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M. B. Rhodes [a] , R. S. Porter [a] , W. Chu [a] & R. S. Stein [a]
[a] Department of Chemistry and Polymer, Research Institute University of Massachusetts, Amherst, Massachusetts
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Light Scattering Studies of Orientation Correlations in Cholesteryl Esters‡

M. B. RHODES, R. S. PORTER, W. CHU and R. S. STEIN

Department of Chemistry and Polymer Research Institute
University of Massachusetts
Amherst, Massachusetts

Abstract—Photographic and photometric light scattering patterns from the myristate, propionate and palmitate esters of cholesterol are analyzed in terms of theories previously developed for the scattering from crystalline polymers. The scattering is shown to result primarily from correlations in orientation of anisotropic elements. The solid state may exist in a negatively birefringent spherulitic form with a size dependent upon crystallization temperature, or may occur in the form of randomly correlated aggregates of crystals best characterized by a correlation function. Such random correlation persists through the smectic state. In the cholesteric state, there is a transition to disc-like non-random correlation with a correlation distance and non-randomness dependent upon the ester, temperature, and thermal history.

Introduction

In a previous report,[1] some illustrations of the application of the photographic light scattering technique to the study of cholesteryl myristate were presented, and means of interpretation of such results in terms of theories used for describing crystalline polymers were reviewed. It was shown, in agreement with earlier reports by Chatelain,[2] that scattering primarily arises from the existence of regions having correlated orientation with dimensions comparable

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with the wavelength of light. As has been demonstrated in considerations of the scattering from polymeric solids,[3,4] this gives rise to a high intensity of depolarized scattering in which the direction of polarization of the scattered light differs from that of the incident light. A quantitative consideration of the polarization of the scattered light and its angular dependence serves to characterize the dimensions, shape and arrangement of these correlated regions.

Types of Correlations

Scattering may arise from any heterogeneity in the polarizability tensor of the medium. This may be a consequence of fluctuations in (1) the average refractive index of the medium, (2) the local anisotropy, (3) the orientation of the optic axis of anisotropic regions, or (4) the optic rotation of locally optically active regions.

Average refractive index fluctuations are most simply described and may arise from local variations in the density or of composition of the medium. Composition fluctuations arise when dealing with multicomponent systems, and are of primary concern, for example, in the determination of molecular weight of polymers by light scattering. We shall restrict our considerations in this paper to single component systems where composition fluctuations cannot occur.

Density fluctuations may arise because of Brownian motion of a single phase system and is related to the compressibility of a medium, or arise from the co-existence of two phases of differing density. The latter is often associated with a high degree of scattering (critical opalescence) at a discrete first order phase transition, or may give rise to scattering over a range of temperature in the case of a diffuse transition. For solids and liquid crystals, phases may co-exist in a metastable state as a result of quenching from a higher temperature. If the refractive index differences are sufficiently small and the correlated regions are not too large (Rayleigh–Gans case[5]), the scattered light will be polarized in the same direction as the incident light. (The absence

of depolarized scattered light may be taken as a criterion of scattering arising from only density fluctuations.)

Scattering from density fluctuations may be described in terms of discrete regions having definite shape, size, and structure. In many cases of scattering from dense media where scattering particles are very close or interpenetrate or where no discrete scattering particle can be identified, a statistical description is required. For the Rayleigh–Gans case, the approach of Debye and Bueche[6] is useful. The Debye–Bueche theory of density fluctuations has been generalized by Goldstein and Michalik[7] and Stein and Wilson[4] to media having fluctuations in both density and orientation of anisotropic elements. The scattering is described in terms of a density correlation function $\gamma(r)$ and an orientation correlation function, $f(r)$. For many systems these correlation functions may be approximated by Gaussian or exponential forms with correlation distances characterizing the size of the regions of correlated density and orientation.

The Stein–Wilson theory involves the assumption of so-called " random orientation fluctuations " for which it is assumed that the correlation in orientation only depends upon the separation of the scattering elements and does not depend upon the orientation of the optic axes with respect to the line interconnecting the two volume elements. Such statistics apply to correlations where the regions within which optic axes tend to be parallel have spherical shape. In actual systems, one may have stronger correlations when the optic axes are parallel to the interconnecting lines. This gives rise to rod or fiber-like domains of parallelness throughout the system such as occur in the nematic liquid crystal state. Alternatively, if optic axes tend more to be parallel when they are perpendicular to the interconnecting line, disc or layer-like domains of correlation result as are characteristic of the cholesteric state.

An experimental consequence[4] of " random orientation fluctuations " is that the scattering pattern is cylindrically symmetrical about the incident beam and independent of the angle of rotation of the polarizer or analyzer with respect to the scattering plane

(but is dependent upon the angle between the polarization directions of the polarizer and analyzer). Thus, if the polarizer and analyzer are simultaneously rotated about their normals through an angle, ψ, keeping their polarization directions parallel (designated $I_{\parallel}$) or keeping them perpendicular (designated $I_{\perp}$), there will be no variation in scattered intensity with ψ at small scattering angles (θ) for samples having no macroscopic orientation. Such experiments have been carried out for crystalline polymers,[8,9,11] and it has been shown that, for many systems, there is appreciable ψ variation of $I_{\parallel}$ and $I_{\perp}$ indicating non-randomness. We shall show in this paper that the scattering from liquid crystal mesophases arises principally from orientation fluctuations, but that the degree of randomness of these fluctuations differs from one mesophase to another, and depends upon temperature, for a given mesophase.

Theories for the scattering from such systems having non-random orientation fluctuations have been developed where the optic axes are confined to a two-dimensional plane.[8,9,10] These theories predict a ψ variation of the scattering which depends upon parameters characterizing the non-randomness. The more general version of the theory introduces additional correlation functions which characterize the way in which the angular dependence of orientation correlation varies with the separation of the scattering elements. These may be determined from an analysis of the way in which the ψ variation of $I_{\parallel}$ and $I_{\perp}$ vary with the scattering angle, θ. Preliminary studies of this nature for the scattering from crystalline polymers have been reported. While the experiments reported here and elsewhere[1] demonstrate the necessity of applying the non-random theory to liquid crystal scattering, quantitative studies, which are now in progress, have not yet been reported. A consequence of the non-random theory is that the separation of the density and orientation contributions to scattering must take non-randomness into account.

An extreme limiting case of non-randomness is a system containing definitely shaped scattering objects such as anisotropic rods or spheres where optic axes are oriented in some definite way

with respect to the dimensions of the object. An example is a spherulite of a crystalline polymer which is a spherical or disc-like assembly of anisotropic scattering entities in which the optic axis is oriented at some definite angle, β, with respect to the radius.[12] The scattering from such spherulites is highly dependent upon ψ as shown in the polar plot of $I_\perp$ in Fig. 1 for the case of $\beta = 90°$.

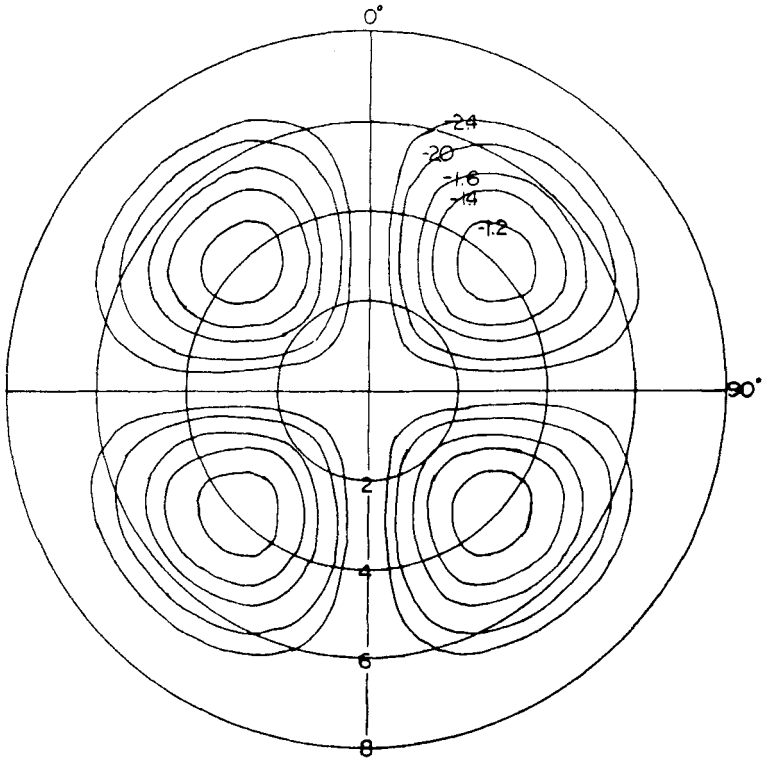


Figure 1. A calculated $I_\perp$ scattering pattern for a two-dimensional anisotropic disk.

The familiar four-leaf clover type scattering pattern falls to zero at $\psi = 0°$ or 90° and is a maximum at $\psi = 45°$. If $\beta = 45°$, however, the $I_\perp$ maximum for disc scattering occurs at 0° to 90°.

The variation of such spherulitic scattering patterns with θ exhibits a maximum. The experimental determination of the θ at which this maximum occurs serves as a convenient way to quantitatively determine the radius of the spherulite, which has been successfully compared with the direct microscopic determination of the radius.[10]

It will be shown that in some cases, cholesterol esters give scattering patterns which are describable in terms of this spherulite theory.

It should be noted that spherulite scattering patterns can also be described by the non-random correlation function type theory, where the functions are more complex than the simple exponential or Gaussian type functions, and may be calculated from geometric considerations.[9] They exhibit maxima and minima in their variation with r. This is what gives rise to the maximum in the variation of scattering with θ, a feature not seen for exponential or Gaussian correlation. Liquid crystals exhibit order intermediate between the non-random correlations describable by the exponential correlation functions and the high degree of order characterized by the spherulitic functions.

Scattering patterns for randomly oriented arrays of anisotropic rods have been calculated.[8,13] These may exhibit four-fold symmetry in ψ as do spherulites, but do not show a maximum in θ. Such patterns are seen for cholesteric phases and are also essentially similar to those predictable by non-random correlation function type theory. The difference is that by assuming a discrete model such as a rod, one neglects correlations between rods which is an important consideration in real systems and is best considered from a statistical point of view.

In summary, the variation of scattering intensity with θ and ψ indicates the statistics of the correlation of orientation of the structural elements. Such a description is ideal for systems such as liquid crystals in which the correlation is intermediate between the perfect correlations of a real crystal and the low degree of correlation characteristic of a true liquid. For correlation over short distances, less than a few hundred Angstrom units, systems may be characterized by X-ray scattering as has been done, for

example, by Hosemann *et al.*,[14] in which the disorder is characterized by a parameter, g, characterizing the fluctuation of the unit cell lattice vector **a**. While the X-ray studies are highly important for characterizing these short range fluctuations, it becomes increasingly difficult to apply them to the longer range fluctuations occurring over distances of many thousands of Angstrom units, encountered with many mesophases, since the X-ray scattering associated with these long distances occurs at small angles, accessible with difficulty. The experimental techniques for studying the light scattering occurring at much larger angles are considerably easier. Also, the X-ray scattering is primarily sensitive to the electron density of the system which is dependent upon the arrangement of all of the electrons of the atoms constituting the system and is only indirectly related to the molecular orientation. On the other hand, as we have seen, the light scattering is extremely dependent upon the anisotropy of the system which is determined by the distortion of the outer electron shells of the system which is determined by the type and orientation of the chemical bonds constituting the molecules. The description of the arrangement of these bonds is of prime importance in describing molecular liquid crystals.

Both X-ray and light scattering provide complementary information about such systems, and it is one of our goals to describe both types of experiments in terms of a set of unified parameters related to the structural statistics.

The conventional descriptions of liquid crystals in general categories such as smectic, nematic or cholesteric are qualitative. A more quantitative description would be in terms of statistical parameters defining the correlation of orientation of molecules. The classification in terms of the various types of mesophases would then be categorizing the system as residing in particular regions of parameter space. Scattering methods provide the best means of quantitative determination of these parameters. Theories of the thermodynamics and statistical mechanics of these systems and the kinetics of their formation are then best formulated in terms of such parameters.

Experimental Methods

The experimental techniques of light scattering measurements have been described. The photographic method[3,10,15,16] is a convenient means of rapidly but qualitatively recording the scattering pattern and its changes with time and temperature. In brief, light from a low-power He–Ne gas laser is passed through a sample of the system being studied, passed through an analyzing polaroid and allowed to fall on a photographic film. For liquid crystal systems, it is most convenient to have the incident light beam pass upward vertically through the sample cell, which may be fashioned from microscopic slides or cover glasses. Indeed, a microscope stage serves as a convenient sample holder in which the sample can be easily positioned and rotated. The temperature of the sample may then be readily controlled and measured using conventional microscope hot stage techniques.

For our apparatus, a Spectra-Physics Model 130 laser was employed for which $\lambda_0 = 6358$ Å. A Corning 6300 Å cut off filter was used to eliminate shorter wavelength radiation coming directly from the discharge tube. Stray radiation was further eliminated by passing the incident laser beam through a 1–2 mm pinhole located about 1 cm below the sample. A camera type shutter in the incident beam defined the exposure time which was usually of the order of 1/25–1/50 sec. A type HN36 plastic mounted Polaroid analyzer was located about 1 cm above the sample. (Plastic mount was found superior to glass laminate in eliminating stray reflections from glass surfaces.) Sample to film distances were in the range of 5″–25″ depending upon the angular range of scattering being studied. This was calibrated by replacing the sample with a diffraction grating and measuring the position of the diffraction spots on the photographic film as previously described.[10] Patterns were recorded on 4″ × 5″ Ansco Super Hypan film.

Photomicrographs were obtained using a Zeiss polarizing microscope equipped with a Koffler hot state which was calibrated with standard melting point substances.

With the exception of cholesteryl acetate (which was studied

from only a qualitative point of view), the esters studied were obtained from Applied Science Laboratories, State College, Pennsylvania, and were better than 99% pure. These were similar to samples studied in previous work by one of the authors.[17] The transition temperatures cited below for these esters as previously obtained by DTA are described in Table 1, where T_1 is the lowest transition temperature, T_2 the intermediate transition, and T_3 the transition temperature to the istropic liquid. The literature values cited below are consistent with the differential scanning calorimetry transition temperatures obtained on the samples actually used in these light scattering studies with differences being in the direction of the DTA values being somewhat higher. A variety of transition temperatures have been reported earlier (see, for example, Gray[18]).

TABLE 1 Transition Temperatures for Cholesteryl Esters in °C

Cholesteryl Ester	T_1	T_2	T_3
n-Propionate	99 ± 1	110	115.3
Myristate	73.6	79.7	85.5
Palmitate	(78.5)	79.7	83.0‡
Stearate	(75.5)‡	(79.5)‡	85.1

‡ Values given by Gray.[18] Parentheses indicate reported monotropic transition observed only on cooling.

The cholesteryl acetate sample studied here was of uncertain origin so that results on this sample should be interpreted with caution.

Temperatures of samples, both for microscopy and light scattering studies, were manually controlled using a Variac and were measured using a thermocouple. Heating and cooling rates were in the range of 1° to 10° per min.

Experimental Results

Preliminary investigations were concerned with the scattering from cholesteryl acetate in the solid state. A common observation

is the occurrence of spherulitic structure for samples quenched from the melt. Figures 2 and 3 show two photomicrographs for samples quenched at two different cooling rates from the istropic liquid by removing them from the hot stage and allowing them to cool in the air.

As can be seen from these photographs, structures are observed which are identical in appearance to spherulites observed for spherulitic high polymers.[19] The spherulites are birefringent, exhibiting a maltese cross when viewed between crossed polars where the dark bands are parallel to the polarization directions, indicating that the optic axes are either parallel or perpendicular to the spherulite radii. Examination with a first-order red plate reveals that the direction of highest refractive index is perpendicular to the radius.

Inspection of the larger spherulites shows the appearance of radial fibrillar structure, much like that seen for polymers.[18] It is

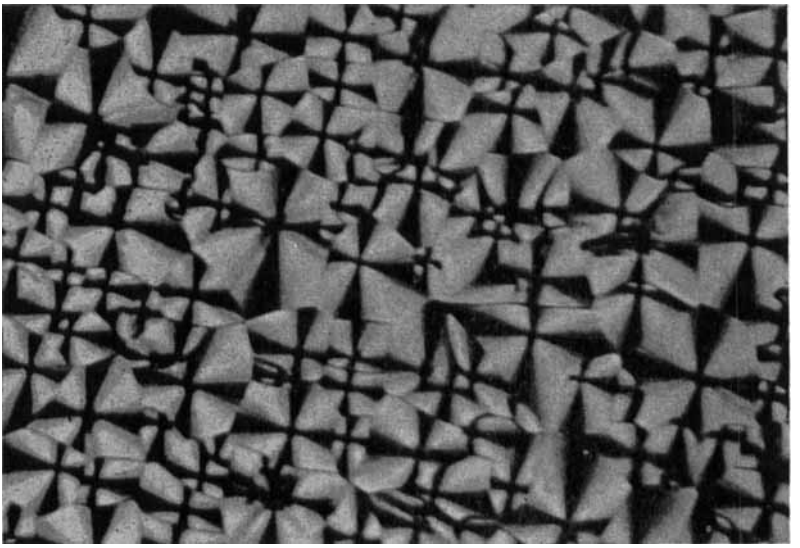


Figure 2. A photomicrograph between crossed polars for spherulites of cholesteryl acetate in the solid state (at room temperature) rapidly quenched from the istropic melt.

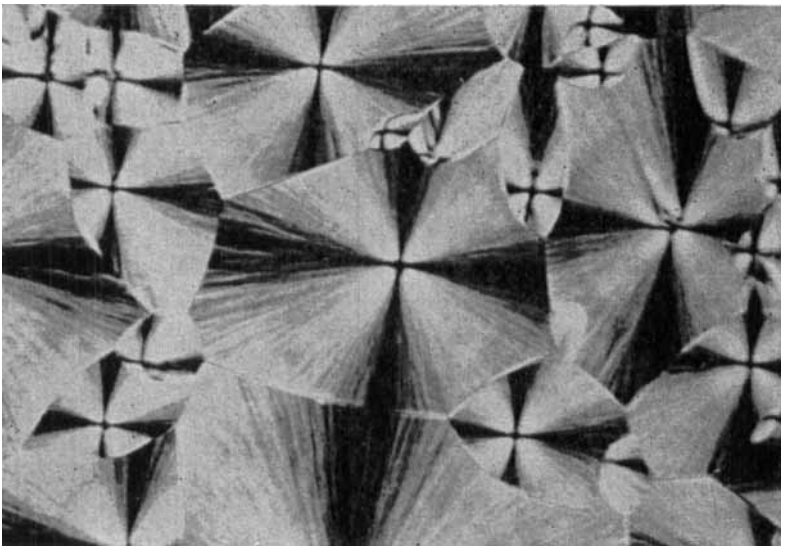


Figure 3. A photograph between crossed polars for spherulites of cholesteryl acetate in the solid state (at room temperature) more slowly quenched from the isotropic melt.

tempting to postulate that, like with polymers, the spherulites are composed of radially oriented crystalline lamellae with the high refractive index direction and hence the molecular plane oriented perpendicular to the lamellae plane.

As with polymer spherulites, the faster quenching rate gives the smaller spherulite. Those in Fig. 2 quenched rapidly average about 26nm in size, while the more slowly cooled spherulites of Fig. 3 are of the order of 68nm. This dependence of spherulite size upon quenching rate suggests that, as with polymers, the spherulitic growth is a nucleated process with the nucleation rate increasing with decreasing temperature.

Qualitative microscopic observation reveals that the spherulites grow radially outward from their centers at a rate which increases with decreasing temperature until they impinge, giving the volume filling structures seen in Figs. 2 and 3. The similarity of these observations to those for the kinetics of growth of polymer

spherulites[20] suggests that much of the theory of polymer crystallization might be carried over to the description of the kinetics of liquid crystal solid state spherulite formation.

Experimental studies of spherulite growth rates for isothermal crystallization are in progress and attempts will be made to interpret them in terms of degrees of supercooling, heats of fusion, and crystal surface energies.

These observations on cholesteryl acetate are typical for the other esters with minor variations in morphology. It has been possible, in some cases, to grow spherulites having banded structure, interpretable as with polymers,[3] in terms of helicoidal twist of the radial lamellae. The continuity of these rings throughout the spherulite indicates continuity of the phase of this twist.

Light scattering patterns were obtained for these spherulites using both parallel (V_V) and crossed (H_V) polars and are presented in Figs. 4 and 5. The resemblance of these patterns with those previously published for polymer spherulites[3] and with theoretically calculated patterns is evident. The 45° orientation of the crossed polar patterns is consistent with the 90° orientation ($\beta = 90°$) of the optic axis with respect to the spherulite radius consistent with the conclusions from microscopy. The extension of the $I_{\parallel}$ pattern in the polarization direction is also in agreement with this conclusion.

The difference in the size of the scattering patterns for the two sizes of spherulites is evident, with the larger spherulites giving the smaller patterns. Sizes calculated from the position of the θ_{max} of the $I_{\perp}$ patterns using the previously quoted equation agree with the average size estimated from the photomicrographs within experimental error.

Scattering patterns have been reported previously[1] for cholesteryl myristate in which the solid state and smectic state exhibit random-type orientation correlations with no azimuthal dependence, but the cholesteric state was non-random with $\beta = 90°$. In this case, changes were reversible upon heating and cooling. This is by no means universal and it is quite common with the other esters, for example, for the non-random cholesteric type pattern to

persist on cooling to the lower temperatures characteristic of the smectic and solid states.

Light scattering offers a convenient way to follow the sequence of structural changes accompanying the changes with temperature, which supplements and provides more complete information than obtainable from depolarized light intensity measurements.[21] Sequences of $I_{\parallel}$ and $I_{\perp}$ photographs obtained during the slow heating of cholesteryl myristate are given in Figs. 6 and 7. As previously reported, both $I_{\parallel}$ and $I_{\perp}$ patterns are of comparable intensity and give azimuthally independent patterns in the range of both the solid and smectic mesostates characteristic of scattering arising principally from random orientation fluctuations. No change in the nature or intensity of either the $I_{\parallel}$ or $I_{\perp}$ pattern occurs at the T_1 transition at 73.6 °C. However, at the T_2 transition at 79.7 °C from the smectic to the cholesteric mesophase, there is a change in shape of the $I_{\parallel}$ pattern, which becomes elongated in the vertical (polarization) direction, indicative of an increase in the non-randomness of the orientation correlations. In this region there is a dramatic drop in the $I_{\perp}$ intensity as evident from the absence of any pattern at 79°C. In the small temperature interval between 79.0 °C and 79.7 °C, there is a rapid increase in non-random $I_{\perp}$ scattering. Thus, it appears that at the T_2 transitions, there is a loss of random correlations prior to the development of non-random ones.

At higher temperatures, between 80° and 85 °C, there is a decrease in size of both the $I_{\parallel}$ and $I_{\perp}$ pattern, indicating an increase in correlation distance. This indicates that structure is not constant throughout the region of the temperature range of the cholesteric state, but there appears to be a continuous change in the extent of correlation with temperature.

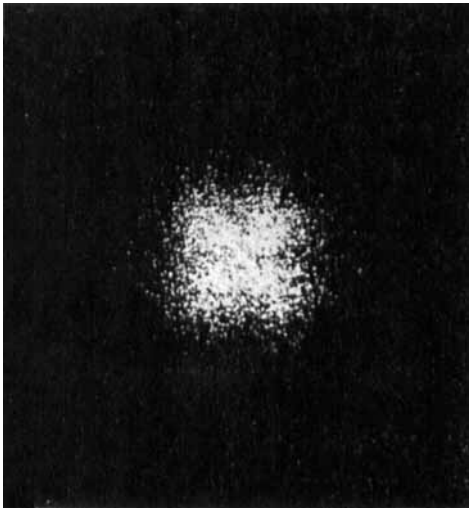
Above the melting point of the cholesteric phase at $T_3 = 85.5$ °C, both $I_{\parallel}$ and $I_{\perp}$ vanish. For the exposure times of our photographs, no detectable scattering is found above this temperature, indicating that the anisotropy associated with the scattering element is negligible in comparison with that in the regions of the mesophase.

(*a*)

(*b*)

Figure 4. Light scattering patterns obtained from the cholesteryl acetate spherulites shown in Fig. 2 obtained with (*a*) parallel and (*b*) crossed polarization. The parallel polarization direction is vertical.

(*a*)



(*b*)

Figure 5. Light scattering patterns obtained from the cholesteryl acetate spherulites shown in Fig. 3 obtained with (*a*) parallel and (*b*) crossed polarization. The parallel polarization direction is vertical.

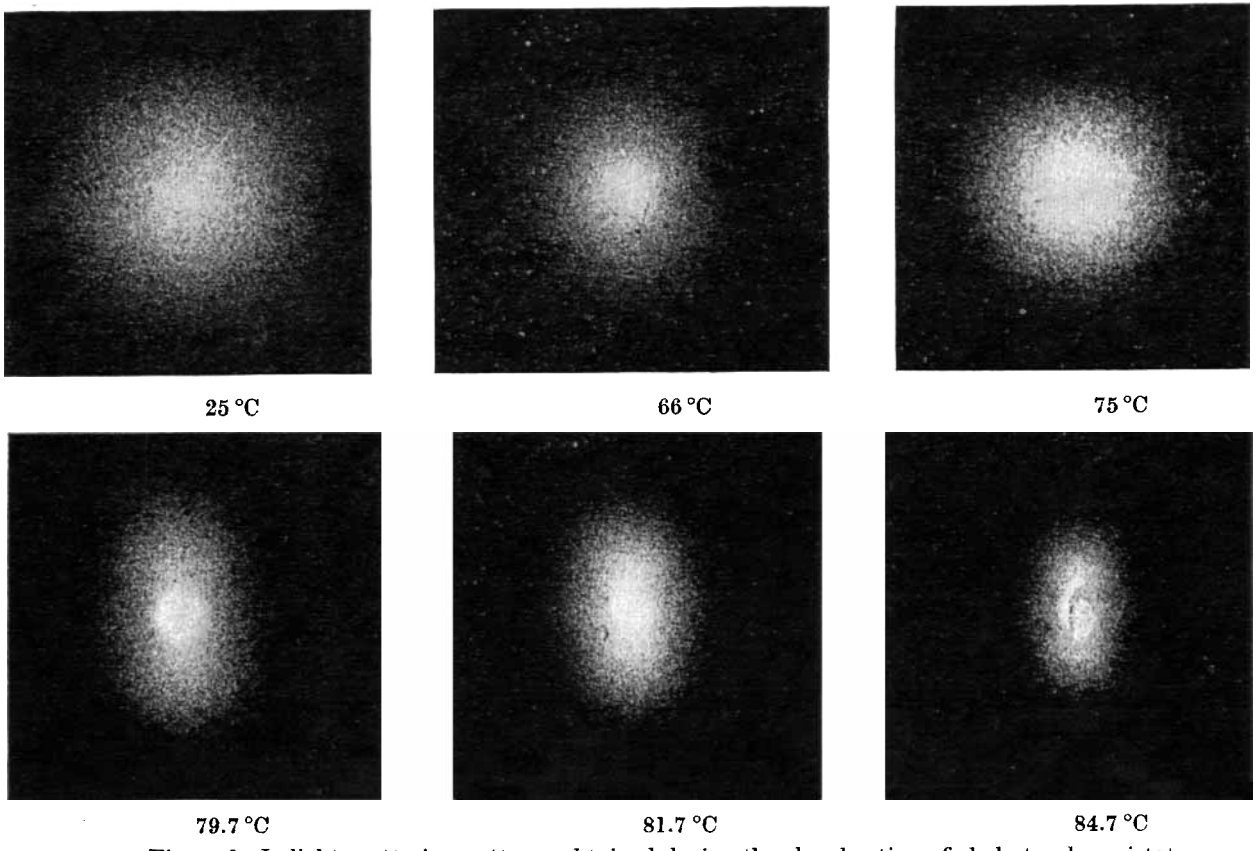
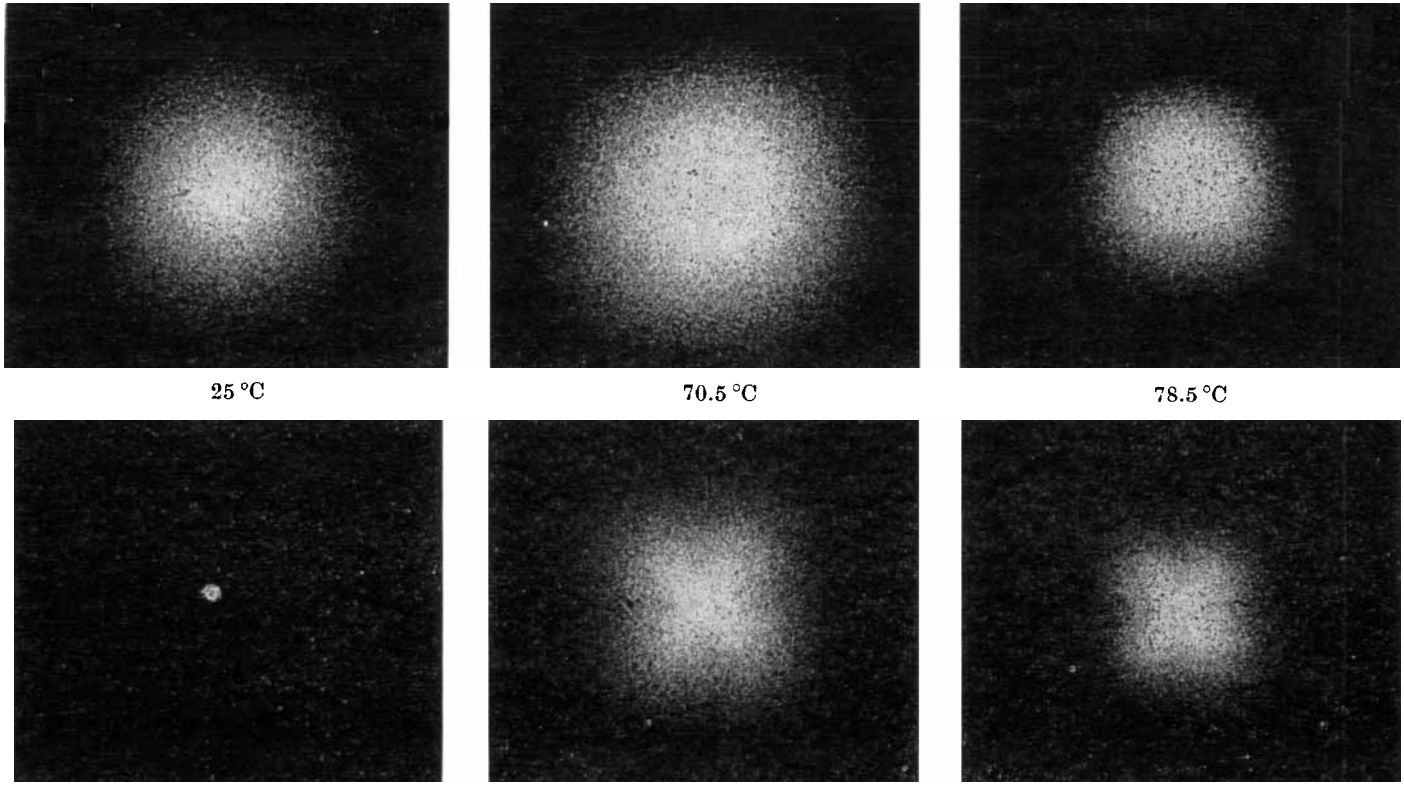


Figure 6. $I_{\parallel}$ light scattering patterns obtained during the slow heating of cholesteryl myristate.



25 °C 70.5 °C 78.5 °C

79 °C 79.7 °C 84.7 °C

Figure 7. $I_{\perp}$ light scattering patterns obtained during the slow heating of cholesteryl myristate.

A sequence of $I_\perp$ patterns observed during the cooling of cholesteryl stearate from the isotropic melt is presented in Fig. 8. A non-random $I_\perp$ pattern suddenly appears in the interval between 78° and 77 °C. By 76° the angular variation in intensity is lost and the pattern becomes random.

The azimuthally dependent scattering patterns for the cholesteric state are typical, and non-random correlation appears characteristic of this state. As we have seen, the type of non-randomness may vary and different esters exhibit characteristic differences. An interesting observation in the $I_\parallel$ and $I_\perp$ patterns shown in Fig. 9 for cholesteryl propionate in the cholesteric state (above the melting point) is that the principal pattern seen in the $I_\parallel$ picture has its maxima at $\pm 45°$ to the vertical (polarization direction) while the maxima for the $I_\perp$ pattern are at 0° and 90° to the vertical. Such patterns, rotated through 45° from the typical ones, have been obtained previously for polytetrafluoroethylene and other polymers and have been explained[21] on the assumption that the optic axis is tilted at approximately 45° to the direction of maximum extension of the structure. Thus maximum correlation in orientation would occur when the angle β between the optic axis of a scattering element and the interconnecting vector between two elements is of the order of 45°. It would appear that such an explanation is also applicable here.

It is noted on further examination of Fig. 9 that, in the center, there are small scattering patterns having the more usual orientation. This would mean that for large correlation distances (scattering at small angles) correlation was greatest for $\beta = 0°$ or 90°. Thus it would appear that in this case, the nature of the non-randomness would depend upon the separation of the scattering elements.

Similar phenomona, not described in detail here, have been observed for cholesteryl palmitate and stearate. It appears that the light scattering patterns are often a more sensitive test of correlated orientation than the appearance of structure with a polarizing microscope. For example, with cholesteryl palmitate, one can obtain a typical $I_\perp$ type pattern in the cholesteric state when no microscopic structure can be detected.

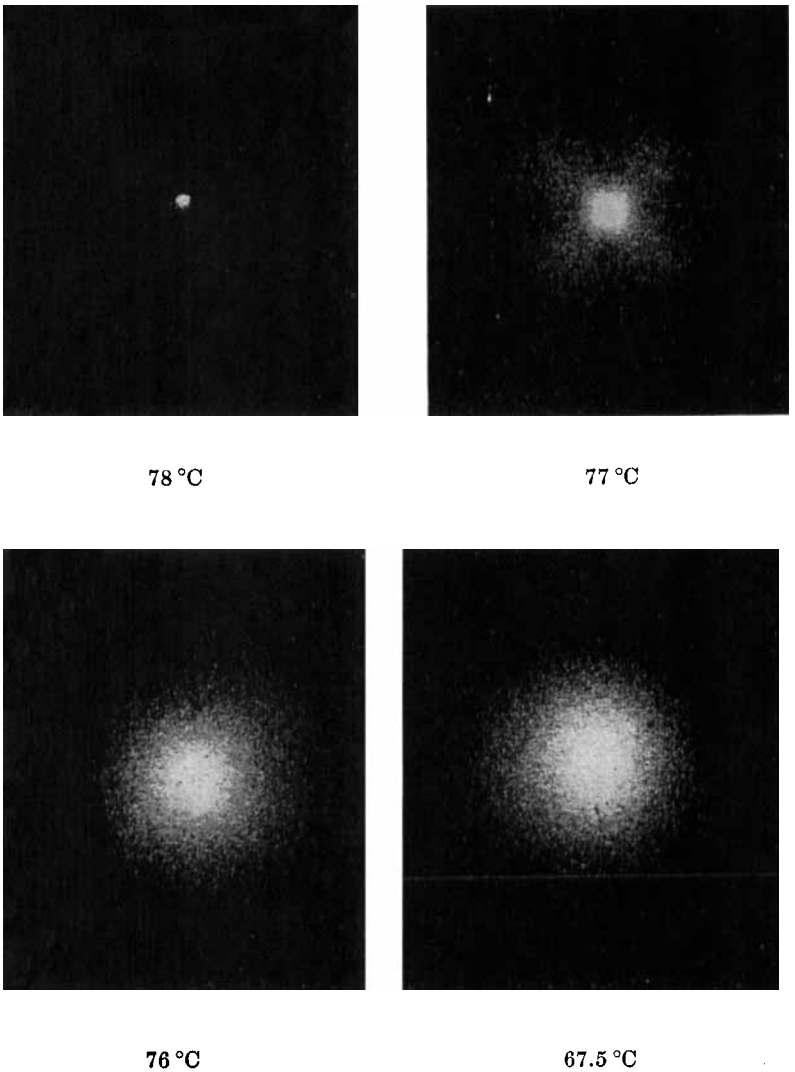
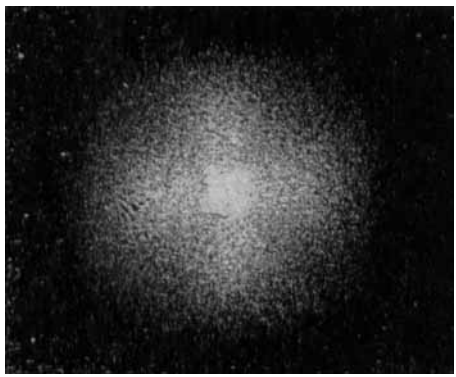


Figure 8. The variation in $I_{\perp}$ light scattering patterns during the slow cooling of cholesteryl stearate from the isotropic melt.

(*a*)



(*b*)

Figure 9. Light scattering patterns obtained from cholesteryl propionate in the cholesteric state using (*a*) parallel and (*b*) crossed polarization.

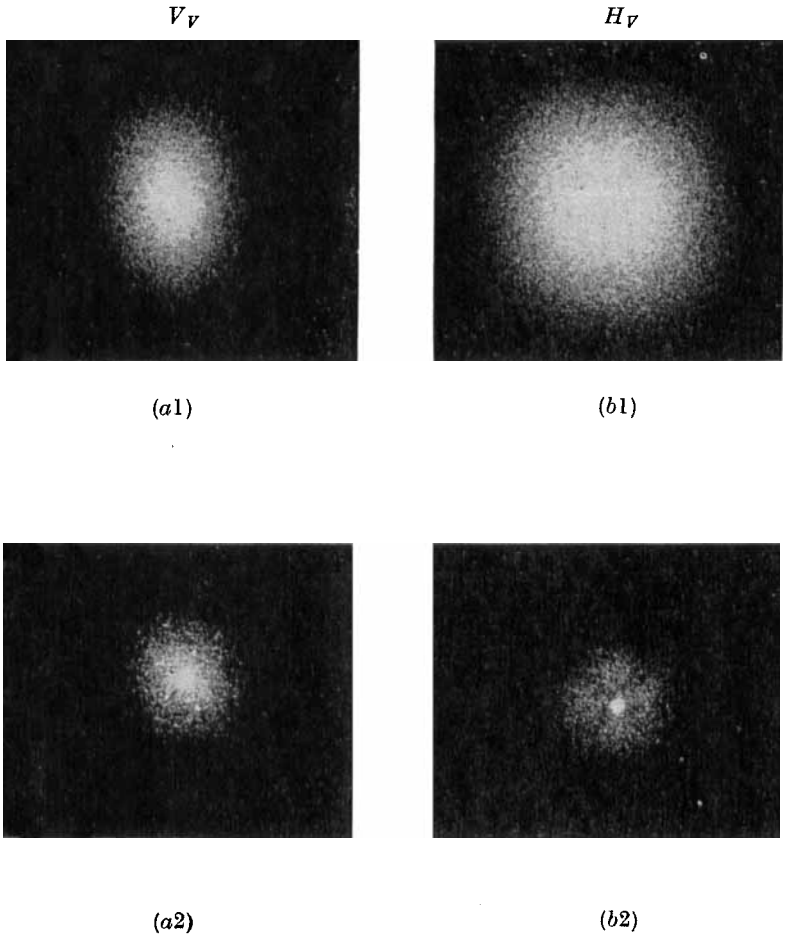


Figure 10. Two types of light scattering patterns obtained for cholesteryl palmitate using (*a*) parallel and (*b*) crossed polarization.

It is apparent from these studies that much interesting information may be acquired from light scattering observations. Quantitative characterization is best carried out from photometric measurements as illustrated in a following paper.

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