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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 studies of the dependence of the crosslinking efficiency and network properties on the state of the system at the time the crosslinks are introduced. In the initial phases of this study, it became readily apparent that appropriate experiments have to be carried out utilizing molecular weight fractions if a quantitative meaningful interpretation could be made. These experiments were thus carried out with molecular weight fractions of linear polyethylene which were crystallized under controlled and defined conditions and irradiated as a function of temperature and state. In contrast with much of the radiation chemistry of polymers that has been reported in the literature, this approach to the problem has involved a subsidiary set of problems concerned with companion studies of crystallite size, degree of crystallinity, and molecular weight. It has been found that in order to make a complete analysis of the problem, the temperature, molecular weight, degree of crystallinity, morphological detail, and interfacial structure must be treated as independent variables. The utilization of molecular weight fractions also involves the additional problems of preparation and characterization of the materials utilized in the irradiation experiments.

The description and analysis of the large amount of data that have been obtained with respect to hydrogen evolution, vinyl disappearance, and the formation of <u>trans</u> unsaturation have been reported at invited Symposium before the Division of Polymer Chemistry, American Chemical Society, San Francisco Meeting, April 1968. In this work the very unique result has been obtained which demonstrates the involvement of the vinyl-end group in the crosslinking and gelation processes. These conclusions were demonstrated by the use of hydrogenated samples. When hydrogenated samples are compared in the highly crystalline and completely amorphous state at the same temperature of irradiation, no difference is observed in the crosslinking efficiency. This is in contrast to the previous reports from this laboratory for the unhydrogenated materials where a much greater efficacy of crosslinking is observed for the very highly crystalline samples. It has also been shown that a serious material imbalance exists for the hydrogenated samples irrespective of the state of the sample at the time of irradiation. This latter result does not permit the previously accepted assumptions that the material imbalance that is observed in the conventional sample are due to the presence of the vinyl-end group. The facts that emerge are that the material imbalance is observed for samples, irrespective of state, in which the vinyl-end group is absent. This imbalance is in the direction that more hydrogen is evolved than can be quantitatively accounted for by the crosslinking process and the formation of <u>trans</u> unsaturation. Detailed studies have been undertaken to see if this excess hydrogen evolution can be attributed to chain scission. Recent results for the partitioning between sol and gel of molecular weight fractions indicate that between 98-100% gel is eventually formed irrespective of molecular weight or the state of the system. This result would appear to rule out any conventional random chain scission process. However, the possibility of random chain scission with some type of recombination is still an admissible possibility. Detailed analysis of the partitioning curves indicate that though some small deviations are observed from the theoretical expectation for molecular weight fractions, no major process which does not involve random crosslinking can be tolerated.

The implication of the vinyl-end group in the crosslinking process leads to the conclusion that for the usual linear polyethylene the critical dosage for gelation should have a dependency on the number average molecular weight which would be superimposed on the classical expected inverse dependence on the weight average molecular weight. The preliminary results previously reported have indicated that this expectation is confirmed for irradiation of the completely amorphous polymer at 130°C. Deviations have been reported for molecular weights less than 1×10^5 where a systematic decrease in the product of the viscosity average molecular weight times the critical dosage for gelation is observed. More recent work with hydrogenated samples, irradiated in the completely molten state, confirm this conclusion since for hydrogenated samples in the lower molecular range, the aforementioned product is the same as for the very high molecular weight polymer. Similar conclusions have also been reached from experiments on molecular weight fractions which could be crystallized to a very high level of crystallinity where different dosage for gelation is observed as a function of molecular weight and the vinyl-end group content. Some discrepancies have now appeared, however, in our results for the higher molecular weight samples ($> 1 \times 10^{-5}$) irradiated in the crystalline state. Here the level of crystallinity is of course decreased as the molecular weight increases and the large difference in crosslinking efficacy previously reported appears to be reduced. This apparent discrepancy could be a consequence of the details of the post-irradiation treatment and the method of sol-gel analysis. This problem is currently receiving strong attention in the hopes that it can be resolved.

In order to prepare highly ordered crystal systems of very high molecular weight chains the properties of crystals formed in dilute polyethylene solutions under a hydrodynamic shear field have been studied. A very high level of axial orientation can be achieved in such a system with an increase in the level of crystallinity as compared to the usual crystallized sample. Detailed dilatometric studies, accompanied by calorimetric measurements, have indicated a melting temperature in excess of 141°C. Because of the concern of the possibility of the presence of internal stresses, in this highly oriented, noncompletely crystalline system, various and detailed annealing procedures were adopted at temperatures above 141°C. From these experiments it was concluded that the melting temperature is greater than 143°C and less than 148°C. This conclusion has been confirmed by measurements of the dissolution temperature (the melting temperature in a dilute solution) where the aforementioned effects should be greatly reduced. In this type of experiment it was found that the dissolution temperature was 116°C which was significantly greater than any dissolution temperature previously observed. For bulk crystallized specimens this temperature is only 2° less than the estimated equilibrium dissolution temperature. This type of work is being continued with a molecular weight fraction of about 75,000 which would further reduce the effect of internal stresses.

The morphological studies of crystalline polyethylene are being continued with major emphasis on the density and enthalpy of fusion of crystals formed from dilute solution. The controversy which has existed with regard to the density of the crystals formed from dilute solution has now been resolved. Measurements have been performed in a specially designed pycnometer in which the crystallization takes place in situ and the density of the precipitated crystals directly determined. Extensive measurements of this type have yielded densities which lie in the range of 0.965 to 0.980 depending on molecular weight and crystallization temperature. These results are in good agreement with those previously reported in a variety of density gradient columns. This quantity is significantly less than 1.00 which is the density required for true single crystals. We have also found that there is an inverse relationship between the density and the crystallite thickness in the chain direction which extrapolates to the appropriate density for a crystal of infinite thickness. These results are compatible with a variety of other physical measurements on such crystals and are most easily interpreted in terms of a disordered amorphous overlayer. Similar conclusions are consistent with more recent measurements of the enthalpy of fusion. These latter measurements are now being extended to very low molecular weight fractions.