MASTER

RADIATION-INDUCED CROSSLINKING AND GRAFTING

REACTIONS IN POLYETHYLENE

BY

WALTER J. CHAPPAS

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APPROVAL SHEET

Title of Dissertation: Radiation-Induced Crosslinking and Grafting
Reactions in Polyethylene

Name of Candidate: Walter J. Chappas ✓
Doctor of Philosophy, 1979

Dissertation and Abstract Approved:

Professor Joseph Silverman
Department of Chemical and
Nuclear Engineering

Date Approved: October 22, 1979

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Curriculum Vitae

Name: Walter John Chappas

Permanent address: 9174 Canterbury Riding
Laurel, MD 20810

Degree and date to be conferred: Ph.D., 1979

Date of birth: February 14, 1953

Place of birth: Omaha, Nebraska

Secondary education: O'Fallon High School
O'Fallon, Illinois
1971

Collegiate Institutions Attended	Dates	Degree	Date of Degree
Southern Illinois University	1971-1975	B.A.	August 1975
University of Maryland	1975-1977	M.S.	May 1977
<i>C. Park</i> University of Maryland	1977-1979	Ph.D.	December 1979

Major: Nuclear Engineering

Professional Publications:

1. Walter J. Chappas, and J. Silverman, "The Effects of Trace Fillers on the Radiation-Induced Crosslinking of Polyethylene," J. Poly. Sci., Polymer Letters Ed., Vol 17, 5-14 (1979).
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ABSTRACT

Title of Dissertation: Radiation-Induced Crosslinking and Grafting
Reactions in Polyethylene

Walter J. Chappas, Doctor of Philosophy, 1979

Dissertation directed by: Professor J. Silverman
Department of Chemical and
Nuclear Engineering ✓

This dissertation is concerned with three aspects of the crosslinking and grafting reactions induced by ionizing radiation.

One is the effect of trace inert fillers on the radiation-induced crosslinking of polyethylene. Work by Gordiyenko et al.¹ showed an unexpected sharp increase in the gel fraction of irradiated polyethylene samples with SiO_2 concentrations of only 0.2%. If confirmed, such a sensitization of crosslinking by a trace additive would be of considerable industrial importance. To check and extend this work, experiments were performed with silica filled samples of low-density polyethylene subjected to 5 and 10 Mrad doses of gammas and electrons. Contrary to Gordiyenko's results the insoluble fraction determined by Soxhlet extraction was found to be independent of SiO_2 concentrations up to 0.5% by volume of both a finely divided (0.007 μm) and a coarse (75 μm) filler. Substantial changes in the conditions of irradiation, and in sample preparation and treatment do not affect gel yields.

Another unexplained phenomenon is the ability of acid to enhance the radiation-induced grafting of styrene to polyethylene. It is well known that the addition of methanol to the solution accelerates the

rate of the radiation-induced grafting of styrene to polyethylene.⁸ Garnett and Yen⁹ have shown that the addition of acid to an air-saturated methanol-styrene system enhances the grafting rate of styrene to polypropylene still further, and attributed the effect to hydrogen atoms. Pinkerton and Stacewicz¹⁰ attributed the effect to a reduction of inhibiting oxygen, which is less soluble in the acidified grafting solution. In this work, experiments were performed using polyethylene films immersed in styrene-methanol solutions both with and without acid and oxygen. The results show the gamma-induced grafting rate (room temperature, 40 krad-h^{-1}) is enhanced by the presence of acid even in O_2 -free systems, despite the fact that the acid does not permeate the film. Experimental results show the grafting rate depends on the composition of both the film and the liquid in which it is immersed. They also show that the existence of hydrogen atoms need not be invoked in order to explain the acid effect. Also, the acid enhancement occurs with grafts greater than 100% where there is little industrial interest.

The radiation chemistry of the amorphous region of polyethylene is understood far better than that of the crystalline region. Experiments were performed with a Varian 4502 ESR spectrometer on single crystals of a model compound which resembles the crystalline region of linear polyethylene. The purpose was to study the relative yields, and the migration and decay mechanisms of the radicals. ESR measurements at low power levels ($< 10 \mu\text{W}$) were made on single crystals of *n*-eicosane ($n\text{-C}_{20}\text{H}_{42}$) which were irradiated with gammas at 77°K . The relative concentrations of the three possible types of

alkyl radicals were examined, first at 77°K and then after warming the crystals up to various temperatures for several time intervals and cooling them to 77°K for measurement. Also the relative concentrations were measured at room temperature as a function of time for several days. Two unexpected results were obtained:

1. The alkyl radicals found in samples with an absorbed dose of 250 krad are almost entirely of the interior type ($-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$). Samples given higher doses show an increasing concentration of the penultimate radical ($-\dot{\text{C}}\text{HCH}_3$). The primary terminal radical is not observed.

2. There is a slow conversion of the interior alkyl radical to the penultimate form particularly at higher temperatures.

These results were used as the basis for explaining the apparent contradictions between Gilbro and Lund,³⁴ and Kimura et al.³⁵ regarding the relative yields of the penultimate and interior radicals in irradiated eicosane. In agreement with Kimura et al., the results suggest that the fracture of C-H bonds in irradiated eicosane favors the yield of the interior secondary alkyl radical far more than is to be expected from a random fracture pattern.

The results of the ESR studies also demonstrate that the intramolecular migration of the alkyl radical site is more rapid than intermolecular migration. This confirms the conclusions of Hama et al.³⁸ obtained by studies on alkane diols but conflicts with the conclusions of Shimada et al.³⁶ on irradiated urea-polyethylene samples.

An ionic mechanism is proposed for the production of the alkyl free radicals in irradiated polyethylene and all other solid linear

alkanes. This mechanism is a modification of one proposed by J. Weiss to explain prompt crosslink formation. According to Weiss the principal initial radiation interaction with an alkane is an ionization producing a cation radical and an electron. The cation radical then reacts in either an inter- or intra-molecular fashion producing molecular hydrogen. The intermolecular reaction converts the original alkane to a carbonium ion adjacent to an alkyl radical; subsequent neutralization produces two adjacent alkyl radicals. The intramolecular reaction produces an unsaturated cation radical which becomes a vinylene group following charge neutralization. This mechanism describes the production of radical pairs, unsaturation, and prompt crosslinks. It also explains the existence of the unsaturated cation observed by Waterman and Dole²⁶ and the observation by Timm and Willard¹⁹ that the radical concentration in irradiated hydrocarbons remains constant upon neutralization. Previous theories of hot hydrogen mechanisms and of ionic processes based on the post-neutralization expulsion of H₂ are unable to explain all of the published results. In addition it is shown that there is no conflict between the existence of the H atoms in irradiated solid CH₄ and their absence in the irradiated higher alkanes. The production of H atoms in CH₄ is assumed to arise from a fast neutralization after the initial ionization step thereby preventing the ionic reactions of the Weiss mechanism. Published electron mobility data support the assumption. The modified Weiss mechanism agrees with all of the ESR and optical spectroscopy data on solid alkanes.

The non-random fracture pattern of the C-H bonds in alkanes is explained in terms of random ionization and positive hole migration to

the energetically favored interior position, after which the ionic processes of the Weiss mechanism ensue. Published experimental evidence of highly mobile positive holes is offered in support of this explanation.

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Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
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To Caprice

For whom this degree was worth attaining

and

My Parents

Who can no longer say I am a perpetual student.

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For all those who follow in my footsteps, through the long hours of studies, the sleepless qualifier nights, and the never-ending laboratory duties that seem even to supersede the attainment of your degree, I have but one word of advice - confide in the wisdom of your advisor. His years of experience are only outweighed by his insight and understanding of science and, more importantly, the qualities that make a good scientist. When in doubt or confused, talk to him; he will always have time in his busy schedule for you and your problems. You have an advisor you can talk to, but never expect compliments for less than Ph.D. level accomplishments. The road toward your Ph.D. is long and rugged, but when completed, the praise of your advisor will be sincere; and only then will you appreciate the past years. Professor Joseph Silverman, my mentor, my advisor, thank you.

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CHAPTER I

CHAPTER I

INTRODUCTION

One of the principal industrial uses of ionizing radiation is associated with the crosslinking of polyethylene. Another potentially large application of ionizing radiation is graft polymerization. It is the purpose of this dissertation to perform a series of studies related to the fundamental problems of practical interest in these areas of radiation processing.

In these areas of applied radiation chemistry there are a series of interesting and unresolved problems. They are:

- (1) the sensitization and enhancement of the crosslinking of polyethylene by the addition of small amounts of inert fillers;
- (2) the acceleration of the grafting rate of styrene to polyethylene by the addition of small amounts of acid; and
- (3) the mechanism by which the radiation-induced free radicals produced in crystalline alkanes migrate and ultimately disappear with the formation of crosslinks.

All of these problems are central to the understanding of how the transient species are produced in irradiated polyolefins and how they can be used toward practical ends.

A. Radiation-Induced Crosslinking Reactions

The two major effects of ionizing radiation on polyethylene are the production of crosslinks and unsaturation. Intermolecular carbon-

carbon bonds are formed with increasing dose and eventually reach the point at which a three-dimensional network is formed. This condition occurs when there is an average of one crosslink per initial weight average polymer molecule. This crosslinked polymer has three important characteristics:

- (1) a portion of the polymer (the gel) becomes insoluble in normal solvents of the unirradiated polymer;
- (2) there is a greater form stability in the presence of solvents, and although the three-dimensional network can undergo thermochemical breakdown, it is infusible; and
- (3) the irradiated polymer has the property of elastic memory. This property has been the basis for major industrial products including heat shrinkable packaging and insulation.

The mechanism is complex but can be reduced to a simple set of reactions for the purpose of this discussion.

The ionizing radiation produces free radicals along the polymer chain. These radicals react and terminate each other producing covalent C-C bonds.

Hydrogen molecules and vinylene unsaturation are other major products.

B. Radiation-Induced Grafting Reactions

Radiation-induced grafting of various monomers to formed polymers is potentially one of the most important applications of ionizing radiation for industrial processes. As most polymers cannot be "alloyed" the technique is a powerful means of obtaining a polymeric material which combines the properties of the two components.

In a common method of radiation grafting, active sites are produced in the polymer which then react with monomer to form a side chain. Grafting of styrene to polyethylene by ionizing radiation is one of the most important model systems for study of the problems associated with this technique. The usual procedure is to place a polyethylene film in a styrene solution and then to irradiate the system. Styrene units propagate a pendant chain on the secondary alkyl radical produced in reaction (1).

After thirty years of research there are still unknowns associated with grafting systems. A principal problem to which this work has addressed itself is the effect of small additions of acid to the monomer solution on the outcome of the grafting reaction.

C. Industrial Aspects

Radiation initiated crosslinking, polymerization, and grafting reactions have many advantages over chemical methods. For example, the initiation step is almost independent of temperature, and radicals are uniformly produced throughout the material at a rate that is only a function of the radiation intensity. This simplifies control over the

reaction rate and the molecular weight of the product. This technique can be applied to many monomer-polymer pairs and sometimes to reactions that are not possible or convenient with other methods. Radiation-induced reactions can also occur at very low temperatures or in the solid state.

The application of high energy radiation to processes on the industrial scale is strongly connected to the convenience, the acceptability and the economics of such processes. This explains why most of the reactions studied are those in which a relatively small dose can produce a large effect. Examples of this type of reaction are the polymerization of vinyl monomers, the grafting of vinyl monomers to different polymers, the crosslinking of polymers, and radiation sterilization. Because only small doses of radiation (~ 15 Mrad) are required in the above reactions, the energy savings are substantial when compared with alternative processes.

D. Some Fundamental Aspects of Radical Behavior

It can be seen that the basic value of these two techniques, crosslinking and grafting, is to modify the physical and chemical properties of polymers. These changes are initiated by radicals, the reactive sites produced by ionizing radiation. It therefore becomes important that the production, migration, and disappearance (in the form of crosslinks and other reactions) be understood.

The answers to many of the questions are of practical value as many of the olefinic polymer systems of great interest to industry are semicrystalline. Glassy alkanes and liquid systems which are similar

to the amorphous region, have been studied with substantial success. There is still no comprehensive understanding of how these radicals form, migrate or disappear in the well-structured crystalline fractions. Polyethylene single crystals are small, typically 150 Å thick and a few millimeters on a side, however large single crystals can be made of lower molecular weight linear alkanes. These have served as model compounds for the study of the crystalline region. This dissertation provides a further contribution to this branch of the literature reporting ESR studies on irradiated $n\text{-C}_{20}\text{H}_{42}$.

CHAPTER II

CHAPTER II

The Effects of Trace Fillers on the Radiation-Induced Crosslinking of Polyethylene

A. Introduction

The effects of additives on the properties of polymer filler systems subjected to ionizing radiation have been observed for many years and, with one notable exception, are reasonably well understood. The exception is a Russian paper reporting an unusual phenomenon. This work by V.P. Gordiyenko et al.¹ describes the effect of low concentrations of SiO_2 and TiO_2 fillers on the radiation-induced crosslinking of polyethylene. The principal results are summarized in Figure 1 taken from their work. It shows that the gel fraction of a low density polyethylene sheet irradiation with a dose of 5 Mrad is increased by 60% by the addition of 0.2 volume percent of finely divided SiO_2 (0.02 μm particles) or 0.5 volume percent of coarse TiO_2 (1 μm). Thus, almost trace quantities of either additive can reduce substantially the dose required to achieve gel contents of industrial interest. The cost of radiation energy is expensive ($\sim \$1/\text{kWh}$). Thus, if these results are readily reproducible, the cost of some industrial radiation processes, particularly the manufacturing of insulation and heat shrinkable packaging, could be cut significantly by the addition of small amounts of an inexpensive inert filler.

The experiments reported are attempts to confirm and extend the results reported by Gordiyenko et al.

B. Experiments

Fumed silica from Sigma Corporation ($0.007\ \mu\text{m}$ diameter and $400\ \text{m}^2\text{g}^{-1}$ surface area) and Fisher Laboratory grade SiO_2 gel ($75\ \mu\text{m}$ diameter) were used as fillers to produce a uniform polymer-filler blend with Microthene polyethylene powder (U.S. Industrial Chemical Company). The samples were blended at 140°C and $470\ \text{kg cm}^{-2}$, and then pressed into $0.8\ \text{mm}$ thick sheets on a Carver hydraulic press. The press was allowed to cool before the pressure was released and the sample removed. The concentration and uniformity of the silica distribution in the filled samples were confirmed by infrared analysis at $475\ \text{cm}^{-1}$ (Figure 2), where there is a strong silica absorption peak and virtually no polyethylene absorption. The optical density at this wavelength was found to be proportional to the silica content, and the spectrum of each sample measured was independent of the position of the sheet under examination (Figure 3). An incidental finding is that the decadic molar extinction coefficient of the fine silica at $475\ \text{cm}^{-1}$ is $70\ \text{M}^{-1}\text{cm}^{-1}$. The samples were cut into rectangular strips ($2 \times 10\ \text{cm}$). Some were subjected to gamma radiation from the 25,000 curie cobalt-60 source at the University of Maryland at a dose rate of $2.2\ \text{Mrad h}^{-1}$; others were irradiated with a $2.2\ \text{MeV}$ electron beam from an RDI Dynamitron at Columbia Research Corporation, Gaithersburg Maryland at a dose rate of $5\ \text{Mrad s}^{-1}$. Fricke dosimetry measurements were performed at Maryland for the Co-60 irradiations; electron beam dosimetry was performed by W.L. McLaughlin using radiochromic dye films. All recorded doses are estimated to be reliable within 5 percent. Also maximum-to-minimum doses in each sample did not exceed 1.07.

Irradiations were done both in air and in a nitrogen atmosphere. The samples were annealed for 15 m at 110°C to minimize post-irradiation reactions. The gel fraction of the annealed strips was determined by Soxhlet extraction with boiling xylene in a nitrogen atmosphere for 70 hours followed by drying in a vacuum oven for another 50 hours at 55°C. Measurements of the elastic modulus at 150°C were made using an Instron 1130 Universal Testing Machine.

The experimental conditions matched those of Gordiyenko et al. in most respects. The principal differences were as follows: (1) the use in this work of 0.007 and 75 μm silica instead of 0.02 μm SiO_2 ; and (2) the post-irradiation conditioning procedure consisted of annealing the samples for 15 minutes at 110°C rather than 1.5 minutes at 130°C. The lower temperature and longer time assured more complete annealing with less thermal degradation. This research went beyond the Russian work in including gamma irradiations in addition to the electron beam irradiations, as well as measurements of the oxygen effect and tensile properties. It did not repeat the Gordiyenko measurements of allyl radical concentration by ESR, and of crystallinity by X-ray diffraction; these results have no direct bearing on the principal phenomenon of interest: enhanced gel yield.

C. Results and Discussion

Prior to the performance of the experiments reported here several possible explanations of the published results were considered. In general, the speculations focused on possible interactions at the interface between the filler and the polymer during the irradiation.

One possibility is the higher dose rate in the polymer near the interface with the filler. This could arise from the following considerations. The energy absorbed per gram in the bulk polymer and the bulk silica should be the same, but the flux density of scattered electrons should vary directly as the density (neglecting differences due to atomic number). Thus, at the interface, the electron flux into the polymer would be perhaps twice that entering the filler. Another mechanism that could lead to an enhanced effect at the interface involves the transfer of electron energy absorbed by the filler to the surface; this effect has been reported² for several systems involving a substance absorbed on silica gel. A third factor that may be involved is some specific chemical interaction that may occur at the interface under the influence of ionizing radiation; this interaction may be enhanced by the increased dose effects suggested above. Even collectively, however, these possibilities do not provide a reasonable basis for explaining the sharp increase in crosslinking caused by the addition of only 0.2 volume percent of the oxide. The volume fraction of the polyethylene at the interface in the 25-50 Å region that would be involved is too small.

At first all samples were blended with the coarse filler (75 µm SiO₂) for 15 min at 150°C in the Brabender Plastograph. We found that higher filler content led to greater discoloration. We decided to reduce the blending time as filler content was increased to produce composites that were colorless to slight yellow. The gel versus filler concentration data (Figure 4) shows no evidence of the reported maximum.

Clearly the discoloration of the polymer was due to the abrasive action of the filler. This abrasive action may be viewed in two

different ways. Although the temperature of the blender was controlled to keep the average temperature of the melt constant, there is a possibility of local microscopic heating. There have been studies of thermal degradation⁵ which arises primarily from breakage of the C-H bonds and the subsequent oxidation of the secondary alkyl radical. The known chemistry associated with this process leads to vinylene unsaturation ($-\text{CH}=\text{CH}-$) at the expense of the pendant vinylidene ($\text{R}_1\text{R}_2\text{C}=\text{CH}_2$) groups, with no net increase in the total concentration of unsaturated species. Another mechanism for the abrasive action could be purely mechanochemical in nature. In this type of degradation, the chains are torn into primary alkyl radicals by the action of the blender. The free radicals produced from the mechanical fracture of polyethylene at 77°K have been studied by Sohma et al.⁶. They suggest that subsequent radical recombination would increase the terminal vinyl unsaturation ($-\text{CH}=\text{CH}_2$) which might be expected to enhance the radiation effect especially in a branched polymer such as low density polyethylene. Thus, even though the initial experiments with coarse silica did not show an increase in the gel content with increasing filler content, finely divided silica could enhance thermal and mechanochemical effects.

Blending experiments were performed using the 0.007 μm SiO_2 . Infrared analysis shows little change in the concentration of the unsaturated species, but a significant increase in the carbonyl absorption band at 1700 cm^{-1} (Figure 5). Blending experiments disclose that the filler content, particle size, blending speeds, and blending times all affect the degree of discoloration and oxidation (Figure 6). Analysis of our samples shows that the principal unsaturation is in

the form of vinylidene groups which build up to a constant level in less than 15 minutes. Vinyl unsaturation builds up more slowly; even after one hour, it is less than 20% of the vinylidene unsaturation. Vinylene unsaturation after 15 minutes of blending is also less than 20% of the vinylidene unsaturation; after 60 minutes it is smaller than but comparable to that of the pendant vinylidene unsaturation. Fifteen minutes in the blender produces carbonyl groups with a yield comparable to that of the unsaturation; after 60 minutes, the carbonyl groups dwarf the unsaturated groups. These data suggest a combination of reactions whose chief consequences are negligible for purposes of this dissertation. The production of unsaturation in the composites by the action of the blender is just too small to have an impact on the subsequent radiation chemistry.

The radiation crosslinking experiments with polyethylene samples containing 0.007 μm silica were performed both in air and in an inert atmosphere with high energy electrons (Figure 7) as well as gammas (Figure 8). Blending time for this series and all the experiments which followed was 20 min. The results shown in Figure 8 reflect the role oxygen plays as a scavenger molecule in the presence of alkyl radicals, and indicate the significance of oxygen diffusion as a rate controlling parameter in the crosslinking reactions; however, the results do not show the enhanced gel yields observed in the work of Gordiyenko et al.

The elastic modulus measurements were made above the crystalline melting temperature to determine whether any unusual viscoelastic behavior could be observed in the filled samples. Figure 9 shows that the modulus measurements of gamma irradiated samples filled with

0.007 μm SiO_2 compare closely with the moduli calculated from the Guth-Gold equation: $M = M_0(1 + 2.5 v_f + 14.1 v_f^2)$ where M_0 is the modulus of unfilled sample, and v is the volume fraction of the filler. (Each experimental point is the mean of four measurements.) Thus, trace fillers do not have any unusual effects on mechanical behavior.

The details of the work by Gordiyenko et al. as outlined in the experimental section of their paper are incomplete. Parameters such as blending time, temperature, and speeds were not reported. On the other hand, all results obtained in this research show that substantial changes in these experimental conditions do not affect the gel content. Nevertheless, one cannot exclude the possibility that a precise replica of their equipment, materials, and conditions could yield their results. Also, it may be useful to examine the mechanochemistry during the blending operation to search for conditions that enhance the yield of vinyl groups; these groups can participate in a chain reaction of radiation-induced crosslinking⁷.

There are publications reporting improved mechanical properties of filled polyethylene after irradiation.^{3,4} They describe room temperature measurements of physical and mechanical properties, primarily creep and tensile strength. However, the samples typically contain 15 percent filler before significant effects are observed. There is nothing in these works that would lead one to expect the effects reported by Gordiyenko et al.

CHAPTER III

CHAPTER III

The Effect of Acid on the Radiation-Induced Grafting of Styrene to Polyethylene

A. Introduction

The radiation-induced graft polymerization of polyethylene immersed in methanol-styrene solutions is described in publications from several laboratories. Recent investigations have led to reports of a substantial enhancement of radiation grafting rates of polyolefins in methanol-styrene solutions brought about by the addition of H_2SO_4 . For example, Garnett and Yen⁹ report that a 70% methanol-30% styrene solution containing 0.1 M H_2SO_4 has a grafting rate 1.75 times that of the acid-free system. A more complete compilation of their results is shown in Figure 10. They attribute the enhanced grafting rate to an increased yield of hydrogen atoms leading to abstraction reactions with the trunk polymer and subsequent chain propagation from the radical sites on the polymer. No data were reported on samples with small amounts of total graft, which is the likely region of industrial interest.

The results of Garnett and Yen are unexpected as the acid should not permeate the polyethylene strip. A possible explanation was advanced by Pinkerton and Stacewicz.¹⁰ They also found apparent acid enhancement of another graft polymerization system, methylmethacrylate-methanol and polypropylene. Their experiments showed the effect was really due to the water introduced into the system along with the acid. They found that the water reduced the solubility of air in the

grafting solution, thereby reducing the concentration of oxygen which ordinarily inhibits the grafting reaction (Figure 11).

Thus the Pinkerton-Stacewicz explanation of the polypropylene-methylmethacrylate system could apply to the Garnett-Yen results. This could be tested by additional experiments performed in the absence of oxygen. We therefore undertook an experimental program to confirm the Garnett and Yen work, and to extend the study to O_2 -free systems, especially low total grafts where there might be some industrial interest.

B. Experiments

Polyethylene films (U.S. Chemical Co.; $M_n = 25,000$; $M_w = 99,600$; density = 0.924 g cm^{-3} ; thickness = 0.065 mm) were soaked in n-hexane for 24 h to remove aromatic impurities and then dried in a vacuum oven at 70°C for 24 h. The styrene (McKesson Chemical Co.) was washed three times with 20% NaOH and then three times with distilled H_2O . The styrene was distilled immediately and collected at liquid nitrogen temperatures in subdued light and stored at -196°C . The methanol used was analytical reagent grade anhydrous methyl alcohol (Mallinckrodt), and the acid used was A.C.S. reagent grade H_2SO_4 (Matheson Scientific). All samples were prepared within 24 h of the distillation and were always free of any polystyrene. Nitrogen was bubbled through the system for 5 min before the containers were sealed.

All samples were subjected to gamma radiation from the 25,000 curie Cobalt-60 source at the University of Maryland at a dose rate of 40 krad h^{-1} and a temperature of 20°C . The grafted polyethylene strips

were removed from the styrene-methanol solutions immediately after the irradiation. Post-irradiation grafting was minimized by washing the strips twice in hexane followed by soaking the samples in benzene for 48 h. The polyethylene strips were then vacuum dried at 70°C until an equilibrium weight was reached. The percent graft was calculated by the following equation:

$$\frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}}$$

The swelling experiments were performed on low density polyethylene with a thickness of 0.8 mm. Strips were immersed in solutions of 70% methanol-30% styrene with and without acid for 24 h in order to insure its equilibration with styrene; methanol does not dissolve in the film appreciably. The samples were then wiped dry and hung on a balance where the weight was measured against time. Extrapolation to zero time yields the saturation concentration of styrene in the strip.

C. Results and Discussion

Experiments with air-saturated samples similar to those performed by Garnett and Yen proved difficult to reproduce. The results of the series, summarized in Figure 12, are the mean values of several runs. Subsequent measurements in nitrogen were reproducible to within 5%. Our results show an increase in the total graft in both air and nitrogen irradiated systems confirming the acid enhanced effect reported by Garnett and Yen. Our experiments demonstrate that the effect cannot be attributed to oxygen as the work of Pinkerton and Stacewicz might suggest.

Figure 13 is typical of our rate data. They show that the acid has little effect on the grafting rate below 100% graft, but is quite substantial with higher grafts. This suggests the effect does not arise from an initiation process caused by H atom abstraction reactions with the trunk polymer as the H atom effect should be as pronounced at low grafts as well as high grafts. We attribute the effect to a combination of changes in the composition of the strip and changes in the outside solution during the irradiation. Clearly at high total grafts we are grafting styrene to a material that is largely polystyrene. The addition of acid in the outside solution resulted in a ten-fold increase in the homopolymerization of styrene. The resultant increase in viscosity as well as the decrease in monomer in the outside solution may affect the grafting rate.

We also measured the desorption of styrene from strips equilibrated with an acidified styrene solution and an unacidified solution. The results shown in Figure 14 indicate a slight change in the steady state monomer concentration in the PE strip with the addition of acid. This change in weight may be due, at least in part, to surface polymerization reactions induced by the acid during the 24 h soaking period. The data also indicate a slight change in the diffusivity, probably resulting from the reactions on the surface.

A result which may be the basis for some meaningful speculation came from the following experiment:

We irradiated two systems for 2 h, one with acid and one without. With the total graft nearly equivalent we switched solutions and strips, placing the strip grafted in acid in the acid-free solution and the strip grafted in the acid-free medium in the acid solution. After

four more hours of grafting, the total graft in the strip initially in acid was only slightly higher than if it had never been in the acid solution. This is probably due to the slightly accelerated graft rate during the first two hours while in the acid. The initially non-acid system after four hours of grafting in acid was only slightly lower than if it had always been in the acid. This tends to indicate that the composition of the film is important. The enhanced grafting rate takes effect at about 100% graft, whether the strip was initially exposed to acid or not.

The dynamics of the grafting system make an analysis of the acid effect exceedingly difficult. The monomer concentration in the external solution is decreasing, while the polystyrene content and viscosity are increasing. The strip is also changing in composition, swelling characteristics, and viscosity. The acid introduced into the system makes it even more difficult to untangle the numerous parameters controlling the grafting reaction. However, it is clear that hydrogen atoms need not be involved in order to explain the acid effect. In addition to this fundamental conclusion, there is an important, practical one. The acid plays a role in highly grafted systems where the strips consist primarily of polystyrene grafted to a polyethylene framework, but there is little industrial interest in such matters.

CHAPTER IV

CHAPTER IV
Production and Migration of Radicals in
Single Crystals

A. Introduction

The irradiation of single crystals of normal alkanes can, in principle, yield radicals of three different types: (1) interior ($-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$); (2) penultimate ($-\text{CH}_2\dot{\text{C}}\text{HCH}_3$); and (3) terminal ($-\text{CH}_2\dot{\text{C}}\text{H}_2$). If the pattern of C-H fracture is random and the species produced do not equilibrate quickly, the relative yields of the three products are readily predictable. Equilibrium would convert almost all of them into interior radicals as the C-H bond energy of the interior methylene groups is lowest. The results published to date on these systems fit neither of these two extremes; furthermore they are in conflict. Experiments were therefore performed to examine the mechanism by which the various radicals migrate and disappear. The normal alkane single crystal used was n-eicosane ($\text{C}_{20}\text{H}_{42}$) and the technique used to study the behavior of the radicals was ESR spectrometry.

The principal works of the past bearing on this subject were performed by Gilbro and Lund,^{13,30-34} Fujimura and Tamura¹¹ and by Iwasaki and his co-workers.²⁰ Most of the results by Gilbro and Lund as shown in Table 1 are consistent with a pattern of random C-H fracture followed by equilibrium of the terminal radical to the penultimate radical. The reason for the terminal instability on the last two carbon atoms may be that the end groups on the unit cell are not rigidly confined thereby leading to transformations favoring the more

stable penultimate radical. They have, however, experimental evidence which conflicts with such a mechanism: the irradiation of a normal chloride produces the normal alkyl radical in which the radical site undergoes slow migration to the interior. The matter is complicated still further by the fact that the data by Kimura et al.³⁵ are in sharp conflict with the work by Gilbro and Lund. They found that almost all radicals are of the interior type in experiments on irradiated single crystals of eicosane prepared by this laboratory.

B. The Model Crystal

A more definitive understanding of radical production and migration of crystalline alkanes can be found by studying the radiation chemistry of a n-eicosane ($C_{20}H_{42}$). The crystalline form of this alkane resembles polyethylene single crystals, although the latter are orthorhombic while the former is triclinic with the following lattice constants and properties¹¹.

$$a = 4.281\text{\AA} \qquad b = 4.820\text{\AA} \qquad c = 25.52\text{\AA}$$

$$\alpha = 91.18^\circ \qquad \beta = 93.53^\circ \qquad \gamma = 107.35^\circ$$

$$\text{melting point} = 36.8^\circ\text{C}$$

$$\text{density} = 1.0 \text{ g-cm}^{-3}$$

The crystal is convenient for use at cryogenic and room temperatures. Its use allows us to examine by ESR the types of free radicals formed on irradiation at low temperatures. Species with absorption lines too broad to be seen in an amorphous or poly-

crystalline sample are sharp and easily analyzed in the single crystal.

C. Experimental Methods

Eicosane ($n\text{-C}_{20}\text{H}_{42}$) from Eastman Organic Chemicals was purified and formed into single crystals by zone melting. The crystals were cleaved into slivers a few millimeters in cross-section and about 10 mm in height. The crystal sample was evacuated to 10^{-5} torr for 24 h in a Vycor tube and then sealed. The irradiations were performed at 77°K with gamma rays from the Co-60 source located at the University of Maryland's Laboratory for Radiation and Polymer Science. The dose rate was $1.5 \times 10^6 \text{ rad-h}^{-1}$. The signal from the ampoule was eliminated by flame annealing the sample tube after each irradiation while keeping the sample at liquid nitrogen temperature.

Spectra were recorded on a specially modified Varian V-4502 X-band spectrometer at 77°K . Magnetic field modulation of 100 kHz was used. The magnetic field was perpendicular to the chain axis.

The Varian spectrometer, designed to operate in the milliwatt region, was specially modified to operate in the microwatt region. This was accomplished by the following modifications developed in this study at the suggestion of Dr. Y. Ito:

- (1) The sample cavity was attached to the high power arm in order to eliminate the noise found in the variable Isolator used when the machine is operated in the low power mode, and

- (2) a fixed 20 db isolator was placed between the klystron and the sample cavity in order to reduce the incident power on the sample yet maximize the reflected signal.

These modifications allowed operation at $4 \mu\text{W}$, which is well below the saturation levels of the alkyl radicals.

The heat treatment experiments were performed in the following manner. The samples which were irradiated at 77°K , were warmed rapidly to fixed temperatures for 5 minutes and then cooled back to 77°K for the ESR measurements.

Samples were analyzed for relative changes in the radical concentration by double integration of the $\Delta M_s = 1$ spectrum. The relative intensities of the two observable alkyl radicals were found by computer simulation. Table 2 lists the parameters used to simulate spectra (Figures 15-20) with various relative interior and penultimate radical concentrations. The relative heights of various peaks were then plotted to form calibration curves (Tables 3,4 and Figures 21-24) from which the unknown spectra could be analyzed.

D. Power Saturation

In order to assure the recorded spectra were not deformed by power saturation, a power saturation curve was constructed for both the interior alkyl and penultimate alkyl radicals. The plots of signal intensity vs. power (Figure 25) show a linear change for both species up to $10 \mu\text{W}$. At higher power levels the signals begin to saturate and depart from the linearity. Noteworthy is the fact that the penultimate radical saturates at a higher power than the interior radical, a result

in agreement with published work by Iwasaki et al.²⁰ In this work, all measurements were performed at power levels well below saturation limits.

E. Results and Discussion

The motivation behind this portion of this research is to determine the relative initial yield of each of the free radical species and to determine the mechanism by which they migrate and annihilate each other, presumably by crosslink formation.

By simulating the recorded spectra of irradiated eicosane, we were able to estimate the relative concentrations of the various types of radicals. Then using warming techniques described in the experimental section, the radicals were allowed to migrate to the surface of the crystal or to defects in the crystal, and react. (Crosslinking reactions do not occur within the crystal.⁴⁰) The results, found in Figures 26-34, show a slight decrease in the relative concentration of the interior type radicals as the system is warmed and the radicals migrate followed by further movement to the interior after several days at room temperature (Figure 35).

The results of the C-H fracture pattern show that shortly after the irradiation at 77°K with a dose of 0.2 Mrad the interior radicals form 95% of the total radical yield and the penultimate species accounts for the other 5%. No terminal radicals are observed. These results agree with those of Kimura et al.³⁵ and are in apparent conflict with observations of Gilbro and Lund. When the crystal is annealed (i.e. stored at room temperature for several days until there

is no ESR signal) and again irradiated with a 0.2 Mrad dose, the penultimate fraction increases to 15%; the remaining 85% of the radicals are in the interior form. Still further, the ratio of the penultimate to interior radicals increases with time. Note that the change in the ratio is slow even at room temperature. Also the total radical concentration is constant with time in the region 77°-200°K.

These two sets of results suggest that the conflict between the Japanese and Swedish laboratories can be resolved by standardizing the experimental conditions. However the conditions employed by Kimura et al. yield results which are fundamentally more meaningful.

In addition to resolving the disagreement in published results, this work leads to important conclusions in two areas: initial fracture patterns and radical migration.

1. Fracture Patterns

The C-H rupture pattern at 77°K is not random even when this assumption is modified by rapid conversion of the terminal to the penultimate species. Thus the interpretation of the Gilbro and Lund data by Iwasaki leading to his assumption of the modified random fracture scheme is not valid. A more reasonable mechanism is one which would be based on the initial formation of interior radicals only, followed by slow migration of the radical site. The rate of the migration and the associated conversion of the interior to the penultimate form increase with temperature. A possible mechanism for these results is given in the next chapter (Section F).

2. Radical Migration

The movement of the alkyl radicals produced during the irradiation of n-eicosane can be considered in terms of intramolecular and intermolecular migration. The radical site can shift by H atom abstraction from a neighboring carbon on the same or an adjacent chain. Which is the more likely process has been the subject of several studies in the past. It was also a subject of this research. Intermolecular migration must take place in order that the radicals disappear by termination. The length of the $C_{20}H_{42}$ molecule (25 Å) is so small and the concentration of the radicals is so low that an alternative mechanism cannot be accommodated. Since there are no terminal alkyl radicals observed during the migration process, intermolecular hydrogen transfer cannot occur solely along the c-axis of the crystal. The migration could take place along the c-axis by a series of intramolecular movements to the penultimate position followed by intermolecular migration to an adjacent chain.

An interesting and potentially important experiment was reported by Shimada et al.³⁶ They examined the migration of alkyl radicals produced in a urea-polyethylene matrix. This system, in which the polyethylene chains are isolated from each other by the urea matrix, shows no migration at room temperature. Since the alkyl radicals on the polyethylene chains are unable to undergo intermolecular migration, and only above 100°C did the disappearance of the alkyl radicals in the urea matrix follow the kinetics of radical disappearance in polymer crystals, they concluded the intramolecular movement had to be very slow compared to the intermolecular migration. This conclusion is valid, however, only if a radical can interact with another radical

on the same chain and terminate. This requires doses which provide more than one radical per chain. Our analysis shows this was not the case in their work so that their conclusions appear to be unjustified.

Seguchi and Tamura³⁹ measured the radical decay kinetics of irradiated polyethylene single crystals. They found that the data give a better fit to a mechanism based solely on isotropic diffusion than one based on radical diffusion along the polymer chain. They conclude that the migration of the radicals occurs intermolecularly.

A more definitive study which provided contrary results was performed by Hama et al.³⁸. They irradiated n-alkane diols and observed the thermal conversion of the secondary alkyl radical to the terminal radical. Also ultraviolet irradiation of the terminal radical induced return to the interior secondary type. Since there is no change with time in the total radical concentration these effects are clearly due to intramolecular movement along the chain. It was not until the temperature was raised above 280°K that the radicals, by this time completely converted to the terminal type, underwent a bimolecular termination reaction.

Results obtained in this research help to resolve the disagreement. Figure 26 shows that the radicals produced in n-eicosane at 77°K move from the interior to the penultimate positions upon warming to room temperature, and that this migration takes place at temperatures where the radical concentration remains unchanged with time. Clearly these results are consistent with those of Hama et al., in showing that the intramolecular radical movement takes place earlier than the intermolecular migration.

It is interesting to apply these conclusions to the observation by Hamanoue et al.¹² that spatially correlated radical pairs disappear in irradiated eicosane with lifetimes of minutes when the mean lifetime for the disappearance of the secondary alkyl radicals may be hundreds of hours. By the mechanism established in this work these data can be explained by intramolecular hopping that would destroy the pair signal yet under conditions of slow intermolecular movement, would keep the alkyl radical concentration constant.

CHAPTER V

CHAPTER V

Mechanisms of Primary Processes

A. Introduction

Extensive studies of the radiolysis of condensed alkanes have provided substantial information on the production of various transient and persistent products. Today's most widely offered explanations, based on hot atom and ion-molecule mechanisms, do not explain the entire process satisfactorily. This chapter is an attempt to provide a more complete explanation of the radiation chemistry of solid alkanes.

1. Older Theories

There are three ways of explaining the mechanism for free radical production in polyethylene.

First, a free radical can be created through simple C-H bond scission induced by either neutralization or by direct interaction. The liberated hydrogen atom is frequently said to be "hot", that is, it has sufficient kinetic energy to initiate non-thermal reactions. Work by Iwasaki and his co-workers support this kind of mechanism.

A second explanation was proposed by Weiss³⁷ in 1958. In this mechanism, ionization is followed by inter- and intra-molecular ionic reactions, H₂ expulsion, followed by neutralization. The Weiss mechanism is a useful one which is consistent with the observations of an unsaturated cation and prompt crosslinking, but it has been largely ignored or rejected.

A third explanation was proposed by Libby¹⁴ in 1961. He concluded that the Weiss suggestion of H₂ expulsion prior to neutralization was, at best barely exothermic. Libby therefore proposed a mechanism based on the following reaction sequence:

1. ionization to form a cation radical and an electron
2. H atom abstraction by the cation radical
3. neutralization
4. H₂ expulsion.

2. Requirements of a Satisfactory Mechanism

Any mechanism proposed to explain the radiation chemistry of polyolefins must be consistent with several experimental observations made on the irradiation of solid alkanes at low temperatures:

- (a) the absence of H atoms in the ESR spectra of all hydrocarbons except methane (Timm and Willard¹⁹);
- (b) the apparent initial production of all alkyl radicals in spatially correlated pairs*, 5-6Å apart (Iwasaki et al.²⁰);
- (c) the production of the unsaturated cation radical, -HC=CH-^+ , as described by Waterman and Dole²⁶;
- (d) the high yield of unsaturation formed during the radiolysis of alkanes; and

*Unless stated otherwise, a "radical pair" is two alkyl radicals which are spatially correlated in close proximity to each other. Only when it is so stated does the phrase refer to an alkyl radical and its geminate hydrogen atom.

- (e) the report by Timm and Willard¹⁹ that a post-irradiation neutralization process at low temperatures does not affect the free radical concentration.

In addition, any mechanism must also give reasonable explanations for other phenomena observed in the radiation chemistry of hydrocarbons, such as the relative initial yields of primary and secondary alkyl radicals, and the results obtained with mixed crystals of protiated and deuterated alkanes.

B. Hot Atom Mechanism

1. H Atom Signal in CH₄

The H atom observed in the ESR spectrum of irradiated solid methane at 4°K is perhaps the strongest evidence for the existence of hot-hydrogen chemistry during the radiolysis of hydrocarbons. This hydrogen atom is not "hot" enough, however, to escape the immediate vicinity of the geminate methyl radical; many, if not all, the H atoms appear in the form of spin coupled pairs with the methyl radicals.

The question arises as to how the hot hydrogen is born. The C-H bond has a dissociation energy of approximately 4 eV. Even in a head-on collision with an H atom, an electron must have a minimum of 1800 eV to rupture the bond; and if the electron hits the H atom in a random classical manner, the average energy required is 3600 eV. The energy of Cobalt-60 gamma rays (~1.25 MeV) is far greater than these energies, but the bulk of the interactions of ionizing radiation with the alkane occur with secondary electrons. These secondaries lose their energy in interactions which have a $1/E^2$ distribution, where E is the

energy loss per collision. Thus less than 1% of the degraded electrons in the secondary electron distribution have sufficient energy to cause C-H scission. Since the G value for the production of these pairs is approximately 4, direct interactions can only account for a small fraction. The usual explanation is based on the fact that the ionization potential of methane (13.1 eV) is much greater than the bond energy. In consequence, hot hydrogen can be born after the neutralization process following an initial ionization. Since the G value for the ionization is 3.6, which is comparable to the yield of H atoms and the methyl radicals, this would appear to be the chief mode for radical production. Thus, in principle, H atoms can be born with an excess kinetic energy of 8 eV. These are potentially capable of producing at least one secondary C-H scission in the immediate vicinity of their creation. After they are thermalized by a few collisions, they are trapped at low temperatures; the evidence is clear that they do not migrate or undergo abstraction reactions below 10°K^{20} . (Section B.2)

The following is a series of reactions based on these considerations which describe the rupture of a C-H bond and the resulting production of an alkyl radical and a trapped H atom.

If this were the only valid mechanism, we would also expect to observe one species in the high pressure mass spectra of methane,

CH_4^+ . We would also expect several species in the ESR spectra of the irradiated solid, including CH_3 , $\text{H}_{\text{trapped}}$, $\text{CH}_3\cdots\text{CH}_3$ pairs, and $\text{CH}_3\cdots\text{H}$ pairs. Some H_2 evolution would also be anticipated.

This is clearly not the only mechanism. One observes in the mass spectrum not only CH_4^+ but CH_2^+ , CH_3^+ , and CH_5^+ , all in abundant quantities. ESR studies of the irradiated solid show the expected species: CH_3 , H , and $\text{CH}_3\cdots\text{H}$ pair signals but no $\text{CH}_3\cdots\text{CH}_3$ pairs. Also H_2 evolution is an observed product of the radiolysis as expected.

There is uncertainty regarding the presence of long-lived electrons after irradiation of CH_4 at low temperatures. Iwasaki et al.²⁰ state that the sharp signal characteristic of electrons does not appear in their spectra, even at 1.6°K; however, electrons at a variety of trap depths could give rise to a more diffuse signal which would be difficult to discern. Also, thermoluminescence studies by Charlesby and co-workers above 77°K give strong evidence for trapped electrons and corresponding cation species in irradiated higher alkanes. Shirom and Willard¹⁹ also conclude there are charged species in the higher alkanes which can be bleached with photons capable of raising the trapped electrons to the conduction band. (It is noteworthy that these two sets of results are for the higher alkanes.)

Even if electrons and positive species in irradiated solid CH_4 are introduced into this mechanism, it does not explain the abundance of certain ionic species observed in the high pressure mass spectral data.

There is another possible mechanism for the production of hot hydrogen atoms. This mechanism is based on the direct excitation of

the alkane followed by the ejection of a hot hydrogen atom.

This mechanism may also represent a reasonable explanation for the radiolysis of solid CH_4 . Clearly, however, additional ionic processes are at work in the gas phase radiolysis as demonstrated by the mass spectral data. Also conductivity measurements demonstrate that ionization takes place in the liquid to yield a cation radical and a highly mobile electron.⁴¹

2. H Atoms in Higher Alkanes

The mechanism described by reactions (1) - (4) fits the ESR results for solid CH_4 but fails to account for similar data for the higher alkanes. For the higher alkanes, the absence of trapped H atoms, even at 1.6°K, and the presence of spatially correlated pairs of alkyl radicals represent a clear conflict with such a mechanism. The mechanism also is inconsistent with the data of Iwasaki²⁰ et al.; they show that H atoms are trapped in methane-ethane mixtures irradiated at 4.2°K, and only upon warming to 10-20°K do the H atoms react to produce the ethyl radical and hydrogen gas.

This is an unexpected result. The ionization potentials of the higher alkanes are lower than that of methane, while the C-H bond energies of all alkanes are almost the same; thus, the energy of the hot hydrogen atoms produced on neutralization of irradiated CH_4 are the greatest of those produced in the entire alkane series. Yet, even

these atoms fail to abstract hydrogen to form H_2 and are trapped. It is therefore impossible to attribute the presence of radical pairs in the irradiated higher alkanes to abstraction reactions by hot hydrogen atoms.

C. The Libby Ionic Mechanism

1. Crosslinking and Unsaturation

An early description of the mechanism for alkyl radical production during the radiolysis of normal alkanes was suggested by Libby¹⁴ and later by Kevan and Libby.²¹ Their explanation was based on an ionic process where a free radical is produced by a hydrogen atom abstraction reaction prior to a neutralization reaction which is accompanied by H_2 expulsion:

The combined reactions (10) and (11) were estimated to be exothermic by a few kilocalories per mole.

It is important to note that the charged species in (9) and (10) are cation radicals, not carbonium ions. Libby¹⁴ believed the cation radical was of great importance to radiation chemistry as it "had the great bonding facility characteristic of ordinary free radicals which is still further enhanced kinetically by the long-range polarization forces."²² These forces were shown to be capable of causing the reactants to be attracted to each other which could bring the chemical

forces into range, resulting in an increased collision cross section.

Libby saw the process in terms of rapid inter- and intramolecular abstraction reactions between the ion radical and neighboring CH_2 groups. This is followed by neutralization with the rapid ejection of an H_2 molecule. When the H atom is abstracted from a neighboring chain by the cation radical, the neutralization and H_2 ejection give rise to two neighboring alkyl radicals. Reactions (10) and (11) show the formation of two radicals in close proximity, which can lead to a "prompt" crosslink. (This sequence could also account for radical pairs which were discovered subsequent to Libby's work.) A closer orientation of the H atom on a CH_2 adjacent to a cation radical site is equivalent to a intramolecular hydrogen abstraction; neutralization takes the following form in Libby's mechanism to produce the vinylene groups observed in the radiolysis of alkanes:

2. Neutralization

Timm and Willard¹⁹ concluded that the Libby mechanism failed to satisfactorily explain the experimentally observed independence of the radical concentration on neutralization. If reaction (11) were the only mechanism for free radical production, then upon neutralization the concentration of free radicals would increase. They referred to work by Shirom and Willard¹⁸ who saw no change in the radical concentration when trapped electrons in gamma irradiated 3 methylpentane at 77°K were bleached.¹⁸

Timm and Willard neglected to consider the possibility of opposing neutralization reactions which could keep the radical concentration constant. It turns out there are two such compensating processes: the production of a free radical upon neutralization of the product formed in the intermolecular abstraction (Reaction 11), and the loss of a radical (namely, the initial cation radical) by the neutralization leading to unsaturation as shown in (12). The G value for alkyl radicals is 4 and the neutralization reaction accounts for half of them (reaction (10) accounts for the other half); the G value for unsaturation is 2. Thus the two neutralization reactions are approximately equal and opposite in their effect so that there should be no change in the radical concentration as a consequence of neutralization.

Waterman and Dole²⁶, however, invalidate this mechanism by providing strong evidence (cf. Section D3) for the unsaturated cation radical $R_1CH = \overset{+}{C}HR_2$ in irradiated polyethylene at 4°K; it is transformed quantitatively into $R_1CH = CHR_2$ on neutralization. The Libby mechanism does not provide for the formation of this unusual cationic species.

D. The Weiss Ionic Mechanism

1. Description of Mechanism

An extension of an early ionic mechanism proposed by Weiss is shown here to be in agreement with all experimental observations on higher linear alkanes but fails to fit the data for methane.

Weiss proposed the following ionic mechanism:

Primary Reaction:

Secondary Reaction:

Tertiary Reaction:

Neutralization Reaction:

Crosslinking Reaction:

Note that one mode of producing alkyl radicals is intramolecular expulsion of H_2 (Reaction 14). The other is based on the reaction sequence 13, 15, and 16; this is equivalent to an intermolecular expulsion of H_2 .

The difference between Libby and Weiss is that the former postulated neutralization prior to H_2 expulsion while the latter maintained that the unimolecular ejection of a hydrogen molecule from the radical cations of the higher alkanes is a relatively rapid process

compared with neutralization. The best test of the two mechanisms could be the results for highly viscous liquids, solids, and ionized gases in which the electrons are collected by application of an electric field. In these systems, H_2 elimination (14, 16, 17) and H abstraction (15) processes can compete more effectively with the neutralization process.

2. Mass Spectral Data

The Weiss mechanism provides the basis for predicting the presence of several positive ions in the mass spectra of various normal alkanes, including $C_n H_{2n+2}^+$, $C_n H_{2n}^+$, $C_n H_{2n+3}^+$, $C_n H_{2n+1}^+$, and $C_n H_{2n-1}^+$. Work by Draper and Green²⁴, and Green and Pinkerton²⁵ shows positive evidence of all of these species. Also their results of yield versus pressure indicate that the method of production of these ions is consistent with the Weiss mechanism.

3. Unsaturation

The radiation-induced production of trans-vinylene unsaturation in normal hydrocarbons appears to be preceded by the formation of the unsaturated ionic species $C_n H_{2n}^+$. This conclusion is based on infrared absorption measurements on irradiated polyethylene performed by Waterman and Dole²⁶. The irradiations were done at 4°K. They found a double absorption band in the region of 966 cm^{-1} , the normal position of the neutral transvinylene group. They suggest the band at 973 cm^{-1} is due to the unsaturated radical cation $-CH=CH^+$, which is an analog of $C_n H_{2n}^+$ species predicted by the Weiss mechanism (reaction 14) and observed in mass spectroscopy. When the sample is warmed to 77°K the

973 cm^{-1} band disappears while the 966 cm^{-1} band increases. It is difficult to account for these results except by attributing the 973 cm^{-1} band to the $\text{C}_n\text{H}_{2n}^+$ species, and the growth in the 966 cm^{-1} band on warming to neutralization and consequent production of the vinylene compound.

It is also important to note that the $\text{C}_n\text{H}_{2n}^+$ species has an unpaired electron. This radical species disappears upon neutralization as the vinylene species is formed. If all the vinylene groups are formed by the neutralization process the decrease in the unsaturated cation radicals would match the increase in the alkyl radicals formed by reaction (18). Such a system would exhibit no net radical change upon neutralization in agreement with the observations by Shirom and Willard.¹⁸

Thus it appears that the Weiss mechanism does extremely well in explaining the radiation chemistry of normal hydrocarbons. His mechanism describes the production of radical pairs (which were unknown when he wrote his paper), although he discussed them only as the precursors to "prompt" crosslinks; it is the only mechanism that predicts the existence of the unsaturated cation radical and it fits the neutralization results of Shirom and Willard. The mechanism does not however explain the existence of H atoms in irradiated methane.

E. General Mechanism

The foregoing section demonstrates that the Weiss mechanism is remarkably consistent with all information in producing a description of the radiation chemistry of linear alkanes. But it has one

conspicuous failing: it does not work for solid methane. The data for solid methane can be described in terms of the hot atom model without reference to any ionic species. At first glance, this is surprising when one considers that the mass spectral data for methane, which are the consequence of a variety of ionic reactions are in agreement with the Weiss mechanism.

The success of the Weiss mechanism with gaseous methane and with higher alkanes (solid or gaseous) and its failure with solid methane suggest a more generalized mechanism of the following form:

1. The principal primary species produced by irradiation of alkanes are radical cations and electrons,
2. in solid methane the neutralization process is rapid relative to H_2 expulsion and H atom abstraction reactions,
3. in solid alkanes and in alkane gases subjected to an electric field the H_2 expulsion (both inter- and intra-molecular) and H atom abstraction reactions are rapid relative to the neutralization process.

Clearly such a mechanism is based on the assumption that the migration of electrons is slower in linear hydrocarbons than methane. The following list of electron mobilities shows this is indeed the case:

methane ⁴¹	$400 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
ethane ⁴¹	$0.9 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
n-pentane ⁴¹	$0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
neo-pentane ⁴¹	$70 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

(These data are for liquids but the sparse data available for solid alkanes follow the same pattern.) This suggests that the mechanism may be of an intermediate nature in branched alkanes; that is, the competition between neutralization and the other reactions may favor the latter somewhat more in branched alkanes than in linear alkanes, but somewhat less than in methane.

F. Mechanism for the C-H Fracture Pattern in Solid Alkanes

The data produced in this research confirm that the free radicals produced in irradiated solid alkanes are of the interior type. None of the previous speculations on the mechanism give any insight as to why this is the case.

We propose the following. The initial ionization process occurs randomly throughout the molecule. The site of the ionization is rapidly transferred by positive hole migration to the interior of the molecule prior to the abstraction and expulsion reactions of the Weiss mechanism. Such a mechanism would be strengthened (1) by experimental evidence of hole migration in irradiated alkanes, and (2) by demonstrating, at least on an energetic basis, that the interior site should be favored over the penultimate and ultimate sites.

The evidence for hole migration can be found in the work by de Haas et al.^{42,43} in pulse conductivity studies in cyclohexane. Meggitt and Charlesby⁴⁴ also find evidence of hole migration in irradiated polyethylene; they do not differentiate between inter- and intramolecular migration.

The interior position is also energetically favored. This is illustrated by the fact that methane⁴⁵ (ip = 13 eV) has an ionization potential 25% greater than that of n-pentane⁴⁵ (ip = 10.6 eV).

CHAPTER VI

CHAPTER VI

CONCLUSIONS

1. The enhancement of the radiation crosslinking of polyethylene said to be associated with the addition of small amounts of inert filler was not substantiated by experiments performed over a much wider range of conditions than reported heretofor. Although, the results were negative, it is still possible that the blending process could lead to the enhancement of radiation crosslinking reactions. This would arise from an increased yield of unsaturated species which might lead to chain reaction crosslinking. The mechano-chemistry associated with this process, although never optimized, is worthy of further study, especially since there are important industrial implications.

2. The radiation-induced grafting reactions reportedly sensitized by acid were observed and substantiated. The results are less impressive when considered for industrial applications. The effect, observed primarily for total grafts above 100% and accompanied by substantial amounts of occluded homopolymer would have no practical value. The mechanism is still unclear, but the sensitization by acid is clearly not caused by an increase in the H atom yield.

3. The relative yields of the various types of alkyl radicals produced in irradiated single crystals of $n\text{-C}_{20}\text{H}_{42}$ were found to be dependent upon experimental conditions, particularly dose, temperature, and time. This leads to the resolution of conflicting data reported by other laboratories and establishment of the conditions

which provide the most meaningful fundamental information. Radical migration to defective crystalline regions either within or on the surface of the sample were found to be by both inter- and intra-molecular motion. The results show that a small fraction of the interior radical sites shift to the penultimate position upon warming; this is followed by intermolecular movement and termination. Intermolecular migration is a prerequisite for radical termination but intramolecular motion is more rapid.

4. A general theory for the radiolysis of linear alkanes is proposed. The differences between the radiolysis products of solid methane and the higher alkanes is explained by the greater mobility of the liberated electron in the methane and thus the smaller geminate recombination time. In higher alkanes the lower electron mobilities allow the ionic processes of the Weiss mechanism sufficient time to occur before neutralization. An explanation of the fracture patterns is offered which involves random ionization, and hole migration to the interior positions prior to the ionic processes of the Weiss mechanism.

TABLES

TABLE 1

Relative Radical Yields Reported
by Gilbro and Lund³²

	Experiment		Theory	
	<u>% Penultimate</u>	<u>% Interior</u>	<u>% Penultimate</u>	<u>% Interior</u>
C_6H_{14}	65.6	34.4	71.4	28.6
$C_{10}H_{22}$	42.5	57.5	45.5	54.5
$C_{16}H_{34}$	33.1	66.9	29.4	70.6
$C_{20}H_{42}$	29.3	70.7	23.8	76.2

TABLE 2

Simulated Parameters

Sextet line width	10.5 gauss
Sextet splitting	36.6 gauss
Penultimate line width	4.5 gauss
Methyl splitting	36.2 gauss
Methylene splitting	27.4 gauss

TABLE 3

Sample Spectrum

Peak to Peak Ratios

$$R_1 = S_3 / \text{methyl right side}$$

$$R_2 = S_3 / \text{methyl left side}$$

$$R_3 = S_4 / \text{methyl right side}$$

$$R_4 = S_4 / T \text{ right side}$$

TABLE 4

Simulated Spectrum

Fraction Sextet	R_1	R_2	R_3	R_4
0.50	0.44	0.62	0.44	0.39
0.70	1.21	1.24	1.21	1.09
0.80	2.38	1.73	2.38	2.20
0.825	2.97	1.89	2.97	2.70
0.85	3.88	2.07	3.88	3.58
0.90	8.25	2.41	8.25	7.61

FIGURES

Figure 1. Effects of SiO_2 and TiO_2 on the radiation induced crosslinking of polyethylene as described by Gordiyenko et al.

Figure 2. Infrared spectra of pure polyethylene (···) and polyethylene filled with 0.5 volume percent of 0.007 μm silica (—).

Figure 3. The concentration and uniformity of the silica in the filled samples as confirmed by infrared analysis at 475 cm^{-1} .

Figure 4. Percent gel as a function of concentration of 75 μm SiO₂.

Figure 5. IR spectra of polyethylene blended for 60 min at 120 rpm and 150°C.

Figure 6. Carbonyl concentration as a function of blending time by IR absorption at 475 cm^{-1} .

Figure 7. The effect of fillers on gel production in PE irradiated by electrons in the presence and absence of oxygen.

Figure 8. The effects of fillers on gel production in PE irradiated by gammas in the presence and absence of oxygen.

Figure 9. The effect of fillers on the elastic modulus of PE irradiated by gammas in the presence of oxygen.

Figure 10. The effect of 0.1 M H_2SO_4 on the grafting of polyethylene immersed in styrene-methanol solutions as reported by Garnett and Yen.

Figure 11. The effect of H₂O on the grafting of polypropylene immersed in methylmethacrylate-water solutions as reported by Pinkerton and Stacewicz.

Figure 12. The effects of $0.1 \text{ M H}_2\text{SO}_4$ on the grafting of polyethylene immersed in O_2 and O_2 -free styrene-methanol solutions.

Figure 13. The effect of $0.1 \text{ M H}_2\text{SO}_4$ on the grafting kinetics of polyethylene immersed in a O_2 -free 70% methanol - 30% styrene solution.

Figure 14. The effect of 0.1 M H_2SO_4 on the swelling characteristics of a 0.8 mm thick polyethylene strip immersed for 24 h in a 70% methanol - 30% styrene solution.

Figure 15. Computer simulated ESR pattern of irradiated eicosane with a .50/50 interior/penultimate alkyl radical composition.

Figure 16. Computer simulated ESR pattern of irradiated eicosane with a 70/30 interior/penultimate alkyl radical composition.

Figure 17. Computer simulated ESR pattern of irradiated eicosane with a 80/20 interior/penultimate alkyl radical composition.

Figure 18. Computer simulated ESR pattern of irradiated eicosane with a 82.5/17.5 interior/penultimate alkyl radical composition.

Figure 19. Computer simulated ESR pattern of irradiated eicosane with a 85/15 interior/penultimate alkyl radical composition.

Figure 21. Calibration curve for the R_1 , the ratio of interior sextet signal to the penultimate signal.

Figure 22. Calibration curve for the R_2 , the ratio of interior sextet signal to the penultimate signal.

Figure 23. Calibration curve for the R_3 , the ratio of interior sextet signal to the penultimate signal.

Figure 24. Calibration curve for the R_4 , the ratio of interior sextet signal to the penultimate signal.

Figure 25. Power saturation curve for the interior and penultimate alkyl signals.

Figure 26. The effect of temperature on the concentration of the interior radical relative to the total radical concentration.

Figure 27. ESR pattern of an irradiated eicosane crystal at 77°K.

Figure 28. ESR Pattern of an irradiated eicosane crystal at 77°K after annealing at 155°K for 5 m.

Figure 29. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 175°K for 5 m.

Figure 30. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 200°K for 5 m.

Figure 31. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 220°K for 5 m.

Figure 32. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 250°K for 5 m.

Figure 33. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 270°K for 5 m.

Figure 34. ESR pattern of an irradiated eicosane crystal at 77°K after annealing at 300°K for 5 m.

Figure 35. Effect of time on the relative concentrations of the interior alkyl radical at room temperature.

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