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An Explanation of Spherulites Growth Rate Change in Cholesteric Liquid Crystals as Investigated by the Microscopic Method

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An Explanation of Spherulites Growth Rate Change in Cholesteric Liquid Crystals as Investigated by the Microscopic Method

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The microscopic method of cholesteric liquid crystal isothermal crystallization investigation has been found to have certain advantages, such as simplicity and enables direct observation of the process. This method enables photographing of individual phases of the crystallization process over a wide range of time. The analysis of particular photographs provides information about the quality and radii of spherulite growths. Furthermore, this measurement renders it possible to find the vôlume changes of crystallized substance and values of these parameters as n and k from the Avrami theory of isothermal crystallization of polymers and liquid crystals.

In previous investigations of isothermal crystallization of polymers[1-5] and liquid crystals,[6-8] it has been found that the radius of the spherulites is a linear function of crystallization time. Recently, similar results were obtained when we investigated the isothermal crystallization of cholesteric liquid crystals using the microscopic method.[9-12]

In this investigation a series of measurements of spherulitic radii in cholesteryl caproate has been performed for various crystallization times and we found that the spherulites growth was characterized by two growth rates, G_i and G_2, in the same temperature of crystallization. The small field of vision is characteristic of the microscopic method and that is why the execution of spherulitic growth rate measurements are difficult in a wedge shaped sample. In this work the spherulitic growth rate G of liquid crystals was measured for different thicknesses of samples at the same temperature. The temperature was constant and controlled by a thermocouple. These results are shown in Figures 1, 2, 3 and 4. It is evident from these figures, that at first the spherulites are growing with a growth rate G_1, then G_2 where $G_2 > G_1$. This phenomenon seems new and can only be observed by use of a microscope. Moreover, it may be associated with the microscopic properties of the investigated substance or with the geometry of the experiment.

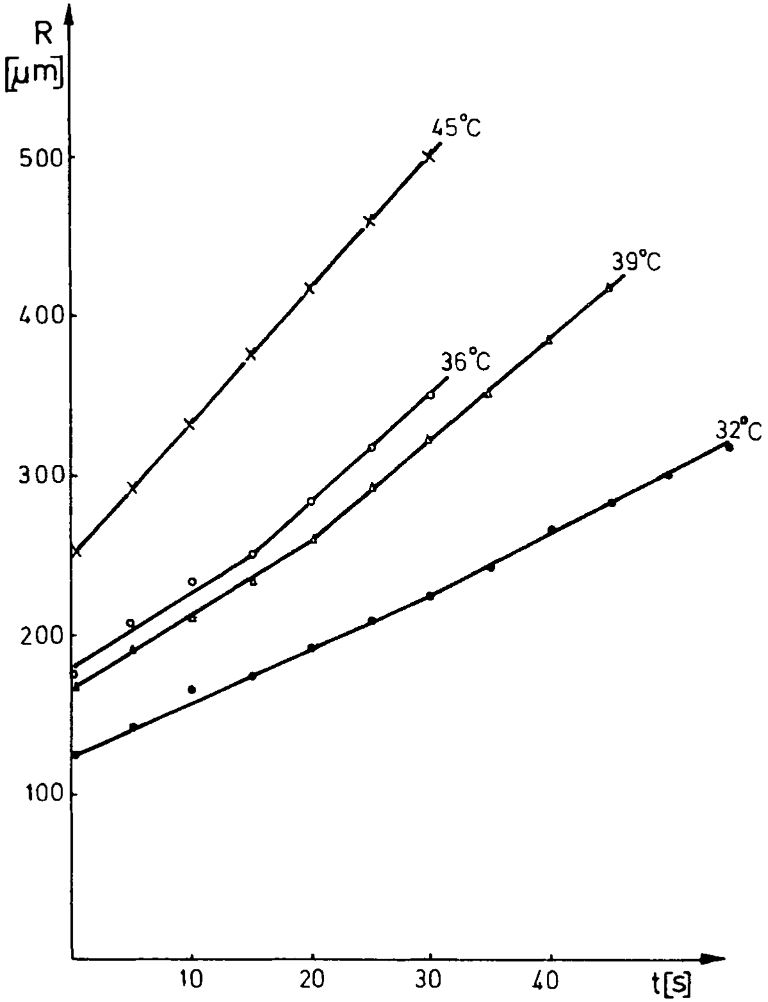

FIGURE 1 The relationship between spherulitic radius R of cholesteryl caproate and temperature for various crystallisation time t.

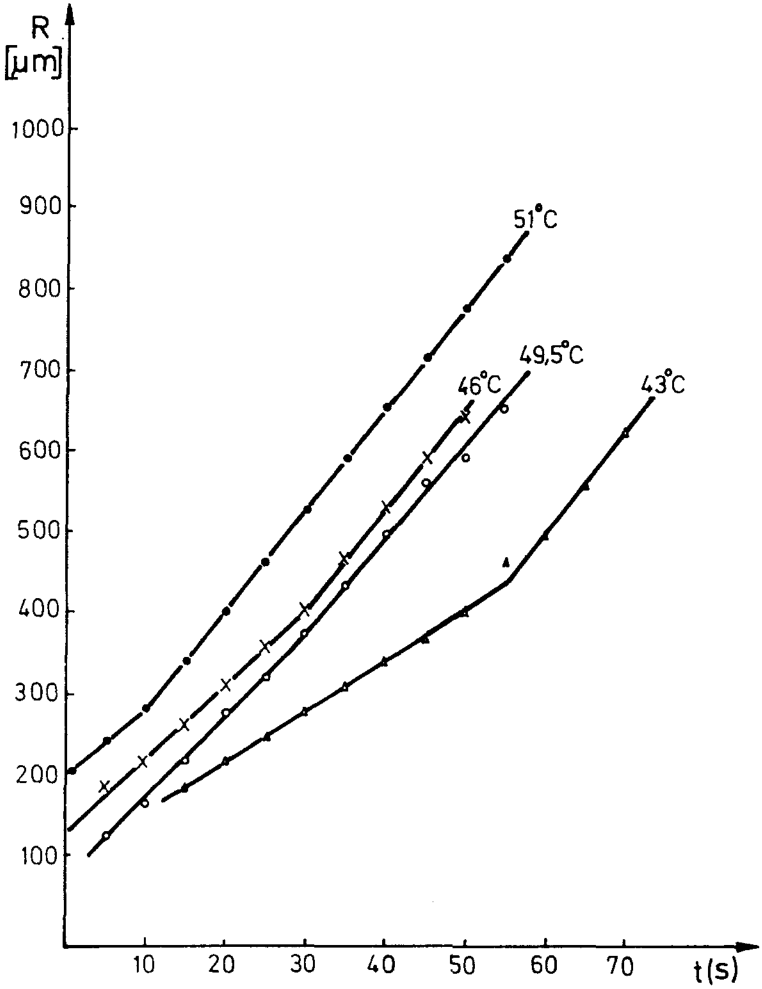

FIGURE 2 The relationship between shperulitic radius R of cholesteryl caproate and temperature for various crystallisation time t.

The aim of the following investigation is to suggest a reason for the phenomenon previously observed. An explanation for the occurrence of the two spherulitic growth rates seems to be impossible when considering them as an aspect of the microscopic properties of the investigated liquid crystal molecules. We assert that this phenomenon is associated with the geometry of the liquid crystal samples. It is known that velocity change of crystallized liquid crystal volume with time, is proportional to its surface area.

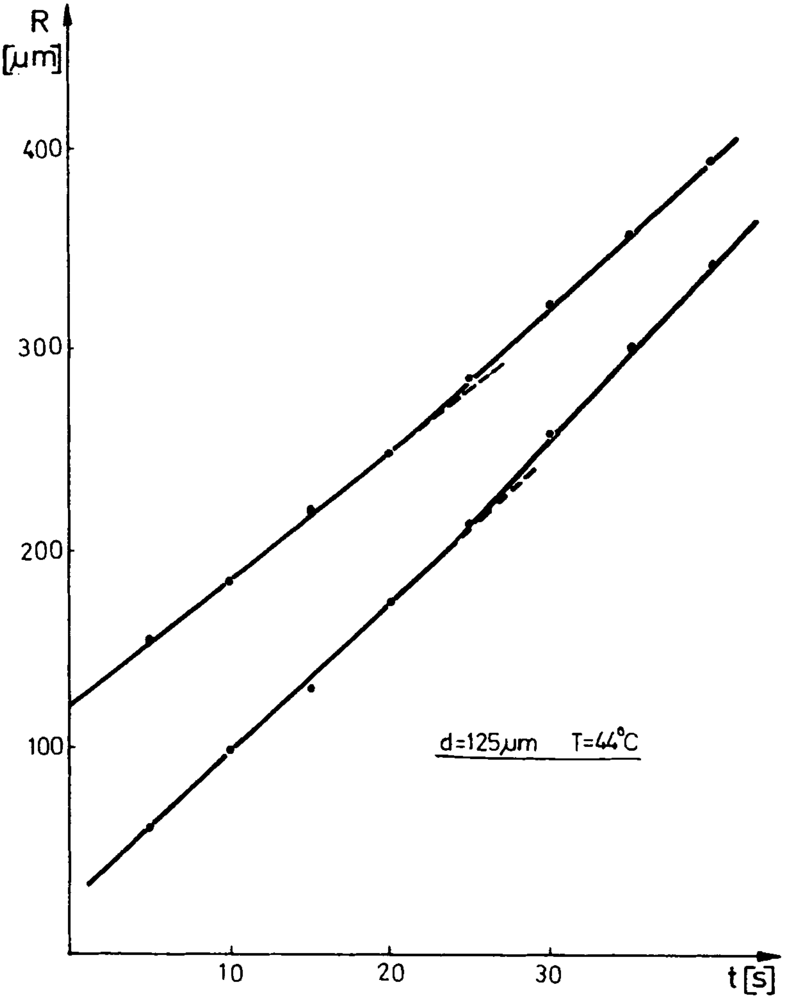

FIGURE 3 The relationship between R and time t given for some spherulites growing in the field of microscope vision in the definite temperature.

$$\frac{dV}{dt} = GS \qquad (1)$$

where: V—crystallized crystal volume
G—spherulitic growth rate = dR/dt
S—surface area of crystallized liquid crystal

The measurement of spherulitic growth was performed by the use of the graphic relationship between spherulite radius and time. The above mentioned

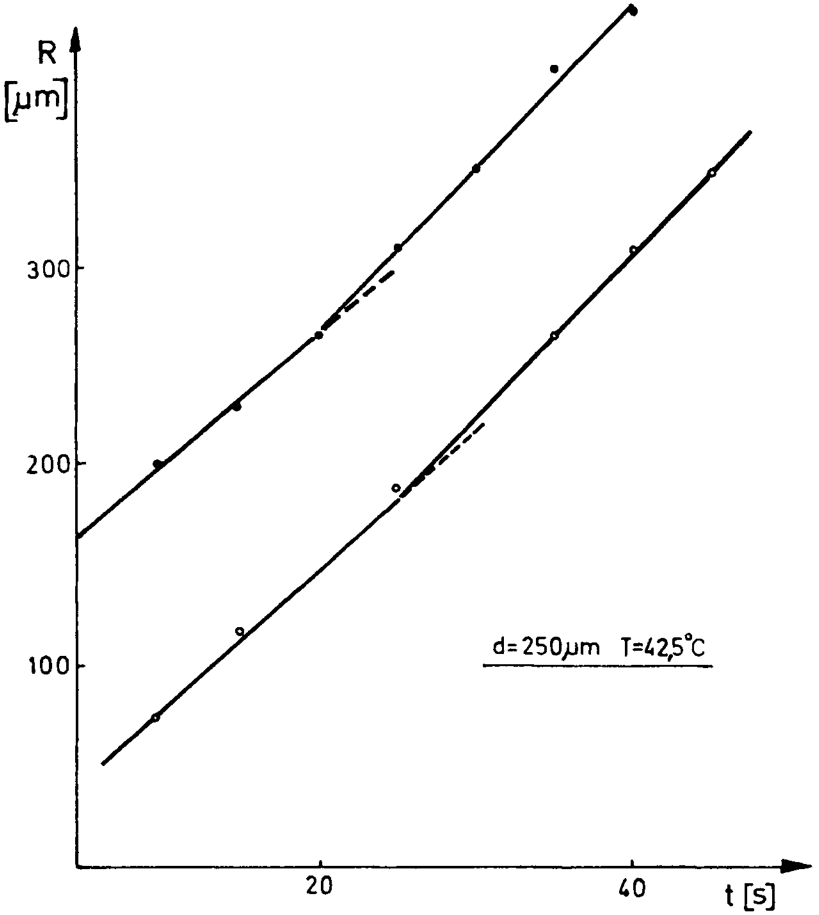

FIGURE 4 The relationship between R and time t given for some spherulites growing in the field of microscope vision in the definite temperature.

growth rates G_1 and G_2 can be combined with the surface area of the spherulite by the first formula. The investigation of isothermal crystallization of cholesteryl caproate with the microscope proves that the relationship between the spherulitic radius and growth time is characterised by two different gradients in the range of the crystallization temperatures. In the first phase of growth, the gradient of the curve is lower than in the second phase $G_1 < G_2$ but $S_{\text{sph}} > S_{\text{dysc}}$. This suggests that the spherulitic growth rate depends on the surface geometry of the spherulite.

The additional information, which can confirm the geometric mechanism of spherulitic growth rate change, is the value of the activation energy of

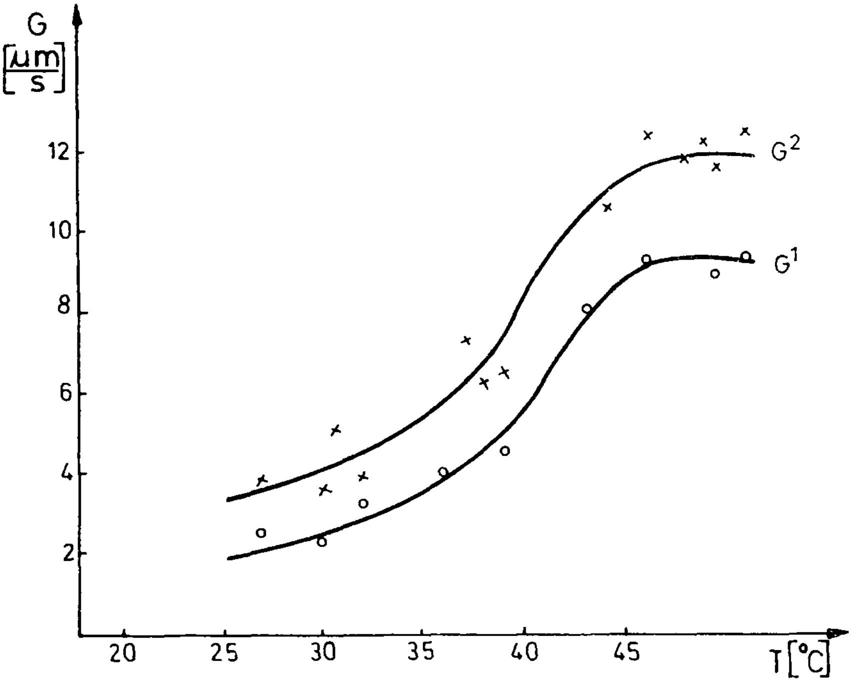

FIGURE 5 The experimental values of G_1 and G_2 for cholesteryl caproate as a function of temperature.

crystallization on the surface of liquid and nuclei. Though two growth rates are found experimentally, the activation energy for the isothermal crystallization of liquid crystals can not achieve two values for the same substance. It is evident then that the investigation of the activation energy is very important in this case. The dependence of spherilitic growth rate in polymers and liquid crystals on temperature is revealed in the bell-shaped bell curve which is also dependent on the activation energy ΔE and the free energy ΔF. If, during crystallization, the temperature is lower than the temperature of maximum G, then the activation energy ΔE has a greater influence on the process of spherulite growth than free energy ΔF. The following can therefore be written:

$$G = G_0 \exp - \frac{\Delta E}{kT} \tag{2}$$

where: G_0 is a constant, ΔE is the free activation energy of the crystallization process on a liquid-nuclei surface
T is the temperature of crystallization.

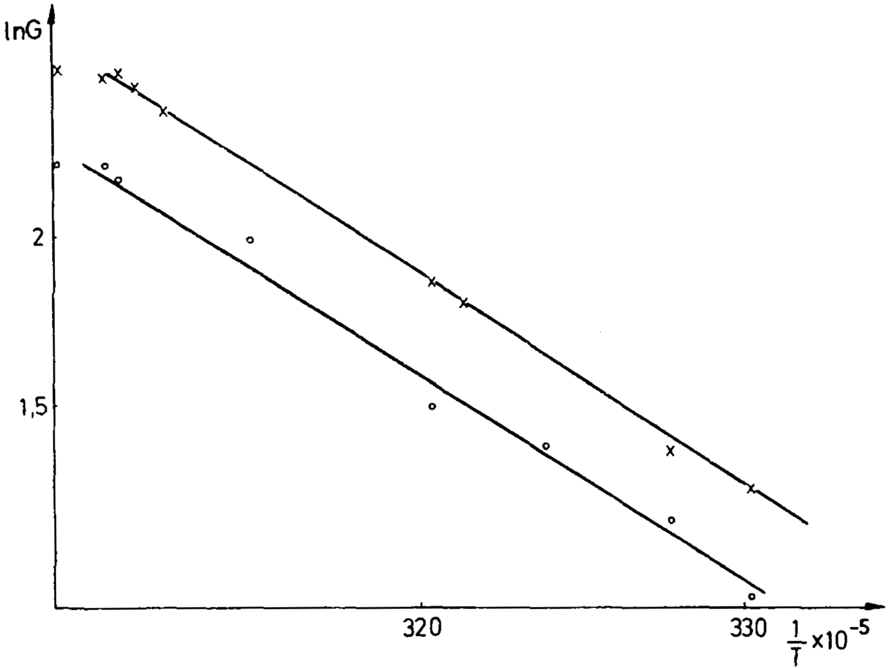

FIGURE 6 The ln G_1 and ln G_2 as linear function of I/T.

The experimental values of G_i and G_2 for cholesteryl capoate are shown in Figure 5 and these values fulfill the conditions of the second formula and they make calculation of the activation energy values possible. In this case ln G_1 and ln G_2 are linear functions of I/T (Figure 6). The calculated activation energy ΔE from Figure 6 is 0.5 eV. In conclusion it can be said that the same value of the activation energy for the two phases of spherulitic growth confirms the geometric mechanism of spherulitic growth rate change.

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