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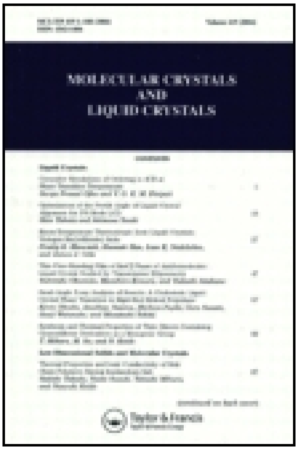

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Study of Isothermal Crystallization in Cholesteryl Nonanoate by Optical Methods

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Recently, there have been published many studies concerned with the physical properties of liquid crystals. Among other things, the optical,[1] dielectric[2] and electro-optical properties and the isothermal crystallization processes[3–6] of liquid crystals are studied. The interest in the properties of liquid crystals is associated with their numerous industrial applications.[7–9]

Liquid crystals are characterised by the molecular arrangement of a higher order than that of an isotropic liquid but lower than that of a solid substance. This molecular arrangement occurs in those compounds of which the molecules have the form of a rod or are flat. Some authors believe that, in addition to that, the molecular arrangement is associated with there being an interaction of dipole moments at the molecular ends.[10,11] The asymmetric structure of liquid crystal molecules imposes limitations on their rotatory motion because of high differences between their inertia moments in relation to their axes of rotation. The limitations result in a definite spacial orientation of the molecules. The liquid crystalline state is moreover characterized by translatory motion which is typical of the liquid state.

In studying the physical properties of liquid crystals it was asserted that liquid crystals may appear in any of a number of mesophases, depending on the degree of the molecular arrangement. The following mesophases are distinguished: nematic; smectic; and cholesteric.

The molecular arrangement in the liquid crystalline state does undoubtedly affect their crystallization processes. It has been confirmed that, in crystallizing, liquid crystals form spherulites. Prerequisite to the crystallization process is the presence of crystallization nuclei, which in turn may be formed either homogeneously or heterogeneously.

In homogenous formation, because of density fluctuations in the liquid crystalline state, a certain volume of the substance may be frozen, upon sufficient cooling, into a crystallization nucleus will then grow into crystallite. The crystallites are randomly distributed in the liquid crystal, but they combine into larger formations, giving spherulites.

The heterogenous formation of the crystallization nuclei takes place on the surfaces of imperfections or on wall surface irregularities. Both analysis of the relation between the dielectric constant and the temperature in cooling and heating,[12] and direct microscopic observation showed liquid crystal crystallization to be associated with the spherulite formation process. This relationship can be described by the dielectric constant temperature hysteresis loop. During crystallization, further molecular arrangement takes place, in the liquid crystal substance, leading to changes in the crystallizing substance properties (e.g., light depolarisation or changed density) The phenomena have been utilized for the study of the crystallization kinetics by measuring the light depolarisation[5,6] and by the dilatometric method.[3,4]

The kinetics of the crystallization process is described by the Avrami equation.[13–15]

$$\frac{V - V_t}{V - V_0} = e^{-kt^n} \tag{1}$$

where: V = final specific volume
V_0 = initial specific volume
V_t = specific volume in t
k,n = Avrami constants

The purpose of this study is to determine the n and k constants of isothermal crystallization by the microscopic method and to compare the results with those obtained by the dilatometric[3] and light depolarisation[6] methods.

EXPERIMENTAL

Cholesteryl nonanoate, obtained from the Medical School of Łódź, was used. The experimental compound was purified by gel chromatography. The measurements were performed on microscope Type MB-30, manufactured by P ZO, Poland.

The specimens were placed in a special thermostatically controlled cell which is diagrammed in Figure 1. A constant thickness of the liquid crystal layer on the slide was assured by using a 12 μm thick ring cut from Teflon film manufactured by I.C.I.

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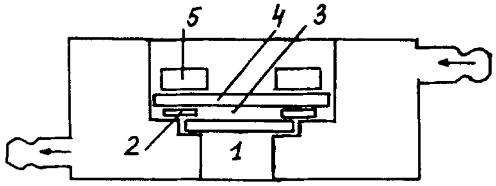

FIGURE 1 Schematic diagram of the measuring cell 1. slide glass; 2. distance film; 3. specimen; 4. cover glass; 5. tightening plate.

The Teflon ring was provided with a side indentation to avoid the risk of any excess amount of specimen affecting the distance between the slide and the cover glass.

Pulverized cholesteryl nonanoate was introduced into the thermostated cell where it was heated to 95°C and left at this temperature for 4 minutes for degassing. Next, the specimen was intensively cooled to the required temperature at which isothermal crystallization was tested. Upon the specimen arriving at the required temperature and upon the appearance of spherulites the specimen was photographed at intervals from 0.5 to 2 min., depending on the crystallization temperature. The photographing was continued until the crystallization of the speciman was completed. The developed negatives were enlarged and the spherulite diameters were measured. The spherulite growth rate G at a given crystallization temperature was determined from the relationship between the spherulite radius and the crystallization time by the least squares method. The relationship between the spherulite radius and crystallization time is shown in Figure 2. The growth rate determined for each spherulite at the same crystallization temperature enabled us to calculate the average rate G for the given temperature. The values of G that have been obtained for various temperatures are listed in Table I. The relationship between the values of G and crystallization temperature obtained here for cholesteryl nonanoate is represented in Figure 3. Because of experimental difficulties it was not possible to obtain values of G for the whole crystallization temperature range, which according to Price[3] begins at 78.8°C. From the test results obtained for the dielectric properties of cholesteryl nonanoate it would follow that the crystallization had begun at a temperature lower than

TABLE I

Spherulite growth rate G in choresteryl nonanoate at different temperatures

Temp. [°C]	24.0	25.6	26.7	27.6	29.1	31.1	32.6	34.9	39.7	43.8
$G \frac{\mu}{\text{min.}}$	14.8	19.1	20.6	22.2	24.1	29.5	29.8	41.5	42.6	44.5

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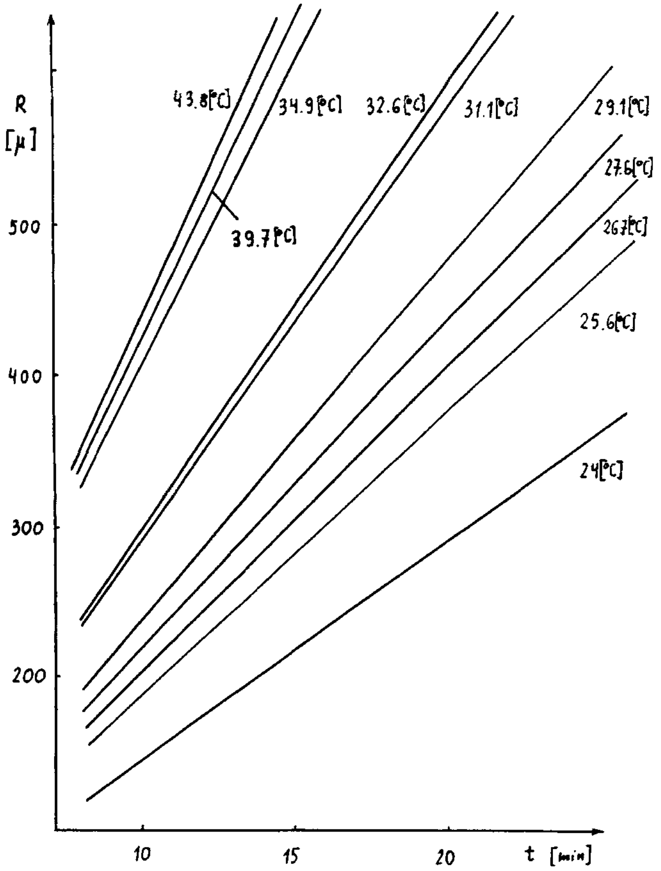

FIGURE 2 Relationship between radial growth and time at various temperatures, measured on 12 specimens.

that reported by Price,[3] but in our experiment the crystallization starting time was difficult to identify. This was particularly so at the higher crystallization temperatures. However, the authors believe that by modifying the microscopic method it will be possible to obtain results for the whole crystallization temperature range.

The photographs of the crystallization process were also used for determining the Avrami constants n and k.

Equation (1) describes the isothermal crystallization process in the case of a speciman of constant weight, whereas in this study specimens were considered that had a constant volume but varied weight. The adoption of the constant volume specimen, instead of constant weight specimen, was dictated

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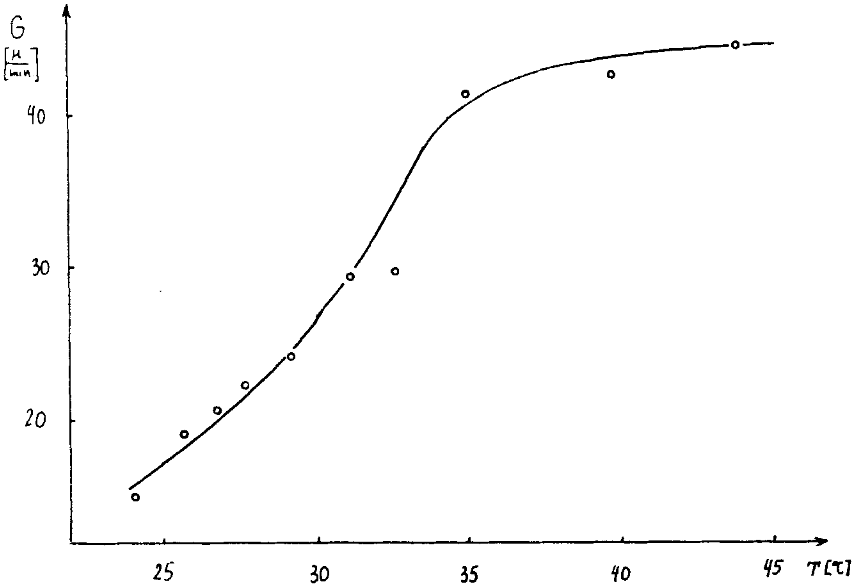

FIGURE 3 Spherulite growth rates in choresteryl nonanoate at various temperatures.

by the microscope field of vision. Accordingly, Eq. (1) had to be transformed as follows:

$$\frac{m_c}{m_0} = e^{-kt^n} \tag{2}$$

where: m_c = mass of liquid not yet crystallized at given time t
m_0 = total mass of liquid subjected to crystallization.
If: v = volume of liquid crystalline substance, confined to the field of vision, after the crystallization process
v_s = volume of the spherulites formed in volume v at the time t
m_s = mass of volume v_s of crystallized substance
ρ_s = density of crystallized substance

we obtain:

$$\begin{aligned} m_0 &= v \times \rho_s \\ m_c &= m_0 - m_s = v \times \rho_s - v_s \times \rho_s \end{aligned} \tag{3}$$

On inserting Eq. (3) in Eq. (2), we have:

$$\frac{v - v_s}{v} = e^{-kt^n} \tag{4}$$

The spherulite volume that is in the vision field of the microscope differs only

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insignificantly from the actual volume of the spherulities formed from mass m_0. The mass m_0, which in the crystallized state does not extend outside the field of vision, has a volume v_1, in the liquid state that is larger than v. It is easy to observe that:

$$\begin{aligned} m_0 &= v \times \rho_s \\ m_0 &= v_1 \times \rho_c \end{aligned} \tag{5}$$

where: ρ_c = density of the substance in the liquid crystalline state.

From relation (5) it follows that:

$$\frac{v}{v_1} = \frac{\rho_c}{\rho_s}$$

In the already dilatometric study[3] it was calculated that $\rho_c/\rho_{c_s} = 0.95$. The maximum volume change of mass m_0 in the crystallization process is approximately 5 per cent. The error in calculating k and n with Eq. (4) must not exceed 5 per cent.

The spherulite volume surface, v_s, areas were measured *versus* crystallization time by means of a planimeter. The observed spherulities are large compared to the thickness of the liquid crystal specimens used in our method. Therefore, it can be assumed, with some simplification, that the volume of a spherulite is equal to the product of its thickness multiplied by its surface area. This is so because a spherulite within the thin microscopic specimen layer grows virtually within two dimensions. Another reason for adopting the above assumption is that at the time the first photograph was made the spherulite which originally had grown in all directions, would have already spanned the distance between the slide and cover glass and would thereafter continue to grow only within its cylindrical cross section. Thus, it was assumed that the volume of the spherulite could be determined by measuring its surface area.

The crystallization time t of Eq. (4) has a substantial effect on the values of k and n. This is why the time t would have had to be measured right from the start of the crystallization process, which was not possible with the method

TABLE II

The values of Avrami constants n and k determined for cholesteryl nonanoate by the microscopic method.

Temp. [°C]	25.6	27.6	31.1	34.9	39.7
n	2.29	2.29	1.95	1.87	1.78
$k \ \frac{1}{\text{min}^2}$	4.71×10^{-4}	6.30×10^{-4}	12.31×10^{-4}	16.95×10^{-4}	22.65×10^{-4}

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TABLE III

The values of Avrami constants k and n determined for cholesteryl nonanoate by the dilatometric method.[3]

Temp. [°C]	26.0	31.5	38.5	44.7	
n	4	3.9	3.9	4.2	$n = 4$
$k\ \frac{1}{\mathrm{min}^4}$	9.2×10^{-3}	6.7×10^{-3}	4.0×10^{-3}	6.7×10^{-4}	

adopted in this study. It was, therefore, necessary to determine the time indirectly, as follows:

In the first measurement of the v_s of a given specimen at a given temperature there were spherulites of different sizes. Now, by measuring the radius of the biggest spherulite and dividing it by the predetermined growth rate G at the given temperature it was possible to determine the time elapsed from the start of the crystallization till the moment the v_s was recorded. The time t in Eq. (4) is a sum of time t_0 and the intervals Δt between the successive photographs.

In order to determine k and n, Eq. (4) was written in the following form:

$$\ln\left(-\ln\frac{v - v_s}{v}\right) = \ln k + n \times \ln t \tag{6}$$

The k and n values for cholesteryl nonanoate calculated from Eq. (5) by the least squares method are given in Table II.

To enable comparison, the corresponding values of k and n obtained by the dilatometric method by F. P. Price[3] are given in Table III.

The microscopic method enables direct observation of the nuclei growth N, see Table IV.

TABLE IV

Nucleus growth rate N determined for cholesteryl nonanoate by direct microscopic observation method.

Temp. [°C]	25.6	27.6	31.1	34.9	39.7
$n\ \frac{1}{\mathrm{min}^3}$	12.5×10^{-9}	7.3×10^{-9}	5.2×10^{-9}	2.3×10^{-9}	1.4×10^{-9}

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CONCLUSIONS

According to Stein *et al.*[6] the spherulite growth rate G is expressed by the relation:

$$G = G_0 \exp\left[-\left(\frac{\Delta E}{nT} + \frac{\Delta F}{kT}\right)\right] \tag{7}$$

where: G_0 = constant

E = activation energy for transport across the liquid-nucleus interface

F = free energy of critical size nucleus formation

k = Boltzman constant

T = temperature in the absolute scale

The function G is represented in Figure 4, and it is similar to the function diagram obtained by I. H. Maggil[16] for polymers.

The results presented in Table I and Figure 3 indicate that the spherulite growth rate in highly supercooled cholesteryl nonanoate is low. With decreased degree of supercooling, the growth rate G increases first rapidly

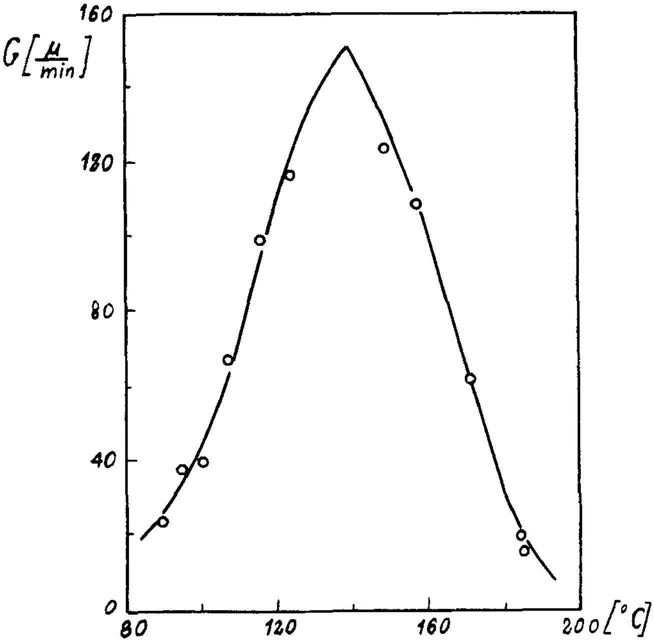

FIGURE 4 The relationship between temperature and spherulite growth rate in nylon.[6,18]

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and then less rapidly, which corresponds to the beginning of the curve plotted in Figure 4. A contrary phenomenon is reported by S. A. Jabarin and R. S. Stein[6] who studied choresteryl myristate where the growth rate G increased with increased degree of supercooling. The fact which accounts for this apparent divergence is that Jabarin and Stein used supercooling from 3.0°C to 4.2°C while in our case the supercooling was in the range of 64.0°C to 34.3°C. With allowance for the different supercooling levels it can be said that the results obtained by the two methods conform with the variation described by Eq. (6).

The results obtained in this study for k and n are substantially different from those reported by F. P. Price and J. H. Wendorff[3] who studied the cholesteryl nonanoate crystallization kinetics by the dilatometric method. It is to be noted that in the dilatometric method specimens of a volume of approximately 5 cm^3 were used, whereas in the described microscopic method the volume of the specimen was 3.2×10^{-2} mm^3 and its thickness was 12 μm. In this case the wall effect on liquid crystals is to be expected. In isothermal crystallization, the process kinetics is affected by the specimen's dimensional asymmetry. This is also suggested by S. A. Jabarin and R. S. Stein.[6]

Precision of determining the crystallization time t is another factor affecting the values of k and n. As it has been mentioned the slight change of the specimen's volume during crystallization makes it difficult to identify the crystallization starting point when using the dilatometric and the light depolarization methods.

This difficulty may lead to substituting incorrect crystallization time (too long or too short) to the Avrami equation and, consequently, to obtaining different values of k and n under the same methods.

For the purposes of the present study a method for determing the crystallization time, consisting in direct observation of the spherulite growth, was developed. Similarly as in the study by Price and Fritzsdze,[4] averaging the value n obtained at different temperatures gives a whole number.

Considering the mentioned differences between the dilatometirc and the microscopic methods the results obtained by the two methods are hardly comparable.

The microscopic method enables direct observation of the nuclei growth rate N. This is simply done by counting the spherulites in the microphotographs and calculating their growth rate against the known time $t_0 + ist$ and known sample volume V.

The advantage of the microscopic method over the two other methods seems to lie in that the microscopic method permits determination of the crystallization starting time, the spherulite growth rate, and the nuclei growth rate.

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SUMMARY

Isothermal crystallization in cholesteryl nonanoate at temperatures from 26 to 42°C was studied by the optical method. From the data obtained. Avrami constants, n and k, for isothermal crystallization were calculated.

In this study the value obtained for n is 2 while with the dilatomatric method it is 4.

The spherulite growth rate G and the nucleus growth rate N were calculated with the crystallization temperature range covered in this study. A method was developed for determining the crystallization starting point.

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