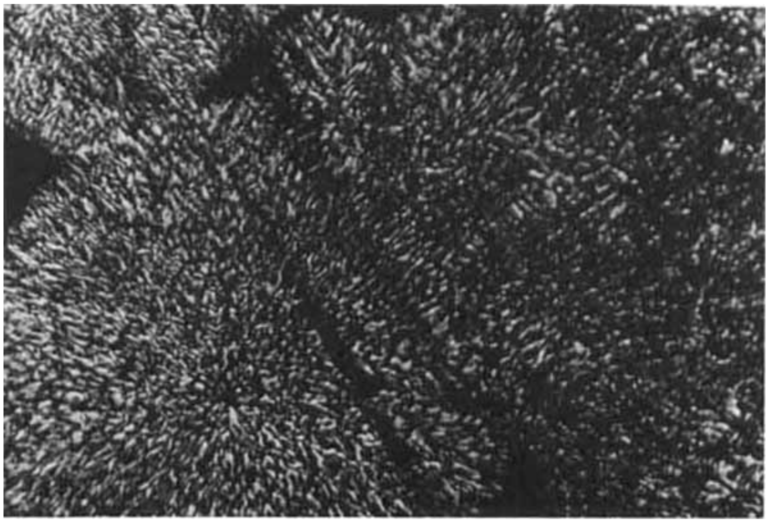

FIGURE 8 (a) Cholesteric spherulites obtained without using electric fields. (b) Cholesteric spherulites grown under electric fields.

When the growth is pursued without electric fields, the agreement between the experimental curve shown in Figure 3 and the theoretical one (Figure 6) is satisfactory. Nevertheless, the slope dv/dT of approach to T_0 is steeper for the theoretical curve when compared to the experimental one. This result is similar to that obtained by Würz, Klar and Chan; it was suggested that the discrepancies could be a consequence of the temperature dependence of the frictional coefficient γ or to the inadequacy of the mean field approximation over a rather wide temperature range.

We may conclude that $\gamma/3(2\kappa a)^{1/2}$ is a function of temperature and that its influence is also effective when the growth is pursued under electric fields. However, when the theoretical and experimental results obtained under electric fields are compared, the agreement is less satisfactory. This shows that the function $\gamma/3(2\kappa a)^{1/2}$ is also dependent on the electric field and that its influence is prevailing when compared to the changes in the transition temperatures.

The experimental results obtained for the temperature dependence of the growth rates under electric fields are given in Figure 7. It may be seen that the growth rates obtained at different temperatures are decreased by the electric field and that the rate of decrease is practically independent on temperature.

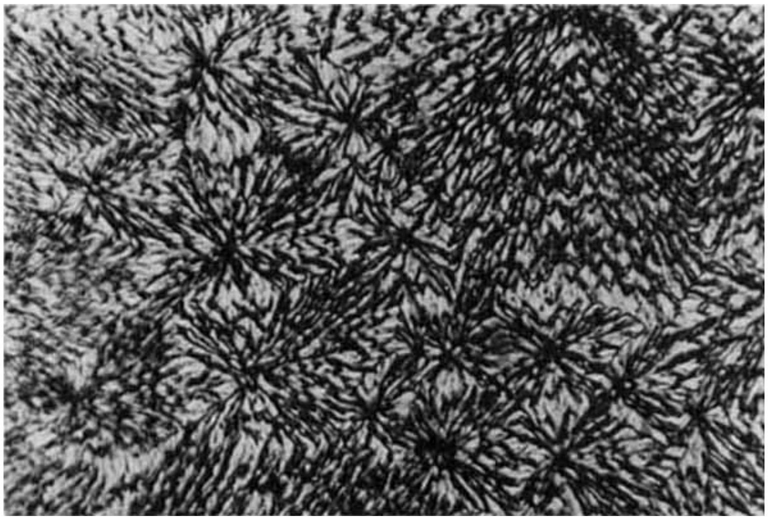

FIGURE 8 (*Continued*)

The influence of d.c. electric fields on growth kinetics is also revealed when the morphologies of the spherulites obtained without or under electric fields are compared. As shown in Figure 8a, the microstructure of the spherulites grown without d.c. fields consists of small focal conic domains symmetrically arranged within the spherulite texture. For the spherulites obtained under d.c. fields the focal conic domains are larger (Figure 8b)†.

Another qualitative explanation of this phenomenon is the field-induced ordering within the mesophase. Jabarin and Stein[4] noticed that the nucleation rate and growth rate decreased with sample thickness. They assumed that the glass surface oriented the mesogenic substance and concluded that the growth is less favoured when one deals with an ordered substance. All the same, under electric fields the phenomenon is more complex as the field-induced alignment of molecules is not the single mechanism involved in the growth process. Polarization phenomena should be more important and, as a result of this, the relaxation kinetics of the molecules in the vicinity of the interface will be affected.

In case of nonmesogenic compounds, the effects of surface charge and dipole distribution on the heterogeneous nucleation were investi-

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†This may be an indication that the growth rates are different.

gated both theoretically and experimentally.[10,11] Changes in critical supersaturation and growth kinetics were found. It is expected to obtain more significant effects when liquid crystals are involved.

References

1. J. M. Pochon and H. W. Gibson, *J. Amer. Soc.*, **93**, 1279 (1971).
2. F. P. Price and J. H. Wendorff, *J. Phys. Chem.*, **75**, 2389, 2849 (1971); **76**, 276 (1972).
3. F. P. Price and A. K. Fritzsche, *J. Phys. Chem.*, **77**, 396 (1973).
4. S. A. Jabarin and R. S. Stein, *J. Phys. Chem.*, **77**, 399, 409 (1973).
5. U. Würz, G. Klar and S. K. Chan, *J. Physique*, **40**, C3-404 (1979).
6. S. K. Chan, *J. Chem. Phys.*, **67**, 5755 (1977).
7. C. Moţoc and M. Honciuc, *Rev. Roum. Phys.*, **28**, 541 (1983).
8. C. Moţoc, M. Honciuc, R. Mitroi and C. Roşu, "Small angle light scattering and polarization phenomena in cholesteryl esters mixtures," 8th Int. Liquid Crystal Conf., Kyoto, Japan, 1980.
9. W. Helfrich, *Phys. Rev. Lett.*, **24**, 201 (1970).
10. A. A. Chernov and L. M. Trusov, *Kristallographyia*, **16**, 601 (1961).
11. C. Moţoc, *J. Cryst. Growth*, **12**, 309 (1972); *Rev. Roum. Physique*, **21**, 513 (1976).