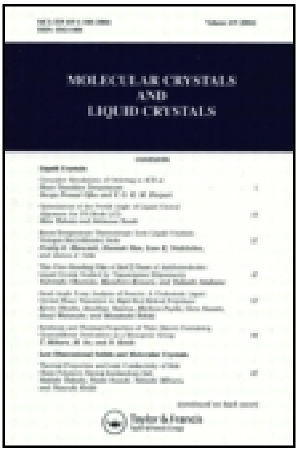


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Optical Effects from Spherulites in Polyethylene

D. Revannasiddaiah [a] , M. S. Madhava [a] , R. Somashekar [a] & S. R. Kumaraswamy [a]
[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, India
Version of record first published: 24 Sep 2006.

To cite this article: D. Revannasiddaiah , M. S. Madhava , R. Somashekar & S. R. Kumaraswamy (1993): Optical Effects from Spherulites in Polyethylene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 217-221

To link to this article: http://dx.doi.org/10.1080/10587259308030137

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 217–221
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Optical Effects from Spherulites in Polyethylene

D. REVANNASIDDAIAH, M. S. MADHAVA, R. SOMASHEKAR and S. R. KUMARASWAMY

Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India

(Received December 12, 1991; in final form November 18, 1992)

The spherulites exhibited by polyethylene samples have an associated ring structure which gives rise to diffraction and other optical effects which are attributed to a periodic variation of the refractive index of the spherulites for light polarized transverse to the radial direction. The periodic and continuous variation of the refractive index is confirmed from sensitive interference experiments. The optical phenomena are illustrated with striking photographs.

Keywords: spherulite, polyethylene, birefringence, interference, phase grating

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.[1–7] The optical behaviour of ringed spherulites in the case of cholesteric liquid crystals has been discussed by us.[8–9] The ring structure is usually attributed to a periodic variation of the refractive index which in effect involves periodic variation of optical thickness. 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 a periodicity in the tangential component of the polarizability of the ringed spherulites, the radial component of which is constant. Presently, using the interference techniques we have not only been able to confirm the results of Stein and Rhodes but also estimated the birefringence.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Commercially available samples of polyethylene (low density, linear low density and high density) have been used by us in our studies. The samples used for optical observations were prepared on a microscope glass side, and had a thickness of about 50 μm. The thin regions of solidified film near the periphery often exhibited striking optical textures characteristic of the spherulites, when observed with a polarising microscope. Figure 1 exhibits the texture typical of ringed spherulites. Unlike in cholesteric compounds where the rings are of uniform spacing, in the case of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) samples the spacing of the rings is large near the centre of the spherulites and away from the centre a uniform spacing of 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. 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 rings 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 with ring structure of very small ring spacing and hence we have not carried out any detailed investigation on 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

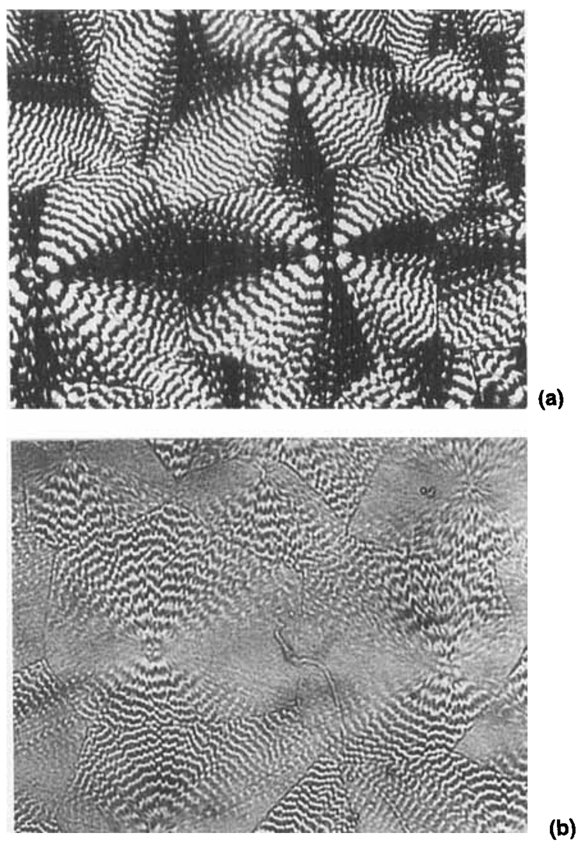
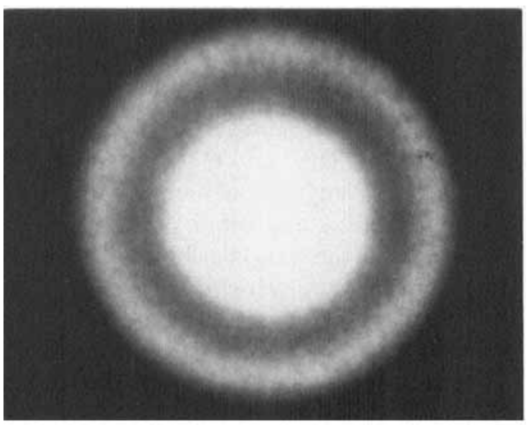


FIGURE 1 Microphotograph of the ringed spherulite texture of high density polyethylene; ring spacing 6 μm, (a) using unpolarized white light and (b) using plane polarized white light, the vibration direction being along the horizontal.

of light normal to the spherulite film) arises only for light polarised with its electric vector transverse to the radial direction. Per contra, for light polarised with its vibration direction along the radius there should be no periodic variation of the refractive index and hence there will be no lense like focusing effect. Therefore, when the incident light is polarised with its vibration direction along any radial direction, the ringed structure is absent along that particular radial direction (see Figure 1(b)).

Assuming that the ringed spherulites behave as phase gratings Keith and Padden[1] have discussed the theory of optical behaviour of the rings in polyethylene to account for their experimental observations. Such phase gratings give rise to optical diffraction which is a consequence of the periodic variation of the refractive index for light polarised transverse to the radial direction. Since the periodic variation of the refractive index is absent for light polarised along any radial direction, the diffraction effect should be absent at points corresponding to the radius along which the incident light is polarised. Figure 2(a) exhibits the diffraction ring photographed


(a)

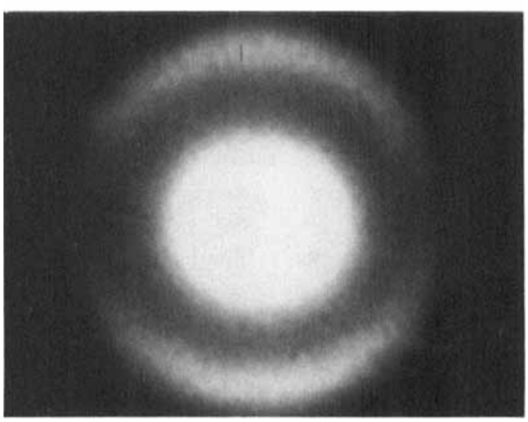

(b)

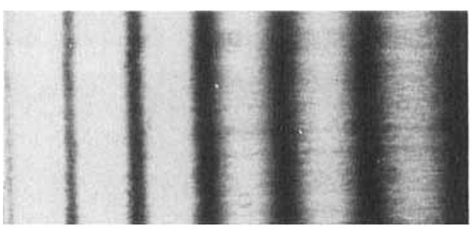
FIGURE 2 Diffraction pattern obtained with the ringed spherulite texture of high density polyethylene using light of wavelength 5461 Å, (a) with unpolarized light and (b) with plane polarized light, the vibration direction being along the horizontal.

with unpolarised light. Figure 2(b) was photographed with the incident light vibration along the horizontal direction 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.

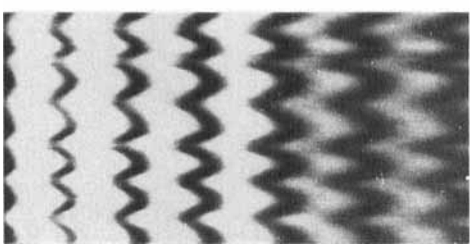
Stein and Rhodes,[2] using low angle light scattering technique, have shown that the principal optical directions in the case of spherulites of polyethylene correspond to the radial direction and the direction transverse to the radial direction. We have reconfirmed this result with the aid of an interference experiment, the details of which are given in an earlier paper.[9] Here, we reproduce the observed interference pattern using ringed spherulites in Figure 3.

From the measurements of the observed shift shown in Figure 3(b) the birefringence associated with polyethylene spherulites, crystallized at room temperature, is estimated and 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 polyethylene chains. Measurements were also made with the spherulites crystallized at higher temperatures i.e., with the spherulites of larger ring spacing. The measured value of Δn, both in the case of LLDPE and HDPE samples, is found to decrease with crystallization temperature. Using the Babinet compensator[9] it is also observed that the spherulites of polyethylene and other polymeric materials give rise to interference fringes which exhibit the periodic shift.

All the above facts confirm that the refractive index is indeed variable continuously and in a periodic fashion. The observed periodic variation of the refractive



(a)



(b)

FIGURE 3 (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 wth a ringed spherulite of high density polyethylene.

index in polymer spherulites is generally due to the periodic twist of the crystalline lamellae and this has been confirmed using electron microscope techniques.[4] 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.

Acknowledgment

One of us (SRK) is thankful to the University of Mysore, Mysore, for the award of University Post-graduate Fellowship.

References

1. H. D. Keith and F. J. Padden, *J. Polymer Sci.*, **31**, 415 (1958).
2. R. S. Stein and M. B. Rhodes, *J. Appl. Phys.*, **31**, 1873 (1960).
3. R. S. Stein, M. B. Rhodes and R. S. Porter, *J. Colloid and Interface Science*, **27**, 336 (1968).
4. F. W. Billmeyer, Jr., *Text Book of Polymer Science,* III Edn., John Wiley and Sons, Inc., New York, 281 (1984).
5. D. R. Uhlmann and A. G. Kolbeck, *Scientific American*, **233**(6), 100 (1975).
6. R. A. Chivers, P. J. Barham, J. Martinez-Salazar and A. Keller, *J. Polymer Sci.*, **20**, 1717 (1982).
7. G. Chiu, R. G. Alamo and L. Mandelkern, *J. Polymer Sci.*, **28**, 1207 (1990).
8. D. Revannasiddaiah, M. S. Madhava and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **39**, 87 (1977).
9. D. Krishnamurti, M. S. Madhava and D. Revannasiddaiah, *Mol. Cryst. Liq. Cryst.*, **47**, 155 (1978).
10. W. A. Wooster and A. Breton, *Experimental Crystal Physics*, Clarendon Press, Oxford 13 (1970).