Semi-Annual Status Report

to

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for

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by

Leo Mandelkern
Principal Investigator
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The major research areas in this program are concerned with the fundamental radiochemical acts that are involved in the crosslinking of polymers by means of high energy radiation and the dependence of crosslinking efficacy and network properties on the state of the system at the time the crosslinks are introduced. As has been detailed in previous reports and publications from this laboratory, it became mandatory that molecular weight fractions be used with controlled crystallization and well defined morphology. Because of this most of the work has been with fractions of linear polyethylene with defined and described morphology and thermodynamic properties.

The morphological studies of crystalline polyethylene have emphasized the density and enthalpy of fusion of crystals formed from dilute solution. In a manuscript, which has been accepted for publication in Macromolecules the controversy regarding the density of such crystals has been resolved. A variety of experimental techniques, which are described in detail, yield densities in the range 0.965-0.980, depending on the molecular weight and crystallization temperature. This large density deficiency from that of the unit cell is explained along with other physical measurements on the existence of a disordered interfacial layer. We have also found that for the lower molecular weights (with the increased end group concentration) for the same crystallite size, the density is greater than for the higher

molecular weight species.

We have also studied the effect of irradiation crosslinking on certain thermodynamic properties of highly crystalline polyethylene, including crystals formed from dilute solution and low molecular weight fractions crystallized in the bulk. Primary attention has been given to enthalpy of fusion measurements and it has been found that there is an initial decrease in this quantity with irradiation dose, a well defined minimum exists and with increasing dosage about 90% of the initial enthalpy of fusion is observed. Two competitive molecular processes appear to be operative; one involves radiation damage and the other appears to be affecting the enthalpic properties of the melt.

In order to prepare highly ordered crystalline systems from very high molecular weight fractions, the properties of crystals formed in dilute solution under a hydrodynamic shear field have been studied. Although a high level of axial orientation can be demonstrated, with some increase in the level of crystallinity for the same molecular weights crystallized in the bulk, density and enthalpy of fusion measurements indicate that the crystallization process is far from complete. On the other hand, dilatometric measurements indicate a melting temperature greater than 145^{o}C and less than 148^{o}C which is in good accord with theoretical

predictions. These directly observed melting temperatures in bulk are confirmed by measurements of the dissolution temperature. The rather high melting temperatures observed could be attributed to either the development of very large crystallites in the chain direction or in a reduction of the interfacial free energy. Low angle x-ray diffraction measurements are planned to attempt to resolve this problem.

The work on the irradiation crosslinking of polyethylene as a function of molecular weight, temperature, and degree of crystallinity as independent variables has been essentially completed and several manuscripts are currently being prepared for publication. The discrepancies that appeared in the high molecular weight range, which were described in the last report, have now been resolved.