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The Temperature Dependence of Birefringence in Irradiated Polyethylene*

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In the past, this laboratory has studied the graft copolymerization of styrene to polyethylene initiated by radiation⁽¹⁾. Part of this work has involved microscopic examination of the grafts⁽¹⁾⁽²⁾. As an aid to understanding the observed phenomena, a preliminary investigation of the temperature dependence of birefringence in irradiated polyethylene was undertaken.

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Experimental

The polyethylene film used here had a density of 0.92 gm/cc, a thickness of 0.13 mm and it was lightly oriented due to processing. It was equivalent to the low density polymer used in our previous investigation, and like it, was not annealed prior to use.

The film was irradiated to the required dose at the rate of 0.51 M rad/hr in a Co^{60} source. Dose rate was determined by the Fricke technique.

The irradiation was performed in air at 25° C to conform to the 2b grafting condition of reference (1) and the type II grafting condition of reference (2). The specimen was placed in a Koeffler hot stage on a Leitz CMU polarizing microscope and heated at the rate of 0.75° C/min. Optical retardance was measured as a function

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of temperature using an elliptical compensator and a sodium vapor lamp as the light source. The melting point was taken as the temperature at which the birefringence disappeared (retardance = zero).

Results and Discussion

Figure 1 shows the retardance plotted as a function of temperature for an unirradiated specimen. The retardance at first increases slowly then drops. At 106° C there is a sharp rise to a peak at about 110° and then a precipitous drop to zero at 113° C. This retardance "spike" was reproducible in all unirradiated specimens but it was completely absent in specimens given a radiation dose of 25 M rad.

On cooling down from the melting point, the specimen recrystallized in its previous orientation, the retardance becoming greater than before. This showed that the nucleation sites were not completely destroyed at the melting point. On reheating the "spike" almost completely disappeared showing that it was due to annealing and recrystallization. If the specimen were heated considerably above the melting point (200° C) and cooled, it recrystallized in random fashion, retaining no trace of its previous orientation.

Figure 2 shows the data for a specimen having a dose of 200 M rad. The annealing spike has disappeared. The melting point is now 105° C. On cooling from the melting point it recrystallizes but this time with the retardance less than before. On heating to 230° however, it recrystallizes but this time the specimen seems to retain a trace of its previous orientation. This can also be seen in the specimen given a dose of 150 M rad.

Figure 3 shows a specimen given a dose of 500 M rad. Here a new phenomenon becomes apparent. The birefringence does not drop precipitously to zero. Instead it drops sharply to a low value then decreases very slowly as a function of temperature. The high temperature birefringence is not due to the presence of crystallites⁽³⁾ since the temperatures involved are considerably above the normal crystalline melting point. If the sharp drop in retardance is extrapolated to zero for this specimen, a melting point is obtained which is consistent with the other observed data. The retention of birefringence above the normal melting point in irradiated polyethylene has been noted by others⁽³⁾⁽⁴⁾.

It may be assumed that, in all cases except the 500 M rad specimen, the disappearance of birefringence correlates with the crystalline melting point. Figure 4 shows that the melting point decreases in a uniform manner with radiation dose, agreeing with the results of Dole and Howard⁽⁵⁾ and others⁽⁶⁾⁽³⁾. In addition, it is seen that the steepness of the retardance-temperature curve near the melting point decreases with dose.

These effects can be explained by a simple picture. The crystallites in polyethylene may be expected to vary in size and perfection. The smaller, more defective ones will have a lower melting point than the larger ones. As the unirradiated material is slowly heated below the melting point, the smaller crystallites melt while the larger ones grow at their expense. Those defects that can be annealed out. The effect is similar to that of aging a precipitate. As a result of this the melting point appears higher and sharper. This explains the annealing "spike" seen on the unirradiated and unannealed samples.

One of the results of irradiation is crosslinking. Even when irradiated in air, this is true, especially if the specimen is subsequently heated. A crosslink may be looked on as an unannealable defect which cannot be incorporated in the

crystallite lattice without causing a great deal of distortion⁽⁷⁾. The crosslinking however, can take place freely in the amorphous regions. The crosslink will prevent the material immediately surrounding it from being incorporated into a crystallite. This would interfere with the recrystallization and annealing and the observable effect would be a decrease in the slope of the melting curve and a disappearance of the annealing spike. Both these effects were observed.

Due to the restraints imposed by the lattice, the formation of crosslinks within the crystallites themselves are extremely improbable compared to the amorphous region⁽⁷⁾. However, active species such as radicals can form and be stored within them. When the crystallites melt these are free to form crosslinks. On cooling down from the melting point, the specimen then can no longer crystallize to the same extent as before. This explains why the retardance in recrystallized irradiated polyethylene is less than the initial retardance while the reverse is true for the unirradiated material.

If polyethylene is heated considerably above the melting point, the nucleation sites are destroyed. On cooling, recrystallization may be expected to occur in random fashion. In irradiated specimens a new phenomenon can occur. As the crystallites approach their melting point, crosslinking occurs while the molecules are still oriented relatively parallel to each other. The result is an oriented crosslinked gel that takes considerably more energy to disorient than in the unirradiated material. Whenever this material is cooled down, a trace of its former orientation is retained as was seen in specimens given a radiation dose of 125 M rad or more.

If the sample is given a high radiation dose, more than one crosslink can be expected to form between molecules originally adjacent to each other in the crystallite. The chain length between crosslinks is then the same for both molecules and

they are forced to remain in each others vicinity and more or less parallel. If the crosslinks are not too close together, the result is an oriented nucleation site which persists to very high temperatures in spite of the fact that the overall melting point is lower. This would help explain the observed high temperature birefringence.

If this were true there should be another observable effect. The polyethylene when cooled from the melt crystallizes at a somewhat lower temperature than it melts. Due to the interference of crosslinks with nucleation, the freezing point should decrease with radiation dose. However, if nucleation sites persist at high temperature due to crosslinking of originally crystallized material, then the freezing point should start to increase with high doses. In Figure 5 the temperature at which measurable retardance first appears is plotted. This temperature first decreases, then increases as expected. The first specimen to show this increase is the first one to show retained orientation on cooling from above the melting point. This is consistent with the presence of oriented nucleation sites formed from crystallites. The freezing point determination shows poor reproducibility due to its extreme sensitivity to such factors as the rate of cooling, etc. However, qualitatively at least, the effect shown in Figure 5 is unmistakable.

The points in Figure 5 with radiation dose of 128 M rad or above are for specimens cooled from 200° C or above. Those for doses less than 128 M rad are for specimens cooled from the melting temperature. This had to be done because retardance could not be measured for the specimens if cooled from 200° C. This in no wise affects the argument.

Synopsis

The birefringence of irradiated polyethylene was observed as a function of temperature. The data is consistent with a mechanism in which crosslinking limits the growth and annealing of crystallites. Crosslinks formed in material which was oriented at the time the crosslinks were formed, results in an oriented gel. This effect explains the birefringence and the persistence of nucleation sites at high temperatures.

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Figure 1
 Unirradiated Control.
 ○ Specimen being heated
 ● Specimen being cooled

Figure 2
Radiation Dose 200 Mrad
○ Specimen being heated
● Specimen cooled from 200°C

Figure 3

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Radiation Dose 500 Mrad

○ Specimen being heated

● Specimen cooled from 200°C

Retardance thickness

A N 52 43593 W 1344024

Figure 4
Melting Point of Irradiated Polyethylene

Figure 5
Freezing Point in Irradiated Polyethylene

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