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Title Page

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1. Introduction

Crystallization in polymers is a complex process. There are many polymers that crystallize, and many other that do not. Crystallization occurs only when the temperature is below the polymer's spontaneous melting point. However, the temperature must be high enough to prevent inhibition of molecular movement. The molecules must have a sufficient degree of freedom to achieve the conformation needed to attach to the crystallizing chain. Most crystallizing polymers have a regular and simple structure that repeat as organized units called 'mers'. These polymers are unlikely to have a huge amount of branching and intertwining.

The rate of crystallization is affected by the rate of crystal nucleation and the rate of crystal propagation. In order to create highly crystalline polymers, the rate of crystal nucleation needs to be small, while the rate of crystal propagation needs to be high. The temperature of the molecules also plays a critical role in uniform crystallization. Polymers which are exposed to great temperature variations undergo crystallization at different rates and in different manners. This usually leads to different crystal phases and morphologies within the same polymeric solid.

The purpose of this experiment is to familiarize ourselves with the use and application of a polarized light microscope. Polarized light microscopy (PLM) is a widely used method for investigating materials, their crystal structures and their performance properties. Although one could use Fourier Transform Infrared Microscopy (FTIM) or Scanning Electron Microscopy for the same task, the optical microscope will help us quickly identify and study spherulites in semi-crystalline polymers in a relatively inexpensive manner. In doing this, we take advantage of the difference in birefringence between the crystal lamellae and the non-crystalline regions of the polymer. In addition, the crystalline lamellae often orient themselves in different arrangements as they grow radially outward in all directions from the spherulite center. This gives rise to an effect commonly known as the Maltese cross effect, or 'extinction cross' when observed under polarized light. [6]

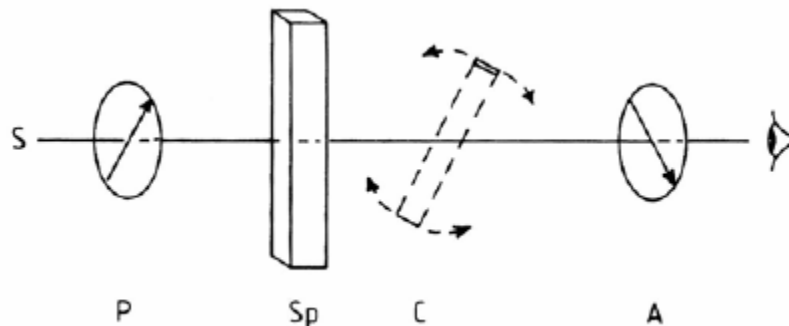


Figure 1 Schematic of a PLM Apparatus

The detailed mechanism and working of a polarizable microscope is outside the scope of this introduction.

2. Materials and Equipment

1. Olympus BX51 upright microscope
2. Polyethylene (PE) samples
 - i. Stretched PE with paralleled orientation
 - ii. Commercial high density PE (HDPE)
 - iii. Metallocene PE 1 (linear PE)
 - iv. Metallocene PE 2 (branched PE)
 - v. Polyethylene-clay nanocomposite based on iv.
3. Data acquisition software
4. Image processing software

3. Procedure

Originally, the procedure was to first form the samples under different conditions to achieve different specimens for analysis with the help of the PLM. We later found that this was not possible within the allotted 3-hour time-frame, so a new procedure was devised as follows.

We first familiarized ourselves with the controls and settings of the Olympus BX51 Upright Microscope. We began our observations at a 20X magnification with sample #1: semi-crystalline polymer film prepared by a melt crystallization technique. We first adjusted the brightness so that we could clearly see the sample's crystalline regions when viewed using the polarizer. This was evident when the sample looked dark except for the crystalline regions. We then moved the sample until we found a representative region and increased magnification to 50X to capture and measure the spherulite diameters using the software. This process was repeated with the other samples (#2: Commercial HDPE, #3: Metallocene PE 1, linear, #4: Metallocene PE 2, branched, and #5: Polyethylene-Clay Nanocomposite based on #4).

It must also be noted that samples 2, 4 and 5 were investigated under transmitted light, whereas samples 1 and 3 were investigated under reflected light. The reason for this being that samples 1 and 3 were too thick for any amount of appreciable light to pass through.

4. Results

The computer-aided data acquisition system provided us with snapshot photographs that we could later analyze. We then used a software program to measure crystal widths and

spherulite radii. The results are tabulated below. A legend for the slide numbers, along with their descriptions, is given in Table 2.

	Crystal #	Diameter (μm)					Average
Slide 1 (low res)	1	3.745	2.774				3.2595
Slide 1 (low res)	2	1.942	1.664				1.803
Slide 1 (high res)	3	20.906	19.512	19.861			20.093
Slide 2 (high res)	1	10.326	12.686	12.04			11.684
Slide 3 (high res)	1	24.69	28.128	22.024			24.95
Slide 3 (high res)	2	19.788	20.588	22.362	27.916		22.664
Slide 4 (high res)	1	9.284	16.232				12.758
Slide 5 (high res)	1	27.875	20.353	18.118	29.821	26.023	24.438
Slide 5 (high res)	2	11.532	9.482	14.379	10.348		11.43525
Slide 5 (high res)	clay	139.723					139.723

Table 1 Crystal Dimensions

Slide #	Description
1	Stretched PE with paralleled orientation
2	Commercial high density PE (HDPE)
3	Metallocene PE 1 (linear PE)
4	Metallocene PE 2 (branched PE)
5	Polyethylene-clay nanocomposite based on #4

Table 2 Slide Descriptions

It is clear from Table 1 that the average diameter of spherulites in sample slide #3 is much higher than that of the sample slide #4 (almost twice). We thus conclude that linear PE has much larger spherulites than branched PE. An explanation for this observation is provided in the following discussion.

5. Discussion

1. *What different morphologies have you observed with each sample? Show the images.*

Morphology is the relative size and shape of phases. Each material in our experiment had a different morphology. Sample 1 had elongated polymer chains. In the picture we see three dark lines which may be due to the differences in depth of the material on either side of the lines.



Figure 2 Sample 1 Images

The second picture shows a region of highly crystalline material.

For sample 2, it was observed that spherulites were embedded in each other and not fully grown which is an indication that crystallization started from many different points. The picture shows two different phases with the spherulites in the middle phase.



Figure 3 Sample 2 Image

Sample 3 had many spherulites in its structure which did not inhibit the growth of neighbouring spherulites. This is evident from the measured diameters of samples 2 and 3 (Documented in Table 1). Diameters of spherulites in sample 3 are nearly twice the diameters observed for sample 2. Note that the picture shows only one phase.

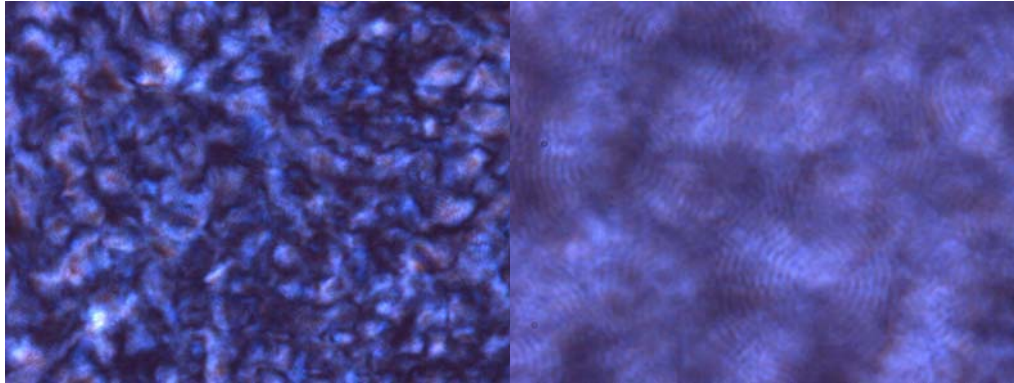


Figure 4 Sample 3 Images

Sample 4, being branched polyethylene, is difficult to crystallize; consequently, few spherulites were seen in its structure. The picture shows two different phases.

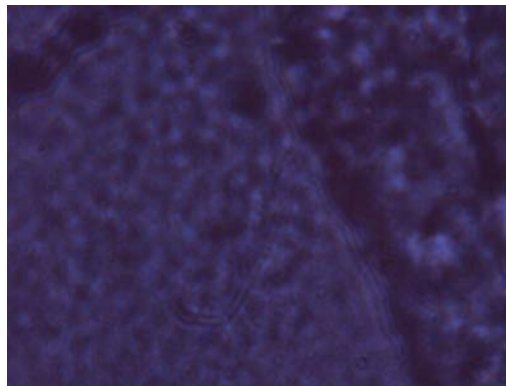


Figure 5 Sample 4 Image

The pictures for sample 5 show a huge clay particle whose diameter is nearly fifteen times the diameters of the spherulites in the structure. The clay composite can change the electrical resistance, optical behaviour and the melting point of the structure.

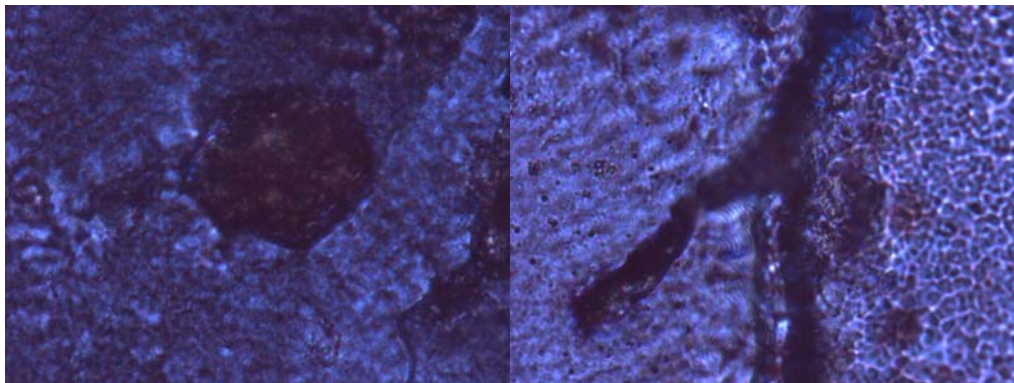


Figure 6 Sample 5 Images

2. *What is the difference between linear PE and branched PE? Provide images to support your explanation.*

Linear and branched are two ways polymer chains are observed in polyethylene (PE). Branching occurs when a very long polymer chain twists and turns (in the nucleation process) and eventually bonds with itself. While uncoiling or during rearrangements in the chain, this connection snaps, leaving a branch at the main polymer backbone.

A linear polymer is quite different as it does not have branching. The phenomenon of branching can create many variations in the properties of the polymer. Hence it is easier to analyze linear PE. Through our analysis of linear polyethylene, it was noticed that linear polyethylene was more ordered and organized than the branched polyethylene. Linear PE has noticeable spherulites that can be observed using the PLM and measured using the software available to us, whereas the Branched PE has no formations of spherulites. With branching, there is a lesser scope for overlapping, folding and the formation of lamellae. Branched polyethylene is more hindering, and disallows the overlap of polymeric structures, restricting the formation of spherulites and lamellae. Also, crystalline structures are of far larger concentration and are more defined in the linear polyethylene when compared to the branched polyethylene.

When we observed the samples, this held true, to an extent. We saw an abundance of spherulites characteristic of the linear PE, but we also saw two spherulite-like regions in the branched sample as well; yet, they were unclear, so it may be said that they are not in fact spherulites but rather irregularities in the structure of the polymer.

(Images on page 8)

3. *What is the difference between Homo PE and Composite PE?*

Homogeneous polyethylene is made of only one type of monomer. Composite polyethylene has clay or other particles or fibers in the dispersed phase. They can also have non-uniformly repeating units of varying monomers. The phase separation is very clear for composite polyethylene while not for homogeneous polyethylene.

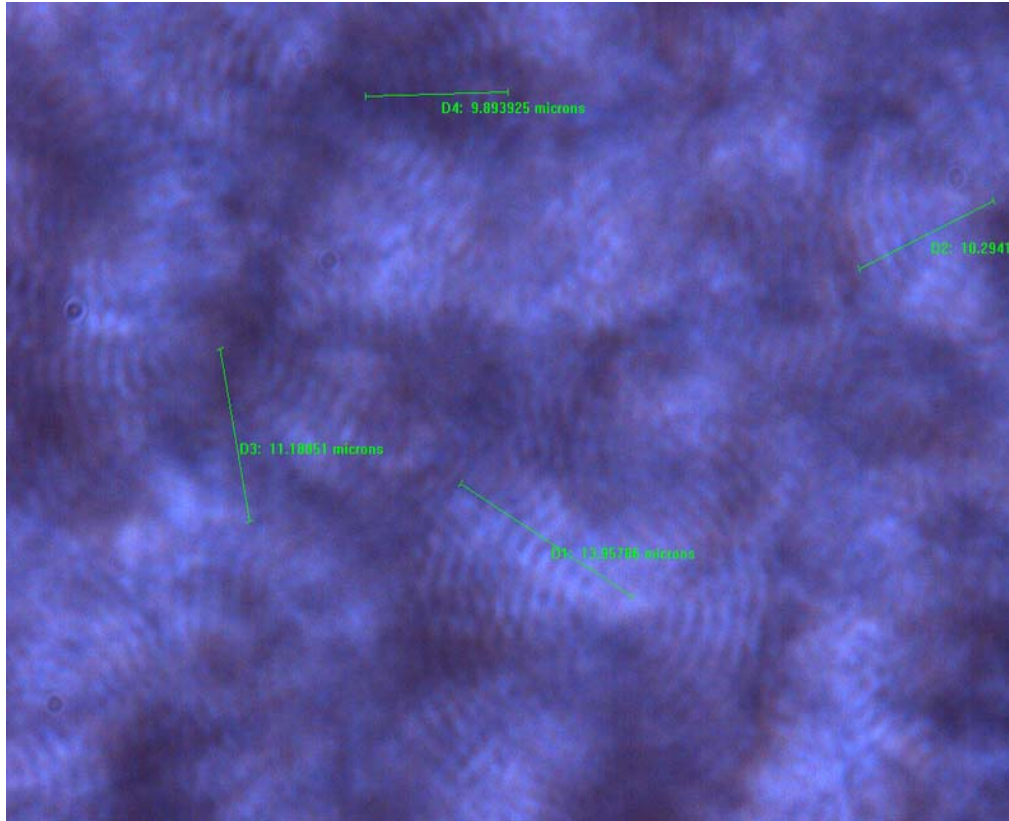


Figure 7 Linear Metallocene Polyethylene

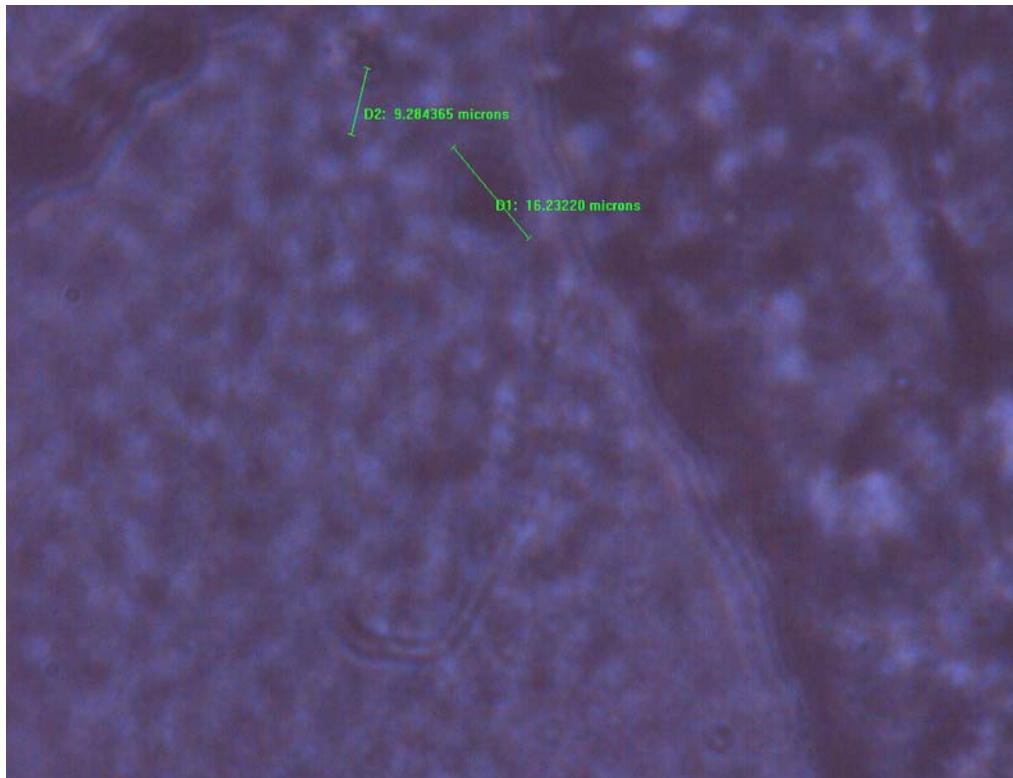


Figure 8 Branched Metallocene Polyethylene

6. Conclusion

From the above results and following discussion, we have seen how to use a polarized light microscope to examine the crystal domains and spherulites within a polymer. We studied different crystal morphologies and related this to the physical dimensions of the spherulites observed under the microscope. We investigated the differences, both in morphology as well as in crystallite domains, between linear and branched polyethylene. We also co-related the diameter of a spherulite to the corresponding polymer's degree of linearity. We found that the more linear a polymer was, the greater the number of spherulites observed, which also had a larger diameter than branched polymers.

More results were apparent upon further examination. In the last part of our discussion, we looked at the basic difference between homogenous PE and composite PE. This proved useful in the analysis of the last sample – a clay nanocomposite. We found that the addition of clay nano-particles to the polymer significantly altered its morphology and average spherulite diameters.

Overall, the experiment was a success. We familiarized ourselves with the basic working and application of a polarized light microscope, including important concepts such as focus, brightness, magnification, transmittance and reflection. This helped reinforce our knowledge on polymer crystallites and also provided insight into how scientific experimentation and materials characterization was to be carried out.

7. Questions

1. *How are polymer chains able to form crystallites?*

Polymers form long macromolecular chains of a certain repeating unit with covalent bonds. The intermolecular forces that the polymer chains experience and the amount of degrees of freedom available within the molecules are responsible for the formation of the crystallites. An ideal example of this is displayed in the slow cooling of a polymer, where van der Waal's, hydrogen bonding, and dipole-dipole forces direct the formation of chains.

As a result of slow cooling of the polymer, an organized system of chains form and overlap onto each other in layers which are formed in an outward manner in all directions from a single point. These continuous stacks of polymer chains are held together by intermolecular forces and exhibit a sphere-like appearance. When the chains are long and branched, they might intertwine and possibly bond between themselves. This leads to a very coiled and looped topology. In this case, structures of the polymer get fixed in certain positions.

Sometimes, these chains also stack on top of each other forming repetitive structures. When a regular row of similar polymer units is formed, a relative

phase is created. This phase then can overlap similar phases, resulting in the formation of crystallites. These polymers may also grow into strands of lamellae, which pile, intertwine and twist together to form spherical crystals called spherulites that grow outward. Each different arrangement of a crystallite has its own topology and arrangement. Lamellae and spherulites are a consequence of an ordered nucleation of crystals. These factors contribute to crystalline structures as well as other morphologies and topologies of polymers.

2. Which distinctive shape is seen when observing a spherulite between crossed polars? Explain why this shape is seen?

The distinctive shape seen when observing a spherulite between cross polars is the Maltese cross, show in Figure 9. These are white regions with black extinction crosses.

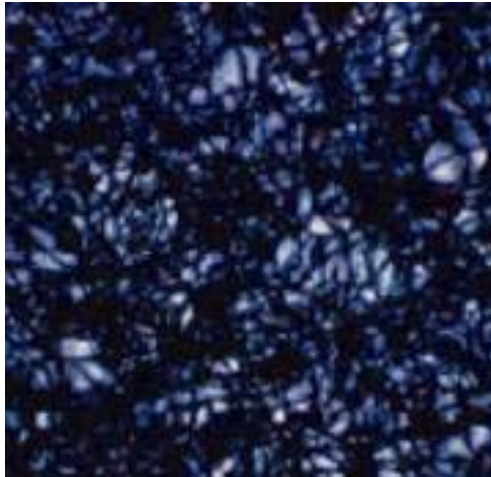


Figure 9 Maltese Cross Effect

(from <http://www.cheng.cam.ac.uk/research/groups/polymer/RMP/nitin/Maltesecross.jpg>)

When a polymer solidifies, the polymer chains reorganize to form a crystalline structure. In semicrystalline polymers especially, there is a difference in birefringence as there exists both crystalline lamellae as well as non-crystalline amorphous regions within the same polymer. As the spherulites are formed, the birefringent lamellae radiate outwards in all directions, taking on different orientations. This gives rise to the Maltese cross effect. This can be seen in crossed polars as white regions with black extinction crosses.

In standard polarized light microscopy, there are two polarizing filters: a) the polarizer, located on one side of the sample, and b) the analyzer, located on the opposite side of the sample. (See Figure 1 on page 2) The polarizer permits the plane of light that has its electric field oriented in the east-west direction. In contrast, the analyzer permits the plane of light with its electric field oriented in the north-south direction. Under these conditions all light is absorbed by the two polars, and the setup is known as a crossed polar setup. Introduction of any

anisotropic material (i.e., any polymer with amorphous regions) into the light path re-polarizes the light between the polars so as to generate interference colors and other effects visible in the eye-piece of the microscope as can be seen in Figure 9. This effect is consequently seen only between crossed polars but not under plane-polarized light.

3. *When increasing the magnification of the microscope, what phenomena will occur?*

The magnification of the microscope significantly affects what is viewed during polarized light microscopy. Increasing the magnification level (i.e. 20X to 100X) allows for the surface to be analyzed in a very different manner. First of all, an increased magnification requires the lens to be refocused on the object. It is important to know that any conclusions synthesized from this study are highly dependent on the magnification and focus settings.

When the magnification is about 20X, the whole surface can be scanned as a whole, with the help of the polarizer, to find general areas of crystallinity. Once the area is identified, the magnification can be increased to zoom into the area of interest. One phenomenon that might occur after this process is that the luminance on the object may change with the magnification. Depending on this, the aperture on the bottom of the microscope needs to be adjusted to allow appropriate amount of light to enter. Now, when the surface is zoomed in upon, the observer may need to readjust the location of the sample to perfectly view the area of interest, namely, crystallites. One may also need to refocus the lens as there may be different levels of depth (valleys) on the surface which may affect what is being seen.

At lower magnification levels, sizes and general areas of crystalline densities can be observed and at higher magnifications, the relative topologies and arrangements of the crystals can be seen.

4. *How should the initial focusing of the microscope be done?*

We first determine whether it is practical to view the sample with either transmitted or reflected light. In most cases, it is best to view thin samples using transmitted light, and the thicker samples using reflected light. We begin with the smallest magnification, i.e. 20X, and adjust the brightness such that when the polar lens is rotated, the crystalline regions are visibly brighter than the other amorphous regions. Once this is done, we focus the lens by rotating the knob on the side of the microscope; this adjusts the spacing between the lens and the sample itself, helping produce a clearer image on the readout. After this it is possible to move the sample horizontally to search for an ideal spot to investigate using the other knobs on the side of the microscope.

8. References

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