CHAPTER 9

CHAPTER 9

Optical effects from spherulites of polyethylene

9.1 Introduction

It has been known for a long time that many polymers like polyethylene, polytrimethylene glutarate and others exhibit spherulite textures with a ring structure. The literature connected with this subject is rather extensive and hence, only a selected list of publications (wherein exhaustive references may be found) are given here [1-10]. A spherulite texture arises when there is a radial growth about a centre of nucleation. The molecular ordering is usually such that the principal vibration directions in the spherulite correspond to the radial directions and the directions transverse thereto. Therefore, a spherulite when observed under the polarizing microscope between crossed polars exihibits the characteristic Maltese-cross similar to the uniaxial figure, the mutually perpendicular directions of the isogyres (extinctions) corresponding to the vibration directions of the polarizer and anlyser. The ring structure is usually attributed to a periodic variation of the refractive index, which in effect involves a periodic variation of the optical thickness. The ring structure arises as a consequence of the lens-like focussing effect associated with the periodically varying optical thickeness along every radial direction. The optical behaviour of ringed spherulites had been discussed by Krishnamurti et.al., [11,12] in connection with the case of spherulites observed with cholesteric liquid crystals and their mixtures. On the basis of the observed low angle light scattering patterns in the case of ringed spherulites of polyethylene Stein and Rhodes [2] have inferred that there is periodicity in the tangential component of the polarizability of the ringed spherulites, the radial component of which is constant. In the present study, using two different interference techniques we have reexamined the optical effects of spherulites in polyethylene.

9.2 Experimental results and discussion

(i) Ringed spherulite textures and ring spacing

Commercially available samples of (i) low density, (ii) linear low density and (iii) high density polyethylene have been used by us in our studies. The refractive index for λ 5893 Å and density of these samples were measured using the well-known hollow prism and floatation techniques and are presented in Table 9.1. For optical observations the specimen was prepared by sandwiching the sample between microscope glass slide and cover glass. The setting points of the three polyethylene samples were determined by slowly cooling the samples from their molten state on a hot stage (described in Chapter-2) till the first traces of crystallinity, as evidenced by the birefringence, begin to appear between the crossed polars. These values are also presented in Table 9.1.

Table 9.1 Refractive indices, Densities and Setting points of polyethylene samples

Samples	Refractive index *n*	Density (g.cm^{-3})	Setting points (°C)
Low density polyethylene (LDPE)	1.453	0.917	105
Linear low density polyethylene (LLDPE)	1.473	0.926	123
High density polyethylene (HDPE)	1.494	0.950	126

The thin regions of the solidified film near the periphery often exhibited striking optical textures characteristic of the spherulites, when observed with a polarizing microscope. Figure 9.1a shows the texture typical of ringed spherulites. Unlike in cholesteryl compounds and their mixtures where the rings are of reasonably uniform spacing, in the case of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) samples, the spacing of the rings is large and non-uniform near the centre of the spherulites and away from the centre

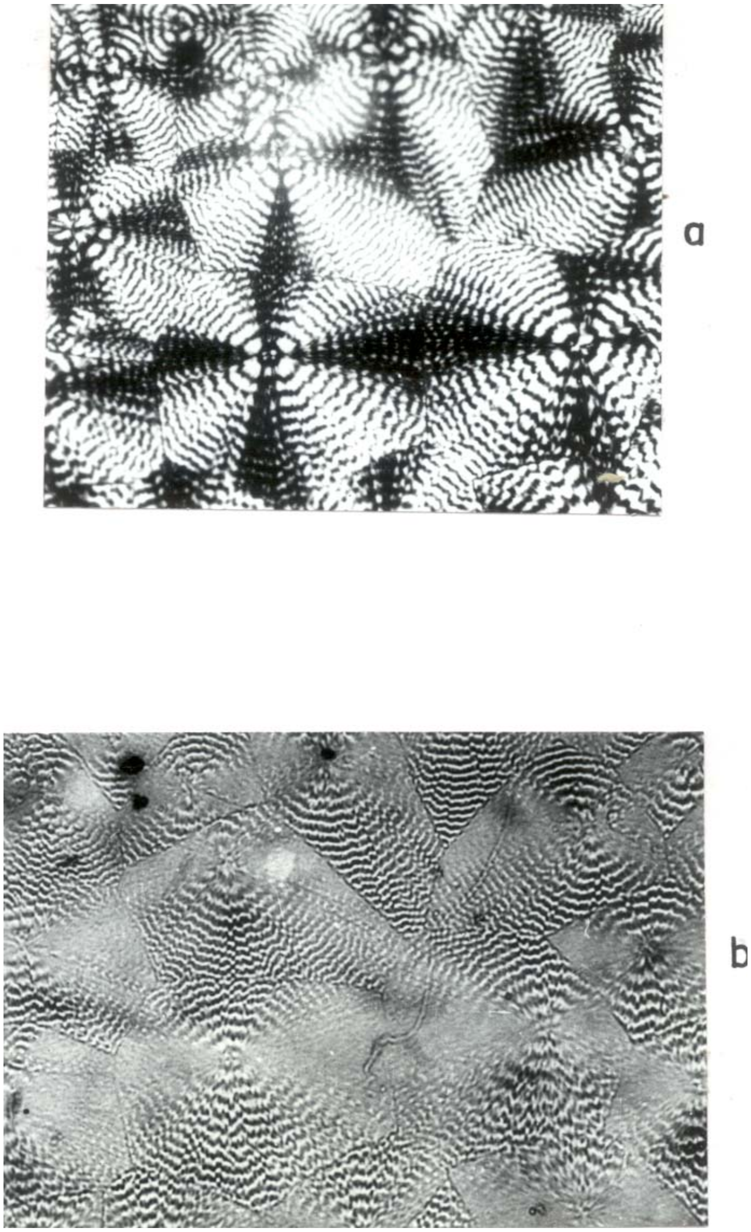


Figure 9.1: Microphotographs of the ringed spherulite texture of high density polyethylene; ring spacing 6 μm.

(a) Specimen between crossed polars

(b) Using plane polarised incident light, the vibration direction being along the horizontal.

a uniform spacing of the ring structure is observed. This is due to the fact that initially when the specimen is suddenly brought to the crystallization temperature from the molten phase, it takes some time to attain this temperature. Here, the crystallization temperature is the temperature at which the ringed spherulites were grown by suddenly cooling the sample from its molten state to any desired temperature below the setting point. Further, the spacing of the ring structure is observed to be a function of the crystallization temperature. This is confirmed by growing the spherulites at different crystallization temperatures. It was found that the ring spacing changes from 2 μm to 15 μm for a change of crystallization temperature from 25° to 125°C. It may be mentioned here that the low density polyethylene sample exhibits the spherulite texture of very small ring spacing and hence we have not carried out any detailed investigation on the spherulites of this sample.

If the principal optical direction transverse to the radial direction rotates in a helicoidal fashion, the periodic variation of the refractive index (for propagation of light normal to the spherulite film) arises only for light polarized with its electric vector transverse to the radial direction. Per contra, for light polarized with its vibration direction along any radial direction, the ringed structure is absent along that particular radial direction. For example, when the incident light is plane polarized with its vibration direction along the horizontal, the ringed structure is hardly visible along the horizontal diameter as may be seen from Figure 9.1b.

(ii) Optical diffraction

Assuming that the ringed spherulites behave as phase gratings Keith and Padden [1] have discussed the theory of optical behaviour of the ringed spherulites in polyethylene to account for their experimental observation. Such phase gratings give rise to optical diffraction which is a consequence of the periodic variation of the refractive index, for light polarized transverse to the radial direction. Since the periodic variation of refractive index is absent for light polarized along any radial direction, the diffraction effect should be absent at points corresponding to the radius along which the incident light is polarized. Figure 9.2a shows the

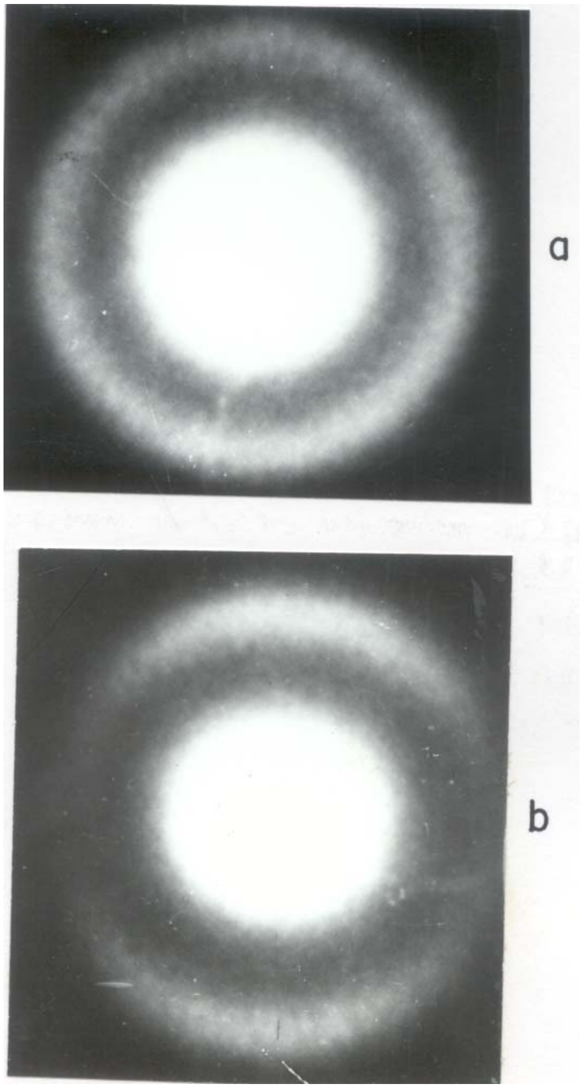


Figure 9.2: Diffraction patterns obtained with the ringed spherulite texture of high density polyethylene using light of wavelength 5461 Å

(a) with unpolarised light and

(b) with plane polarised light, the vibration direction being along the horizontal.

diffraction ring photographed with un polarized light. The diffraction ring photographed with the incident light vibration along the horizontal direction is shown in Figure 9.2b and it may be noticed that the diffraction effect is absent along the horizontal direction. It may also be pointed out that the phase gratings here are not perfect in the sense that the dark rings are not narrow and the fibrils encroach irregularly upon the edges of these dark rings to some extent. Hence, this irregular phase grating gives only the diffused first order diffraction ring. The wrinkles observed in the ring structure also indicate that the orientations of the structural units in different regions are subject to fluctuations.

(iii) Experimental verification of the periodic variation of the refractive index

The series of methylene groups in polyethylene forms long continuous chain lying normal to the crystalline lamellae in which the local optic axes correspond to the normals to the lamellae. Evidently, for light polarized along the longitudinal direction of the chains the refractive index will be higher than the index for light polarized along directions transverse to the chains. Under these circumstances, where the ribbon-like lamellae along the different radial directions undergo twist like deformations about the radial axes, the longitudinal directions of the chains (optic axis) would rotate, and along the different points of the radial direction there will arise a periodic variation of the refractive index for light polarized with its vibration direction transverse to the radial direction. This is the view proposed for the origin of the optical effects of the ring structure in polymers [4,13]. However, direct experiments do not appear to have been carried out till now, to verify the periodic variation of the refractive index referred to above in the case of polymers. In this connection it may be mentioned that Stein and Rhodes [2] from their studies on low angle optical scattering, in the case of ringed spherulites of polyethylene, have shown that there is a periodicity in the tangential component of the polarizability of the ringed spherulites, the radial component of which is constant. In the following, with the aid of an interference experiment we have confirmed this result by showing that the refractive index is indeed variable continuously and in a periodic fashion. In the case of spherulites of cholesteric compounds and their mixtures, the periodic variation of the refractive index was confirmed unambiguously by Krishnamurti *et al.,* [12] with the aid of an elegant interference experiment. The same technique has been adopted in the present investigations. Only a brief account of the experimental technique is given here. It is well-known that when a birefringent crystal (with its principal directions horizontal and vertical) is kept between crossed polars at 45° to the vertical, white light transmitted through the combination produces a spectrum showing a series of extinctions at different wavelengths. In fact, such a phenomenon cannot be observed here with the spherulites alone, because the specimens are too thin to give rise to significantly large phase difference. Therefore, a modified experimental arrangement shown in Figure 9.3 was used. The experimental set-up essentially consisted of a tungsten ftlament lamp *S*, followed sequentially by a condensing lens L, a polarizer P, cleaved plate of a crystal of barite ($BaS0_4$) B, the spherulite sample SS, a microscope T M which focuses the enlarged image of the spherulite (magnified about 50 times) on the slit of the spectrograph SP, an analyzer A. The polarizer and analyser are crossed, their vibration directions being at 45° to the horizontal and vertical. The suitable " apertures D, D are introduced in the path of the beam in order to secure the depth of focus of the enlarged image formed on the slit of the spectrograph. The cleavage plate of a crystal of barite was oriented normal to the incident beam with the principal vibration directions along the vertical and horizontal, the refractive index corresponding to the horizontal direction being greater than the index corresponding to the vertical direction.

In the absence of the spherulite the vertical dark bands are observed in the spectrum at different wavelengths (Figure 9.4a), which satisfy the equation [14],

$$m\lambda = t_1 \Delta n_1 (\lambda) \qquad (9.1)$$

where m is an integer and, t_l and Δn_l (λ) correspond respectively to the thickness and the birefringence of the barite crystal, for the horizontal and vertically polarized components passing through it. Let us consider a particular dark band of given m, at $\lambda = \lambda_o$ so that,

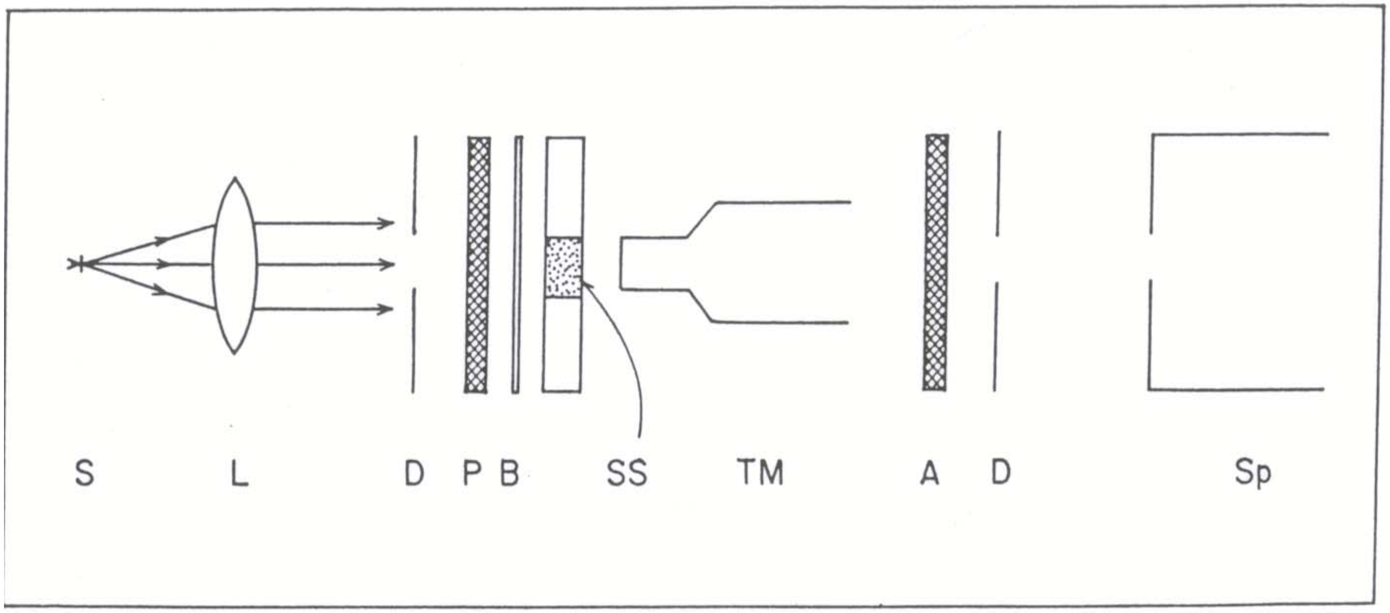


Figure 9.3: Plan view of the experimental arrangement used to study the birefringence of the spherulite sample.

$$m\lambda_o = t_1\, \Delta n_1\, (\lambda_o) \qquad (9.2)$$

If a spherulite is interposed in juxtaposition with the barite an additional path difference arises and the extinctions shift their positions and satisfy an equation of the form,

$$m\lambda = t_1\, \Delta n_1\, (\lambda) \pm t_2\, \Delta n_2\, (\lambda) \qquad (9.3)$$

where λ is the wavelength corresponding to the extinction, t_2 is the thickness of the spherulite sample and Δn_2 is the birefringence associated with the spherulite. The positive sign applies when the fast direction of the spherulite coincides with the fast direction of the crystal, and the negative sign when the slow direction of the spherulite coincides with fast direction of the crystal. Since the phase difference introduced by the spherulite is usually less than 2π, m will have the same value and $(\lambda\text{-}\lambda_o)$ is small. In the "above we have not explicitly considered the dispersion of birefringence in the region $(\lambda\text{-}\lambda_o)$ but have assumed that $t_1\, \Delta n_1\, (\lambda) = m\lambda_o$ and $t_2\, \Delta n_2\, (\lambda) = t_2\, \Delta n_2\, (\lambda_o)$ Hence for a given *m,*

$$m(\lambda\text{-}\lambda_o) = t_2\, \Delta n_2 \qquad (9.4)$$

It is evident from this equation that when the spherulite is mounted such that its diameter is along the slit of the spectrograph, owing to the periodic variation of the refractive index for light polarised transverse to the diameter, Δn_2 varies from zero to a maximum and hence the wavelength at which the extinction occurs, changes from λ_o to λ. When the fast direction of the crystal coincides with the fast direction of the spherulite, it is evident that λ is greater than λ_o and hence the extinction should shift towards the red region of the spectrum. Figure 9.4b exhibits the periodic shift of extinctions towards the red.

From measurements of the extinctions, the birefringence associated with the polyethylene spherulites can be determined if the value of m corresponding to each band is known. The following procedure was adopted to estimate the value of *m* of bands.

From equation 9.1, it may be written that

$$m\lambda = \text{constant} = \text{c} \tag{9.5}$$

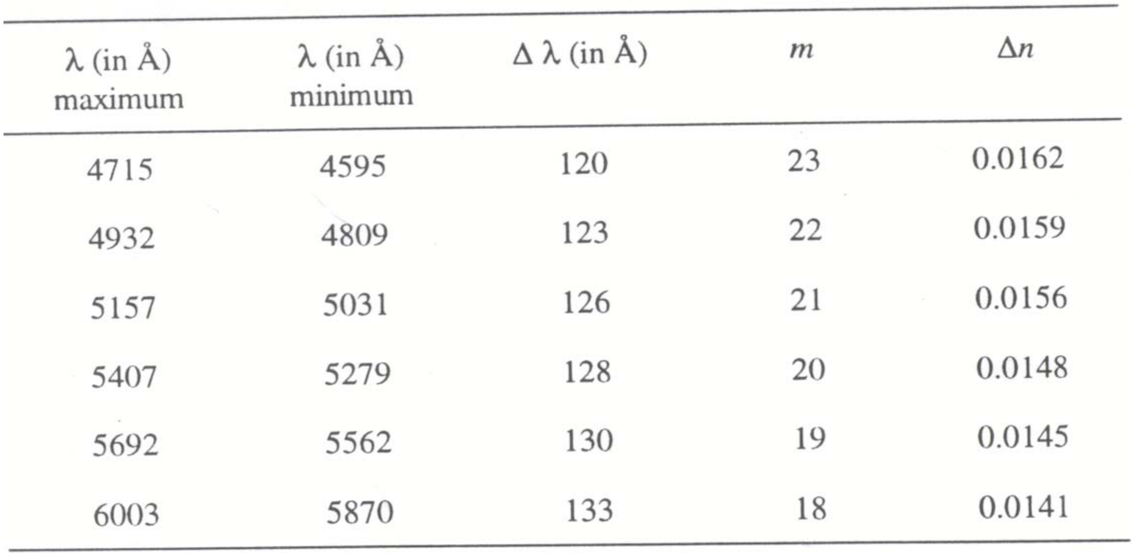
$$\textit{i.e.,}\ \log m - \log\left(\frac{1}{\lambda}\right) = \log \text{c} \tag{9.6}$$

By preparing a chart of $\log\left(\frac{1}{\lambda}\right)$ with the measured value of λ of the bands, and matching it with another chart of log m (drawn to the same scale for various integral values of m) it was possible to obtain uniquely coincidences between and $\log\left(\frac{1}{\lambda}\right)$ for all the bands in the region of the spectrum. Hence, the value of m for each band was ascertained unambiguously. Assuming the same values of m for the corresponding bands shown in Figure 9.4b and using the measured values of λ the birefringence of the sphrulite was calculated. Tables 9.2 and 9.3 give the calculated values of Δn_2 of the spherulites of HDPE and LLDPE crystallized at room temperature, at several wavelengths.

Table 9.2 Birefringence of low density polyethylene ($t_2 = 20\ \mu$m)

λ (in Å) maximum	λ (in Å) minimum	$\Delta\ \lambda$ (in Å)	m	Δn
5967	5845	122	18	0.0109
5658	5537	121	19	0.0115
5374	5254	120	20	0.0120
5124	5006	118	21	0.0124
4900	4784	116	22	0.0128
4684	4570	114	23	0.0129

Table 9.3 Birefringence of high density polyethylene (t_2 = 17 μm)



λ (in Å) maximum	λ (in Å) minimum	Δ λ (in Å)	*m*	Δ*n*
4715	4595	120	23	0.0162
4932	4809	123	22	0.0159
5157	5031	126	21	0.0156
5407	5279	128	20	0.0148
5692	5562	130	19	0.0145
6003	5870	133	18	0.0141

It may be seen from Tables 9.2 and 9.3 that the birefringence of the polyethylene spherulites is found to be positive and has a value of 0.014 in the case of HDPE and 0.011 in the case of LLDPE, for λ 5893 Å. These values are of the same order of magnitude as what one would expect from considerations of the anisotropy of the bond polarizabilities associated with the C-C bonds in the polyethylene chain. Measurements were also made with the spherulites crystallized at higher temperatures i.e., with the spherulites of larger ring spacing. The measured values of Δn_2, both in the case of LLDPE and HDPE samples, are found to decrease with crystallization temperature.

In the same fashion, the phase difference which arises between the two principal vibrations for light passing normally through the spherulite, may be experimentally determined using the Babinet compensator. The interference fringes in the Babinet compensator should also exhibit the periodic shift and this has been confirmed in the case of spherulites of cholesteric compounds [12]. It is observed that the spherulites of polyethylene and other polymeric materials also give rise to interference fringes which exhibit the periodic shift as shown in Figure 9.5.

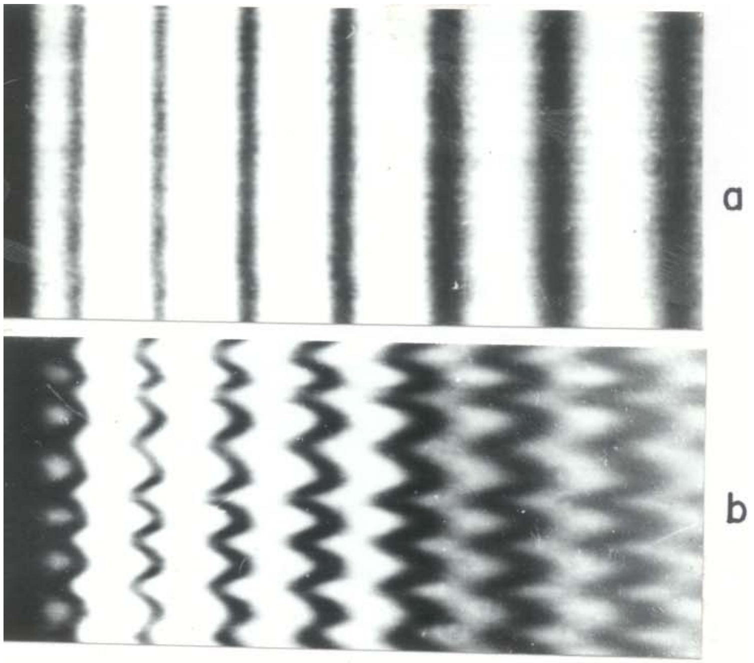


Figure 9.4: (a) Banded spectrum obtained with a crystal of $BaSO_4$ ($t = 0.1$ cm) kept between crossed polars. The left end corresponds to the red region of the spectrum.

(b) Banded spectrum showing the periodic shift of the extinctions observed with a ringed spherulite of high density polyethylene.

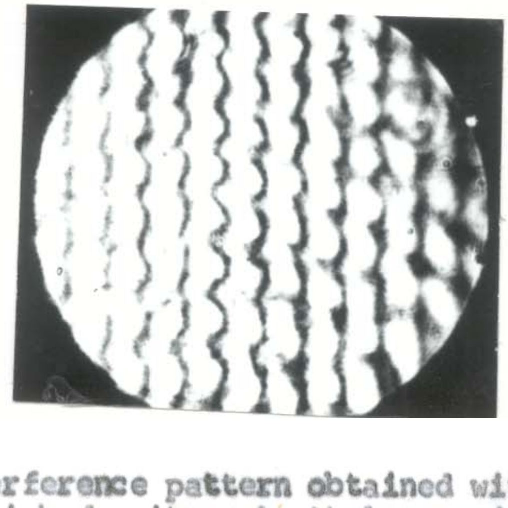


Figure 9.5: Interference pattern obtained with a spherulite of high density polyethylene using the Babinet compensator and with radiations of λ 5893 Å.

These facts confirm that the refractive index is indeed variable continuously and in a periodic fashion. The observed periodic variation of the refractive index in polymer spherulites is generally due to the periodic twist of the crystalline lamellae and this has been confirmed using electron microscope technique [6]. Since there are various factors like chemical bonding, molecular weight, density, thermal effects etc., which are responsible for this twisting, the particular cause is still not known.

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