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AN ELECTRON SPIN RESONANCE STUDY OF TRAPPED ELECTRONS

IN γ -IRRADIATED HYDROCARBON POLYMERS

A Dissertation

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

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by

Ronald Melvin Keyser

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ABSTRACT

Trapped electrons have been detected by ESR spectroscopy in polyethylene, isotactic polypropylene, and poly(4-methylpentene-1) following γ -irradiation at 77°K. In all cases, the ESR spectrum consists of a narrow singlet at $g = 2.0023 \pm 0.0002$ superimposed on a broad free radical spectrum. The singlet can be photobleached by near infrared light ($\lambda > 1000$ nm) and is readily saturated at low microwave powers. The singlet is assigned to a trapped electron since this behavior is analogous to that known to be characteristic of trapped electrons in γ -irradiated alkane glasses.

Initial G-values for trapped electrons in these systems range from 0.46 for linear polyethylene down to 0.08 for isotactic poly(4-methylpentene-1). Both G-values and the maximum value attained in the concentration-dose curve for trapped electrons appear to be correlated with the crystallinity of the polymer and decrease with decreasing crystallinity. Little or no trapped electrons could be detected in non-crystalline polymers such as atactic polypropylene or polyisobutylene. These results strongly suggest that the electron trap is associated with crystalline regions of the polymer.

The linewidth, ΔH_{ms} , of the trapped electron singlet is significantly less in these polymers than in alkane glasses. ΔH_{ms} ranges from 3.4 gauss in polyethylene down to 2.6 gauss in poly(4-methylpentene-1). The spin-lattice relaxation time of trapped electrons in polyethylene has been found to be $T_1 \geq 2 \times 10^{-2}$ sec from microwave power saturation measurements. This value is an order of magnitude greater than for alkane glasses. Both the linewidths and relaxation times indicate that

trapped electrons interact less strongly with their surroundings in semi-crystalline polymers than in alkane glasses.

Enhanced optical absorption between 700-2000 nm has been observed in poly(4-methylpentene-1) following γ -irradiation at 77°K. This absorption can be eliminated by photobleaching with near-infrared light and is therefore assigned to trapped electrons. The band maximum presumably lies beyond 2000 nm but this region is beyond the range of the spectrometer. The absorption band is evidently strongly red shifted compared to alkane glasses.

In terms of a model in which vacancies or voids act as electron trapping sites, the decreased linewidth, longer T_1 , and red shift of the absorption spectrum in polymers relative to alkane glasses imply that the vacancy is significantly larger in polymers. The possibility that the electron is trapped in a row-vacancy defect associated with crystalline regions of the polymer is discussed and evidence derived from ESR studies of electron trapping in n-hexatriacontane is presented in support of this hypothesis.

The thermal decay of trapped electrons in linear polyethylene has been investigated in detail over the temperature interval 77-127°K. The results suggest that there are populations of trapped electrons which are relatively stable toward thermal decay until the temperature is raised to a point where they become vulnerable.

A correlation of trapped electron concentration with free radical concentration in γ -irradiated polyethylene has been observed. The trapped electron yield decreases with increasing free radical concentration, suggesting that free radicals may scavenge electrons.

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CHAPTER I

SOLVATED AND TRAPPED ELECTRONS IN RADIATION CHEMISTRY

A. Introduction

Radiation chemistry is the study of the chemical effects obtaining when molecules are subjected to high energy radiation. The deposition of large amounts of energy in a molecular system results in the formation of a variety of highly reactive intermediates such as free radicals, electronically excited molecules, and ionic species including electrons. Many of these intermediates are unusual in the sense that they are not commonly observed in the more conventional areas of low-energy chemistry. Consequently there has been considerable interest in their behavior, properties, and reactions.

The primary mechanism through which energy is transferred from the radiation field to the chemical system is by ionization and excitation of molecules in the medium. Prior to 1962, the fate of the electron ejected in this process was the subject of intense speculation among radiation chemists. Does it undergo rapid geminate recombination with a positive ion or can it escape the ion and go on to behave as a distinct chemical entity? These speculations were laid to rest in 1962 with the discovery of solvated electrons in irradiated water¹ and trapped electrons in frozen aqueous solutions^{2,3} and in rigid organic glasses⁴ following irradiation.

The term solvated electron as used here is meant to imply an electron physically localized in the medium in such a manner that it is bound to no single molecule and does not reside entirely within the

molecular orbitals of the surrounding molecules. The classic example of a solvated electron is the species responsible for the blue color when an alkali metal is dissolved in liquid ammonia.⁵ Many of the properties of solvated electrons can be qualitatively understood in terms of an electron localized in the liquid and surrounded by a solvation sphere comprised of polarized solvent molecules.

A trapped electron, on the other hand, may be simply regarded as the solid state analogue of a solvated electron. Trapped electrons in radiation chemistry display certain similarities to the familiar F-center. The F-center consists of an electron trapped in the field of a negative ion vacancy in an ionic crystal.⁶ The analogy should not be pushed too far, however, since in radiation chemistry one is dealing mainly with molecular systems as opposed to the ionic crystals in which F-centers are found.

The study of trapped and solvated electrons has received increasing attention in the years since 1962. This results not only from the importance of electronic intermediates in radiation chemistry but also because their behavior and properties have piqued the curiosity of chemists. As Jortner et al.⁷ have pointed out, one would like to know what the electron is "doing" in the system. Many of the more recent investigations have dealt with the phenomenon from the standpoint of the trapped electron. This follows from the fact that, at low temperatures, trapped electrons can be made rather stable with respect to recombination with positive ions and other reactions. Hence their properties can be studied at a relatively leisurely pace as compared to solvated electrons which, in irradiated systems at least, have only a transitory

existence. The presence of trapped electrons has now been unequivocally demonstrated in a wide variety of irradiated systems ranging from ice to frozen hydrocarbons at 77°K. Methods of detection and identification have centered primarily on optical spectroscopy, electron spin resonance (ESR) spectroscopy, and scavenger studies.

In addition to those systems in which trapped electrons are known, many other systems display properties which are best interpreted as deriving from trapped electrons even though their existence can only be indirectly inferred. An important case in point is that of irradiated hydrocarbon polymers such as polyethylene. Following irradiation, polyethylene not only displays enhanced electrical conductivity but thermoluminescence as well, both effects being postulated as resulting from trapped electrons.⁸⁻¹²

Recent work¹³ has employed both optical and ESR techniques to characterize trapped electrons in irradiated alkane glasses. In view of the similarity between an alkane and polyethylene, at least from a chemical standpoint, it seems not unreasonable to suppose that similar techniques might provide a means to obtain direct physical evidence for trapped electrons in irradiated hydrocarbon polymers as well. This dissertation reports the results of an investigation in which the consequences of this supposition are explored.

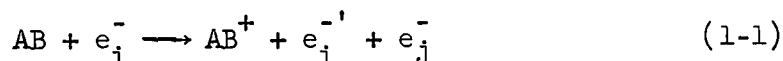
The balance of this chapter is concerned with a somewhat cursory discussion of the effects of radiation on matter, a more detailed discussion of trapped and solvated electrons in both aqueous and organic media, intermediates in irradiated polymers, and finally a more detailed proposal of the problem. Subsequent chapters deal with experimental

methods, results, and lastly, a discussion of the significance of the results.

B. Interaction of High Energy Radiation with Chemical Systems

1. Mechanism of Energy Deposition

Highly energetic electromagnetic radiations such as gamma rays deposit energy in a chemical system primarily as a result of interaction of photons with electrons in the molecular orbitals of the system. For typical photon energies of 1 Mev and for materials of low atomic number, this interaction is mainly by means of Compton scattering.¹⁴ The recoil electron produced in the scattering event possesses energy up to a considerable fraction of the incident photon and consequently may cause considerable further ionization and excitation by means of coulombic interaction with electrons in molecules along its path. These processes may be represented by the following equations¹⁵



where e_i^- is the incident recoil electron, $e_i^{-'}$ and $e_i^{-''}$ represent an electron now of less energy, and e_j^- is a secondary electron formed in the secondary ionization process. AB represents a substrate molecule, AB^+ an ionized AB, and AB^* an electronically excited AB.

The secondary electrons e_j^- are often only of the order of 100 ev or less in energy and their range in condensed-phase materials is short. Consequently any further ionization or excitation which they may produce is located in a cluster close to the site of the original ionization.

On the other hand, the scattered electrons $e_1^{-'}$ and $e_1^{-''}$ usually possess sufficient kinetic energy to initiate a substantial number of additional primary ionization and excitation events along their track. The picture that emerges is a series of volumes containing ionized and excited molecules strung out along the track of the high energy electron. These volumes are called "spurs" and in a condensed system are thought to have a radius of some 10 to 100 Å and are separated by about 10^3 Å along the track.¹⁶

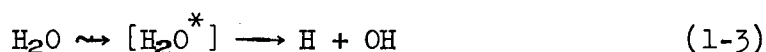
2. Reactions of Intermediates

The primary intermediates resulting from the irradiation of a chemical system are, according to Equations 1-1 and 1-2, positive ions, secondary electrons, and excited molecules. The subsequent reactions of these species determine overall chemical effects resulting from irradiation. Excited molecules are assumed to decompose either by means of homolytic bond scission to give two free radicals or else by decomposition into molecular products. The behavior of the free radicals so produced has been recently reviewed for organic liquids^{16,17} and solids¹⁸ and for aqueous systems.¹⁹ For this reason, little more will be said regarding excited molecules and free radicals except in passing. This is not meant to minimize the importance of free radicals since they are undeniably very important in radiation chemistry, but results from a desire on the part of the author to concentrate on the role of electrons in this introductory chapter.

If the secondary electron produced in Equation 1-1 can escape immediate recombination with the positive ion, both the ion and electron may participate in various chemical reactions. On the other hand, if

rapid recombination is favored, then an excited molecule results and subsequent events are governed by the possible decomposition modes of the excited species as mentioned above.

Early in the development of radiation chemistry, Samuel and Magee²⁰ considered theoretically the problem of escape versus recombination of the secondary electron in liquid water. By ascribing transport properties to the electron similar to those in the gas phase, they deduced that the electron reached thermal energies within about $15 \text{ \AA}$ of the positive ion and was subsequently attracted back to the ion and underwent recombination in a time of the order of 10^{-13} sec. Although some expressed a contradictory viewpoint,²¹ most workers accepted the results of these calculations and used them as a basis for ignoring ionic reactions, attributing the effects of radiation on liquid water to the process



where the symbol $\rightsquigarrow$ stands for absorption of radiation.

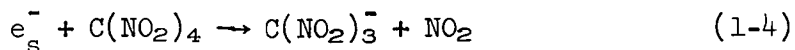
C. The Solvated Electron

1. Discovery and Reactions

In the period from 1958 to 1962, several lines of evidence developed which implied that the radiation chemistry of water could not be so simply accounted for as indicated by Equation (1-3). Thus evidence from scavenger studies²²⁻²⁴ indicated the presence of a second reducing species besides the H atom. Furthermore, this second species was shown to possess unit negative charge on the basis of the effect of ionic strength on the rate constants for its reactions with scavengers,^{25,26}

strongly suggesting the possibility of a solvated electron. Spectroscopic evidence for the solvated electron in water came finally from the classic experiments¹ of Hart and Boag and of Keene. These workers discovered a transient optical absorption in the visible region of the spectrum following a short pulse of intense radiation. The band maximum was observed at 7200 Å.

The evidence for assigning this band to a solvated electron is quite convincing and has been summarized in a recent review.²⁷ Thus the shape, properties, and asymmetry of the band are similar to solvated electron optical bands in metal-ammonia systems. Moreover, if tetranitromethane, $C(NO_2)_4$, is added to the system, the decay of the 7200 Å band occurs concurrently with the appearance of a band corresponding to the known absorption of the tetraform anion.²⁸ This result is explained in terms of scavenging a solvated electron according to Equation 1-4.



where e_s^- stands for a solvated electron. From the known extinction coefficient of $C(NO_2)_3^-$, the extinction coefficient for e_s^- can be obtained as well. The results of other scavenger studies also support the assignment. Scavengers known to react with electrons suppress the 7200 Å band whereas those unreactive to electrons do not. These considerations as well as others²⁷ leave little doubt that the 7200 Å band is to be associated with a solvated electron.

The solvated electron is an extremely reactive species. Rate constants for its reaction with over several hundred organic and inorganic solutes in irradiated water have now been measured. Most of this information is summarized in the literature.^{27,29,30} Unfortunately, however,

much of the kinetic data have been obtained by simply following the rate of disappearance of the e_s^- optical band and in only a few instances has the nature of the final products of the reaction been determined. Many of these reactions are among the fastest known, approaching the theoretical limit for an encounter-controlled reaction. In carefully purified water, on the other hand, the solvated electron decays by a first-order process with a half-life of 800 μ sec.³¹ It has been suggested³¹ that this decay corresponds to the reaction



Recently a report has appeared attributing a transient ESR signal to the solvated electron.³² The spectrum consists of a narrow singlet of width less than 0.5 gauss and g factor of 2.0002 ± 0.0002 . The lifetime of the signal is only 10 msec and its detection requires highly sophisticated instrumentation.

Observations of solvated electrons are not limited to irradiated water alone. Optical absorption bands attributable to solvated electrons have been observed in a variety of alcohols including MeOH, EtOH, *n*-PrOH, and *i*-PrOH.³³ Band maxima range from 6300 Å for MeOH up to 8200 Å for *i*-PrOH. Teply³⁴ has recently reviewed the radiation chemistry of alcohols in this connection and also discussed several reports of solvated electrons in ethers.

2. Structure of the Solvated Electron

Although much information has been amassed regarding kinetic and other properties of the solvated electron, a detailed picture of its structure has yet to emerge. It is generally accepted that a solvated

electron is not an electron bound to a solvent molecule to form a conventional anion, i.e., H_2O^- . The electron affinity of water is not suitable nor are there suitable low-lying orbitals to accommodate the electron. At the other extreme, it is also clear that a solvated electron is not "free" in the sense of a conduction electron in a metal. The mobility and diffusion coefficient of the solvated electron are not much greater than typical anions.³⁵ Furthermore, the existence of a well defined optical absorption band also implies a localized system.

Early theoretical work on the problem of electron binding in solution stems from the properties of solvated electrons in metal-ammonia solutions. The properties of these solutions have been recently reviewed.^{5, 36} In dilute alkali metal-ammonia solutions, the nature of the cation seems to have little effect on the properties of the solvated electron. This fact suggests that the stabilization of the electron derives solely from electron-solvent interactions, i.e., polarization. A second point of interest is that the solutions occupy very much larger volumes than the sum of the volumes of the pure constituents. On the basis of considerations such as these, Ogg proposed³⁷ a model in which the electron is regarded as being localized in a cavity in the liquid, the cavity walls being comprised of polarized solvent molecules. Cavity formation then accounts for the volume expansion. Ogg treated the electron bound to the cavity by means of a particle-in-a-box calculation and concluded that for minimum energy, the cavity radius would be some 10 Å. This is substantially greater than the value of 3 Å obtained by assuming the volume expansion of the solution arises from cavity formation.

Jortner^{7,38,39} has recently extended the "polaron" concept⁴⁰ to the problem of the solvated electron in both liquid ammonia and in water. According to this model, cavity formation arises from short-range repulsion between the solvated electron and electron clouds of surrounding molecules. The electron is bound to the cavity by the polarization field from surrounding solvent molecules which have been oriented and polarized by the field of the electron itself. By using a self-consistent field approach and 1s and 2p hydrogenic-type wave functions for the ground and excited states, Jortner was able to calculate the energy of the electron in the 1s ground state and 2p excited state as a function of cavity radius.

For metal-ammonia systems, the model is rather successful. Thus, for a cavity radius of $3 \text{ \AA}$, Jortner calculates a 1s $\rightarrow$ 2p transition energy of 0.93 ev, which is in rather good agreement with the experimental value of 0.80 ev for the maximum in the optical absorption band of the solvated electron in ammonia. In the case of water, best agreement is obtained in the limit of zero cavity radius, the calculated transition energy being 1.35 ev compared to the observed value of 1.7 ev. Thus the cavity size in water appears to be vanishingly small. This has been interpreted as meaning that no expansion of a normal cavity in water (i.e., a cavity intrinsically associated with the water structure) is necessary to solvate the electron.⁴¹ A further point in this connection is that despite the necessity of using a vanishingly small cavity radius, Jortner calculates a mean radius of the ground state charge distribution of some $2.5\text{--}3.0 \text{ \AA}$, indicating that the electron is diffusely spread out over several surrounding molecules. It is interesting to

note that the collision radius of the solvated electron as estimated from kinetic parameters is also of this order.⁴²

Despite these evident successes of the Jortner treatment, the model is inherently unsatisfactory in the sense that it is a semi-empirical model with the cavity size as an adjustable parameter. Thus, for example, the model is incapable of predicting or dealing with the variations in optical band maxima found for solvated electrons in alcohols.³³ It would seem that some type of cavity or vacancy model is required in which explicit account could be taken of the interaction of the electron with its surroundings. Recent work along these lines has been reported by Natori and Watanabe.⁴³ These authors propose a specific model for the solvated electron in water in which the electron occupies a vacancy in the water structure surrounded by four tetrahedrally disposed water molecules. Although the initial calculations based on this model gave too low a value of the optical transition energy, it has been suggested that the agreement would be substantially improved if better account of long-range polarization interactions were taken.⁴⁴ This model is attractive and should receive further work.

D. Trapped Electrons

1. Frozen Aqueous Systems

Because of the transient nature of radiation-produced intermediates in the liquid state, specialized methods such as pulse radiolysis are required for their study. Work in frozen systems on the other hand affords the possibility of trapping or isolating the intermediates and studying them by means of standard optical and ESR techniques. For this reason, frozen systems have been intensively investigated.

Four possible intermediates in ice might be expected to be observed on the basis of the previous discussion of water:



Here e_t^- symbolizes a trapped electron. H, OH, and e_t^- in fact have been observed. The properties and behavior of all three have been recently reviewed.⁴¹ The discussion here centers on the trapped electron.

It has been only recently that trapped electrons have been observed in irradiated pure ice at 77°K, an optical band at 6300 Å having been assigned to the trapped electron.⁴⁵ The yield of trapped electrons is very low at 77°K and $G(e_t^-)$ has been estimated to be $\sim 2 \times 10^{-4}$. (G is the radiation chemical symbol for yield and represents the number of molecules of a species produced per 100 ev of energy absorbed.) No ESR work has been reported on the trapped electron in pure ice since it appears that the yield is much too low to permit observation by ESR.

In contrast to the very low yields of trapped electrons in pure ice, large yields are obtained if the ice is made strongly alkaline by adding 1-10 M NaOH or other alkali hydroxide prior to freezing. Such systems form clear transparent glasses when frozen.

As discussed by Kevan,⁴¹ irradiated alkaline ice, at 10^{-3} M NaOH, is colored blue but there is no evidence of any species other than OH in the ESR spectrum. With increasing hydroxide concentration, the blue color intensifies until at about 1 M NaOH, a new resonance with $g = 2.001$ and linewidth of 16 gauss between points of maximum slope appears in the ESR spectrum. An optical band with $\lambda_{\text{max}} = 585 \text{ nm}$ is present as well.^{2,3}

Optical bleaching of this band causes it to disappear along with the ESR line at $g = 2.001$. Thermal bleaching accomplishes the same result.

Both the 585 nm band and the resonance at $g = 2.001$ are assigned to a trapped electron. The evidence is as follows. The optical and thermal bleaching experiments indicate both the optical band and ESR resonance belong to the same species. The optical band, although shifted to shorter wave length compared to the solvated electron in water, is similar in shape. The most convincing evidence arises from scavengers. Thus if electron scavengers such as N_2O , CH_3Cl , $ClCH_2COOH$, and others are added to the system, the blue color, the 585 nm band, and the ESR singlet all fail to appear.^{41,46}

Kevan has discussed the various models which have been proposed for the electron trapping site in these alkaline glasses.⁴¹ The most satisfactory model seems to be that of an electron trapped in a hydroxide anion vacancy analogous to the F-center trap in alkali halides.⁴⁷ The hydroxide anion vacancy is formed during irradiation as a result of proton transfer from H_2O^+ to a hydroxide anion. The trap then consists of the solvation shell of polarized water molecules originally oriented about the anion. Support for this type of model comes from ESR linewidth studies. Whereas the trapped electron ESR singlet linewidth is 16 gauss in H_2O systems, it is only 7 gauss in D_2O alkaline ices.⁴⁸ Thus the major interaction of the trapped electron is with surrounding protons and is consistent with the hydroxide anion vacancy model.

As an alternative to generation of trapped electrons in aqueous ices by means of radiation, Bennett et al.⁴⁹ have found that they may be produced by chemical techniques. By clever use of a rotating cryostat

whereby alternate layers of alkali metal and water vapors were frozen onto the cryostat walls at 77°K, trapped electrons could be observed in the deposit. An ESR singlet of $g = 2.008$ and width 9 gauss was associated with the trapped electron and the singlet spectrum gave evidence of unresolved hyperfine lines. On warming, the resolution increased until at 173°K a resolved septet with 5.6 gauss hyperfine splitting and binomial line intensities was observed. Experiments with D₂O indicated the septet arose from equal interaction with six equivalent protons. These results indicate electron trapping in a well defined trap. Bennett et al.⁴⁹ suggested that the electron was trapped in the center of a puckered hexagon with six oxygen atoms at the corners and six hydrogen atoms lying along lines joining adjacent oxygens.

2. Frozen Organic Systems

At the same time as the early experiments involving trapped and solvated electrons in aqueous media, Hamill and co-workers reported the identification of a trapped electron in gamma-irradiated 2-methyltetrahydrofuran (MTHF) glass.⁴ MTHF forms a clear transparent glass when plunged into liquid N₂. Following irradiation at 77°K, the glass turned blue and optical spectroscopy revealed a broad band extending from 400 nm to 1600 nm with a maximum at 1200 nm.^{4,50} This band can be eliminated (photobleached) by exposing the sample to relatively intense light whose wavelength is in the region of the band maximum. The blue color disappears as well.

If several tenths mole percent of naphthalene or biphenyl are added to the system, the 1200 nm band is diminished and new bands at shorter wavelengths appear. These latter bands are identical to those of

naphthalene and biphenyl radical anions prepared by conventional chemical means. Moreover, if the 1200 nm band is photobleached with red light, the anion bands are observed to increase. These facts offer compelling proof that the 1200 nm band results from a solvent-trapped electron.

Dyne and Miller⁵⁰ have summarized these observations in terms of a simple mechanistic scheme. Thus radiolysis of MTHF yields a positive ion P^+ and a secondary electron e_k^- having kinetic energy in excess of thermal.



The secondary electrons lose energy to their surroundings, become thermalized (e_{th}^-), and ultimately may become physically trapped in the matrix as in (1-9).



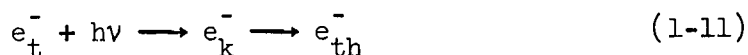
If a solute possessing a high electron affinity such as naphthalene or biphenyl (ϕ_2) is present in the system, then e_{th}^- may be scavenged by the additive:



Hamill et al.⁴ found that, as the concentration of solute was increased, the yield of trapped electrons as represented by the 1200 nm band fell to zero and the radical anion yield reached a plateau. They interpreted these results to mean that all electrons normally trapped in the matrix as a result of (1-9) had been scavenged by the additive. Since the extinction coefficients are known for the biphenyl and naphthalene anions, their limiting concentrations enable a yield for electrons trapped in reaction (1-9) to be determined. On the basis of this method, $G(e_t^-)$ was

found to be 2.6 using naphthalene and 3.0 using biphenyl. The 2.6 value seems to be the better of the two and is in good agreement with ESR results discussed subsequently.

The photobleaching effect may be represented by Equation (1-11):



The mobile electron e_{th}^- so produced may be retrapped, may be scavenged by solute if one is present, or may recombine with the positive ion. Prolonged photobleaching in the absence of solute would of course lead eventually to total recombination.

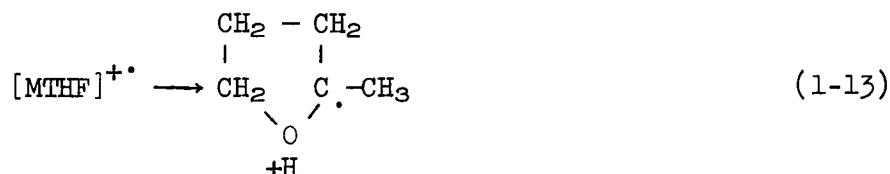
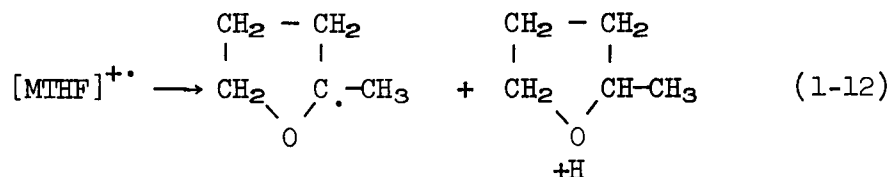
Further evidence regarding the nature of the trapped electron in MTHF comes from ESR spectroscopy. Salmon observed that the ESR spectrum of MTHF glass irradiated at 77°K consisted of a narrow singlet superimposed on a seven-line background spectrum with 20.5 gauss hyperfine splitting.⁵¹ He suggested the singlet was associated with the trapped electron since (1) it could be photobleached with red light, only the septet spectrum remaining after this treatment, and (2) both the singlet and the 1200 nm optical band disappeared together on warming the sample to 90°K. This assignment was confirmed by Smith and Pieroni⁵² who studied the effects of adding biphenyl (ϕ_2) to the glass. At low ϕ_2 concentration, both the singlet and a spectrum attributable to ϕ_2^- were present. Photobleaching removed the singlet and enhanced the intensity of the ϕ_2^- spectrum. The intensity of the singlet decreased with increasing ϕ_2 concentration. These effects are analogous to the optical work and confirm the assignment of the singlet to a trapped electron. From concentration measurements, $G(e_t^-)$ was established to be 2.6.

Several unusual features of the trapped electron ESR singlet in MTHF have been pointed out.⁵³ The linewidth of the singlet, which is Gaussian shaped, is 4.5 gauss between derivative maxima. Typical free radicals with α -protons commonly display an isotropic hyperfine splitting of 20-40 gauss and dipolar line broadening of 10-15 gauss. The lack of hyperfine structure and the narrowness of the line indicate that the trapped electron experiences weaker interactions with protons than does an unpaired electron on a free radical.

A similar conclusion is reached from power saturation studies. The trapped electron singlet undergoes microwave power saturation of the inhomogeneous broadening type at low powers. The singlet intensity reaches a maximum at a microwave field strength of $H_1 = 0.04$ gauss. Thereafter, the intensity decreases with further increase in H_1 until it virtually disappears at $H_1 = 0.25$ gauss.⁵³ Typical free radicals do not saturate in this region and, in fact, the intensity of the underlying septet spectrum increases monotonically over this range. Smith and Pieroni interpret the unusual susceptibility of the trapped electron toward power saturation as reflecting the fact that the spin density of the trapped electron at nearby protons is less and the electron-proton distance greater than for unpaired electrons in free radicals.

Thus the linewidth, absence of hyperfine structure, and saturation behavior imply a wave function for the trapped electron that is essentially independent of surrounding molecular orbitals of MTHF such that the trapped electron acts as an independent chemical entity. On this basis, the trapping site was suggested to be a void or cavity in the matrix surrounded by oriented MTHF dipoles.⁵³

Some comments may be in order regarding the fate of the positive ion in the MTHF system. $G(e_t^-) = 2.6$ implies a similar yield of cations. It is interesting to note in this connection that the septet spectrum underlying the trapped electron corresponds to a G-value of 3.0. Two possibilities have been suggested as in reactions (1-12) and (1-13).



Reaction (1-12) corresponds to intermolecular proton transfer from the primary cation radical to give a free radical and a protonated MTHF molecule.⁵⁴ The free radical then accounts for the septet spectrum with three methyl protons and one β proton each having a 20.5 gauss hyperfine constant while the remaining β proton has a 41 gauss hyperfine splitting constant. Reaction (1-13) corresponds to intramolecular proton transfer, the resulting cation radical having an ESR spectrum identical with that of the free radical in (1-12).⁵³

The trapped electron in MTHF has been discussed in some detail in order to illustrate the optical and ESR characteristics of trapped electrons in slightly polar organic systems. In more polar media such as frozen alcohols, trapped electrons are also readily observed but only in glassy systems. Trapped electrons in frozen glassy alcohols are

characterized by both an optical and ESR spectrum at 77°K. Depending on the alcohol, the optical band of the trapped electron is shifted anywhere from 100 to 300 nm toward shorter wavelengths as compared to the corresponding solvated electron band in the liquid state.³⁴ The ESR spectrum of the trapped electron in alcohols consists of a singlet of 10-15 gauss width which is saturated by microwave power. Both the optical band and ESR singlet disappear on photobleaching with light in the same spectral region as the optical band.³⁴ Deuterium substitution for the hydroxyl proton drastically reduces the singlet linewidth; substitution in the hydrocarbon portion of the molecule has little effect.^{55,56} It has been inferred from these results that the electron is trapped in a cavity in the alcohol matrix and is surrounded by alcohol molecules oriented so that their hydroxyl group points at the electron.⁵⁷ Such a view is consistent with the failure to observe trapped electrons in crystalline alcohols. The well ordered crystalline state would be expected to possess few cavities or vacancies suitable for electron trapping. Neither would reorientation of solvent dipoles be expected to be a facile process in the crystalline state.

Currently, much interest has been generated among radiation chemists by the finding that electrons may be trapped in non-polar alkane glasses at 77°K. Gallivan and Hamill reported⁵⁸ a broad optical band centered at 1600 nm in the near infrared following gamma irradiation of 3-methylpentane glass at 77°K. This band could be eliminated by photobleaching with near infrared light. Experiments involving addition of electron acceptors such as naphthalene or biphenyl to the system resulted in effects analogous to those discussed in the case of MTHF. The 1600 nm band can therefore be attributed to trapped electrons.⁵⁸

Several groups have reported an ESR singlet from trapped electrons in 3-methylpentane glass.⁵⁹⁻⁶² The singlet is narrow with a linewidth of 3.9 gauss, can be photobleached with near infrared light, and is saturated at low microwave power. Conclusive evidence that the singlet is due to trapped electrons comes from the work of Lin, Tsuji, and Williams. For a variety of alkane glasses including 3-methylpentane, they noted an exact correspondence of yields of trapped electrons as measured by ESR techniques with yields determined by optical means.⁶³ Furthermore, the rate of thermal decay of the species is the same both by optical and by ESR measurements provided care is taken to glass the samples used for both types of experiments in the same way.⁶³ Thus both the optical band and the ESR singlet belong to the same species. That this species is a trapped electron follows first from the effects of naphthalene and biphenyl on the optical band as noted above and second by the observation⁶⁴ that when CH_3I is present in the system, the narrow singlet is no longer observed but is replaced by the spectrum of the methyl radical. This latter effect is the result of dissociative capture by CH_3I prior to trapping of the electron:



Tsuji and Williams have investigated the microwave power saturation behavior of the trapped electron in several alkane glasses.⁶⁵ The trapped electron in these systems is even more susceptible to saturation than in MTHF glasses. In alkane glasses the maximum in the saturation curve occurs at about 0.025 mW of microwave power for an irradiation dose of 2×10^{19} ev g^{-1} and shifts to higher powers with increasing dose. This behavior has been interpreted in terms of a spin-lattice

relaxation time of the order of 10^{-3} sec and a spin-spin relaxation time which decreases with dose.

The picture of the trapped electron in alkane glasses that emerges from these various considerations is one which implies an electron more weakly trapped than in the polar organic systems. This follows from the fact that the optical band maximum in alkanes is shifted substantially to lower energies compared to polar media. Furthermore, the narrower linewidths and greater ease of saturation of the ESR singlet in alkanes compared to the polar systems indicates a relatively weak interaction of the electron with its surroundings.

Willard has proposed a model wherein electron trapping occurs in pre-existing voids and vacancies that are frozen into the glass structure.⁶⁶ He correlates the shift in optical band maxima to lower energies as the polarity of the system decreases with an increase in the size of the void. Such behavior would be expected if an electron in a void can be qualitatively considered to behave as a particle-in-a-box since the optical transition energy decreases as the size of the box increases.⁶⁷ The narrowing of the ESR singlet linewidth as the polarity decreases is also in accord with the void concept if the major contribution to the linewidth is from unresolved hyperfine interaction of the electron with surrounding protons in the void boundary. The effects of deuterium substitution on the ESR linewidth indicate such an interaction is important at least in alcohols as previously discussed but whether similar effects occur in hydrocarbons is not yet clear.⁶³

To summarize then, the most generally accepted model at present for the electron trap in frozen organic glasses involves trapping in

pre-existing voids frozen into the matrix. The electron is stabilized as a result of the lower energy state available to it when localized in the void. Additional stabilization is possible in polar media through orientation of solvent dipoles. Whether such orientation occurs as a result of electron trapping or whether arrangements of suitably oriented dipoles already exist prior to trapping has not yet been resolved. Few voids would be expected to occur in crystalline systems because of the high degree of structural regularity characteristic of the crystalline state. Hence trapping should not be an efficient process in crystals. This is in agreement with the failure to observe trapped electrons in crystalline alcohols³⁴ and in several crystalline alkanes.⁶³

Mention should, however, be made of two recent reports of electron trapping in polycrystalline media. First, Iwasaki *et al.* have observed⁶⁸ trapped electrons in several polycrystalline n-alkanes. It may nevertheless still be possible to interpret these results within the void framework as will be discussed in a subsequent chapter. Second, Bonin has observed trapped electrons in polycrystalline acetonitrile following gamma irradiation at 77°K.⁶⁹ The dipole moment of the cyanide group is very large, 4.0 Debye, and it appears that in this instance trapping occurs by a fundamentally different mechanism, the electron being trapped in the dipole field of the cyanide group.

E. Radiation Chemistry of Polyethylene

1. Chemical Effects of Irradiation of Polyethylene

The radiation chemistry of polymeric systems has received a great deal of attention principally because of their commercial importance,

the fact that many polymers are used in radiation fields around reactors and knowledge of their stability to radiation is vital, and finally because of an intrinsic interest in their radiation chemistry. Despite a great deal of effort, much is still unknown about the basic mechanisms involved in the radiation-induced reactions because polymers are difficult to analyze. The major reactions observed when a saturated hydrocarbon polymer is irradiated are (1) crosslinking, (2) main chain scission, (3) H_2 production, and (4) olefin formation.¹⁴

Polyethylene, being the simplest of olefin polymers, has received the greatest amount of study. The "best" values for the yields of the various products are summarized in Table I. The data are taken from the work of Dole and co-workers⁷⁰ and are the product yields extrapolated to zero dose since buildup of radiation products in the system affects the yields at higher doses. An important check on the validity of the G-values in Table I is given by a material balance calculation for hydrogen. For material balance, $G(H_2)$ should be given by the following expression (neglecting the effects of chain scission):

$$G(H_2) = G(X) + G(t-Vl) + 2G(\text{diene}) \quad (1-15)$$

where $G(X)$ and $G(t-Vl)$ represent the G-values for crosslinking and trans-vinylene production respectively. Adding the corresponding values on the right side of Equation (1-15) gives $G(H_2) = 3.9$ in good agreement with the experimental value of 3.7.

2. Intermediates in Irradiated Polyethylene

Polyethylene has been extensively studied by means of ESR spectroscopy subsequent to irradiation and three different radicals have been identified depending on experimental conditions of temperature and

TABLE I

PRODUCT YIELDS EXTRAPOLATED TO ZERO DOSE FROM
THE GAMMA RADIOLYSIS OF POLYETHYLENE AT 35 °C^a

Product	G-Value
Hydrogen	3.68
Crosslinks	1.0
<u>Trans</u> -Vinylene Unsaturation	2.4
Conjugated Diene Unsaturation	0.25
Chain Scission	0.19

^aSource: H. Y. Kang, O. Saito, and
M. Dole, J. Am. Chem. Soc., 89, 1980 (1967).

radiation dose. The subject has been recently reviewed.⁷¹ After irradiation at 77°K, the ESR spectrum consists of six broad lines with a hyperfine splitting constant of about 30 gauss. The spectrum has been assigned to the alkyl free radical $-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$. The assignment is supported by orientation effects on the hyperfine splitting of the α -proton in studies of stretched samples and in solution-grown single crystals of polyethylene.^{72,73} The G-value for production of the alkyl free radical has been found to be $G(\text{R}\cdot) = 3.0$ where $\text{R}\cdot$ stands for a free radical.⁷⁴ Recombination of two adjacent alkyl free radicals is the generally accepted mechanism for crosslink formation although the possibility of ion-molecule condensations leading to crosslinks has also been suggested.¹⁴

If irradiated polyethylene is warmed from 77°K to room temperature, the alkyl free radical decays and ESR reveals the presence of a second species characterized by a seven-line spectrum with a hyperfine splitting constant of 21 gauss. The spectrum of this latter species has been assigned to an allyl free radical, $-\text{CH}_2\text{CH}=\dot{\text{C}}\text{HCH}_2-$.⁷⁵ This species may also be observed following irradiation directly at room temperature. At very high radiation doses, the ESR spectrum consists of a broad singlet whose width is 26 gauss. The spectrum is stable even after several days at 150°C and has been attributed to a polyenyl radical,
 $-\text{CH}_2(\text{CH}=\text{CH})_n\dot{\text{C}}\text{HCH}_2-$.⁷⁴

While the free radical intermediates in irradiated polyethylene have been well characterized, the role of ionic intermediates is still a matter of speculation. Fowler¹² has postulated the existence of trapped electrons in order to explain postirradiation electrical conductivity. Charlesby and Partridge have also invoked trapped electrons in

order to explain the luminescence emitted by polyethylene as it is warmed to room temperature following irradiation at 77°K.^{8-11,76} These authors observed three peaks in a plot of luminescence intensity versus temperature as a sample of oxygen-free polyethylene was warmed up. Partridge⁷⁷ has suggested that these luminescence peaks result from the freeing of electrons trapped on the molecular chains themselves and subsequent recombination with positive ions. The existence of three peaks was interpreted as reflecting the onset of different structural transitions in polyethylene.

Polyethylene and other saturated hydrocarbon polymers have been extensively studied by means of ESR spectroscopy and in only one instance has there been a report of spectral features which might be associated with trapped electrons as opposed to free radicals. Thus Alfimov et al.⁷⁸ observed a broad singlet superimposed on the sextet spectrum of the alkyl free radical in polyethylene irradiated at 77°K. The line-width of the singlet was 20 gauss or greater and from an analysis of photobleaching effects, it was suggested that the broad singlet might be due to trapped electrons. The radiation dose was too low to make likely the possibility that this broad line resulted from a polyenyl free radical. A broad singlet could as well be due to unresolved hyperfine structure from a paramagnetic species produced by electron capture. In this connection, it is of interest to note that a similar broad singlet was observed by these same authors when polyethylene containing benzene was irradiated. For reasons which will become apparent in subsequent chapters, the broad singlet cannot be ascribed to an electron physically trapped in the polyethylene matrix but seems more likely to be the

result of some electron capture process yielding a chemically trapped electron, i.e., a radical anion or free radical.

To the author's knowledge, the only other report in the literature regarding ESR identification of trapped electrons in polymeric systems is by Ormerod and Charlesby.⁷⁹ These authors observed a singlet in the ESR spectrum of polymethacrylic acid following irradiation at 77°K. From scavenger studies, they found that an electron was the precursor of the species responsible for the singlet and suggested the singlet was the result of electron capture by monomeric impurities which are difficult to remove from this particular polymer.

F. Proposal of the Problem

In view of the electrical conductivity work of Fowler and the thermoluminescence experiments of Charlesby and Partridge, it seems likely that electrons may be trapped at low temperatures in irradiated polyethylene. Direct identification of trapped electrons by ESR or optical techniques would therefore be of importance to the radiation chemistry of polyethylene. The experiments of the Russian workers are inconclusive in this respect and all other ESR investigations of polyethylene have failed to provide any evidence for trapped electrons. The recent discovery of trapped electrons in alkane glasses suggests a possible reason for this. Trapped electrons in these glasses are extremely light-sensitive and are readily photobleached by room light. Therefore experiments must, of necessity, be performed in the dark. Furthermore, trapped electrons are very susceptible to microwave power saturation and their presence is only revealed at microwave powers very much lower than commonly employed to observe free radicals.

These features suggest that the inability of earlier workers to observe trapped electrons in polyethylene resulted from failure to exclude light from the sample and failure to work at low enough microwave power. Therefore, the ESR spectroscopy of irradiated polyethylene and several other saturated hydrocarbon polymers was re-examined in this dissertation under conditions experimentally favorable for the observation of trapped electrons.

CHAPTER II

ELEMENTARY THEORY OF ELECTRON SPIN RESONANCE

A. Introduction

In this chapter, a very elementary account of electron spin resonance theory is presented. The energy levels available to an unpaired electron in a magnetic field are discussed as well as the transitions between these levels which account for the resonant absorption of energy. The phenomenon of microwave power saturation is also described. The theory of hyperfine splitting, although extremely important in most electron spin resonance experiments, is treated in a rather cursory fashion here inasmuch as the trapped electron ESR spectra obtained in this investigation show no evidence of resolved hyperfine structure. For a more detailed presentation of the theory of electron spin resonance, the reader is referred to two recent books on the subject.^{80,81}

B. The Phenomenon of Electron Spin

In an effort to explain certain unexpected splittings of lines in atomic spectra, Goudsmit and Uhlenbeck proposed⁸² in 1925 that an intrinsic angular momentum be associated with an electron. This postulate was later placed on a firm theoretical foundation by Dirac who showed that the existence of this intrinsic angular momentum arose naturally when relativity effects were included in the Shrodinger equation.⁸³ The validity of these predictions has now been amply demonstrated by experiment and indeed, this intrinsic angular momentum property of an electron forms the basis of electron spin resonance spectroscopy.

It is convenient to think of the intrinsic angular momentum as resulting from a spinning motion of the mass of the electron about an axis through its center.⁸³ In terms of this simple picture of a spinning electron, Dirac's theory shows that an electron may only exist in either of two states of spin. These two spin states are distinguished by the value that a component of the spin angular momentum along a chosen direction may assume; in one state this value is $+1/2 \hbar$ and is $-1/2 \hbar$ in the other state. (Here the symbol $\hbar$ stands for Planck's constant divided by 2π .)

These properties of electron spin are conveniently expressed in the language of quantum mechanics by the following eigenvalue equations:

$$\bar{S}^2 [|\alpha\rangle \text{ or } |\beta\rangle] = s(s+1) \hbar^2 [|\alpha\rangle \text{ or } |\beta\rangle] \quad (2-1)$$

$$S_z [|\alpha\rangle \text{ or } |\beta\rangle] = m_s \hbar [|\alpha\rangle \text{ or } |\beta\rangle] \quad (2-2)$$

Here $\bar{S}^2$ and S_z are the operators associated respectively with the square of the total spin angular momentum and with a component of the spin angular momentum along some chosen axis (arbitrarily designated as the Z axis). The two possible spin states are represented by the spin functions $|\alpha\rangle$ and $|\beta\rangle$ where the Dirac bra-ket notation has been used. These functions are orthonormal: $(\alpha|\alpha)$ and $(\beta|\beta)$ equal one whereas $(\alpha|\beta)$ and $(\beta|\alpha)$ vanish.

The terms s and m_s appearing in Equations (2-1) and (2-2) represent spin quantum numbers. For a single electron, $s = 1/2$ and $m_s = \pm 1/2$, the positive m_s value being associated with the $|\alpha\rangle$ state and the negative value with the $|\beta\rangle$ state. The total spin angular momentum $\bar{S}$ is then evidently represented by a vector of length $[s(s+1)]^{1/2} \hbar = (3/4)^{1/2} \hbar$.

The only two possible orientations of this vector with respect to the Z-direction are those with components along the Z axis of magnitude $\pm 1/2 \hbar$.

In the absence of perturbing effects, the $|\alpha\rangle$ and $|\beta\rangle$ spin states are of equal energy. However, in the presence of a magnetic field, this degeneracy is lifted and the two states are separated in energy. The electron spin resonance experiment then consists of measuring the magnitude of this energy separation. The manner in which this is accomplished is the subject of the next section.

C. The Electron Spin Resonance Experiment⁸⁰

The discussion to follow in this section centers on the behavior of a free electron or "spin." It should be recognized that the equations which are developed apply to any system containing an unpaired electron. Free radicals are typical examples in this respect.

The properties of spin and charge possessed by an electron confer a magnetic moment on it. This magnetic moment $\bar{\mu}$ is given by the expression

$$\bar{\mu} = - \frac{g\beta}{\hbar} \bar{S} \quad (2-3)$$

where $\bar{S}$ is the spin angular momentum vector, β is the Bohr magneton equal to 0.927×10^{-20} ergs/gauss, and g is a dimensionless constant whose value depends on the magnitude of the orbital angular momentum of the electron. For a free electron with no orbital momentum, the value of g is 2.0023. In the presence of an applied static magnetic field $\bar{H}$, $\bar{\mu}$ will interact with $\bar{H}$ according to the Hamiltonian

$$\mathcal{H} = - \bar{\mu} \cdot \bar{H} \quad (2-4)$$

Substitution for $\bar{\mu}$ gives the corresponding equation

$$\mathcal{H} = \frac{g\beta}{\hbar} \bar{S} \cdot \bar{H} \quad (2-5)$$

Since the direction of the applied field defines what may be called the Z-direction, Equation (2-5) may be rewritten as

$$\mathcal{H} = \frac{g\beta}{\hbar} S_z H \quad (2-6)$$

The allowable values of the energy are then given by the expressions (in bra-ket notation)

$$E_\alpha = (\alpha | \mathcal{H} | \alpha) = \frac{1}{2} g\beta H (\alpha | \alpha) = \frac{1}{2} g\beta H \quad (2-7)$$

$$E_\beta = (\beta | \mathcal{H} | \beta) = -\frac{1}{2} g\beta H (\beta | \beta) = -\frac{1}{2} g\beta H \quad (2-8)$$

The interaction of the electron magnetic moment with the static magnetic field is thus seen to separate the $|\alpha\rangle$ and $|\beta\rangle$ states in energy depending on the value of H . The effect is shown schematically in Figure 1 where the energies of the two states are plotted versus magnetic field strength. This splitting of the energy levels is known as the Zeeman effect.

Electron spin resonance spectroscopy simply involves inducing transitions of electrons in the lower energy spin state to the higher energy spin state. It can be shown that such transitions will occur in the presence of an oscillating electromagnetic field of appropriate frequency, ν . The required frequency is obtained by setting the difference in energy of the two spin states equal to $h\nu$:

$$h\nu = g\beta H \quad (2-9)$$

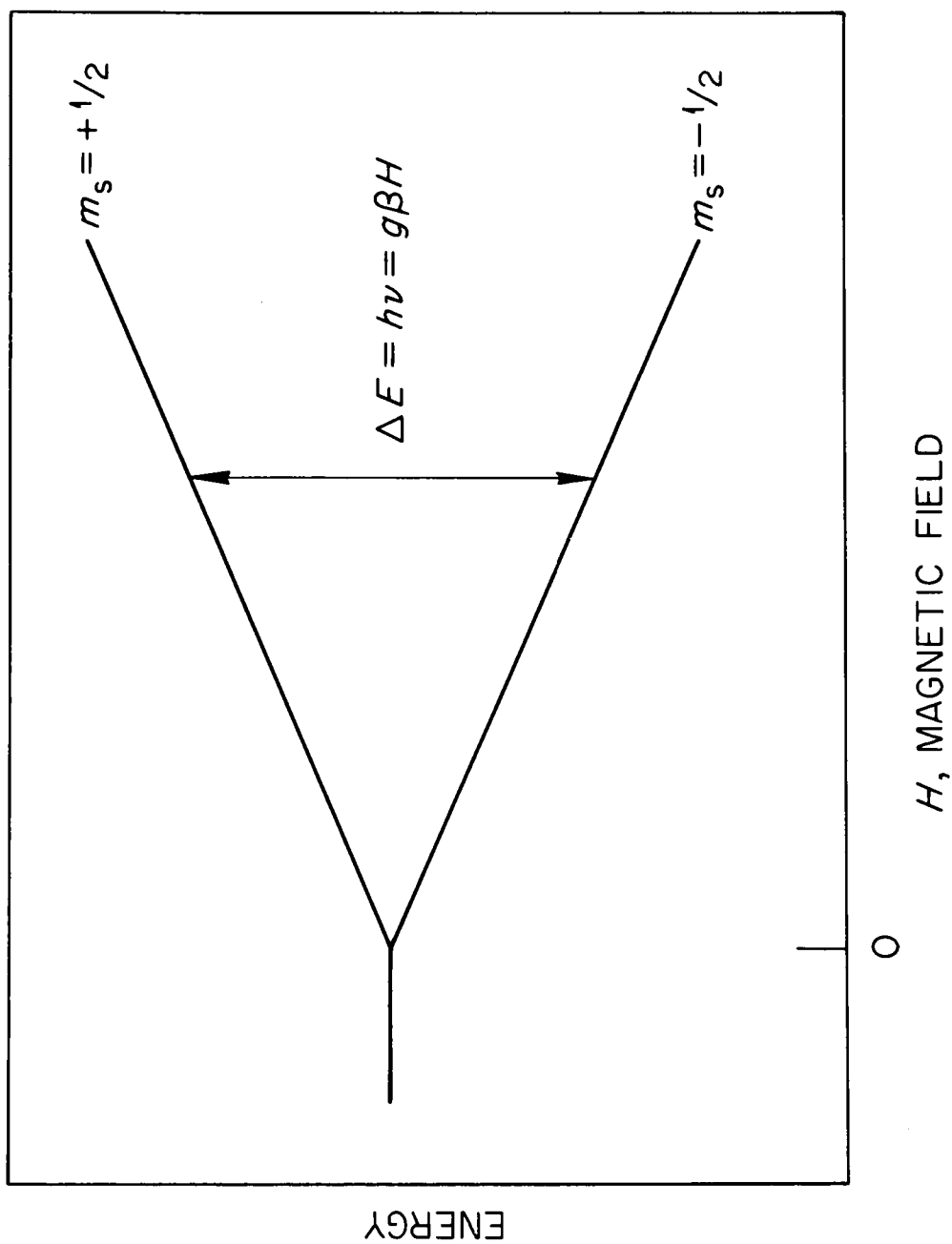


Figure 1. Energy levels for an unpaired electron in a magnetic field.

In ESR spectroscopy, it is customary to use magnetic fields of the order of 3000 gauss. Thus ν is about 9 GHz (gigahertz) and is in the microwave region. The frequency is maintained constant while H is slowly swept through resonance as dictated by Equation (2-9). Resonance is detected by noting the absorption of energy from the oscillating electromagnetic field as electrons are promoted to the upper energy level. The experimental features of a typical ESR spectrometer are given in Chapter III.

Before passing on to the next section, it is worthwhile to bring up one further point. Up to now, the discussion has centered around promoting an unpaired electron from a lower energy spin state to a state of higher energy. Any real paramagnetic sample will of course contain a large number of unpaired electrons. At thermal equilibrium, these will be distributed between the $|\alpha\rangle$ and $|\beta\rangle$ states according to the Boltzman relation:

$$\frac{N_\alpha}{N_\beta} = \exp \left(- \frac{g\beta H}{kT} \right) \quad (2-10)$$

For $g = 2$, $H = 3000$ gauss, and $T = 77^\circ\text{K}$, the exponential term in Equation (2-10) is 0.995. Hence, there is only a slight excess of electron spins in the lower energy state. Since it can be shown that the transitions $|\beta\rangle \rightarrow |\alpha\rangle$ and $|\alpha\rangle \rightarrow |\beta\rangle$ occur with equal probability when stimulated by the oscillating microwave field, it is clear that only the excess population of the lower state gives rise to resonance absorption of energy. Furthermore, in the absence of some mechanism to maintain the population ratio at the thermal equilibrium value, the population of the two states would soon be equalized by the influence of the oscillating microwave field and resonance absorption would cease.

Fortunately a mechanism for maintaining the populations of the two states at their thermal equilibrium value does exist and is known as the spin-lattice interaction. According to this mechanism, spins in the upper energy state can give up energy to their surroundings and revert back to the ground state. The characteristic time required for this process to occur is known as the spin-lattice relaxation time and is given the symbol T_1 . T_1 can be regarded as a measure of the strength of the interaction of a spin with its environment; a short T_1 implies an efficient interaction while a long T_1 results from a weak interaction.

The rate of change of the difference in population of the $|\alpha\rangle$ and $|\beta\rangle$ states as a result of interaction with the oscillating microwave field is proportional to the product of the population difference with the transition probability and the square of the amplitude of the microwave magnetic field, H_1 . If this rate is made large compared to the rate at which the spin-lattice interaction occurs, by increasing H_1 for example, then the population difference will decrease and so will the observed amplitude of the ESR line. This phenomenon is known as saturation. Its occurrence is commonly observed by plotting the amplitude of the line, or signal height, as a function of H_1 . Such a plot is known as a saturation curve. At low values of H_1 , the signal intensity is directly proportional to H_1 . At high values of H_1 , two types of behavior may be observed; the signal intensity either passes through a maximum and then decreases with increasing H_1 , or the signal intensity reaches a plateau where further increase in H_1 results in no change in the signal intensity. These types of behavior are discussed subsequently in Section E of this chapter.

D. The Hyperfine Interaction⁸⁰

In a large majority of the paramagnetic systems investigated, the ESR spectra do not consist of a single line as might be inferred from the preceding discussion. Rather, several lines are observed and in some instances several hundred lines have been resolved. This additional line splitting, known as hyperfine splitting, arises from interactions between the unpaired electron and nearby magnetic nuclei in the sample. The magnetic field that the unpaired electron experiences is thus not simply the applied field but rather the sum of the applied field and local fields from the magnetic nuclei.

The hyperfine splitting can be accounted for theoretically by adding two terms to the spin Hamiltonian. The first of these terms is known as the Fermi contact interaction and has no analogue in classical mechanics. It arises out of the fact that an unpaired electron has a finite probability of being at various nuclei in the molecule. The form of the contact interaction is given by

$$\mathcal{H}_{\text{contact}} = \frac{8\pi}{3} g\beta_N\beta_N |\psi(0)|^2 \bar{\mathbf{I}} \cdot \bar{\mathbf{S}} \quad (2-11)$$

for a simple paramagnetic system like the hydrogen atom. Similar expressions hold for more complicated systems. In Equation (2-11), g_N and β_N are the nuclear g-factor and nuclear Bohr magneton respectively, and $\psi(0)$ is the unpaired spin density evaluated at the nucleus in question. $\bar{\mathbf{I}}$ is the spin operator for the nucleus.

The contact interaction is isotropic and does not depend on the orientation of the sample with respect to the applied field. It can be shown that for a single nucleus of spin I , $(2I + 1)$ lines are observed

in the ESR spectrum as a result of the contact interaction.⁸⁰ For n equivalent nuclei, $(2nI + 1)$ lines result. Moreover, if groups of n and m equivalent nuclei all with the same I are present, the ESR spectrum will contain $(2nI + 1)(2mI + 1)$ lines. The complexity of the spectrum is seen to increase enormously. The line spacings are governed by the quantity $(8\pi/3) g\beta_N\beta_N |\psi(0)|^2$ so that it is apparent that an analysis of the spacings can yield important information regarding the wave function of the unpaired electron.

The second term which must be added to the Hamiltonian accounts for the orientation dependence of the hyperfine splitting which is frequently observed when an oriented specimen such as a single crystal is rotated in the applied field. This term has the form

$$\mathcal{H}_{\text{dipolar}} = -\frac{g\beta_N\beta_N}{r^3} \left[\bar{\mathbf{I}} \cdot \bar{\mathbf{S}} - \frac{3(\bar{\mathbf{I}} \cdot \bar{\mathbf{r}})(\bar{\mathbf{S}} \cdot \bar{\mathbf{r}})}{r^2} \right] \quad (2-12)$$

and arises from the classical dipolar interaction between two magnetic dipoles with spin operators $\mathbf{I}$ and $\mathbf{S}$ separated by distance r . Where more than one magnetic nucleus is present, additional terms of this form must be used.

In liquid systems, the molecules are tumbling about rapidly and the dipolar term averages to zero. In amorphous solids or polycrystalline systems, the interaction is not averaged to zero and lines corresponding to all possible orientations of magnetic nuclei with respect to the unpaired electron contribute to the spectrum. In simple cases where the dipolar interaction is either less than or of comparable size to the isotropic splitting, this may merely serve to broaden the lines resulting from the isotropic contact interaction. In general, however, this is not the case and the resulting spectra are often complex. In these

instances, experiments with single crystals are necessary to interpret the spectra.

E. Line Broadening and Saturation Behavior

In Section C of this chapter, the fundamental equation underlying the electron spin resonance phenomenon was developed in terms of a system of independent and non-interacting electron spins. This is an idealized situation however. In any real system, the electron spins will interact magnetically not only among themselves, but also with their environment. The hyperfine interaction discussed in the previous section is one example but there are others as noted below. As a consequence of these interactions, the spectral lines observed in ESR are not infinitely sharp as might be expected, but are broadened so as to have a finite width.

Portis⁸⁴ has classified all ESR lines into two types; those which are homogeneously broadened and those which are inhomogeneously broadened. The width of a homogeneously broadened line reflects the "intrinsic linewidth" and results from relaxation processes which serve to limit the lifetime of the spin states. These relaxation processes are the spin-lattice relaxation and the spin-spin relaxation involving interaction between like spins, according to Portis. Homogeneously broadened lines result from spins which experience the same type environment and are Lorentzian in shape.

On the other hand, an inhomogeneously broadened line results from spins which are in different environments. The dominant mechanism leading to this type of broadening is the isotropic and anisotropic hyperfine

interaction of an electron spin with surrounding magnetic nuclei. The electron spins therefore experience different local magnetic fields and consequently undergo resonance at different values of the applied field. The observed resonance line is thus an envelope comprised of a superposition of a number of homogeneously broadened lines which are called "spin packets." In a randomly oriented solid, the nuclei responsible for the distribution of local fields are randomly oriented with respect to the electron spin so that the observed line shape of the envelope is Gaussian.

As previously discussed, a system of electron spins is said to saturate when the ratio of the number of spins in the upper energy state to that in the lower state deviates from the value expected for thermal equilibrium. This can occur when the microwave power incident on the sample is large enough that electrons are promoted to the upper level faster than they can lose energy to their surroundings and revert back to the lower level. Portis⁸⁴ has shown that the type of saturation curve observed depends markedly on whether the ESR lines are homogeneously or inhomogeneously broadened.

For homogeneously broadened lines, Portis obtains the following equation for the signal intensity as a function of H_1 :

$$V_R \propto \frac{H_1}{1 + \gamma^2 H_1^2 T_1 T_2} \quad (2-13)$$

In this equation, V_R is the signal intensity, γ is the gyromagnetic ratio of the electron and is equal to 1.76×10^7 gauss⁻¹ sec⁻¹. T_2 is the spin-spin relaxation time measuring the interaction of an electron spin with neighboring unpaired spins and T_1 is the spin-lattice relaxation time. H_1 is the amplitude of the circularly polarized magnetic component

of the oscillating microwave field. It is seen from the equation that at low H_1 , V_R increases linearly with H_1 , then reaches a maximum, and finally decreases as $1/H_1$ at high H_1 .

For inhomogeneous lines the behavior is different. In the case that the width of the homogeneously broadened lines or spin packets comprising the envelope is negligible compared to the overall width of the envelope, Portis finds

$$V_R \propto \frac{H_1}{[1 + \gamma^2 H_1^2 T_1 T_2]^{1/2}} \quad (2-14)$$

In this instance, V_R again is proportional to H_1 at small H_1 but becomes independent of H_1 at high values. In contrast to the preceding case, V_R thus reaches a limiting value and does not decrease with further increase in H_1 .

Castner has extended the treatment to those cases where the linewidth of the spin packets comprising the envelope is not negligible compared to the overall envelope width.⁸⁵ Castner's results are expressed by

$$V_R \propto \frac{X}{(1 + X^2)^{1/2}} \exp(a^2 X^2) \frac{\{1 - \Phi[a(1 + X^2)]^{1/2}\}}{[1 - \Phi(a)]} \quad (2-15)$$

where $X = H_1/\gamma(T_1 T_2)^{1/2}$, Φ represents the error function, and a is the ratio of width of a spin packet to the overall linewidth. The behavior of V_R is intermediate between the two cases treated by Portis. Castner has also given curve fitting procedures for extracting the important quantities a , T_1 , and T_2 from the experimental saturation curve. Use will be made of Castner's treatment in analyzing the saturation of trapped electrons in polyethylene.

CHAPTER III

EXPERIMENTAL METHODS

A. Introduction

This chapter contains an account of the various experimental procedures and techniques employed in this study of trapped electrons. The materials investigated and their properties are discussed first, followed by an account of methods of sample preparation, handling, and irradiation. The procedures involved in the ESR measurements are described and the chapter concludes with a discussion of methods for detecting trapped electrons by means of optical absorption spectroscopy.

B. Materials and Purification Techniques

1. Polyethylene

A variety of polyethylenes ranging from essentially linear high-density material to a branched low-density polymer was used. The various samples, together with their manufacturer and some pertinent physical properties are compared in Table II. The term melt index in Table II refers to the amount of polymer which can be made to flow in a certain time through a capillary of specified size and under specified conditions of temperature and load.⁸⁶ It is thus a measure of the molecular weight of the polymer, although effects such as branching also influence the melt index.⁸⁶

The samples of Phillips Marlex 50 and Marlex 6050 are typical linear high-density polyethylenes. Marlex 50 has been shown to contain less than 1.5 methyl branches per 1000 carbon atoms.⁸⁷ It also contains

TABLE II
 PROPERTIES OF POLYETHYLENE SAMPLES^a

Material	Density g/ml	Antioxidant Concentration (wt %)	Melt Index
Marlex 50 ^b	0.966	0.02 Ionol ^d	5.0
Marlex 6050 ^b	0.965	0	5.5
Marlex 6050 ^b	0.966	0.02 Ionol ^d	5.6
Saturated ^b Polyethylene	0.96	Not known	12
PE-106 ^c	0.929	0	2.8
Alathon 1414 ^c	0.910	0	1.2

^aSource: Manufacturer's data.

^bManufactured by Phillips Petroleum Co., Bartlesville, Oklahoma. The term "Marlex" is Phillips' trademark for its series of polyolefin plastics.

^cManufactured by E. I. du Pont de Nemours Co., Wilmington, Delaware. "Alathon" is duPont's trademark for its series of polyethylenes.

^dThe antioxidant Ionol is 2,6 Di-*t*-butyl-4-methylphenol.

approximately 1.5 double bonds per 1000 carbon atoms, the distribution being 94% terminal vinyl, 1% branched vinyl, and 5% internal trans olefinic double bonds. Although similar data are unavailable for the 6050 samples, the values are typical of linear polyethylene and presumably apply in this case also. The saturated polyethylene sample is a linear high-density material which had been hydrogenated to remove olefinic groups.

Alathon 1414 is a branched low-density polyethylene having a number average molecular weight of 3.1×10^4 as reported by the manufacturer. The PE-106 sample is representative of polyethylenes having properties intermediate between the linear and branched cases.

With the exception of Marlex 50 and the saturated polyethylene, all samples were used without further purification. An effort was made to remove the antioxidant from powdered Marlex 50 samples by extraction with boiling acetone for four days followed by drying under a vacuum of 10^{-5} torr at 115°C for two days. As received, the sample of saturated polyethylene appeared yellow-brown in color, an obvious indication of the presence of impurities since pure linear polyethylene is white. The impurities may be due to catalyst from the hydrogenation process, antioxidants added to the material, or both. Two purification procedures were adopted in an effort to purify the material.

In the first, one gram samples were dissolved in boiling octane precipitated by cooling the solution, and then collected by filtration. This process was repeated five times and then the polymer was dried for several days in a vacuum oven at 80°C. The alternative process involved precipitation three times by cooling a boiling xylene solution of the

polymer, washing in boiling acetone, and finally precipitation twice by cooling a boiling octane solution followed by drying in the vacuum oven. Despite either of these treatments, a slight yellow tinge remained to the material indicating that some impurities were not removed.

The effectiveness of the hydrogenation process in removing double bonds in saturated polyethylene was assessed by means of infrared spectroscopy. A Perkin-Elmer Model 221 infrared spectrometer was used for this purpose. Suitable films 0.01 inches thick were prepared by pressing pellets of the polymer between the heated platens of a Carver Laboratory Press using 0.01 inch shims.

2. Polypropylene

Two samples of isotactic polypropylene and one of atactic polypropylene were obtained from Hercules, Inc., Wilmington, Delaware. The isotactic samples were designated as Profax 6301 powder and Profax 6323 pellets by the manufacturer. According to Hercules, the 6301 material was free of antioxidants and stabilizers but the 6323 sample did contain an antioxidant although the type and amount were not specified. Additional data supplied by Hercules revealed that these samples are greater than 95% isotactic, have a density of 0.907 g/ml, and an intrinsic viscosity of 1.7 dl/g in tetralin. The atactic material was designated as X 16348-2-1 and contained no antioxidants. The sample was rubber-like.

A second sample of isotactic polypropylene powder was obtained from the Phillips Petroleum Co. This material was also antioxidant-free and greater than 95% isotactic. According to Phillips, the material was 70% crystalline as determined by x-ray diffraction. All polypropylene samples were used as received without further purification.

3. Poly(4-methylpentene-1)

A sample of poly(4-methylpentene-1) in powder form was obtained from Imperial Chemical Industries Ltd., England. The material is predominantly isotactic and about 40% crystalline. It contained no antioxidant and was used without further purification.

4. Polyisobutylene

Polyisobutylene free of antioxidant and with a number average molecular weight of 1.8×10^6 was obtained from Enjay Chemical Company. This material was rubber-like and was cut into small pieces before use.

5. n-Alkanes

Samples of n-tetracosane, n-octacosane, n-dotriacontane, and n-hexatriacontane were obtained from Lachat Chemicals, Inc., Chicago Heights, Illinois. These materials have 24, 28, 32, and 36 carbon atoms respectively in the chain. The purity of these hydrocarbons was assessed by gas chromatography and the results are presented in Table III.⁸⁸ All the samples contained small amounts of higher molecular weight homologues as impurities. The major impurity in the octacosane and dotriacontane samples appears to be of a polar nature. This conclusion follows from the appearance of a peak in the chromatogram of these compounds which exhibited considerable tailing. All the alkanes were used as received.

6. 2-Methyltetrahydrofuran (MTHF)

Reagent grade MTHF was obtained from Eastman Organic Chemical Company. The purification of this material was carried out by Bonin and a full description of the techniques involved may be found in his

TABLE III
PURITY OF n-ALKANES

Compound	Purity (percent)
n-tetracosane	99.2
n-octacosane	92.9
n-dotriacontane	96.6
n-hexatriacontane	98.9

dissertation.⁶⁹ Briefly, the MTHF was first washed with 1 N sodium hydroxide, then with distilled water, and finally dried over sodium metal. The dried material was fractionally distilled and the middle fraction boiling at 78-79°C was introduced onto a vacuum line. This fraction was then degassed, dried over sodium mirrors and stored on the line in a reservoir coated with sodium.

7. 2,2-Diphenyl-1-picrylhydrazyl (DPPH)

A sample of the stable free radical DPPH was obtained from Eastman Organic Chemical Company and was used without further purification.

8. Potassium Nitrosodisulfonate (Freymy's Salt)

A sample of Freymy's salt, $K_2(SO_3)_2NO$, was obtained from Alfa Inorganics, Inc., and used without further purification.

9. Solvents

Octane of Puriss grade was obtained from Aldrich Chemical Company. Reagent grade acetone and xylene were obtained from Mallinkrodt Chemical Company and J. T. Baker Chemical Company, respectively. All these were used as received.

C. Methods of Sample Preparation

1. Bulk Crystallized Polymer Samples

The majority of ESR experiments involving polymers were performed on cylindrical rod-shaped specimens 0.48 cm in diameter and 5 cm long. This is the maximum size of sample which can be conveniently accommodated in the dewar which fits the V-4531 cavity of the ESR spectrometer. Preparation of cylindrical specimens was accomplished using a vacuum

molding technique. This technique is important in assuring reproducible results and will be described in detail.

The device used to mold the samples is shown in Figure 2. Approximately 1 g of polymer (in either powder or pellet form) was placed into a 7 mm OD by 5 mm ID glass tube, one end of which had been sealed off. The glass tube served as the mold itself. A 5 mm diameter, 1/8 inch thick Teflon disc was placed on top of the polymer and the mold tube then attached to one arm of a glass "Tee" by means of a short length of rubber tubing. The side arm of the "Tee" was connected to a mechanical vacuum pump. The remaining arm of the "Tee" was fitted with a rubber stopper through which passed a 1/8 inch steel rod, serving as a plunger. A coating of stopcock grease provided a sliding vacuum seal between the plunger and the rubber stopper.

The molding operation itself is begun by first evacuating the entire device. Then the end of the molding tube containing polymer was placed in a cylindrical heater maintained at a temperature 5 to 10° above the melting point of the polymer. A suitable heater was simply constructed using a piece of glass tubing wrapped with Nichrome wire. Temperature was measured with an Iron-Constantan thermocouple and could be varied by adjusting the voltage across the heater windings by means of an autotransformer. After all the polymer had melted, it was molded by manually pressing downward on the Teflon disc with the plunger. Crystallization was finally induced by slowly raising the heater upward about the sample. Molding temperatures for the various materials are shown in Table IV.

The major difficulty encountered in the molding operation was the formation of macroscopic bubbles in the specimen. Inhomogeneities of

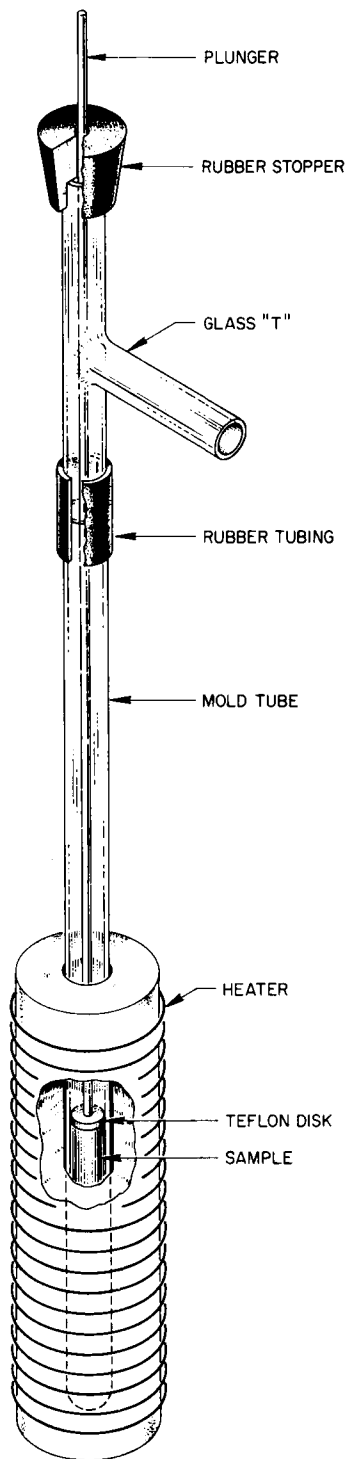


Figure 2. Apparatus for molding polymer specimens.

TABLE IV
MOLDING TEMPERATURES FOR VARIOUS SAMPLES

Sample	Apparent Melting Temperature, (°C) ^a	Molding Temperature (°C)
Linear Polyethylenes	140	145-150
Branched Polyethylenes	115	120-125
PE-106	130	140
Isotactic Polypropylene	160-165	170
Atactic Polypropylene ^b	---	130
Poly(4-methylpentene-1)	240	250
Polyisobutylene ^b	---	150
n-Hexatriacontane	79	85
n-Dotriacontane	70	75
n-Octacosane	62	70
n-Tetracosane	51	60

^aTemperature at which sample became clear.

^bNon-crystalline sample.

this sort are particularly troublesome when trying to determine concentrations of trapped electrons. Bubble formation results from the fact that the specific volume of crystallized polymer is less than that of the melt. Hence, as crystallization proceeds, the solidified polymer tends to draw away from the crystal-melt interface. The viscosity of the melt is too great to allow the molten polymer to adjust itself to the volume changes accompanying crystallization so that the net result is the freezing of bubbles into the specimen.

It was found possible to eliminate bubble formation by the simple expedient of applying a compressive load with the plunger on the sample during crystallization. This assured that the molten phase was always in intimate contact with the growing crystalline portion. Also, crystallization must be initiated at the bottom of the sample and be made to proceed upward in order that the load be always applied to the molten phase.

After crystallization was completed, the specimen was cooled to room temperature and removed from the molding tube. A small hole was drilled approximately 0.5 cm deep into one end of the sample along its axis. A handle, made from a 10 cm length of 3 mm diameter glass rod, was attached to the specimen by warming one end of the rod with a torch and then pushing it into the hole. Samples were then stored in a dewar filled with liquid N_2 until used.

In several instances, molding tubes of other than the standard 7 mm OD by 5 mm ID size were used. Thus, poly(4-methylpentene-1) samples for the optical experiment were molded in 12 mm ID tubes, the procedure being exactly the same as described above. Also, for each of the

materials investigated, ESR determinations of trapped electron concentrations require a comparison with the trapped electron concentration in a standard MTHF sample. It is important that the sample geometries of both standard and unknown samples be the same. Therefore several samples of each polymer were molded in the same type tubes used for MTHF (see p 55). In these cases, the specimen was left inside the tube which was sealed off under vacuum.

2. Oriented Polyethylene Samples

Mats of partially oriented polyethylene single crystals were prepared by methods similar to those described by Salovey⁷³ and Sinnott.⁸⁹ Polyethylene single crystals are microscopic and occur in the form of thin platelets, or lamellae. The lamellae are typically of the order of 100 Å thick with lateral dimensions ranging from 10 to 100 μ. The polymer chains are folded back and forth through a lamella with the folds forming the top and bottom surfaces. The chain axes are oriented perpendicular to the lamellar plane. The single crystals themselves were prepared by first dissolving 1 g of Phillips 6050 antioxidant-free polyethylene in 500 ml of boiling octane. The hot solution was then poured into 1500 ml of octane in a 3 liter flask immersed in a constant-temperature oil bath maintained at $90.00 \pm 0.05^\circ\text{C}$. After about 20-30 minutes, this solution began to appear cloudy as the polyethylene precipitated out. Precipitation was allowed to proceed over a period of 5-6 hours at which point the material in the flask had the appearance of a very finely divided milky-white suspension. The bath was then turned off and the suspension allowed to cool overnight to room temperature. This process was repeated four times, yielding a total of 4 g of solution-crystallized polyethylene.

The suspension of polyethylene crystals was poured into a 150 ml Buchner funnel fitted with a filter containing a 60 mm fritted glass disc. After all the crystals had been transferred to the funnel and most of the octane had been removed by slow filtration under gravity, a 60 mm diameter, 1/8 inch thick Teflon disc was placed on top of the caked crystals. A 1 kg weight was placed on the Teflon disc and a vacuum pulled on the filtration flask for three days to remove remaining solvent. The weight compacted the cake of crystals into a mat 2 mm thick by 60 mm in diameter. It also served to prevent cracking and curling of the mat during solvent removal. After this initial drying treatment, the mat was removed from the filter and placed in a vacuum desiccator and continuously pumped on for four more days.

Samples 5 cm long and 3 mm wide were cut from the mat and used for ESR measurements. These mats were very fragile and shattered easily when cut with a knife. This difficulty was readily avoided by using a razor blade warmed in a torch to a temperature great enough to melt the polymer slightly as it was cut. The amount of polymer melted along the cut edge was insignificant compared to total volume of the sample.

Samples prepared in this manner have been shown to contain stacks or layers of polyethylene single crystals oriented with the plane of the crystal lamellae parallel to the plane of the mat.⁷³ Since the axes of polymer chains in the lamellae are normal to the lamellar plane, the chain axes are also oriented normal to the plane of the mat.

Besides the solution-crystallization method for orienting polyethylene, it is also possible to prepare oriented samples by simply stretching the polymer. In this instance, the polymer chain is oriented

parallel with the axis of stretch.⁷² Samples of antioxidant-free Marlex 6050 were oriented in this way. Cylindrical samples 1.2 cm in diameter and 7 cm long were prepared by the molding techniques of the preceding section. These samples were warmed to a temperature of 130°C where they became noticeably soft and then stretched by manually pulling outward on the two ends. The extent of stretching was about ten times the original length and the final diameter was about 0.3 cm. A section 5 cm long was cut from the stretched material, a glass rod handle attached and the sample stored under liquid N₂ until use.

3. Alkane Samples

Cylindrical samples of n-tetracosane, n-octacosane, n-dotriacontane and n-hexatriacontane were fabricated using essentially the same technique as for bulk crystallized polymers but with the exception that no force was exerted on the material during the crystallization process. These samples were very fragile and tended to break apart when immersed in liquid N₂ for storage or irradiation. This difficulty was circumvented by leaving the sample inside the mold tube and slowly lowering the entire tube containing the sample into liquid N₂, having first cut off the closed tip of the tube.

Several samples of hexatriacontane doped with one to ten mole percent of the shorter chain alkanes dotriacontane, octacosane, and tetracosane were also prepared. These samples were made by weighing out an appropriate amount of the short-chain material, adding it to the hexatriacontane, and then molding the sample as described above. Sample handling techniques were also analogous.

4. MTHF Samples

For ESR experiments, sample tubes to contain MTHF were constructed from high-purity Spectrosil quartz tubing 4.0 mm OD by 3.5 mm ID and about 4 inches long. One end of the tube was sealed closed while a quartz-to-pyrex graded seal was sealed onto the other end. These tubes were attached to the vacuum line, a suitable quantity of MTHF condensed into them, and then sealed off under vacuum.

5. DPPH

A sample consisting of 8.2×10^{-3} g of DPPH dispersed in 2.0004 g of NaCl was used for ESR magnetic field measurements as discussed below on p 64 of this chapter. The mixture was prepared by Bonin⁶⁹ and was contained in a 3 mm ID pyrex tube.

6. Peroxylamine Disulfonate Free Radical

Freymy's salt, $K_2[(SO_3)_2NO]$, dissolves⁹⁰ in a saturated aqueous sodium carbonate solution to give the peroxylamine disulfonate free radical, $[(SO_3)_2NO]^{\cdot -2}$. The sample used in this study was also prepared by Bonin and details of the preparation are to be found in his dissertation.⁶⁹ When not in use, the sample was stored in a refrigerator so as to inhibit decay of the radical.

D. Irradiation Procedures

1. Description of the Radiation Source

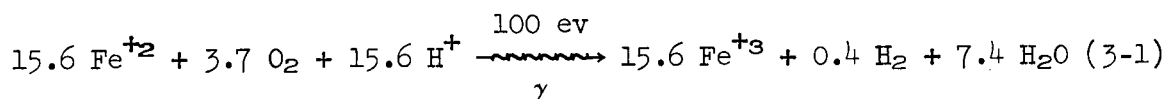
All samples investigated by ESR in this work were irradiated with cobalt-60 gamma rays in a Gammacell 200 Irradiator made by Atomic Energy of Canada Ltd. This source consists of capsules of cobalt-60 arranged

concentrically about a movable cylindrical plug which could be raised or lowered through the lead shielding by actuating an electrical drive motor. The activity of the cobalt-60 was 3,055 curies when the source was loaded in November, 1963.

The cylindrical plug contains a sample compartment 7 inches high and 4 inches in diameter. Irradiations were carried out by simply placing a sample in the compartment and lowering the plug to the bottom of its range. In this position, the sample is located centrally within the cobalt-60 array and in the region of maximum dose rate. All irradiations were carried out with the sample at liquid N₂ temperature, 77°K. A Thermos Co. half-pint vacuum bottle is a convenient size dewar for this purpose. All irradiations were done in darkness to avoid accidental photobleaching of the sample.

2. Dosimetry

The dose rate in the source was determined by Taylor⁹¹ using the Fricke dosimeter⁹² to be $2.87 \times 10^{17} \text{ ev g}^{-1} \text{ min}^{-1}$ in the dosimeter solution on March 21, 1967. Full details of the measurement are reported in Taylor's thesis.⁹¹ Briefly, the Fricke dosimeter depends on the radiation-induced oxidation of ferrous ion to ferric. The overall stoichiometry of the reaction is⁹²



The dosimeter solution consists of $1 \times 10^{-3} \text{ M}$ ferrous sulfate in 0.4 M sulfuric acid. The usual precautions of using triply distilled water and adding a small amount of chloride ion were observed by Taylor so as to inhibit oxidation of the ferrous ions by organic impurities.⁹² The

number of ferric ions formed is directly proportional to the amount of radiation energy deposited in the solution, $G(\text{Fe}^{3+})$ being 15.6.⁹³ Hence, a determination (spectrophotometrically) of the number of ferric ions formed during a given time of irradiation enables the dose rate to be calculated.

It was necessary to apply two corrections to the value for the dose rate obtained for 0.4 M sulfuric acid. The first results from the fact that energy deposited per gram in gamma-irradiated organic materials is predominantly by Compton scattering and is therefore dependent on the number of electrons per gram. Thus, the dose rate in a particular organic sample is related to that in the dosimeter solution according to the equation⁹²

$$D_{\text{sample}} = D_{\text{dosimeter}} \frac{(\sum_i w_i Z_i / A_i)_{\text{sample}}}{(\sum_i w_i Z_i / A_i)_{\text{dosimeter}}} \quad (3-2)$$

where D is the dose rate, w_i is the weight fraction of element i in the molecule, and Z_i and A_i are the atomic number and weight of element i . The summation term in Equation (3-2) is 0.553 for the Fricke dosimeter solution and 0.571 for the polymer used in this work. The correction is therefore only some three percent.

The second correction takes into account the radioactive decay of the cobalt-60 during the time between the dosimetry measurements and the experiments of this dissertation. If the dose rate in the source is known to be I_0 at some time t_0 , then at a later time t , the dose rate I is given by the equation

$$I = I_0 e^{-k(t-t_0)} \quad (3-3)$$

where the decay constant k is known to be 0.0110 month⁻¹.⁹² Applying

both corrections to the dosimetry data yields a dose rate of $2.50 \times 10^{17} \text{ ev g}^{-1} \text{ min}^{-1}$ in the initial stages of the experiments and which subsequently decreased to $2.12 \times 10^{17} \text{ ev g}^{-1} \text{ min}^{-1}$ during the course of the work.

A second ^{60}Co source was used to irradiate a sample of poly(4-methylpentene-1) in an effort to detect the optical absorption spectrum of trapped electrons in this material. This source belongs to the Radiation Chemistry Group of the Chemistry Division at Oak Ridge National Laboratory and a full description of it has been published.⁹⁴ The dose rate at the time of irradiation was $9.18 \times 10^{17} \text{ ev g}^{-1} \text{ min}^{-1}$.⁹⁵

E. ESR Measurements

1. Description of the Spectrometer

The ESR spectrometer used in these studies was the V-4502 unit of Varian Associates, Palo Alto, California. This instrument employs a 12 inch electromagnet and operates in the X-band region of the electromagnetic spectrum. The low power arrangement of the microwave bridge was used. A block diagram showing some of the more essential instrument components appears in Figure 3. A brief description⁹⁶ of these components and their function follows:

- a. The electromagnet together with its power supply provides a magnetic field in the neighborhood of 3000 G at the sample position. Provision is made so that the magnetic field may be swept linearly with time.
- b. The klystron oscillator is used to irradiate the sample with microwave energy. In the Varian V-4502 spectrometer, the klystron frequency is nominally about 9 GHz.

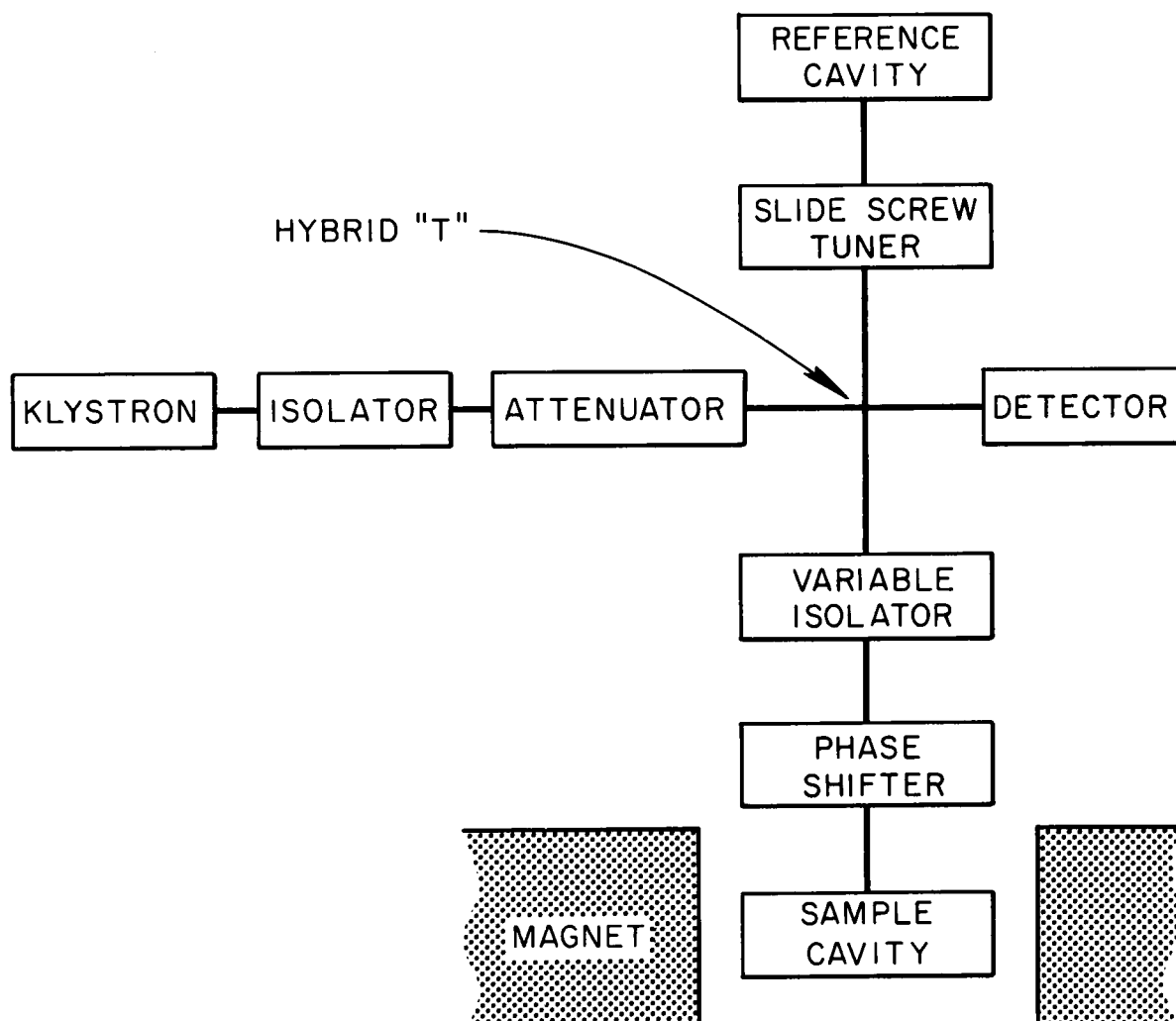


Figure 3. Block diagram of the ESR spectrometer.

- c. The sample itself is located in a resonant cavity within the magnet air gap. When the klystron is tuned to the resonant frequency of the cavity, microwave energy is effectively stored in the cavity with very little reflected back out.
- d. The hybrid T acts much like a balanced bridge device in conventional electronic circuitry. It has the property that it will pass microwave energy from one arm into both adjacent arms but not into the opposite arm. Thus power from the klystron arm is divided equally between the reference and sample cavity arms but is not passed to the detector arm. When both the reference and sample cavities are properly adjusted, the incident microwaves will be stored within them and the detector will receive no signal. If now the magnetic field is moved onto resonance for the sample, the sample will absorb microwave energy as unpaired electrons are promoted from lower to higher energy spin states as was discussed in Chapter II. It can be shown⁹⁶ that this energy absorption changes the impedance of the sample cavity which in turn causes some microwave power to be reflected back out of the cavity. This reflected power divides at the hybrid T, half going into the klystron arm (where it is absorbed by the isolator) and the other half proceeds to the detector.
- e. The crystal detector rectifies the signal, passes it

on to an amplifier system where it is amplified and ultimately displayed on a chart recorder. The detection scheme also makes use of magnetic field modulation and phase sensitive detection. These components are not shown in Figure 3 (p 59), however. This method of detection results in the ESR information being displayed on the chart recorder as the first derivative of microwave power absorption versus magnetic field strength rather than as the absorption itself versus field.

2. General ESR Experimental Procedures

Immediately following gamma irradiation, the sample was transferred as rapidly as possible to an ESR dewar containing liquid N_2 . This was a quartz dewar of double wall construction with a narrow unsilvered tail section sealed to a larger reservoir section. The ESR dewar was then placed in the sample cavity (Varian V-4531) and the entire magnet air gap covered with a black cloth shroud. The entire transfer operation was carried out in the dark with the room lights off in order to avoid accidental photobleaching of the sample. Once the sample was covered by the cloth shroud, however, the lights could be safely turned back on, the spectrometer adjusted, and a spectrum obtained. The elapsed time between removal of the sample from the radiation source and recording the spectrum was typically about five minutes.

No difficulty was encountered in the transfer of polymer samples but special care was required with the alkane samples because of their

fragility. For these latter samples, the transfer operation was accomplished by placing the mold tube containing the samples over the entry to the tail section of the ESR dewar and then carefully pushing the sample into the tail section with a glass rod. Care was taken to ensure that the sample remained under liquid N_2 during the entire process.

Most ESR spectra were recorded at a magnetic field sweep rate of 25 G/min and a modulation frequency of 100 kHz, the peak-to-peak amplitude being 1.5 G. The microwave power level incident on the sample was 2 microwatts (μW). The power level was established by means of a variable isolator and was measured using a Hewlett-Packard Model X 486A thermistor probe connected to a Hewlett-Packard Model 431C power meter. The thermistor probe was attached to the sample cavity of the microwave bridge by means of a 3 db directional coupler and a waveguide shorting switch.

Intentional photobleaching of the sample was accomplished in situ by passing filtered light from a General Electric Co. 1 kwatt tungsten light bulb through slots in the front face of the sample cavity and onto the sample itself. Two glass filters, Corning Nos. 2030 and 4308, were placed immediately in front of the cavity and the cloth shroud over the magnet air gap adjusted about the filters so as to admit to the sample only that light which had passed through the filters. The filter combination passes only that light from the tungsten lamp whose wavelength is greater than 1μ . The light beam was focused onto a circular spot 3 cm in diameter on the front face of the cavity by means of a plano-convex lens 12.5 cm in diameter located between the lamp and the filters. In

all photobleaching studies, the lamp was used at full line voltage (~110 volts).

3. Thermal Decay Studies

For ESR studies of the thermal stability of trapped electrons at temperatures above 77°K, use was made of the Varian V-4557 Variable Temperature Accessory. This device operates by passing a stream of cold N₂ gas through a dewar insert located in the cavity and in which the sample sits. Cooling of the N₂ stream is accomplished by passing the gas from a storage cylinder through a heat exchanger coil immersed in liquid N₂ and thence to the sample by means of a transfer dewar. Temperature at the sample is adjusted by varying the flow rate of the gas through the heat exchanger and also by means of a resistance heater located in the gas stream close to the sample. Temperature is sensed with a platinum resistance thermometer. Temperature control is achieved by means of a control circuit which senses differences in temperature from the set point and then varies the current through the resistance heater accordingly. The minimum temperature possible with this apparatus was 84°K and was controllable to about $\pm 1^\circ\text{K}$ with an absolute accuracy of $\pm 3^\circ\text{K}$. ESR experiments involving the variable temperature accessory were carried out in the usual manner.

4. Determination of g-Factors

In order to determine the g-factor for a paramagnetic species, it is evident from a consideration of Equation (2-9) (p 32) that both the microwave frequency, ν , and the magnetic field strength, H , must be known at resonance. The microwave frequency was determined by using an

Acto Model 1255 transfer oscillator to convert a 50 MHz counter, Model 1037, manufactured by the Systron-Donner Corp, to an 8-12 GHz range.

The magnetic field strength was measured by an indirect method, using a Varian V-4532 dual sample cavity. The special features of this cavity are two-fold. First, spectra from two samples can be recorded simultaneously on a dual-channel recorder using the 100 kHz and 400 Hz detection systems available on the spectrometer. Second, both samples are exposed to the same microwave frequency in the cavity. Thus if a sample whose g-factor is unknown is examined in the dual cavity together with a sample of DPPH whose g-factor is known, the magnetic field strength at the center of resonance for the unknown can be determined from the distance between the centers of the two spectra on the chart. This follows from the fact that since ν is measured and g is known for DPPH, H at resonance can be calculated for DPPH. This value, plus knowledge of the magnetic field scan rate, chart speed, and distance between the two spectra on the chart, enables H at resonance for the unknown to be calculated.

The method thus depends on knowing the rate at which the magnetic field is scanned. This was determined from the hyperfine splitting in a sample of the peroxyamine disulfonate radical. The ESR spectrum of this radical consists of a triplet due to interaction of the unpaired spin with the nitrogen nucleus ($I = 1$). The magnitude of this splitting is 13.00 ± 0.07 gauss.⁹⁰ Thus, a measurement of this splitting plus knowledge of the chart speed gives the field scan rate directly.

F. Optical Spectroscopy

1. Description of the Apparatus

The optical absorption spectra of trapped electrons in hydrocarbon matrices are generally obtained as the difference in optical absorption before and after photobleaching the sample.⁵⁸ This fact, as well as the necessity of working at liquid nitrogen temperatures, imposes certain requirements on the spectrometer and ancillary equipment used in the measurement. First, the sample must be exposed only to a low intensity monochromatic light beam so as to avoid the possibility of accidentally photobleaching (e_t^-) prior to the point at which it is intentionally photobleached. Second, the intentional photobleaching of (e_t^-) must be carried out with another light source of higher intensity and must be done without moving the sample so as to make meaningful comparison of optical absorption before and after photobleaching. Finally, the sample compartment of the spectrophotometer must be large enough to accept the necessarily bulky dewar used to maintain the sample at 77°K.

The Cary Model 14R spectrophotometer satisfies these requirements and was employed in this work to investigate the optical absorption spectrum of (e_t^-) in poly(4-methylpentene-1). The model 14R is a double-beam recording spectrophotometer operating from 1900 Å to 2.65 μ. In the spectral region of interest in this study, 0.7 to 2.0 μ, two light sources are available. Source No. 1 is a low-intensity tungsten-infrared source which is monochromatized before passing through the sample. This light source was used for the optical absorption measurements. Source No. 2 is of higher intensity and is non-monochromatic. It was used to intentionally photobleach the sample.

An optical dewar suitable for use at 77°K has been described by Hamill⁵⁸ and one constructed by Lin⁶⁴ of similar design was employed in this study. As shown in Figure 4, the dewar contains a sample positioning device and is itself contained in a vacuum tight metal housing. The housing serves a two-fold purpose. After filling the dewar with liquid nitrogen and inserting the sample, a partial vacuum is pulled on the housing. This eliminates bubbling of the liquid nitrogen apparently by destroying bubble nucleation sites.⁵⁸ Liquid nitrogen bubbling in the light path can be particularly troublesome as it results in extremely noisy spectra. When bubbling has ceased, the vacuum is removed from the housing and dry air admitted so as to prevent the formation of frost on the dewar windows.

2. Experimental Methods

The first step in the experiment was to obtain the spectrum of an unirradiated poly(4-methylpentene-1) sample in terms of optical density as a function of wavelength. The sample was then removed from the optical dewar, gamma irradiated, and re-introduced into the dewar. Care was taken to protect the sample from exposure to light during the irradiation and transfer.

After recording the spectrum of the irradiated material, the sample was intentionally photobleached by exposing it to light from Source No. 2. Corning 2030 and 4308 filters were interposed between the light source and the sample prior to photobleaching. This filter combination allowed only light of $\lambda > 1 \mu$ to reach the sample. All spectra were obtained versus air in the reference beam.

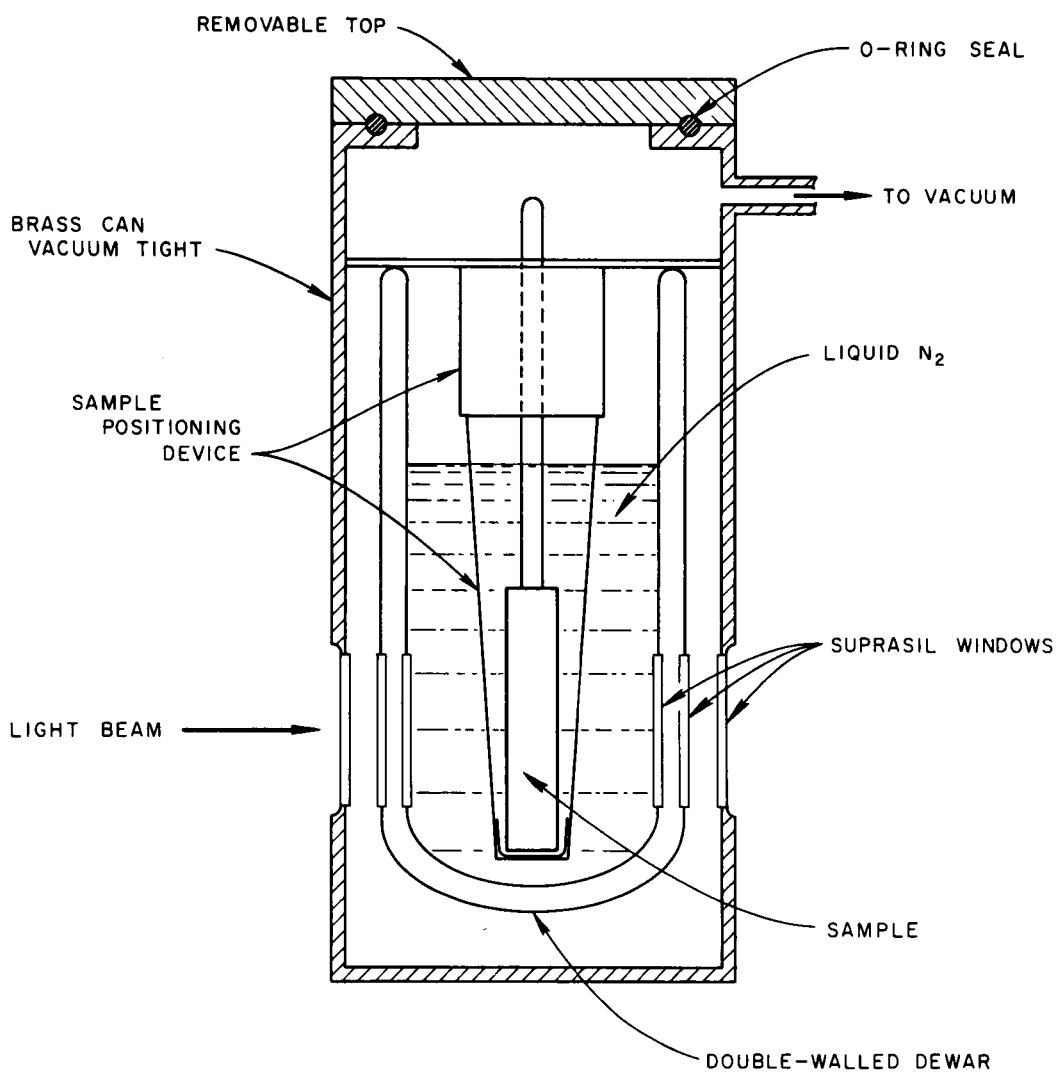


Figure 4. Optical dewar for use at 77°K.

CHAPTER IV

RESULTS

A. Introduction

The results of a number of investigations concerning trapped electrons and their behavior in hydrocarbon polymers are presented in this chapter. The identification, yield, thermal stability, microwave power saturation, and various other characteristics of trapped electrons are discussed first for polyethylene and then for a series of poly(α -olefins). The chapter concludes with some observations of trapped electrons in n-alkanes.

B. Linear Polyethylene

1. Identification of the Trapped Electron

Following gamma-irradiation in the dark at 77°K, a typical first-derivative ESR spectrum also at 77°K of bulk-crystallized antioxidant-free Marlex 6050 polyethylene appears as shown in spectrum A of Figure 5. The most prominent feature of spectrum A is the intense narrow singlet in the center of the spectrum. When the sample is exposed in situ in the cavity to infrared light of wavelength greater than 1000 nm, the spectrum changes from that of A to spectrum B. The narrow singlet has been completely eliminated, i.e., photobleached by this treatment. Only a broad six-line spectrum with approximately 30 gauss splitting remains. Exposure of the sample to unfiltered room light produces an entirely equivalent effect.



Figure 5. First-derivative ESR spectra of γ -irradiated antioxidant-free Marlex 6050 polyethylene at 77°K.

The irradiation dose was 1.1×10^{19} ev g^{-1} . Spectrum A was recorded in the dark and spectrum B was obtained after photobleaching with infrared light ($\lambda > 1000$ nm). The spectra were recorded at a microwave power level of 2 μ W, at a spectrometer gain setting of 200, and at a modulation amplitude dial setting of 250 corresponding to a peak-to-peak modulation amplitude of 1.5 gauss.

Spectrum B has been observed previously in irradiated polyethylene by a number of workers⁷¹ and has been assigned to an alkyl free radical, $\text{-CH}_2\dot{\text{C}}\text{HCH}_2\text{-}$, formed by rupture of a C-H bond along the polyethylene chain. Spectrum A therefore is evidently a superposition of spectra from two distinct species, one being the alkyl free radical and the other a previously undetected species which is light sensitive and whose ESR spectrum consists of a narrow singlet.

The linewidth, ΔH_{ms} , of the singlet is 3.4 ± 0.2 gauss as measured horizontally between the positions of maximum amplitude of the line. These positions correspond to points of maximum slope on the curve which would have resulted had the spectrometer response been plotted as power absorption versus field strength rather than as the first-derivative representation. Hence the subscript ms (maximum slope) on ΔH . For linewidth measurements, the chart speed of the recorder was increased from 1 in/min to 4 in/min in order to increase the accuracy of the measurement. The ± 0.2 gauss uncertainty in ΔH_{ms} arises primarily from difficulty in locating the exact positions of maximum amplitude of the singlet.

The singlet readily underwent microwave power saturation at low microwave power. Below 7 μW the signal height increased as the power was increased. At 7 μW the signal height passed through a maximum and thereafter decreased with further increase in microwave power. At a power level of 100 μW , the signal height had fallen to only one-half the value at the maximum. These data pertain to observations at a modulation frequency of 100 kHz. At lower modulation frequencies, the maximum in the saturation curve shifts to lower microwave power. Such effects will be discussed in a subsequent section.

The narrowness of the linewidth of the singlet in spectrum A of Figure 5 (p 68), the fact that it saturates at very low microwave power, and finally the photobleaching effect are all analogous to the behavior observed for trapped electrons in alkane glasses which has been discussed in Chapter I. Therefore, the singlet in spectrum A is assigned to electrons trapped in the polyethylene matrix. The inability of earlier workers to detect this species can be plausibly ascribed to (1) failure to protect the sample from light and (2) failure to work at sufficiently low microwave power.

2. Antioxidant Effects

The presence of antioxidants in polyethylene can significantly effect the yield of trapped electrons. Figure 6 shows the ESR spectrum at 77°K of a sample of Marlex 50 polyethylene which had received an irradiation dose of 1.1×10^{19} ev g⁻¹ also at 77°K. Marlex 50 contains 0.02 weight percent of the antioxidant 2,6 di-t-butyl-4-methylphenol.

Spectrum A of Figure 6 shows a narrow ($\Delta H_{ms} = 3.4 \pm 0.2$ gauss) singlet superimposed on a broad background similar to the spectrum of the alkyl free radical. The singlet saturates at about 7 μ W and is readily photobleached as shown by spectrum B. The singlet is therefore assigned to a trapped electron.

The spectra in Figure 6 differ in two respects from those of antioxidant-free Marlex 6050 polyethylene. First, the yield of trapped electrons in Marlex 50 is only about one-half that in the antioxidant-free 6050 material when the comparison is made on samples which had received the same irradiation dose. (It may be well to interject a note of caution at this point. The reader is advised against attempting to

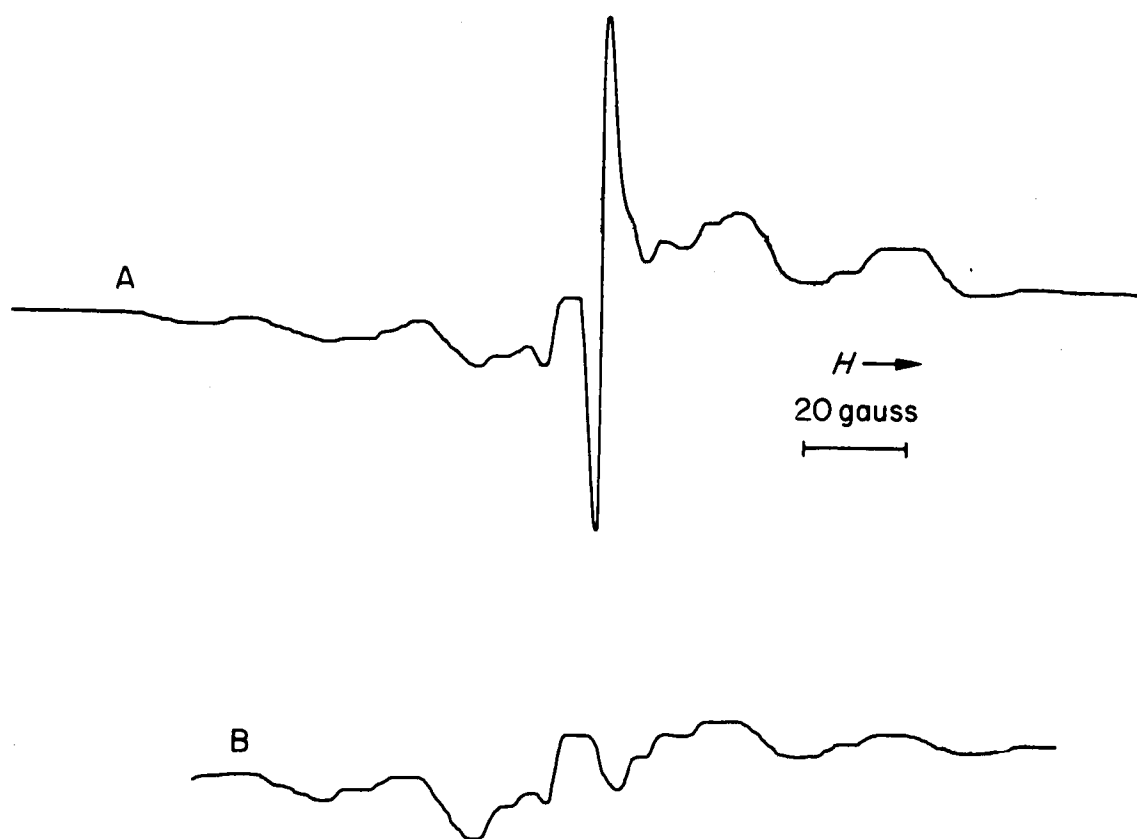


Figure 6. First-derivative ESR spectra of γ -irradiated Marlex 50 polyethylene at 77°K.

The irradiation dose was 1.1×10^{19} ev g^{-1} . Spectra A and B were recorded before and after photobleaching with infrared light ($\lambda > 1000$ nm) respectively. The microwave power level was 2 μ W and the spectrometer gain setting was 400 for both spectra. The modulation amplitude was 1.5 gauss.

draw his own conclusions regarding relative yields solely from a comparison of signal amplitudes in spectra appearing in the various figures of this dissertation. These spectra were prepared from actual photographs of chart recordings. In some instances the extent of photographic reduction may vary from figure to figure although not between spectra within the same figure. Furthermore, a gradual loss of sensitivity of the spectrometer occurred during the course of this work. For this reason, spectra in different figures may correspond to varying spectrometer sensitivities although the sensitivity is the same for spectra within a given figure. In all cases in the text where a statement is made regarding the yield of a species, the statement is supported by a comparison of signal amplitude with that of a secondary standard such as the Varian strong pitch sample or irradiated MTHF.) Second, there is evidence of additional hyperfine structure on either side of the trapped electron singlet in Marlex 50. This structure is not removed by photobleaching and still remains in spectrum B of Figure 6. Entirely similar effects were observed with a sample of Marlex 6050 which also contained antioxidant.

Efforts were made to remove the antioxidant from Marlex 50 by extraction with boiling acetone as noted in Chapter III. Following irradiation, the yield of trapped electrons in Marlex 50 treated in this fashion was virtually identical to that in the antioxidant-free Marlex 6050 sample. Most of the additional hyperfine structure on either side of the trapped electron singlet was lost as well.

The inference to be drawn from these observations is that antioxidant competes with electron traps for electrons. Thus, in the presence

of antioxidant, the yield of trapped electrons is reduced and additional hyperfine structure appears in the ESR spectrum due to the product (free radical or radical anion) resulting from electron capture by the antioxidant. Because of these complicating effects in the presence of antioxidant, all further work to be described was carried out using materials free of antioxidant.

3. Determination of the Trapped Electron g-Factor

The g-factor for the trapped electron in Marlex 6050 polyethylene was measured using the dual cavity procedure discussed in Chapter III. The procedure involves simultaneous recording of spectra from both the unknown and a reference sample of DPPH. Since both samples are exposed to the same microwave frequency, the g-factor of the unknown is related to that of the reference by the equation

$$g(e_t^-) = g_{\text{DPPH}} H_{\text{DPPH}} / H(e_t^-) \quad (4-1)$$

where the subscripts (e_t^-) and DPPH refer respectively to the trapped electron and DPPH reference sample and H is the value of the magnetic field corresponding to the center of resonance.

H_{DPPH} was calculated from Equation (2-9) (p 32) using the measured klystron frequency and $g = 2.0036 \pm 0.0002$ for DPPH.⁹⁷ $H(e_t^-)$ was calculated from the value of H_{DPPH} and the measured distance between the centers of the two resonances. This measured distance was converted into gauss using the known chart speed of the recorder and the scan rate of the applied field. The field scan rate was determined from the hyperfine splitting of the peroxyamine disulfonate radical as discussed in Chapter III. For a nominal setting of 10G/min, the measured scan rate

was 10.3G/min. The measured distance between the two resonances was corrected for the fact that the pens on the dual-channel recorder are offset by 0.40 cm.

Four measurements on the trapped electron singlet in Marlex 6050 by this procedure gave identical values of 2.0022 for $g(e_t^-)$. In view of the uncertainty in g_{DPPH} , it seems best to report the g -factor as 2.0022 ± 0.0002 for the trapped electron in polyethylene. The value is virtually identical to that of an electron with free spin.

4. The Dependence of Trapped Electron Concentration on the Radiation Dose

In common with most other forms of spectroscopy, the area under the ESR absorption curve is proportional to the number of absorbing species. The term absorption curve is used here to refer to a plot of energy absorbed from the microwave field as a function of applied field strength. Since the ESR spectra in this dissertation are all obtained as the first-derivative of the absorption curve, the required area would be that given by the double integral of the spectrometer output.

Ayscough⁸¹ has pointed out, however, that the absolute determination of unpaired spin concentration is impractical in ESR spectroscopy due to difficulties in controlling and measuring the various spectrometer parameters which establish the proportionality constant between area and the number of absorbers. Consequently, most workers resort to comparison methods in which the spectrometer response from the unknown is compared with that from a suitable reference material whose unpaired spin concentration has already been determined by some other technique. This latter procedure has been adopted here.

The reference sample used was an MTHF sample which had received a dose of 2.5×10^{18} ev g^{-1} at $77^\circ K$. $G(e_t^-)$ for MTHF has been determined to be 2.6 trapped electrons/100 ev as discussed in Chapter I. Hence, the trapped electron concentration in the reference was 6.5×10^{16} electrons/g. The linewidth of the trapped electron singlet in MTHF was found to be 4.4 ± 0.2 gauss in good agreement with the published value of 4.5 gauss.⁵³

The ESR singlet of the trapped electron in MTHF has a Gaussian line shape.⁵³ Similarly, it was found that the trapped electron singlet in polyethylene is also characterized by a Gaussian line. This conclusion follows from a comparison of the observed line shape with that expected for the first-derivative of a Gaussian curve with peak-to-peak derivative amplitude and ΔH_{ms} equal to that of the experimental line. It is readily shown that the area under a Gaussian line is directly proportional to the product of the square of ΔH_{ms} and A, the peak-to-peak amplitude of the derivative curve.

Assuming equal densities of polyethylene and MTHF at $77^\circ K$, it follows from these considerations that the number of trapped electrons per gram in polyethylene, N_{PE} , is related to the number per gram in the MTHF reference sample by the equation

$$N_{PE} = N_{MTHF} F \frac{A_{PE} \Delta H_{PE}^2}{A_{MTHF} \Delta H_{MTHF}^2} \quad (4-2)$$

where the subscript ms has been left off ΔH for clarity. A factor F has been included in Equation (4-2) to take account of the fact that the diameter of the polyethylene samples was greater than that of the MTHF standard, i.e., 0.48 cm versus 0.32 cm respectively. The necessity of using different diameter samples arises from the fact that the yield of

trapped electrons in polyethylene is substantially lower than that in MTHF so that for reasons of sensitivity at low doses, it was necessary to use the maximum size polyethylene sample commensurate with the limitations imposed by the geometry of the dewar.

The factor F was taken equal to the ratio of the trapped electron singlet amplitude for a polyethylene sample molded in one of the 0.32 cm ID Spectrosil tubes used to contain MTHF samples to that for the usual 0.48 cm diameter polyethylene sample. Values of F determined in this fashion were 0.425, 0.410, and 0.399 in three separate experiments in which each polyethylene sample was irradiated to a dose of 1.10×10^{19} ev g^{-1} . The average of these values, 0.411, was used in Equation (4-2). This value is close to the ratio of the squares of the radii of the two samples, 0.445, as would be expected.

The trapped electron signal amplitudes were obtained by superposing tracings of spectra recorded before and after photobleaching. The required amplitude was taken as the sum of the measured vertical distances from the maximum and minimum points in the first-derivative trapped electron spectrum to the underlying spectrum recorded after photobleaching.

The trapped electron concentration in terms of electrons per gram of Marlex 6050 polyethylene obtained through use of Equation (4-2) is shown in Figure 7 for irradiation doses up to 6×10^{19} ev g^{-1} . The concentration rises to a maximum at 3×10^{19} ev g^{-1} and thereafter decreases with further increase in dose. At low irradiation doses, below 5×10^{18} ev g^{-1} , the trapped electron concentration increases linearly with dose as shown in Figure 8. From the slope of the line in Figure 8, the

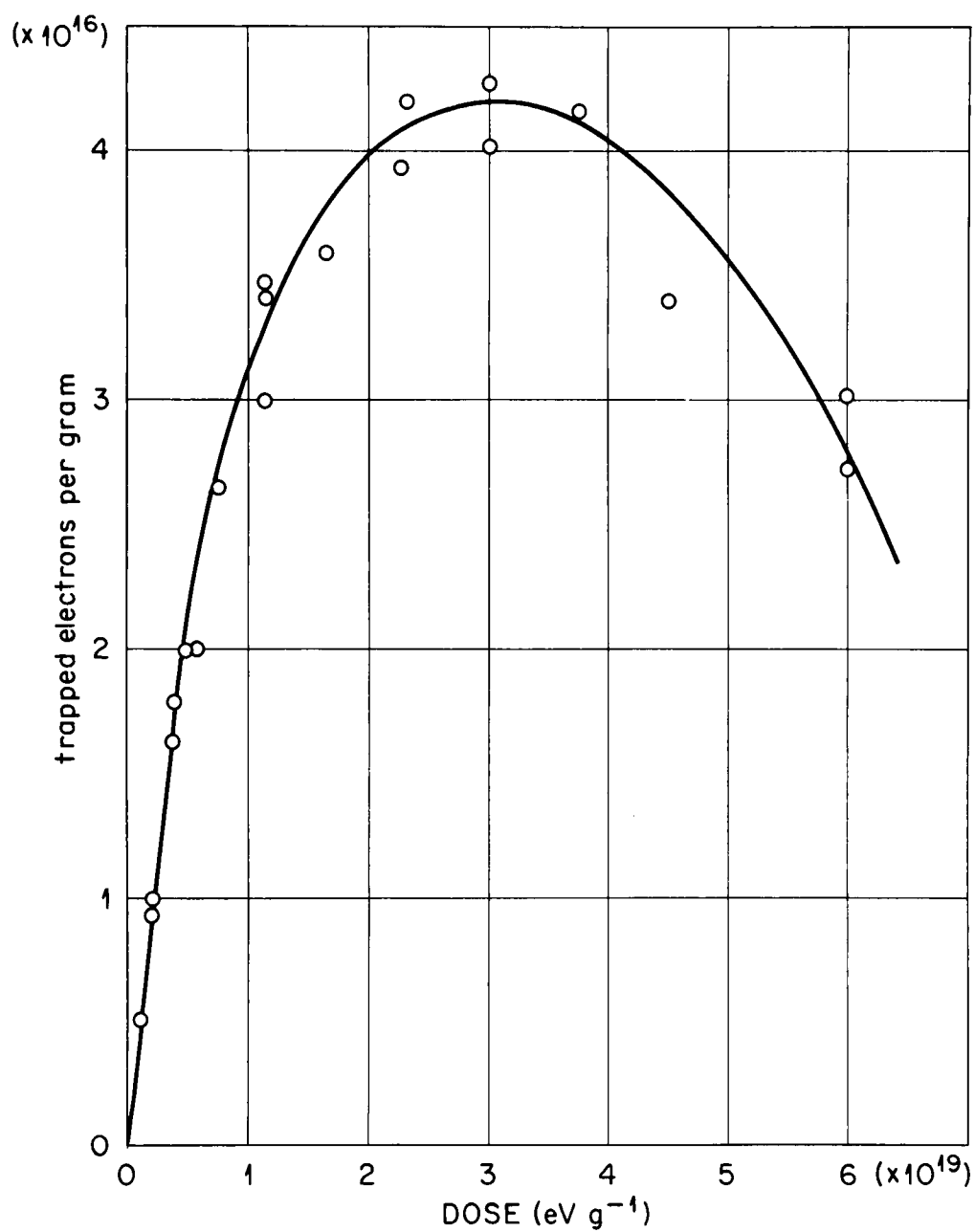


Figure 7. Concentration of trapped electrons as a function of dose in Marlex 6050 polyethylene γ -irradiated at 77°K.

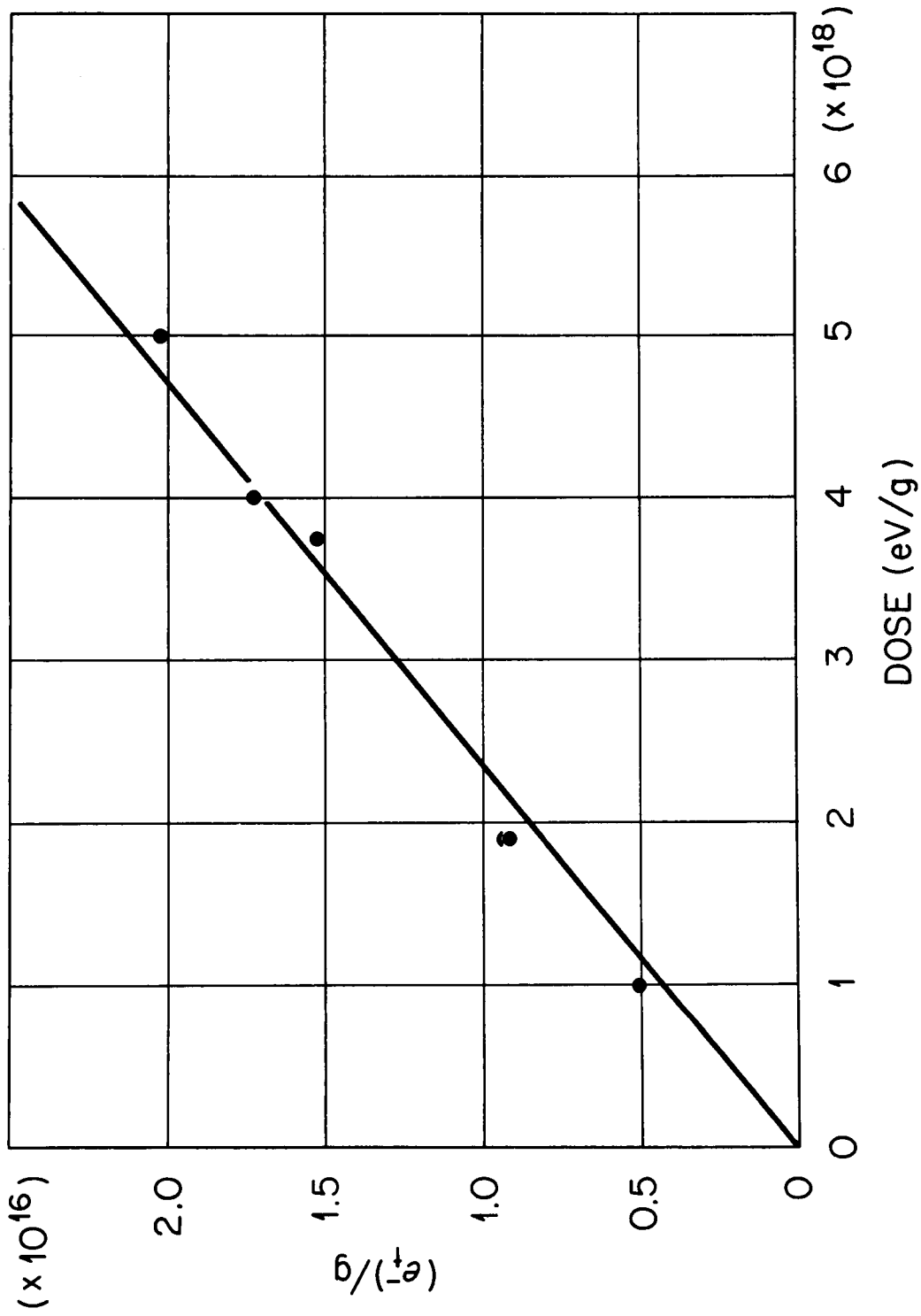


Figure 8. Concentration of trapped electrons at low doses in Marlex 6050 polyethylene γ -irradiated at 77°K.

limiting value of $G(e_t^-)$ at low doses was established to be 0.46 trapped electrons per 100 ev of energy deposited in the sample.

In order to examine the possibility that free radicals may affect the trapped electron yields, a Marlex 6050 sample was irradiated at 77°K to a dose of 3×10^{19} ev g^{-1} which produced a maximum concentration of 4.2×10^{16} trapped electrons per gram (see Figure 7, p 78). The sample was then photobleached with near infrared light, eliminating the trapped electron ESR singlet. No change in the underlying free radical signal was observed to occur as a result of the photobleaching treatment. The sample was then given a second 3×10^{19} ev g^{-1} irradiation at 77°K. This second irradiation doubled the intensity of the free radical signal but produced a new trapped electron ESR singlet whose intensity was only one-half of that which resulted from the initial irradiation. This result suggests that the trapped electron yields are influenced by the buildup of free radicals, the trapped electron yield decreasing with increasing free radical concentration.

The possibility that some other radiation product whose yield is proportional to dose might be responsible for the effect can be ruled out on the basis of thermal annealing experiments. A typical experiment of this type was carried out by irradiating a Marlex 6050 sample at 77°K to a dose of 3×10^{19} ev g^{-1} , photobleaching the sample to remove trapped electrons, and then allowing the sample to warm to room temperature where it was maintained in a stream of dry nitrogen gas for seven hours. During this period, 90 percent of the free radicals decayed out as revealed by the fact that the intensity of the free radical signal subsequent to annealing was only one-tenth of the original intensity prior to

annealing. A second irradiation at 77°K of 3×10^{19} ev g^{-1} following this treatment produced a trapped electron concentration of 3.8×10^{16} electrons/g, nearly equal to the maximum concentration in Figure 7 (p 78). Thus annealing the sample to the point where virtually all the free radicals have been destroyed restores the trapping ability of the matrix. A second annealing experiment was carried out in a similar fashion except that the annealing period was terminated when approximately half the free radicals had been destroyed. The intensity of the trapped electron signal after a second 3×10^{19} ev g^{-1} irradiation at 77°K corresponded to a trapped electron concentration intermediate between the values of 2.1×10^{16} and 3.8×10^{16} electrons/g found in the two preceding experiments.

Thus the yield of trapped electrons observed in experiments of this type appears to be correlated with free radical concentration. This suggests the possibility that electrons may react with free radicals. If such a reaction occurs after the electron is trapped, then this could serve to account for the decrease in trapped electron concentration observed above doses of 3×10^{19} ev g^{-1} in Figure 7 (p 78).

5. Thermal Decay of Trapped Electrons in Marlex 6050 Polyethylene

The thermal stability of the trapped electron in Marlex 6050 polyethylene was investigated by means of ESR as the temperature of the sample was increased in 10° steps from -196°C (77°K) to -146°C (127°K). The results of a typical experiment are shown in Figure 9. The top curve in Figure 9 reflects the extent of thermal decay over a two hour interval at -196°C for a sample which had received a radiation dose of 1.1×10^{19} ev g^{-1} . The rate of decay is greatest in the first 30 minutes

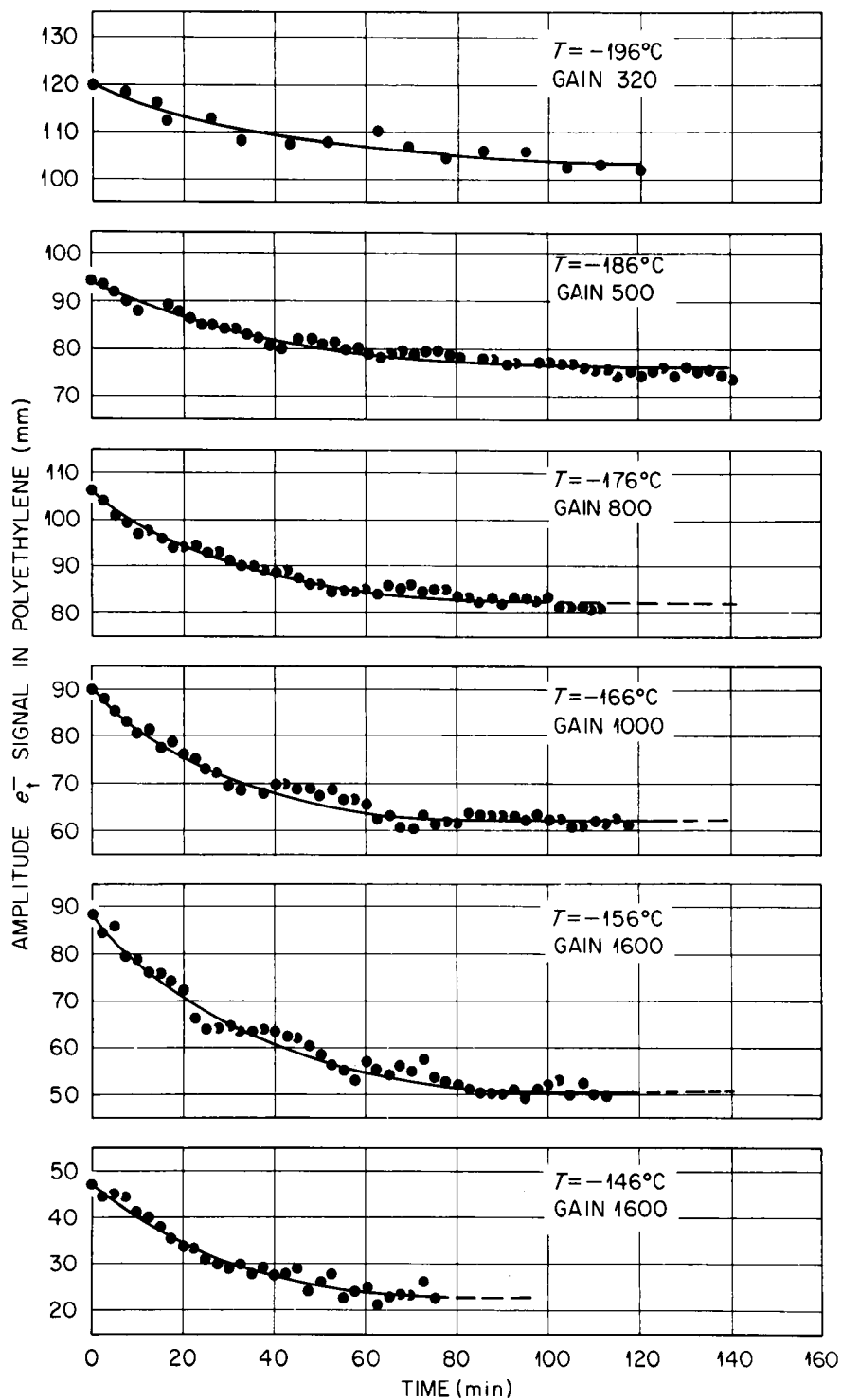


Figure 9. Stepwise thermal decay of trapped electrons in Marlex 6050 polyethylene.

Comparison of amplitudes at one temperature with those at another does not accurately reflect concentration changes since the temperatures are different.

after irradiation. At longer times, the decay becomes very slow and the signal amplitude appears to approach an asymptotic value.

The remaining decay curves in Figure 9 at temperatures above that of liquid N_2 were obtained using a second sample also irradiated to a dose of 1.1×10^{19} ev g^{-1} . After irradiation, this latter sample was stored in the dark under liquid N_2 at $-196^\circ C$ for 120 minutes. The trapped electron decay during this period was assumed to proceed in accordance with the $-196^\circ C$ curve in Figure 9. After the two hour storage period, the sample was removed from the liquid N_2 and inserted in the Varian variable temperature apparatus described in Chapter III. The trapped electron ESR signal amplitude was then monitored at $-186^\circ C$ for 140 minutes. The results are shown as the $-186^\circ C$ curve in Figure 9. The zero of time for these data was taken as corresponding to the first scan of the trapped electron spectrum which was obtained three minutes after removing the sample from liquid N_2 .

After 140 minutes at $-186^\circ C$ the temperature of the sample was raised 10° and the decay of the trapped electrons was followed isothermally for 115 minutes at $-176^\circ C$. The data so obtained are plotted as the $-176^\circ C$ curve in Figure 9. In this instance the zero of time again refers to the first measurement taken 1.5 minutes after raising the temperature to $-176^\circ C$. The remaining curves of Figure 9 were obtained in an analogous fashion, the temperature in each instance having been raised 10° over that of the preceding series of measurements. All the curves are similar in the sense that the decay is fastest during the first 60 minutes at a given temperature and thereafter becomes very slow, the signal height of the trapped electron seeming to approach an asymptotic

value at long times. After 80 minutes decay at -146°C , it became difficult to resolve the trapped electron signal from that of the underlying free radical and the experiment was terminated at this point.

The decay of the trapped electron at the various temperatures in Figure 9 was tested for first-order kinetics according to the method of Guggenheim.⁹⁹ The essence of the method is as follows. Since the peak-to-peak amplitude of the trapped electron singlet, A_t , is proportional to the concentration of trapped electrons at time t , Equation (4-3) is valid for a first-order process.

$$(A_t - A_{\infty}) = (A_0 - A_{\infty}) e^{-kt} \quad (4-3)$$

A_0 and A_{∞} refer to the value of the singlet amplitude at zero and infinite times, respectively, and k is a first-order rate constant. An analogous expression holds for time $t + \Delta$ where Δ is a constant increment of time:

$$(A_{t+\Delta} - A_{\infty}) = (A_0 - A_{\infty}) e^{-k(t+\Delta)} \quad (4-4)$$

Subtracting Equation (4-4) from (4-3), rearranging terms, and taking logarithms results in

$$\ln(A_t - A_{t+\Delta}) = -kt + \ln \left[(A_0 - A_{\infty})(1 - e^{-k\Delta}) \right] \quad (4-5)$$

Thus a plot of $\ln(A_t - A_{t+\Delta})$ versus t should yield a straight line for a first-order process with slope equal to $-k$ and intercept given by the last term in Equation (4-5). Since k may be determined and Δ is fixed, A_{∞} may be calculated from the value of the intercept if A_0 is known.

Plots derived from the data in Figure 9 (p 82) according to the Guggenheim method with $\Delta = 40$ minutes are shown in Figure 10. The scale of the ordinate in Figure 10 is logarithmic. Note also that Figure 10 has been broken into two portions for clarity in displaying the data.

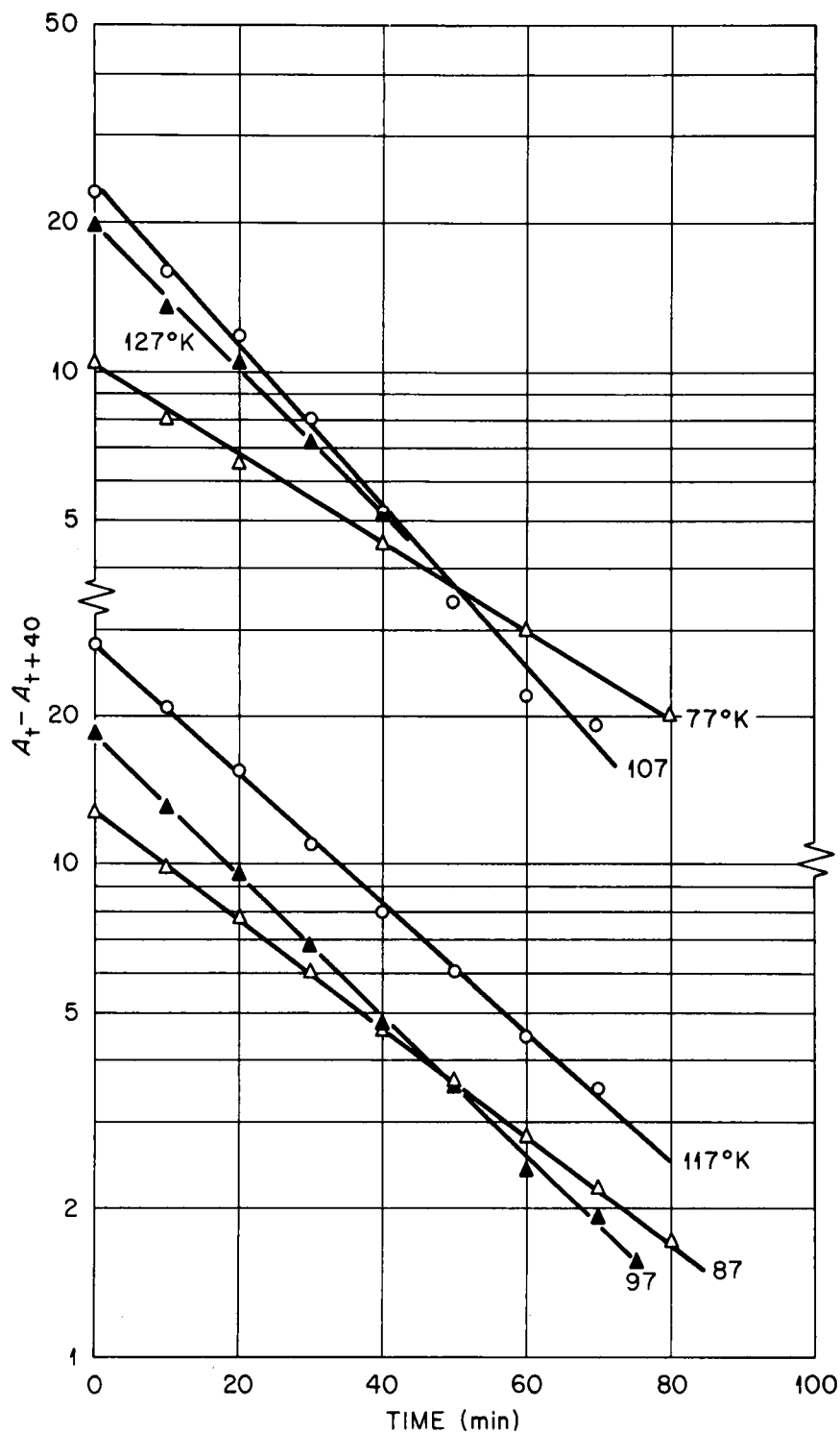


Figure 10. Test of first-order kinetics for the stepwise thermal decay of trapped electrons in Marlex 6050 polyethylene by the Guggenheim method.

The fact that straight lines are obtained at all temperatures indicates that in each case, the decay corresponds to first-order kinetics. The rate constants, k , and the value of the trapped electron singlet amplitude at infinite time, A_{∞} , were obtained from plots of $\ln(A_t - A_{t+40})$ versus t in accordance with Equation (4-5). They are tabulated in Table V. The rate constants were obtained from the slopes of the lines and the A_{∞} values were derived from the intercept at $t = 0$ using the corresponding A_0 values from Figure 9 (p 82). The A_{∞} values are in all cases close to the signal amplitudes observed at long times in Figure 9.

The fact that the amplitude of the trapped electron singlet in these experiments appears to decay to an asymptote represented by the A_{∞} values in Table V can be taken to imply that there are populations of trapped electrons relatively stable toward thermal decay until the temperature is raised to a point at which they become vulnerable to decay. On this basis, it is possible to calculate the fraction of electrons stable toward further thermal decay at each of the 10° intervals between -196°C and -146°C . By assigning a relative value of 1.0 to the trapped electron singlet amplitude measured immediately after irradiation at -196°C and making use of the A_0 and A_{∞} values in Figure 9 (p 82) and in Table V respectively, the fraction of trapped electrons remaining after decay at each of the 10° intervals was calculated. The results are displayed in Figure 11. It is evident from this figure that 0.16 of the initial number of trapped electrons decay on standing for two hours at -196°C and that 0.16 more decay over a similar interval each time the temperature is stepped upward by 10° .

TABLE V

FIRST-ORDER RATE CONSTANTS AND SIGNAL AMPLITUDES
AT INFINITE TIME FOR THE THERMAL DECAY OF TRAPPED
ELECTRONS IN MARLEX 6050 POLYETHYLENE AT VARIOUS
TEMPERATURES

Temperature (°C)	(°K)	First-Order Rate Constant, k (min ⁻¹)	A _∞ (mm)
-196	77	0.021	102
-186	87	0.025	74
-176	97	0.037	82
-166	107	0.036	60
-156	117	0.030	49
-146	127	0.033	20

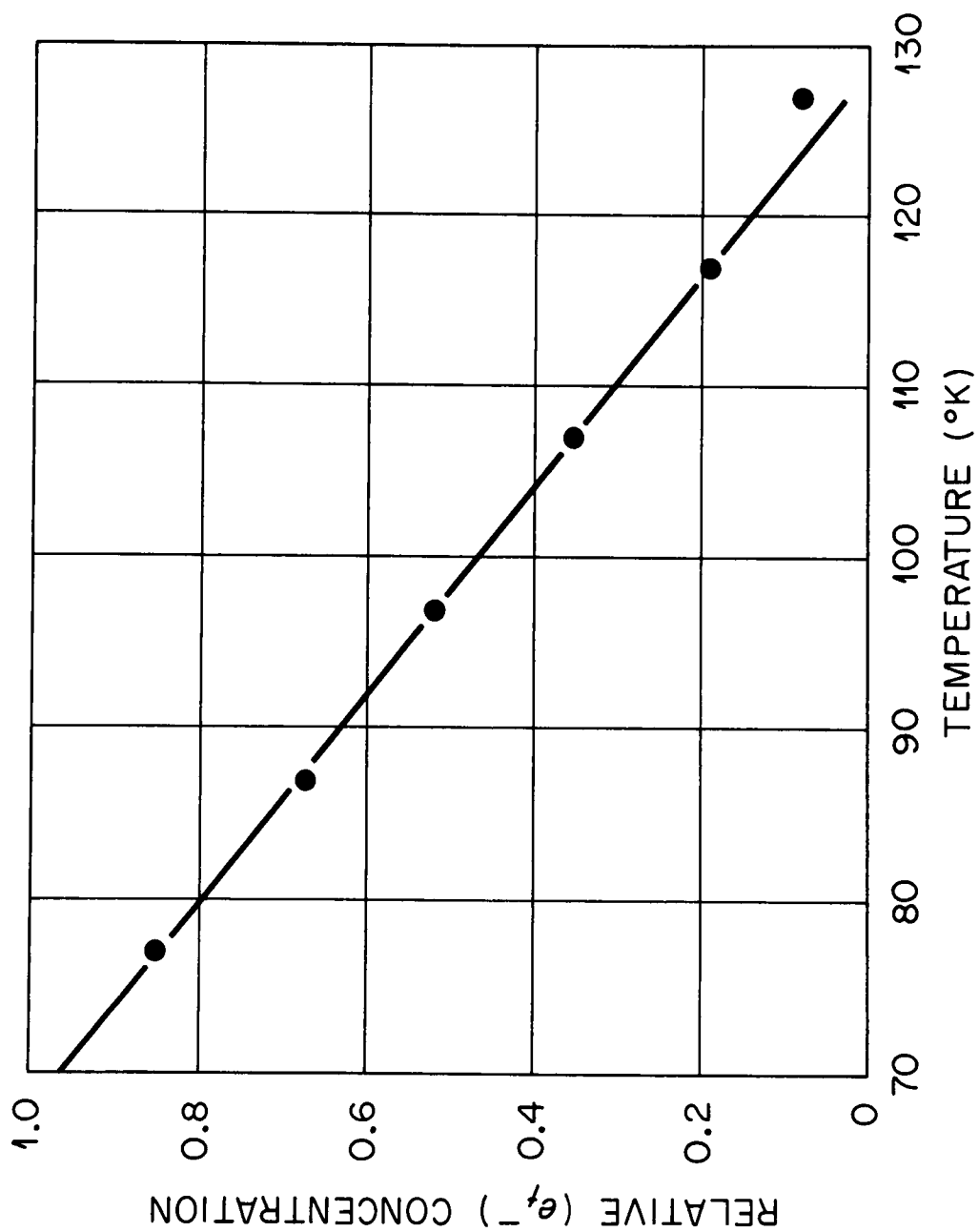


Figure 11. Fraction of trapped electrons thermally stable at various temperatures.

While this type of analysis is attractive, additional thermal decay experiments indicate that it is oversimplified. The results of three such experiments are summarized in Figure 12. The three curves in this figure represent separate experiments involving three samples for which the thermal decay of the trapped electron was followed isothermally at the indicated temperatures. All three samples received an identical irradiation dose of 1.1×10^{19} ev g^{-1} . The signal amplitudes for each experiment were normalized to the initial amplitudes observed about three minutes after removal of the sample from the radiation source. Zero on the time scale refers to these initial measurements.

The $-196^{\circ}C$ curve in Figure 12 may be compared to the corresponding curve in Figure 9 (p 82), the only difference between the two being that in the former case, the decay was followed over a longer time period. It is evident that over a long period of observation, the signal amplitude does not decay to an asymptotic value. There is a slow decay even out to 350 minutes. During the first 100 minutes however, the decay is first-order as determined from a Guggenheim plot. The rate constant is 0.019 min^{-1} , virtually the same as that given in Table V (p 87) at $-196^{\circ}C$. For the experiments at $-175^{\circ}C$ and $-155^{\circ}C$, there is also a slow decay evident at long times but the decay during the first 100 minutes of observation corresponds to no simple kinetic order.

It is of interest to note that after about 100 minutes of decay in Figure 12, 84% of the trapped electrons remain at $-196^{\circ}C$, 50% remain at $-175^{\circ}C$, and lastly, 20% remain at $-155^{\circ}C$. These percentages are very close to those expected on the basis of a 16% decay for each 10° temperature interval as previously discussed and suggests that a model

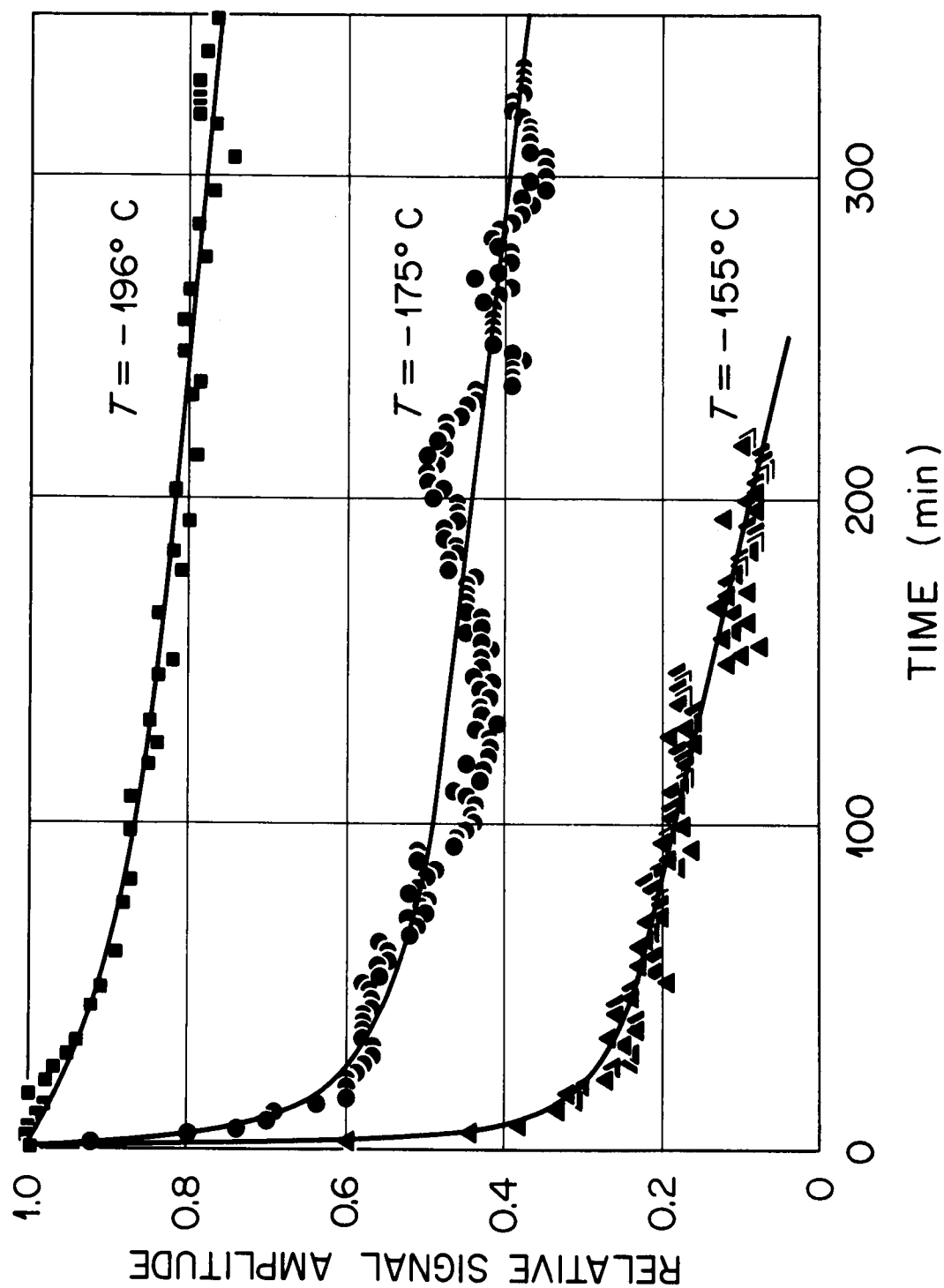


Figure 12. Isothermal decay of trapped electrons in gamma irradiated Marlex 6050 polyethylene at various temperatures.

involving populations of electrons with varying stabilities toward thermal decay has some merit. In fact, as will be discussed in Chapter V, it is possible to account for both the warm-up type experiment of Figure 9 (p 82) and isothermal decays of Figure 12 in terms of such a model.

6. Microwave Power Saturation Behavior of the Trapped Electron in Marlex 6050 Polyethylene

The microwave power saturation behavior of the trapped electron in Marlex 6050 polyethylene is shown in Figure 13 where the relative ESR signal amplitude of the trapped electron singlet is plotted versus the square root of microwave power in mW. Signal amplitudes were obtained by the same procedure as previously discussed in connection with concentration measurements. They were also normalized to the maximum amplitude observed which corresponded to a microwave power level of 4 μ W. All spectra in this experiment were recorded at a modulation frequency of 200 Hz. The polyethylene sample received an irradiation dose of 1.1×10^{19} ev g^{-1} .

In performing saturation experiments of this type, it is important that the concentration of the trapped electron remain constant over the period of measurement. Therefore the sample was stored in the dark at 77°K for three hours after irradiation prior to initiating the measurements in order to allow the major portion of those electrons which were thermally unstable at 77°K to decay out. The amplitude of the trapped electron signal after completing the series of measurements was within 10% of that observed at the start.

The line shape of the trapped electron singlet is closely Gaussian at a power level of 2 μ W and as nearly as could be determined, the line

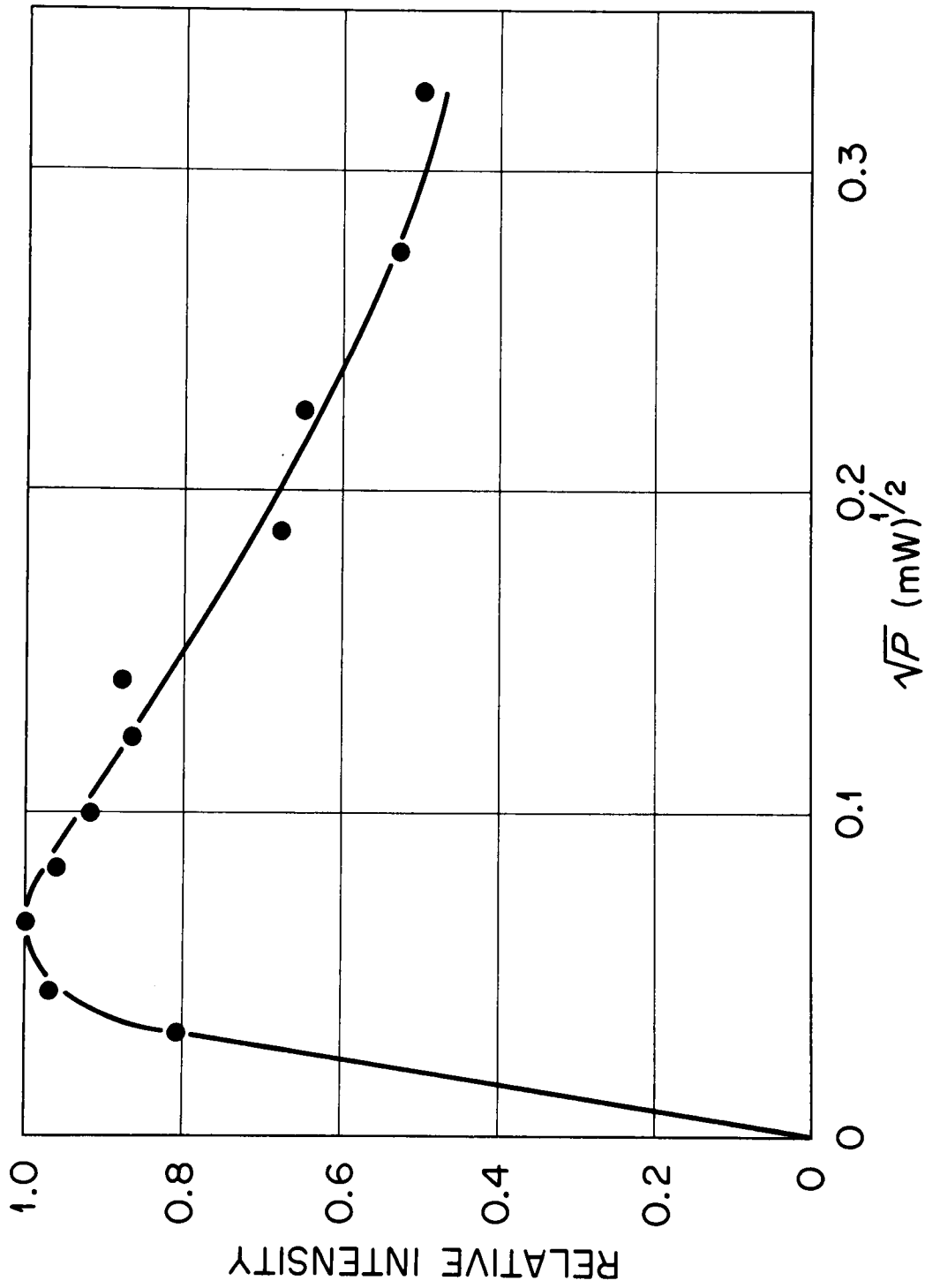


Figure 13, Microwave power saturation behavior of the trapped electron in Marlex 6050 polyethylene at a modulation frequency of 200 Hz.

shape and width (3.4 ± 0.2 gauss) remained constant over the range of microwave power employed in this experiment. These facts indicate that the saturation behavior is of the inhomogeneous type where the width of the homogeneously broadened lines, i.e., spin packets, constituting the line envelope is of comparable magnitude to the observed linewidth. This case has been treated by Castner⁸⁵ as discussed in Chapter II.

On the basis of Castner's treatment, the spin-spin relaxation time T_2 may be obtained from the equation

$$T_2 = \sqrt{2}/a\gamma\Delta H_{ms} \quad (4-6)$$

where ΔH_{ms} is the linewidth between maximum and minimum points in the first-derivative spectrum of the trapped electron, γ is the gyromagnetic ratio of the electron, and a is the ratio of the spin packet width to ΔH_{ms} . Castner has also shown that the product $T_1 T_2$ may be found from

$$T_1 T_2 = 1/\gamma^2 H_{1/2}^2 \quad (4-7)$$

where $H_{1/2}$ is the value of H_1 at which the signal amplitude is one-half of what it would be in the absence of saturation. Castner has given curve-fitting procedures whereby a and $H_{1/2}$ can be determined from saturation curves of the type shown in Figure 13. These have been adequately summarized^{65,85} in the literature and will not be discussed further here since in practice they are rather cumbersome to employ. In applying these procedures, microwave power was converted to H_1 with sufficient accuracy for present purposes by means of the relation⁶³

$$H_1 = 3.7 \times 10^{-2} \sqrt{P} \quad (4-8)$$

The values of T_1 and T_2 which result from application of Castner's treatment to the data of Figure 13 are 2×10^{-2} sec and 5×10^{-8} sec

respectively. These values however represent only a lower limit to T_1 and T_2 . This arises because the modulation frequency of 200 Hz used in the experiment is too high to strictly satisfy certain theoretical restrictions on which Castner's treatment is based. Efforts to work at lower modulation frequencies were unsuccessful as a result of the reduced sensitivity of the spectrometer. Nevertheless, it is felt that these values may be reliably used in a qualitative sense to compare these relaxation times with those derived⁶⁵ for the trapped electron in alkane glasses under similar experimental conditions. This comparison will be discussed in Chapter V.

7. Oriented Samples of Marlex 6050 Polyethylene

Several experiments involving polyethylene samples in which the polymer chains were oriented in known directions were undertaken. It was thought that if electrons could be trapped in these oriented specimens, the ordered nature of the matrix might enable hyperfine interaction of the trapped electron with its surroundings to be observed. Such information would be very important in elucidating the nature of the trap. Unfortunately, although trapped electrons were observed in the oriented materials, no evidence of hyperfine splitting was obtained.

Spectrum A in Figure 14 is the ESR spectrum observed at 77°K after γ -irradiation of a stretched sample of Marlex 6050 polyethylene to a dose of 1.1×10^{19} ev g⁻¹ at 77°K. Stretching the sample orients the polymer chains along the axis of stretch as discussed in Chapter III. The spectra in Figure 14 were obtained with the axis of stretch perpendicular to the applied magnetic field. Spectrum A was recorded with a modulation amplitude of 1.5 gauss corresponding to a spectrometer dial

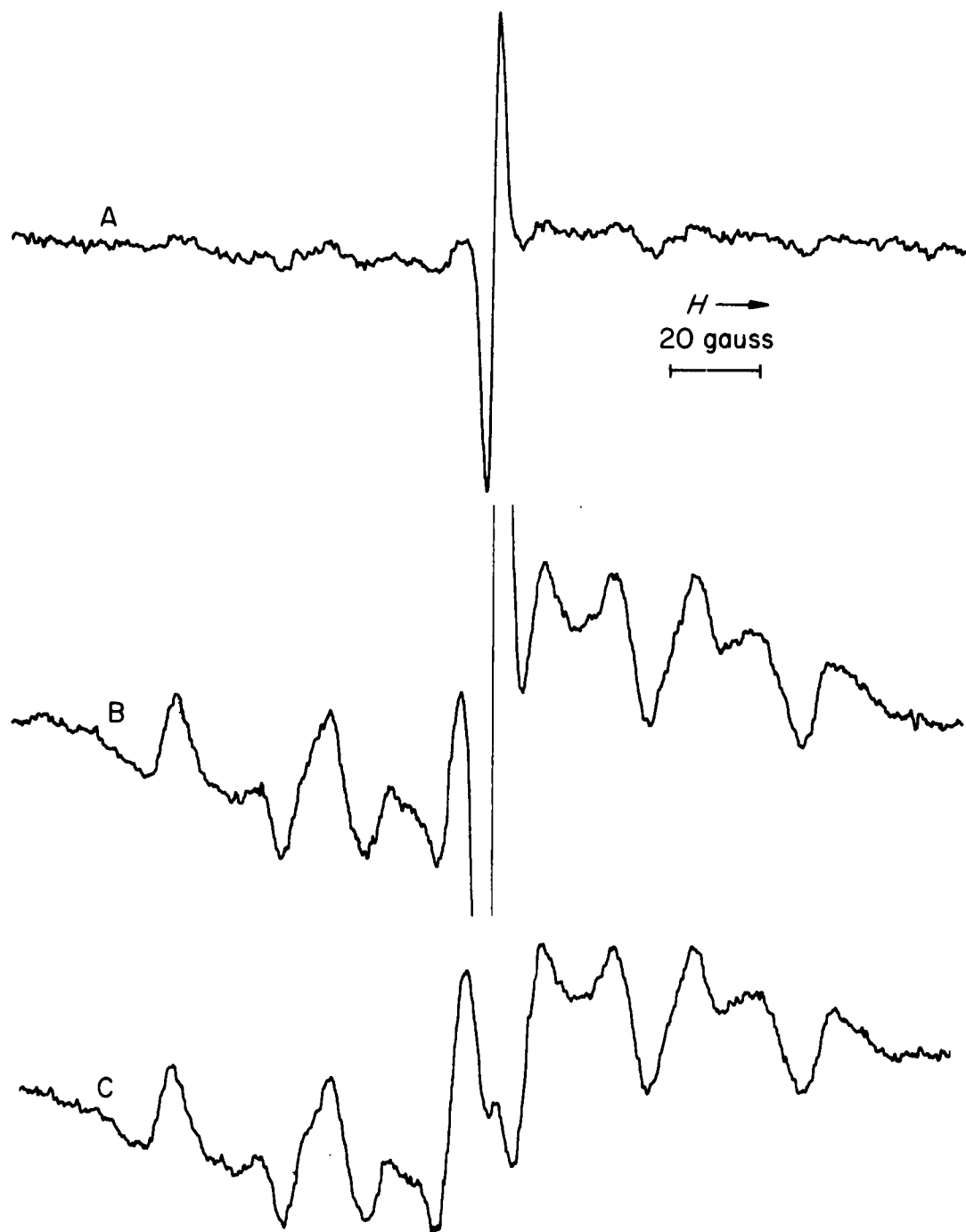


Figure 14. First-derivative ESR spectra at 77°K from a sample of stretched Marlex 6050 polyethylene after γ -irradiation also at 77°K. The axis of stretch is perpendicular to the applied magnetic field.

The sample received an irradiation dose of 1.1×10^{19} ev g^{-1} . Spectra A and B were recorded in the dark and spectrum C was re-recorded after photobleaching with infrared light ($\lambda > 1000$ nm). All three spectra were obtained at 2 μW microwave power and at a spectrometer amplifier gain setting of 1250. The modulation amplitude corresponds to a dial setting of 250 for spectrum A and 1600 for spectra B and C.

setting of 250. Spectrum B corresponds to that of A but with the exception that the modulation amplitude was increased to a dial setting of 1600 in order to increase the sensitivity of the spectrometer. Spectrum C results after photobleaching the sample in light of $\lambda > 1000$ nm and was recorded under conditions identical to those for spectrum B. The narrow singlet in the center of spectrum A is removed by photobleaching. Its linewidth is $\Delta H_{ms} = 3.4 \pm 0.2$ gauss, the same as that for trapped electrons in unstretched Marlex 6050 polyethylene discussed in Section B-1 of this chapter. The singlet is therefore assigned to a trapped electron. Comparison of the trapped electron signal amplitude in spectrum A with that for an unstretched sample which had received an identical irradiation dose revealed that the trapped electron yield is the same in both instances. Thus, no differences in the characteristics of the trapped electron ESR spectrum are observed as a result of orienting the polymer chains by stretching the specimen.

On the other hand, stretching the sample does change the spectrum of the alkyl free radical, $-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$. Spectrum C consists of ten lines with a hyperfine splitting constant of approximately 16 gauss whereas the spectrum of the alkyl free radical in unstretched polyethylene, spectrum B in Figure 5 (p 69), consists of six lines with about 30 gauss splitting. These differences have been observed previously by other workers and have been shown to arise as a result of the anisotropy of the hyperfine splitting from the α -proton in the alkyl free radical.⁷² No evidence for trapped electrons was reported in these latter studies, however.

An alternative method of orienting the polymer chains involves growing single crystals of polyethylene and orienting them by compaction

into the form of a mat. The manner in which this is accomplished has been discussed in Chapter III. The mats are composed of layers of microscopic polyethylene single crystals. The crystals, in the form of tiny lamellae, are composed of folded polyethylene chains such that the chain axis is perpendicular to the plane of the lamellae. Since the lamellar plane is parallel to the plane of the mat, the polymer chains are oriented perpendicular to the plane of the mat.

Figure 15 shows ESR spectra obtained at 77°K from a mat of single crystals after γ -irradiation also at this temperature. The irradiation dose was 5×10^{19} ev g⁻¹. These spectra were obtained with the plane of the mat oriented parallel to the direction of the applied magnetic field; hence, the polymer chains are oriented perpendicular to the field. Figure 16 displays spectra obtained from the same sample but with the plane of the mat oriented perpendicular to the applied field. In this instance, the polymer chains are oriented parallel to the field.

The spectra labelled A in both figures reveal a narrow singlet in the center. This singlet was removed by photobleaching with near infrared light of $\lambda > 1000$ nm as shown by the spectra labelled B. The singlet is assigned to a trapped electron on this basis. The linewidth of the trapped electron singlet in both Figures 15 and 16 is $\Delta H_{ms} = 3.4 \pm 0.2$ gauss, the same as for bulk-crystallized polyethylene in which the polymer chains are randomly oriented. No indication of hyperfine splitting in the trapped electron singlet is evident. The differences in the underlying spectra of the alkyl free radical on change in orientation of the mats with respect to the field direction have also been observed by others and have been attributed to the anisotropy of the hyperfine

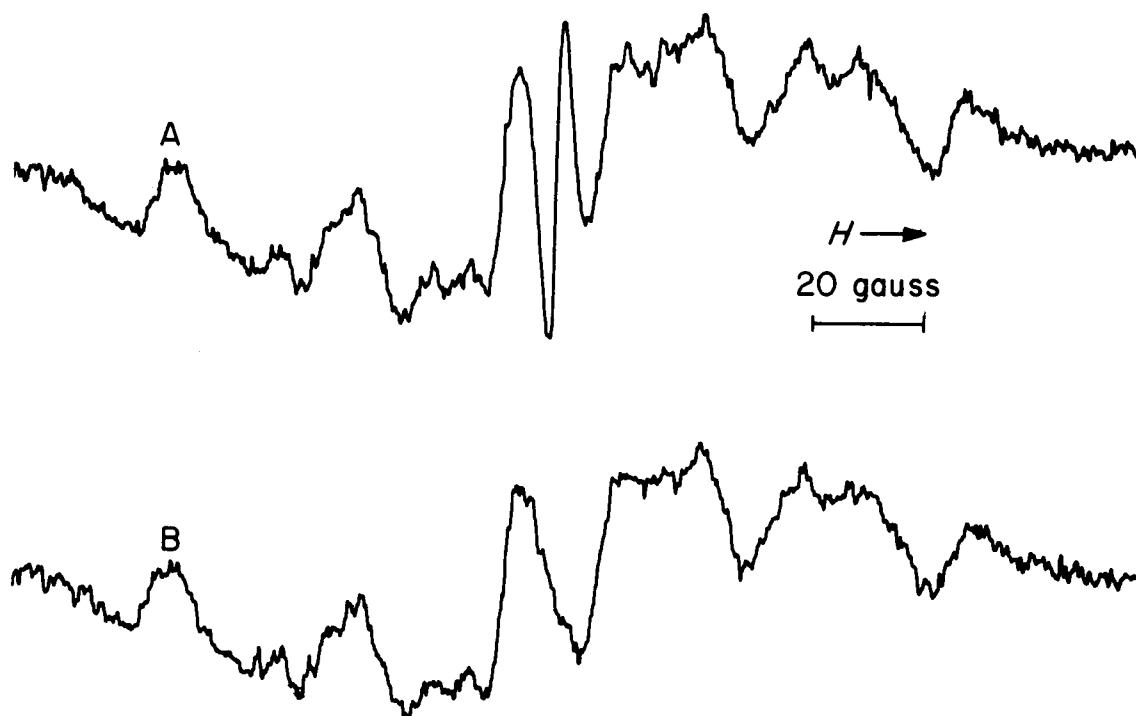


Figure 15. First-derivative ESR spectra at 77°K from a mat of single crystals of Marlex 6050 polyethylene after γ -irradiation also at 77°K. The plane of the mat is parallel to the applied magnetic field.

The sample received an irradiation dose of 5×10^{19} ev g^{-1} . Spectrum A was recorded in the dark after irradiation and spectrum B was recorded after photobleaching with infrared light ($\lambda > 1000$ nm). Both spectra were obtained at 2 μW of microwave power. The amplifier gain setting was 2000 and the modulation amplitude dial setting 630 in both instances.

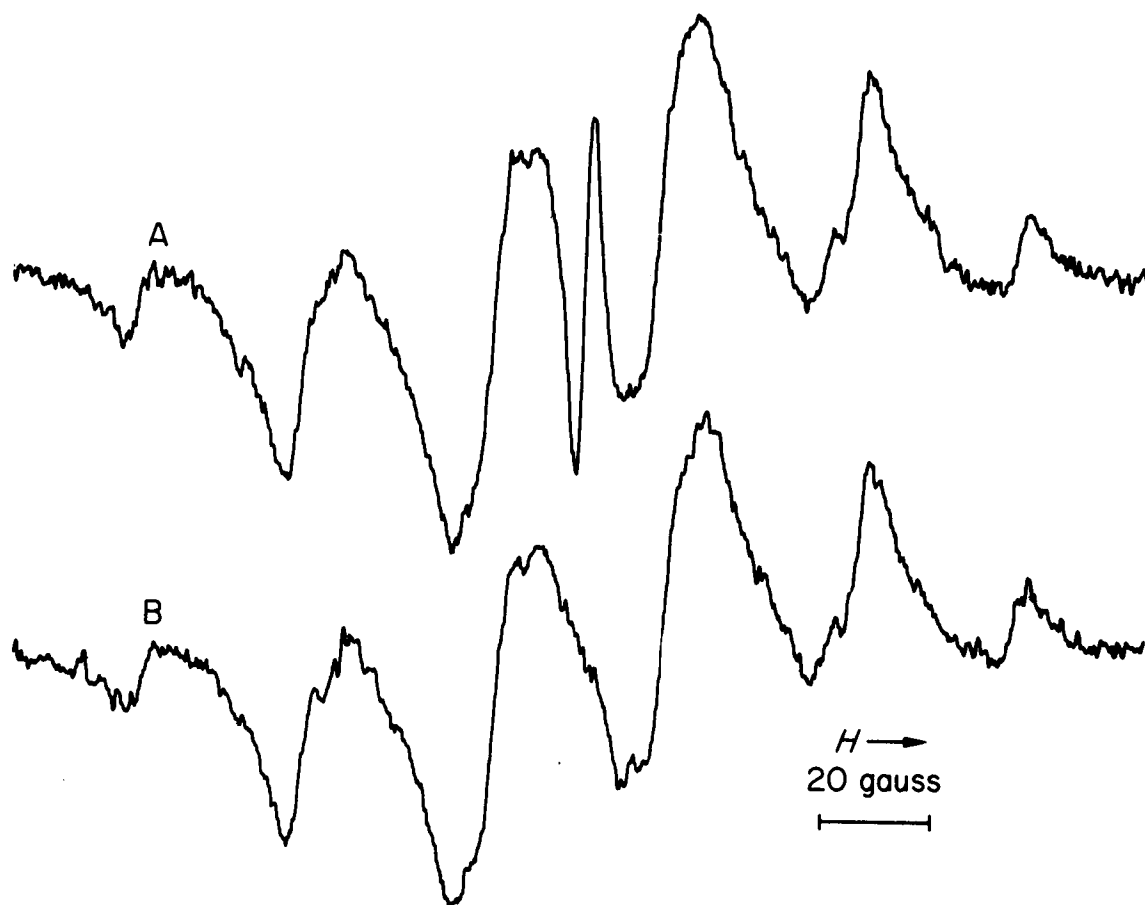


Figure 16. First-derivative ESR spectra at 77°K from a mat of single crystals of Marlex 6050 polyethylene after γ -irradiation also at 77°K. The plane of the mat is perpendicular to the applied magnetic field.

The sample, irradiation dose, and spectrometer variables are the same as in Figure 15.

splitting constant of the α -proton.⁷³ In this connection, spectrum B of Figure 15 is similar to spectrum B of Figure 14 (p 95) although the resolution is poorer in the former case. The similarity is, of course, expected since in both cases, the polymer chains are oriented perpendicular to the applied field.

The concentration of trapped electrons in the single crystal mats appears to be significantly lower than in either bulk-crystallized polyethylene or in samples of stretched polyethylene. This conclusion follows from a comparison of the amplitude of the trapped electron singlet with that of the underlying free radical signal in all three cases. This may indicate that the single crystal mats contain fewer trapping sites. Alternatively, the decreased concentration may simply reflect a dependence of trapped electron concentration on dose similar to that observed in Figure 7 (p 78) for bulk-crystallized polyethylene. Experiments involving single crystal mats irradiated to doses below 5×10^{19} ev g⁻¹ were not carried out, however.

8. Hydrogenated Polyethylene

As noted in Chapter III, linear polyethylenes typically contain small amounts of terminal vinyl unsaturation. Trapped electrons have been observed in several branched chain terminal olefins such as 2-methylpentene-1 following γ -irradiation at 77°K and it is also known that adding several mole percent 2-methylpentene-1 to 3-methylpentane enhances the yield of trapped electrons in the latter material.¹⁰⁰ Therefore the possibility exists that the small amount of vinyl unsaturation present in Marlex 6050 polyethylene may influence the trapping of electrons in this material. To investigate this possibility, a sample

of polyethylene which had been hydrogenated in order to remove double bonds was examined. Terminal vinyl unsaturation in polyethylene, $-\text{CH}_2-\text{CH}=\text{CH}_2$, is characterized by infrared bands at 990 and 910 cm^{-1} . Examination of films made from hydrogenated material by means of infrared spectroscopy revealed the absence of any absorption at these two wavelengths, attesting to the efficiency of the hydrogenation process.

ESR spectra at 77°K from the hydrogenated polyethylene are shown in Figure 17. The sample received a dose of γ -irradiation of 1.1×10^{19} ev g^{-1} at 77°K. Spectrum A was recorded in the dark immediately after irradiation. There is a broad line in the center of the spectrum which obscures the central portion of the underlying alkyl free radical spectrum. This line was still present after exposing the sample to light of $\lambda > 1000$ nm as shown in spectrum B. The broad line was, however, removed by exposing the sample to unfiltered light from a tungsten lamp. The effect is shown in spectrum C.

The broad line in spectrum A is clearly distinguishable from the typical trapped electron singlet in polyethylene on the basis of both linewidth and photobleaching behavior. A broad line in the center of the spectrum could well be due to unresolved hyperfine structure from some paramagnetic species resulting from electron capture by an impurity in the material. The fact that the material was yellow in color, whereas polyethylene is normally white, supports the possibility that these effects result from impurities. In an effort to improve the purity of the hydrogenated polyethylene, the material was recrystallized several times from various solvents as discussed in Chapter III. The yellow color was substantially diminished by these treatments but not completely eliminated.

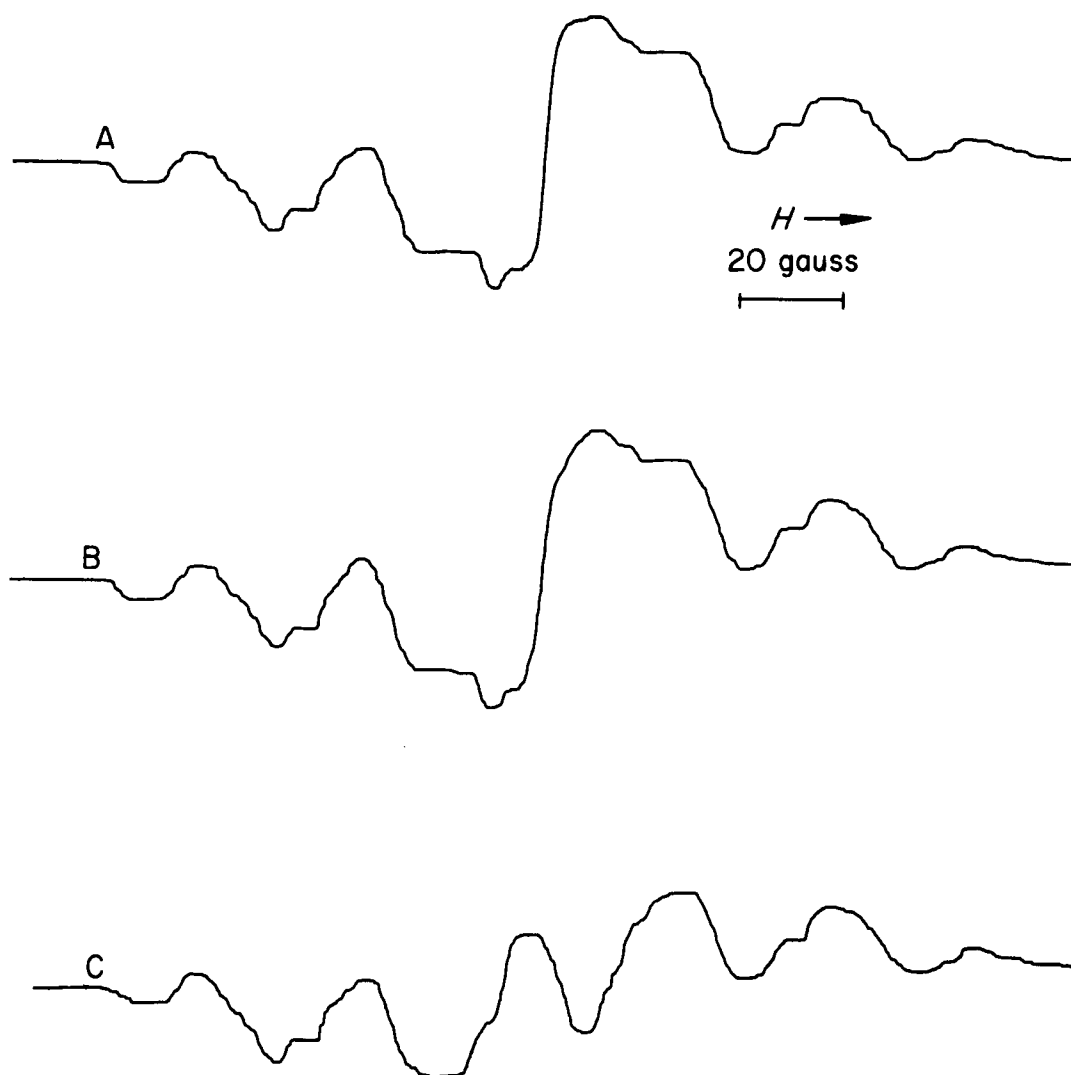


Figure 17. First-derivative ESR spectra at 77°K from a sample of hydrogenated polyethylene after gamma irradiation also at 77°K.

The irradiation dose was 1.1×10^{19} ev g^{-1} . Spectrum A was recorded in the dark, spectrum B after photobleaching with infrared light ($\lambda > 1000$ nm), and spectrum C after exposure of the sample to unfiltered light from a tungsten lamp. All three spectra were obtained at 2 μW of microwave power, an amplifier gain setting of 630, and a modulation amplitude of 1.5 gauss.

ESR spectra at 77°K from a sample of hydrogenated polyethylene which had been recrystallized five times from octane are shown in Figure 18. Samples which had received alternate treatments as described in Chapter III gave entirely similar spectra after γ -irradiation. The irradiation dose for the sample in Figure 18 was 1.1×10^{19} ev g⁻¹. Spectrum A reveals the presence of a narrow singlet of width $\Delta H_{ms} = 3.4 \pm 0.2$ gauss. The singlet is removed by photobleaching with near infrared light of $\lambda > 1000$ nm as shown by spectrum B. Since the linewidth and photobleaching behavior are analogous to that observed for trapped electrons in Marlex 6050 polyethylene, the singlet in Figure 18 is also attributed to trapped electrons.

The amplitude of the trapped electron singlet in the hydrogenated material is 25% of that from a sample of bulk-crystallized Marlex 6050 polyethylene which had received an identical irradiation dose and whose ESR spectrum was obtained under conditions identical to those pertaining to the spectra in Figure 18. Thus the trapped electron yield appears to be somewhat lower in the hydrogenated sample than in Marlex 6050 polyethylene. In view of the questionable degree of purity of the hydrogenated material, the reduced yield of trapped electrons cannot unambiguously be ascribed to the absence of olefinic groups. Even after the extensive recrystallization treatment given the sample, a slight yellow color remained indicating that not all impurities had been removed. It may well be that the remaining impurities scavenge electrons which might otherwise be trapped. The experiments involving hydrogenated polyethylene which had received no purification treatment lend support to this possibility. Alternatively, the lower trapped electron yield

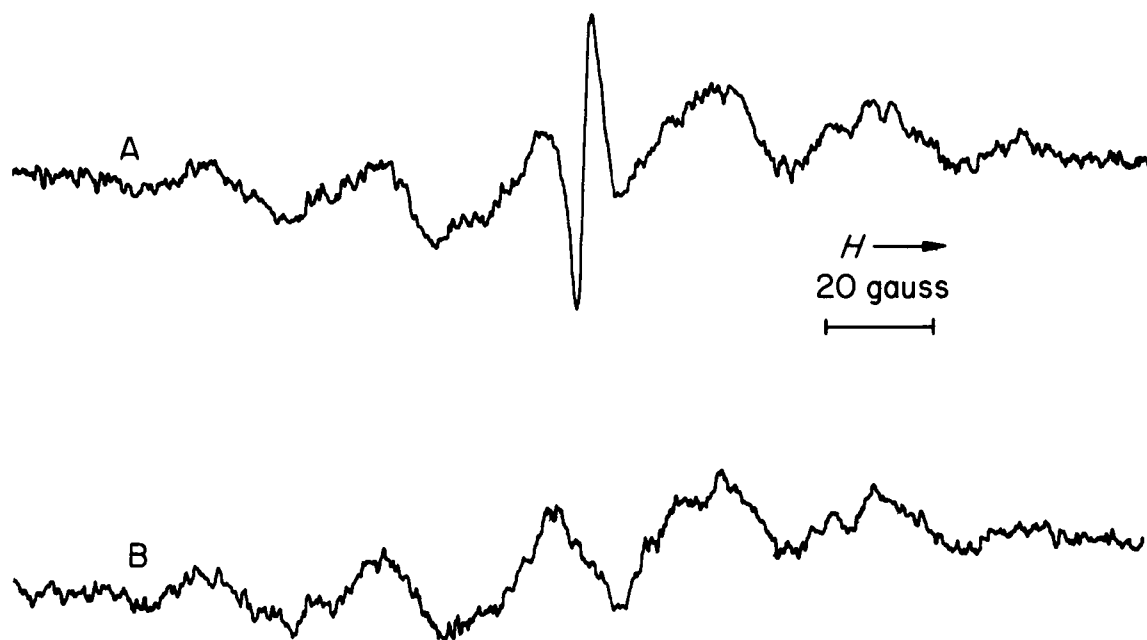


Figure 18. First-derivative ESR spectra at 77°K from a sample of hydrogenated polyethylene recrystallized five times from octane.

The irradiation dose was 1.1×10^{19} ev g^{-1} at 77°K. Spectrum A was recorded in the dark and spectrum B was obtained after photobleaching the sample with infrared light ($\lambda > 1000$ nm). The microwave power was 2 μW , the amplifier gain was 1600, and the modulation amplitude was 1.5 gauss.

may result in some manner from the recrystallization treatment itself. The trapped electron yield in a Marlex 6050 sample which had received the same recrystallization treatment as the hydrogenated material was 50% lower than in a second Marlex 6050 sample which had not received any such treatment. Both samples received an identical irradiation dose of 1.1×10^{19} ev g⁻¹ in making this comparison.

It must be admitted that these experiments are not particularly definitive regarding the possibility that olefinic groups may play a role in the electron trapping process. However, since the trapped electron yield in hydrogenated polyethylene is not dramatically lower by factors of ten or more than in Marlex 6050, it seems unlikely that olefinic groups exert any significant influence on electron trapping in polyethylene. The lower yields in hydrogenated polyethylene can be interpreted as arising simply from impurity effects or from some effect of the recrystallization treatment.

C. Branched Polyethylene

1. Identification of the Trapped Electron in Alathon 1414

The molecular structure of the polyethylene chain depends markedly on the method of polymerization.¹⁰¹ Methods such as coordination polymerization of ethylene or polymerization over supported metal oxide catalysts yield an essentially linear polymer chain with very few chain branches. Marlex 6050 polyethylene is typical in this respect. On the other hand, radical polymerization of ethylene at pressures of 1000-3000 atm yields a polyethylene in which the polymer chain is significantly branched. Polyethylenes of the latter type are therefore known as

"branched" polyethylenes. A molecule of branched polyethylene typically contains about 50 short chain branches, mostly ethyl and butyl, and one long branch which may be as long as the main polymer chain itself. The existence of these branches prevents branched polyethylene from achieving the high degree of crystallinity characteristic of linear polyethylene. Whereas linear polyethylenes are 80-90% crystalline, branched polyethylenes are only 50-60% crystalline.

In view of the identification of trapped electrons in the linear Marlex 6050 material, it is of interest to examine branched polyethylene in this regard. A typical branched polyethylene, Alathon 1414, was selected for this purpose. The ESR spectrum of Alathon 1414 obtained in the dark after gamma irradiation at 77°K is shown as spectrum A in Figure 19. This spectrum exhibits many features in common with that for irradiated linear polyethylene (Figure 5, p 69). First, spectrum A consists of a narrow singlet superimposed on a broad background spectrum. The linewidth of the singlet is $\Delta H_{ms} = 3.4 \pm 0.2$ gauss and $g = 2.0023 \pm 0.0002$, both values being the same as for linear polyethylene. Second, the singlet saturates at microwave power levels in the neighborhood of 10 μ W. Finally, the singlet is eliminated by photobleaching the sample with near infrared light as shown by spectrum B. These three observations are characteristic of trapped electrons as pointed out in connection with the results for linear polyethylene. Therefore, the singlet in spectrum A of Figure 19 is assigned to trapped electrons. The six line background spectrum is that of the alkyl free radical.

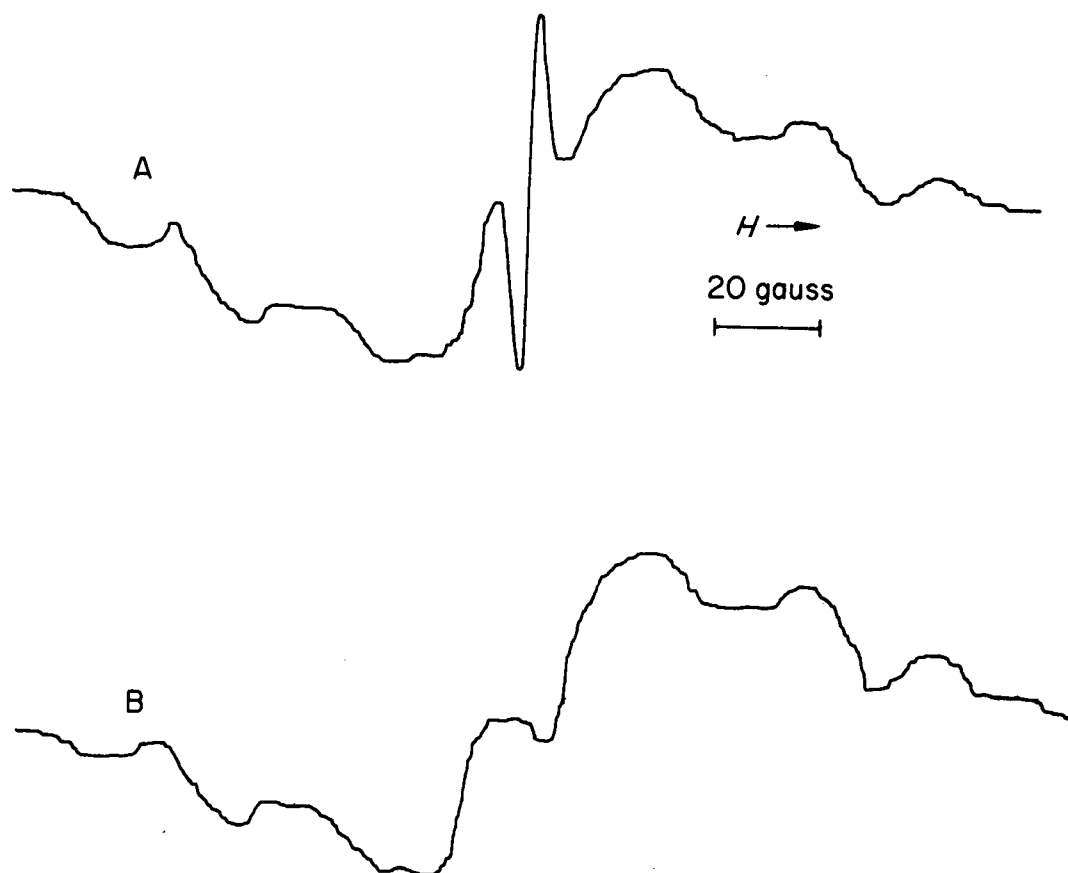


Figure 19. First-derivative ESR spectra of γ -irradiated Alathon 1414 polyethylene at 77°K.

Spectrum A was recorded before and spectrum B after photobleaching with near infrared light ($\lambda > 1 \mu$). The irradiation dose was 1.1×10^{19} ev g⁻¹, also at 77°K. The microwave power level was 2 μ W, the amplifier gain setting was 1200, and the modulation amplitude was 1.5 gauss.

2. Trapped Electron Yields in Alathon 1414

The free radical spectra in Figure 19 and Figure 5 (p 69) correspond to equal numbers of free radicals since both samples received the same dose and $G(R\cdot)$ is approximately the same for branched and linear polyethylenes.¹⁰² The spectra in Figure 19 were recorded at higher amplifier gain than those of Figure 5, thereby accounting for the greater amplitude of the free radical signal. The amplitude of the trapped electron singlet in Alathon 1414, however, is nearly the same as that of the free radical whereas the trapped electron singlet in Marlex 6050 dominates the spectrum.

These observations seem to indicate a lower yield of trapped electrons in branched polyethylene than in linear polyethylene and indeed, this conclusion is born out by the data of Figure 20. In Figure 20, the number of trapped electrons per gram, $(e_t^-)/g$, in irradiated Alathon 1414 is plotted as a function of irradiation dose. Equation 4-2 (p 76) was used to relate signal amplitudes to $(e_t^-)/g$ as previously discussed. The slope of the line gives $G(e_t^-) = 0.12$ electrons/100 ev. This value is substantially lower than $G(e_t^-) = 0.46$ found for linear polyethylene. The yield of trapped electrons at doses larger than those of Figure 20 has not been investigated for Alathon 1414.

Since branched polyethylene differs from linear polyethylene mainly by being less crystalline, the G-value results for the two types suggest that the degree of crystallinity may play a role in determining the ability of a polymer to trap electrons. In this connection, it is worth noting that the amplitude of the trapped electron singlet in a sample of PE-106 polyethylene was intermediate between that of Alathon 1414 and

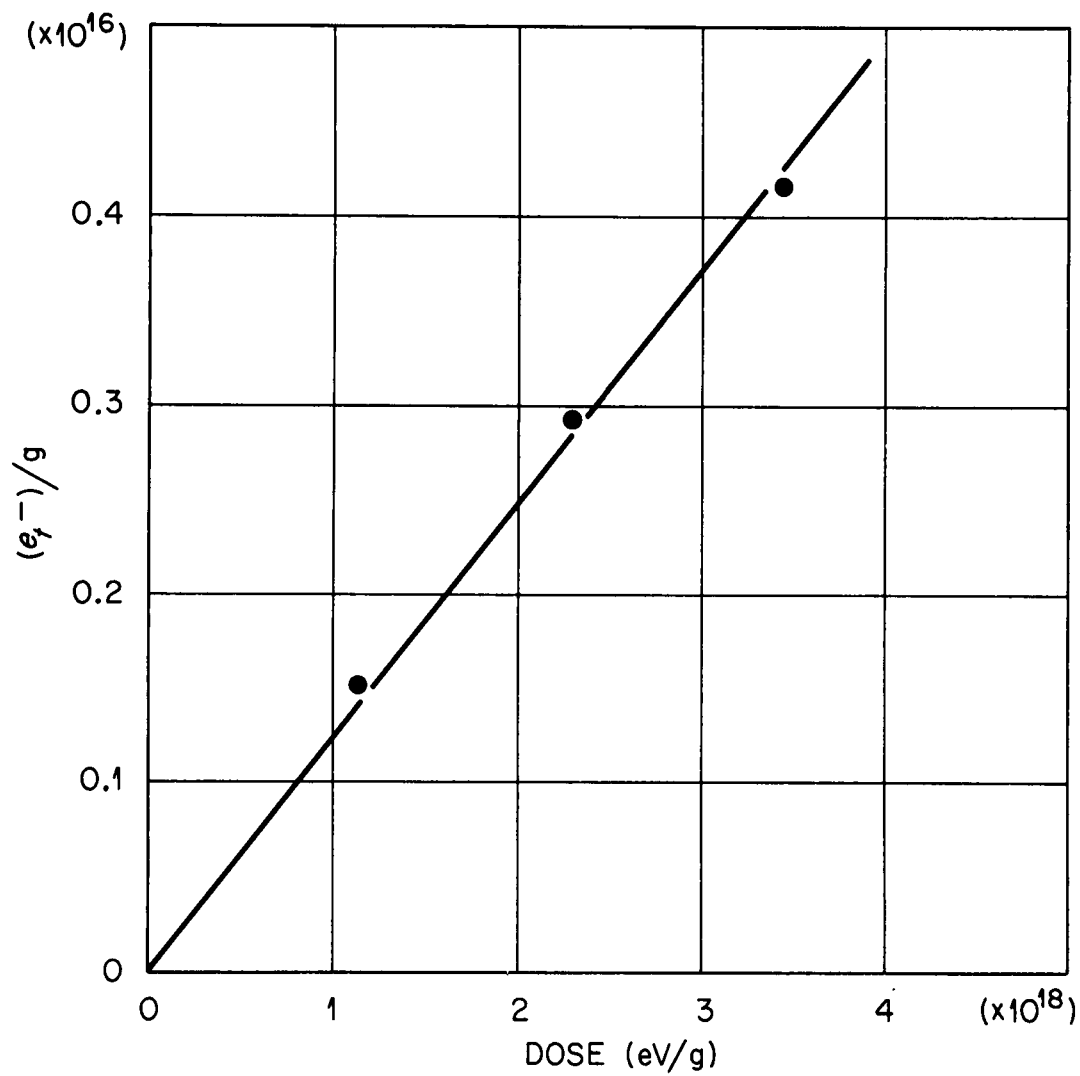


Figure 20. Concentration of trapped electrons in Alathon 1414 as a function of irradiation dose at 77°K.

Marlex 6050. PE-106 polyethylene is of intermediate crystallinity as reflected by the intermediate value of its density (Table II, p 42).

3. Thermal Decay of the Trapped Electron in Alathon 1414

The amplitude of the trapped electron singlet at 77°K in Alathon 1414 is plotted as a function of time after irradiation in Figure 21. The decay curve corresponds to no simple kinetic order but is similar to that for Marlex 6050 polyethylene in the sense that there is a relatively rapid decay in the first 30 minutes followed by a much slower decay at longer times. However, in Alathon 1414 the percentage rate of decay is greater than in Marlex 6050 as shown by the fact that more than 35% of the trapped electrons in Alathon 1414 decay out within one-half hour at 77°K whereas only 7% decays during the corresponding time interval in Marlex 6050 (Figure 12, p 90).

D. α -Substituted Olefin Polymers

1. ESR Studies of Trapped Electrons in γ -Irradiated Isotactic Polypropylene and Poly(4-methylpentene-1)

Figure 22 shows ESR spectra at 77°K from γ -irradiated Phillips isotactic polypropylene recorded before and after photobleaching. The sample received an irradiation dose of 1.1×10^{19} ev g⁻¹, also at 77°K. The prominent singlet in the center of spectrum A of Figure 22 is assigned to trapped electrons. The linewidth of the singlet is $\Delta H_{ms} = 2.9 \pm 0.2$ gauss and is thus somewhat narrower than the trapped electron singlet in polyethylene. The g-factor for the trapped electron in isotactic polypropylene was found to be $g = 2.0021 \pm 0.0002$ by means of the techniques previously discussed. A sample of Hercules isotactic polypropylene

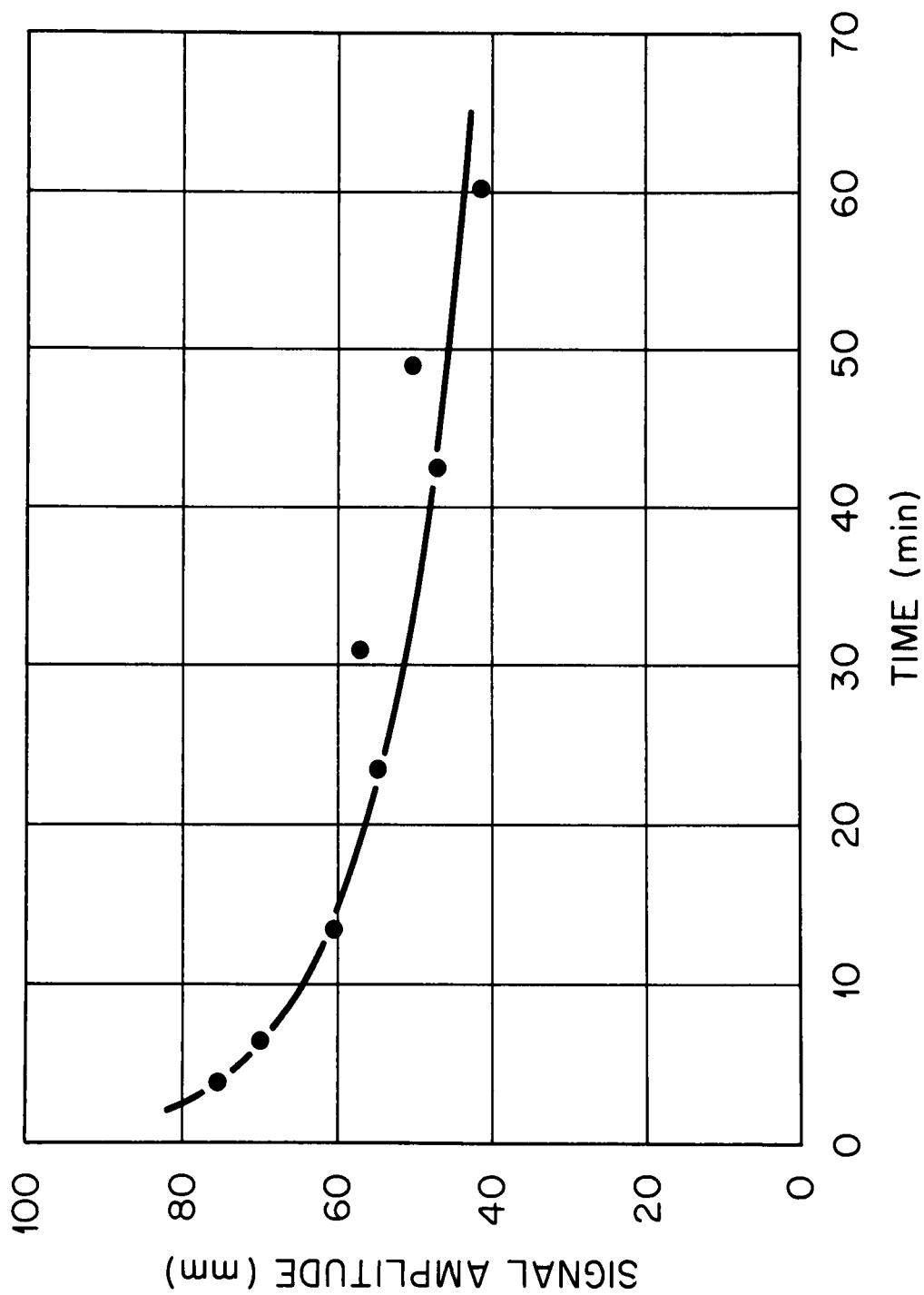


Figure 21. Thermal decay at 77°K of the trapped electron singlet in Alathon 1414 irradiated to a dose of $1.1 \times 10^{19} \text{ ev g}^{-1}$.

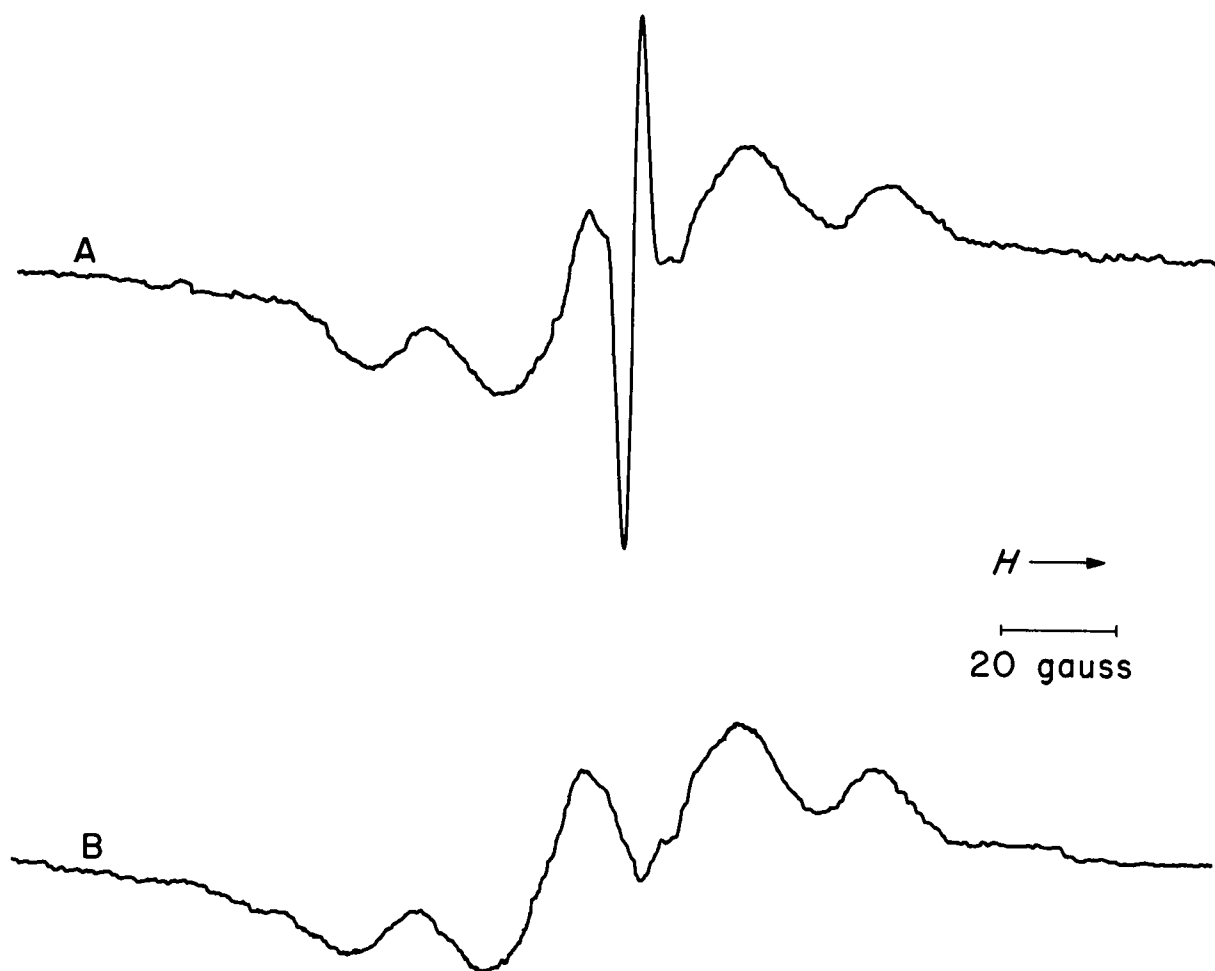
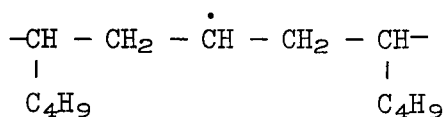


Figure 22. First-derivative ESR spectra at 77°K from γ -irradiated isotactic polypropylene.

The irradiation dose was 1.1×10^{19} ev g^{-1} at 77°K. Spectrum A was recorded in the dark and spectrum B was recorded after photobleaching the sample with infrared light ($\lambda > 1000$ nm). Both spectra were obtained at 2 μW of microwave power, at an amplifier gain setting of 400, and with a modulation amplitude of 1.5 gauss.

gave results identical to those in Figure 22. All subsequent work involved the Phillips material, however. The assignment of the underlying free radical spectrum is uncertain. Several different radical species have been proposed in the literature but so far, no general agreement on a specific assignment has been reached. The problem has been recently reviewed⁷¹ and it seems possible that the spectrum may result from more than one radical structure.

Figure 23 displays ESR spectra at 77°K from a sample of isotactic poly(4-methylpentene-1) following γ -irradiation also at 77°K. The irradiation dose in this instance was again 1.1×10^{19} ev g^{-1} . The trapped electron singlet in spectrum A of Figure 23 is characterized by $\Delta H_{ms} = 2.6 \pm 0.2$ gauss and by $g = 2.0021 \pm 0.0002$. The underlying free radical spectrum, most clearly revealed after photobleaching as in spectrum B of Figure 23, consists of six lines with approximately 23 gauss splitting. An entirely similar free radical spectrum has previously been reported from poly(4-methylpentene-1) γ -irradiated at 77°K and has been assigned to the radical



formed as a result of side-chain scission.¹⁰³

The concentration of trapped electrons in both isotactic polypropylene and isotactic poly(4-methylpentene-1) as a function of irradiation dose at 77°K is shown in Figure 24. The concentration measurements were performed in exactly the same manner as previously described for Marlex 6050 polyethylene. As is evident in Figure 24, the trapped electron concentration in both samples first increases as the dose increases,

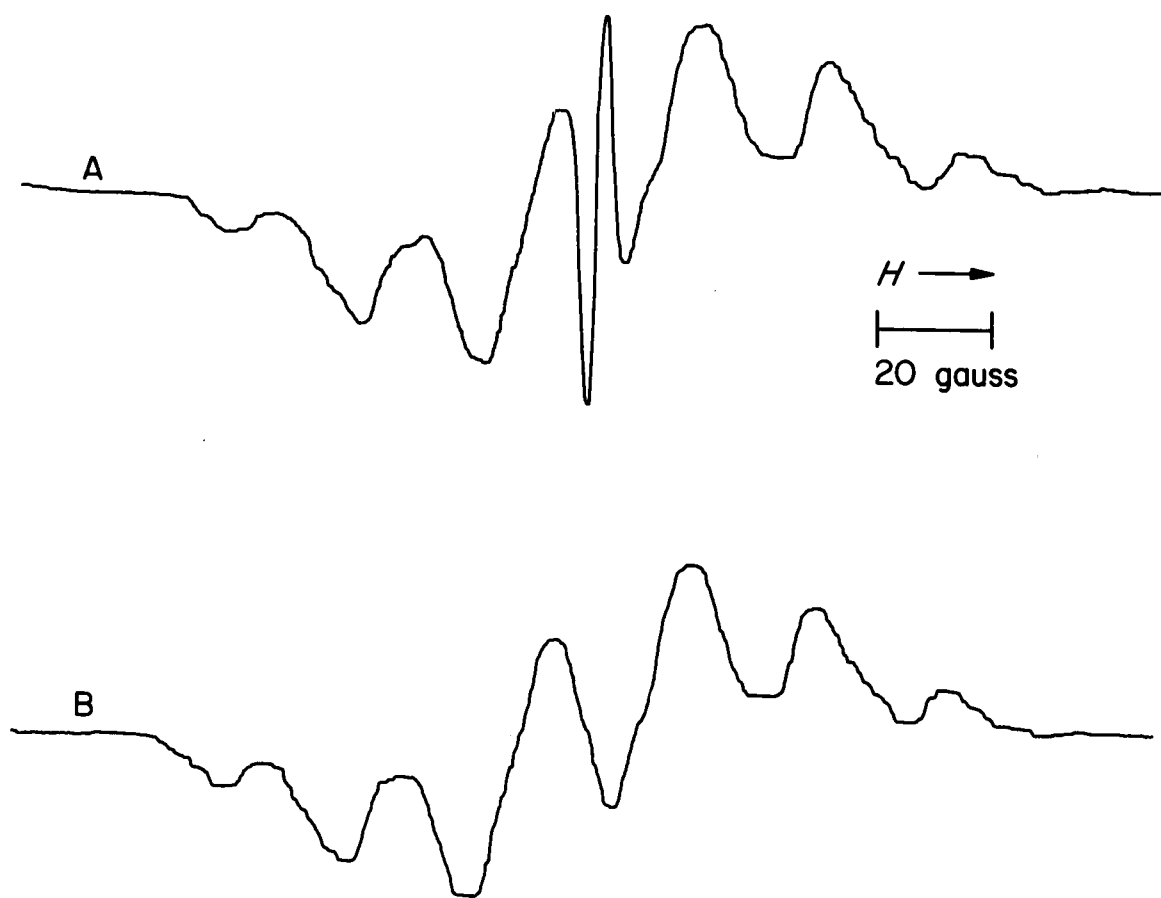


Figure 23. First-derivative ESR spectra at 77°K from γ -irradiated isotactic poly(4-methylpentene-1).

The irradiation dose was 1.1×10^{19} ev g^{-1} . Spectrum A was recorded in the dark and spectrum B was recorded after photobleaching the sample with infrared light ($\lambda > 1000$ nm). Both spectra were obtained at 2 μ W microwave power with an amplifier gain setting of 800, and a modulation amplitude of 1.5 gauss.

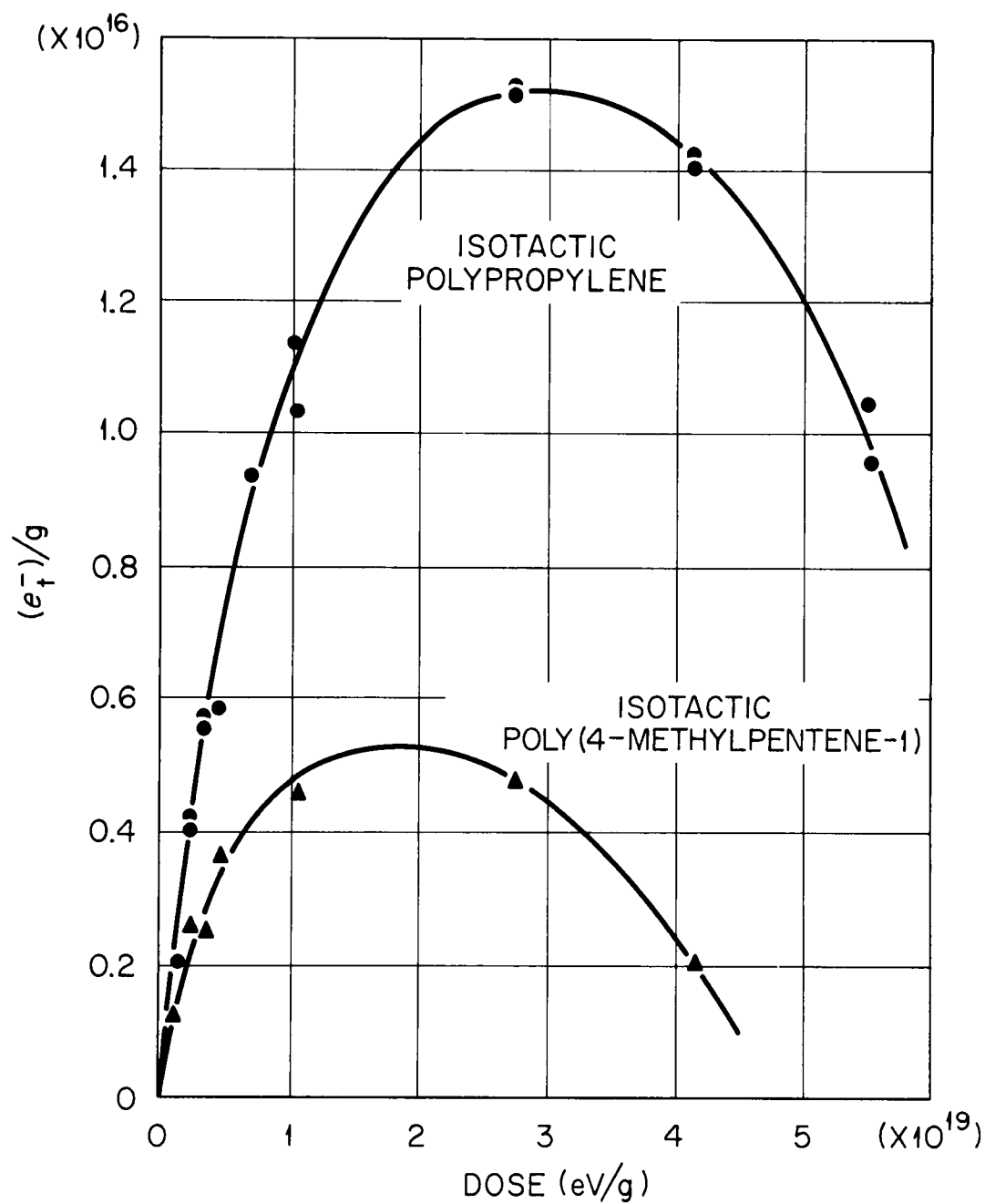


Figure 24. Trapped electron concentration as a function of dose in isotactic polypropylene and isotactic poly(4-methylpentene-1) γ -irradiated at 77°K.

then reaches a maximum, and thereafter decreases with further increase in dose. The effect is similar to that observed in Marlex 6050 polyethylene except that the maximum trapped electron concentration observed in both the polypropylene and poly(4-methylpentene-1) samples is substantially lower than the 4.2×10^{16} electrons/g value found for Marlex 6050. Figure 25 shows that at doses below 5×10^{18} ev g⁻¹, the trapped electron concentration in both polypropylene and poly(4-methylpentene-1) increases linearly with dose. From the slopes of the lines in Figure 25, initial G-values for trapped electrons were established to be 0.17 and 0.08 trapped electrons/100 ev, respectively.

The results of several experiments involving the thermal stability of the trapped electron in isotactic polypropylene and poly(4-methylpentene-1) are summarized in Figure 26. For isotactic poly(4-methylpentene-1) at 77°K, the relative signal amplitude of the trapped electron decreases with time following irradiation as shown by curve C in Figure 26. Curve A depicts the thermal decay in this same material at a temperature of ca. 70°K. This temperature was produced by means of the cryogenic cooling technique¹⁰⁴ whereby a stream of helium gas was passed through a finely drawn capillary tube into the liquid N₂ at the bottom of the ESR dewar. It is evident that the fractional rate of decay of the trapped electron is significantly slower at ca. 70°K. Curve B of Figure 26 depicts the thermal decay of the trapped electron in isotactic polypropylene at 77°K. For all three curves, the trapped electron signal amplitudes were normalized to the amplitude initially observed five minutes after removing the sample from the radiation source. The decay curves correspond to no simple kinetic order.

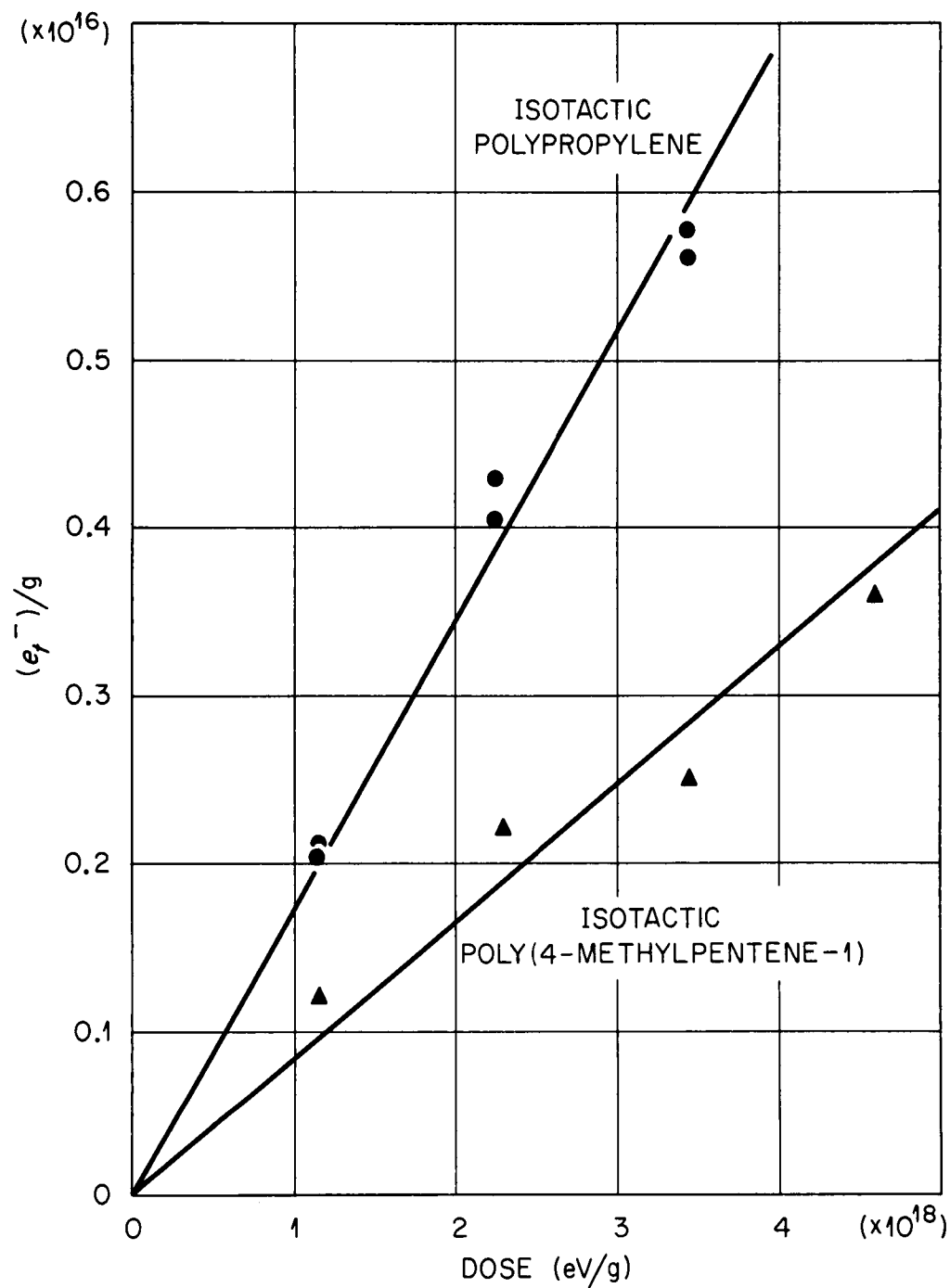


Figure 25. Trapped electron concentration at low doses in isotactic polypropylene and isotactic poly(4-methylpentene-1) after γ -irradiation at 77°K.

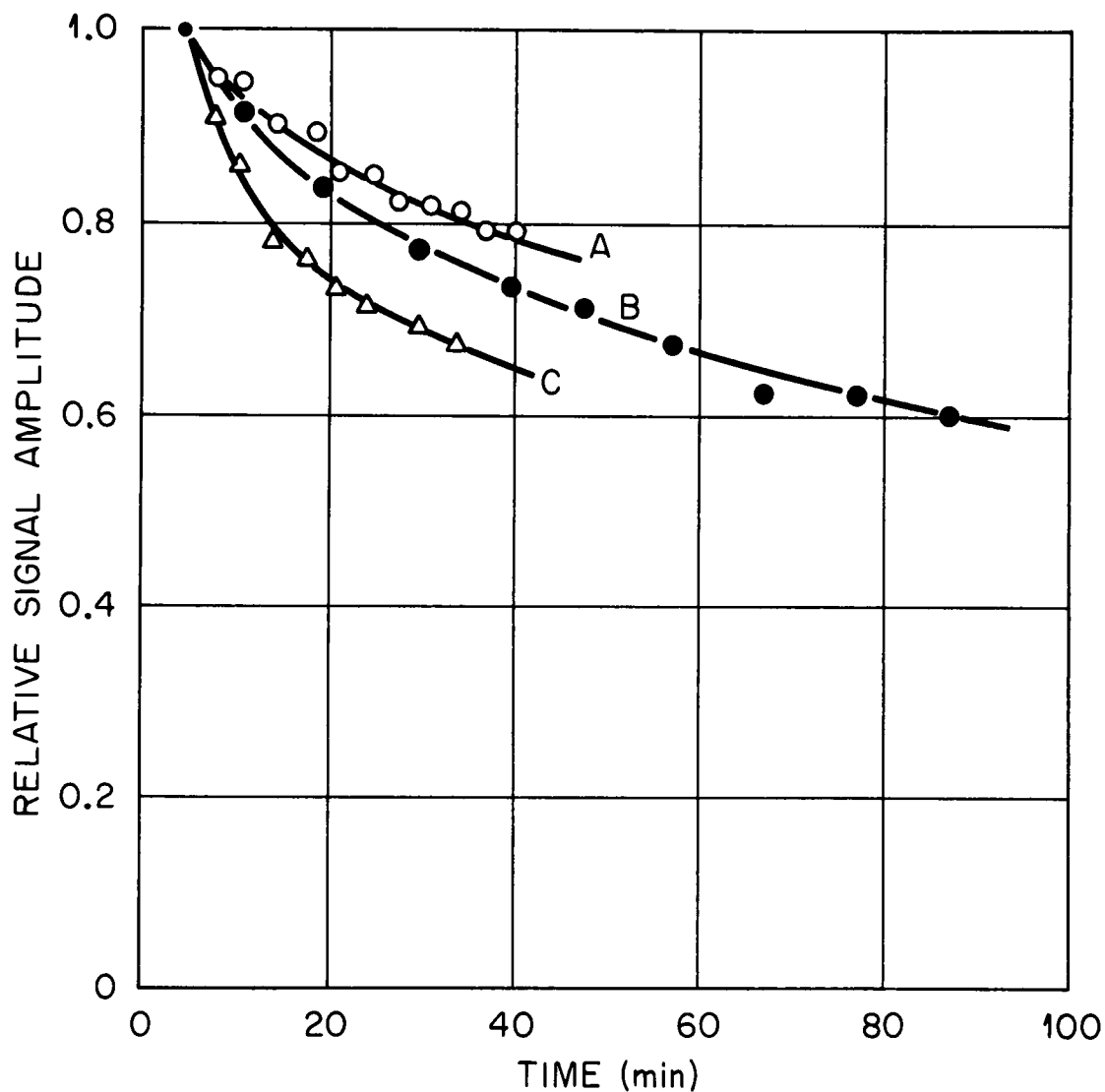


Figure 26. Thermal decay of trapped electrons in γ -irradiated polypropylene and isotactic poly(4-methylpentene-1).

Curve A, isotactic poly(4-methylpentene-1) at a temperature of ca. 70°K; Curve B, isotactic polypropylene at 77°K; Curve C, isotactic poly(4-methylpentene-1) at 77°K. All these samples received an irradiation dose of 1.1×10^{19} ev g^{-1} at 77°K.

2. Optical Absorption of Trapped Electrons in Poly(4-methylpentene-1)

In contrast to polyethylene and polypropylene which are opaque toward light, isotactic poly(4-methylpentene-1) is essentially optically clear. This fact suggests the possibility that trapped electrons in this material might be observed by optical means. The Cary 14R spectrometer and the techniques for making optical measurements at 77°K have been described in Chapter III. The poly(4-methylpentene-1) sample used in this experiment was in the form of a cylinder 1.2 cm in diameter.

Prior to irradiation, the sample was introduced into the optical dewar at 77°K, and its spectrum scanned from 2000 nm to 500 nm. The sample was then removed from the dewar and γ -irradiated at 77°K. The sample received a dose of 2×10^{19} ev g⁻¹, corresponding to the maximum concentration of trapped electrons observed by ESR. Following irradiation, the sample was quickly transferred back into the optical dewar and its spectrum again scanned from 2000 nm down to 500 nm. This scan of the spectrum revealed an increase in optical absorption in the region from 700 to 2000 nm compared to that observed prior to irradiation. The sample was then photobleached in situ for 10 minutes with filtered light of $\lambda > 1000$ nm using the intense beam from the IR-2 lamp of the spectrometer. During this treatment, the position of the sample was not disturbed.

After photobleaching, the spectrum was again scanned from 2000 nm to 500 nm. The increased absorption observed after irradiation had been completely eliminated by the photobleaching treatment, the spectrum being virtually identical to that observed prior to irradiation. The difference in optical density observed before and after photobleaching is

plotted in Figure 27. (The wavelength scale in Figure 27 is in microns; one micron equals 1000 nm.) The increased absorption is attributed to trapped electrons since the photobleaching behavior is the same as that observed in the ESR study of trapped electrons in poly(4-methylpentene-1).

The absorption band maximum is not observed in Figure 27 and evidently lies beyond 2000 nm (2 microns). Unfortunately, 2000 nm is the upper wavelength limit of the Cary 14R spectrometer so that the measurements could not be extended beyond this point. It is of interest to note that λ_{max} for the absorption bands of trapped electrons in alkane glasses lie in the region of 1600-1700 nm.⁶³ Therefore λ_{max} for the trapped electron in poly(4-methylpentene-1) is apparently shifted to significantly longer wavelengths than for trapped electrons in the glasses.

3. Atactic Polypropylene and Polyisobutylene

All the preceding experiments have involved semi-crystalline polymers. It is therefore of interest to examine the possibility of trapping electrons in amorphous polymers, particularly in view of the fact that rather high yields of trapped electrons are readily observed in amorphous alkane glasses.⁶³ Atactic polypropylene and polyisobutylene are typical examples of amorphous polymers. Atactic polypropylene is chemically identical to isotactic polypropylene but differs with respect to the configuration of methyl groups about the main polymer chain. If the polymer chain is imagined to be in a fully extended planar zigzag conformation, then the material is termed isotactic if the substituent methyl groups lie either all above or all below the plane of the chain. If the arrangement of methyl groups is random with respect to the plane of the main chain, the material is termed atactic. The isotactic

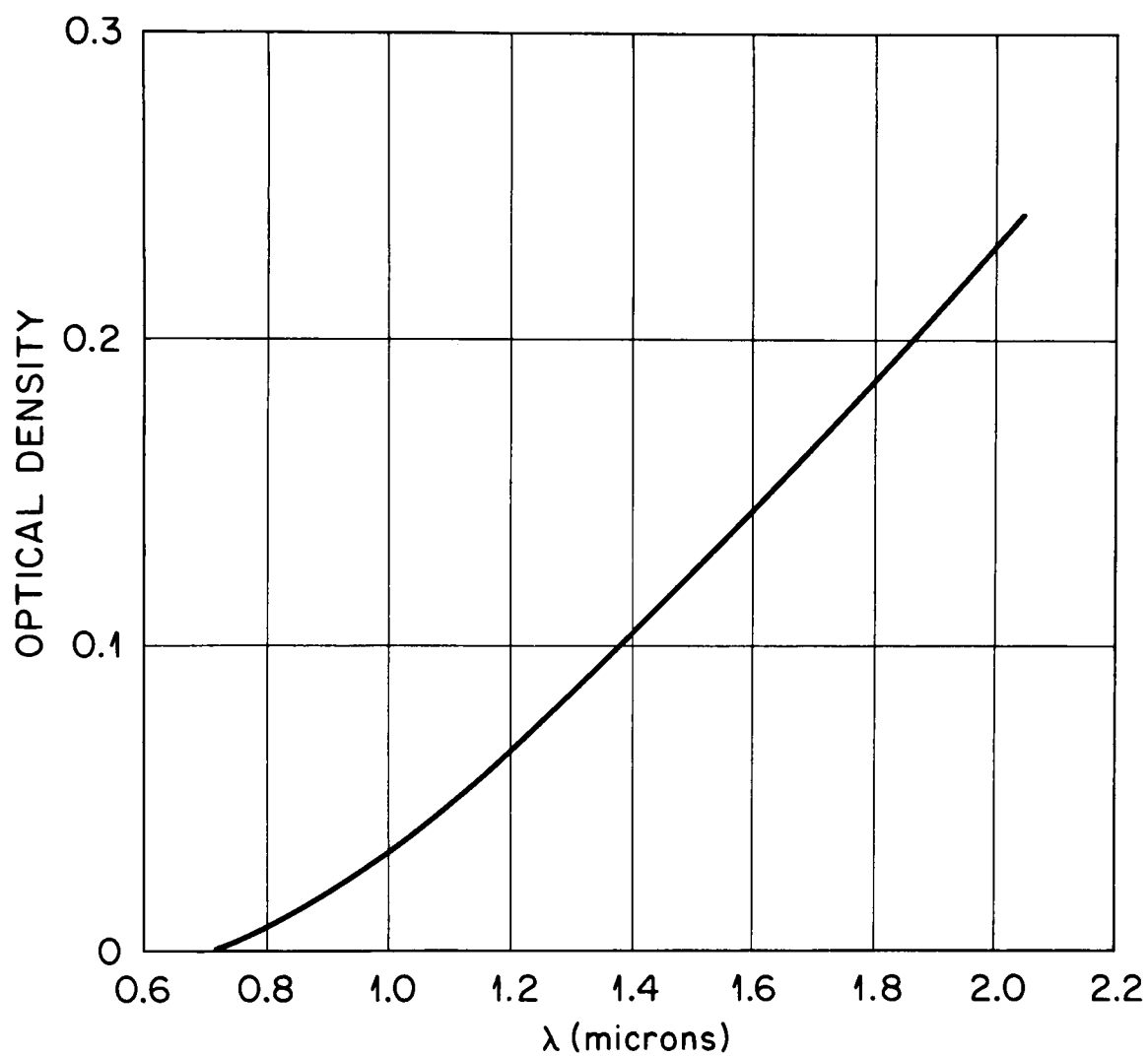


Figure 27, Optical absorption spectrum of trapped electrons in γ -irradiated poly(4-methylpentene-1) at 77°K.

configuration of polypropylene confers sufficient geometrical regularity to the polymer structure to allow it to exist in a substantially crystalline state. On the other hand, the disordered features of the atactic configuration prevent crystallization. In the case of polyisobutylene, the occurrence of two bulky methyl groups on the same carbon atom prevents the polymer chains from getting close enough together to crystallize.

Spectrum A of Figure 28 shows the ESR spectrum at 77°K of γ -irradiated atactic polypropylene. The sample received an irradiation dose of 1.1×10^{19} ev g^{-1} also at 77°K. The small "blip," or singlet, in the center of the spectrum can be removed by photobleaching the sample, as shown by spectrum B, and is assigned to a trapped electron on this basis. The singlet in spectrum A underwent no appreciable thermal decay during the 20 minute period between observation of spectrum A and photobleaching of the sample. A concentration measurement based on the technique described for polyethylene indicates that the yield of trapped electrons in spectrum A corresponds to $G(e_t^-) \leq 0.02$. The yield is therefore quite low.

The ESR spectrum in Figure 29 results from polyisobutylene which had received a dose of 1.1×10^{19} ev g^{-1} at 77°K. No changes were observed in the spectrum after photobleaching with light of $\lambda > 1000$ nm. Therefore, there is no evidence for trapped electrons in this material.

E. n-Alkanes

1. Identification, Yield, and Thermal Decay of the Trapped Electron

It is of interest to examine the possibility of observing trapped electrons in γ -irradiated n-alkanes since they may be regarded as short

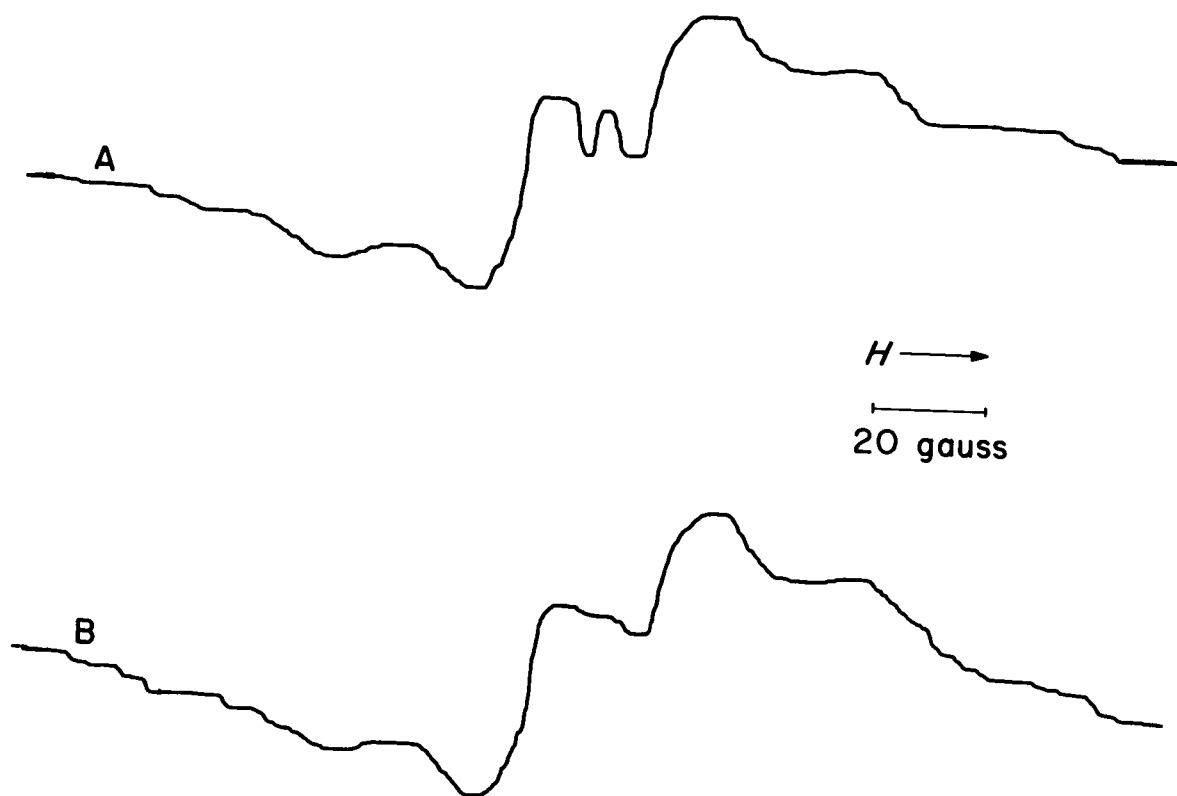


Figure 28. First-derivative ESR spectra at 77°K from γ -irradiated atactic polypropylene.

The sample received an irradiation dose of 1.1×10^{19} ev g⁻¹ at 77°K. Spectrum A was recorded in the dark after irradiation and spectrum B was recorded after photobleaching the sample with infra-red light ($\lambda > 1000$ nm). Both spectra were obtained at 2 μ W microwave power, an amplifier gain setting of 400, and a modulation amplitude of 1.5 gauss.

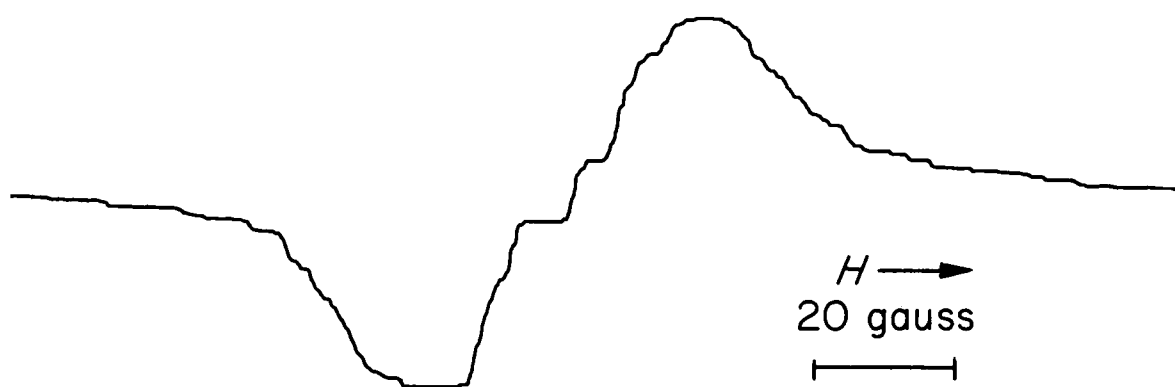


Figure 29. First-derivative ESR spectrum at 77°K from γ -irradiated polyisobutylene.

The sample received an irradiation dose of 1.1×10^{19} ev g^{-1} at 77°K. The spectrum was recorded in the dark immediately after irradiation at 2 μ W microwave power, an amplifier gain setting of 1000, and a modulation amplitude of 1.5 gauss.

chain analogues of polyethylene. ESR spectra following γ -irradiation in the dark at 77°K of a sample of n-hexatriacontane, $C_{36}H_{74}$, are shown in Figure 30. The prominent singlet in the center of spectrum A is assigned to a trapped electron on the now familiar basis of the narrow linewidth of $\Delta H_{ms} = 3.6 \pm 0.2$ gauss, the photobleaching effect as shown by spectrum B, and the fact that saturation of the signal was observed at microwave powers of the order of 5-10 μW . The g-factor of the trapped electron singlet is $g = 2.0021 \pm 0.0002$ as determined by methods previously discussed for the experiments on linear polyethylene. Samples of n-dotriacontane, $C_{32}H_{66}$, and n-tetracosane, $C_{24}H_{50}$, gave entirely similar spectra after γ -irradiation at 77°K. In the case of n-octacosane, $C_{28}H_{58}$, only a small yield of trapped electrons was evident. The amplitude of the trapped electron singlet in this material was substantially lower than the amplitude of the underlying free radical signal.

The dependence of trapped electron concentration on irradiation dose for n-hexatriacontane is depicted in Figure 31. Concentration measurements were performed in a manner analogous to those previously described for linear polyethylene. The shape of the curve in Figure 31 is similar to that observed for the polymers; the trapped electron concentration rises to a maximum and thereafter decreases with further increase in dose. The maximum concentration of trapped electrons observed in n-hexatriacontane, 1.8×10^{16} electrons/g, is lower than the 4.2×10^{16} electrons/g value found for Marlex 6050 polyethylene. At doses below 7×10^{18} $ev\ g^{-1}$, the trapped electron concentration in hexatriacontane rises linearly with increasing irradiation dose and the initial G-value for trapped electron formation was determined to be $G(e_t^-) = 0.17$ trapped

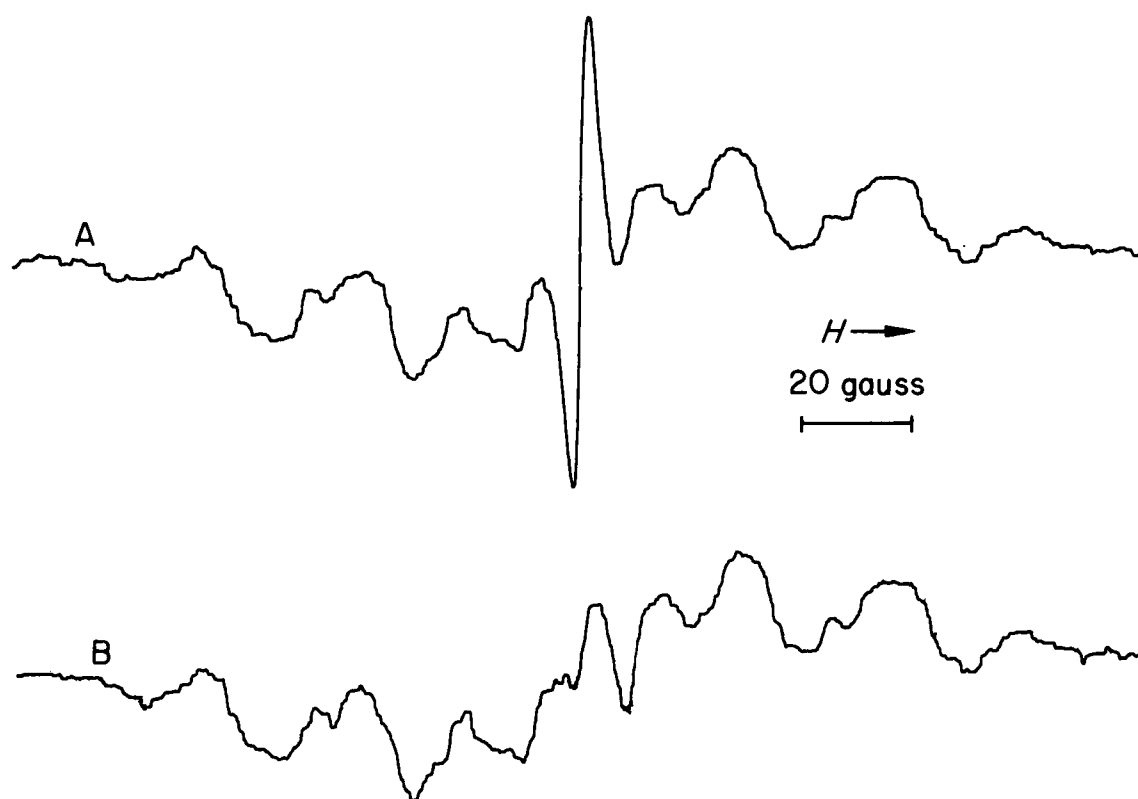


Figure 30. First-derivative ESR spectra at 77°K from γ -irradiated n-hexatriacontane.

The sample received an irradiation dose of 1.1×10^{19} ev g^{-1} . Spectrum A was recorded before and spectrum B after photobleaching the sample with infrared light ($\lambda > 1000$ nm). Both spectra were obtained at 2 μW microwave power, an amplifier gain setting of 1000 and a modulation amplitude of 1.5 gauss.

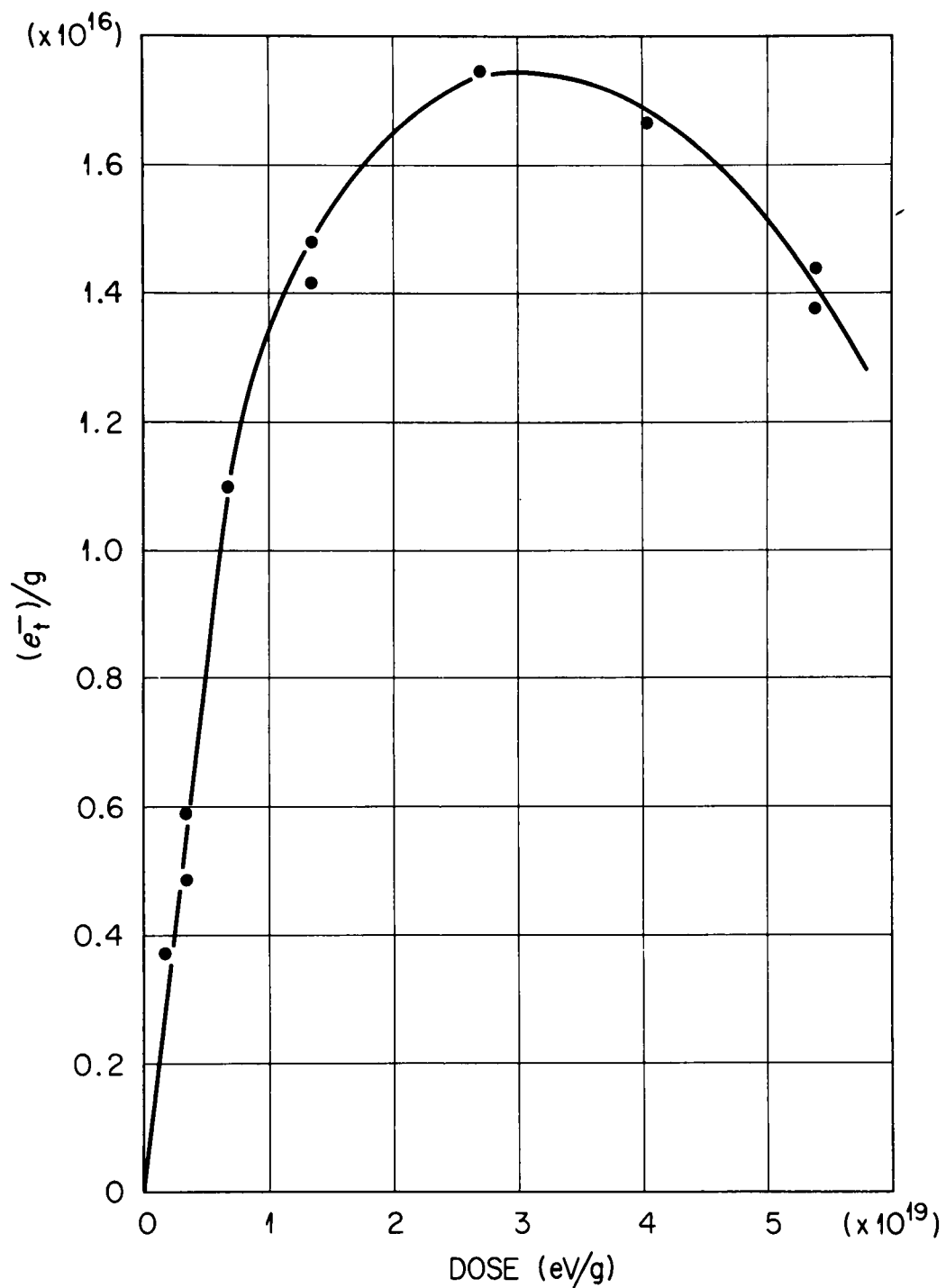


Figure 31. Trapped electron concentration as a function of dose in n-hexatriacontane γ -irradiated at 77°K.

electrons per 100 ev. This value is also lower than $G(e_t^-) = 0.46$ found for Marlex 6050 polyethylene. No detailed investigation of the dose dependence of trapped electron concentration in the shorter chain n-alkanes was attempted. At an irradiation dose of 1.1×10^{19} ev g^{-1} , however, the signal amplitudes of the trapped electron singlet in $C_{32}H_{66}$ and $C_{24}H_{50}$ were approximately the same as that in hexatriacontane when the comparison was made under conditions of equivalent spectrometer sensitivity.

The thermal decay of the trapped electron in hexatriacontane at 77°K is reflected by the data in Figure 32. Zero time in this figure corresponds to the initial observation of the trapped electron singlet made three minutes after removal from the radiation source. Signal amplitudes were normalized to that obtained in the initial observation. The sample received an irradiation dose of 1.1×10^{19} ev g^{-1} . Comparison of Figure 32 with Figure 12 (p 90) reveals that the fractional rate of thermal decay of the trapped electron in n-hexatriacontane is only slightly greater than that in Marlex 6050 polyethylene at 77°K.

2. Trapped Electrons in n-Hexatriacontane Samples Containing Small Amounts of Shorter Chain n-Alkanes

Several interesting observations regarding the effect of adding small amounts of shorter chain alkanes to n-hexatriacontane prior to irradiation are summarized in Table VI. All samples received an irradiation dose of 3×10^{19} ev g^{-1} at 77°K, corresponding to the maximum in the trapped electron concentration versus dose curve for n-hexatriacontane containing no additives. As is evident from Table VI, adding one and ten mole percent dotriacontane to n-hexatriacontane results in a

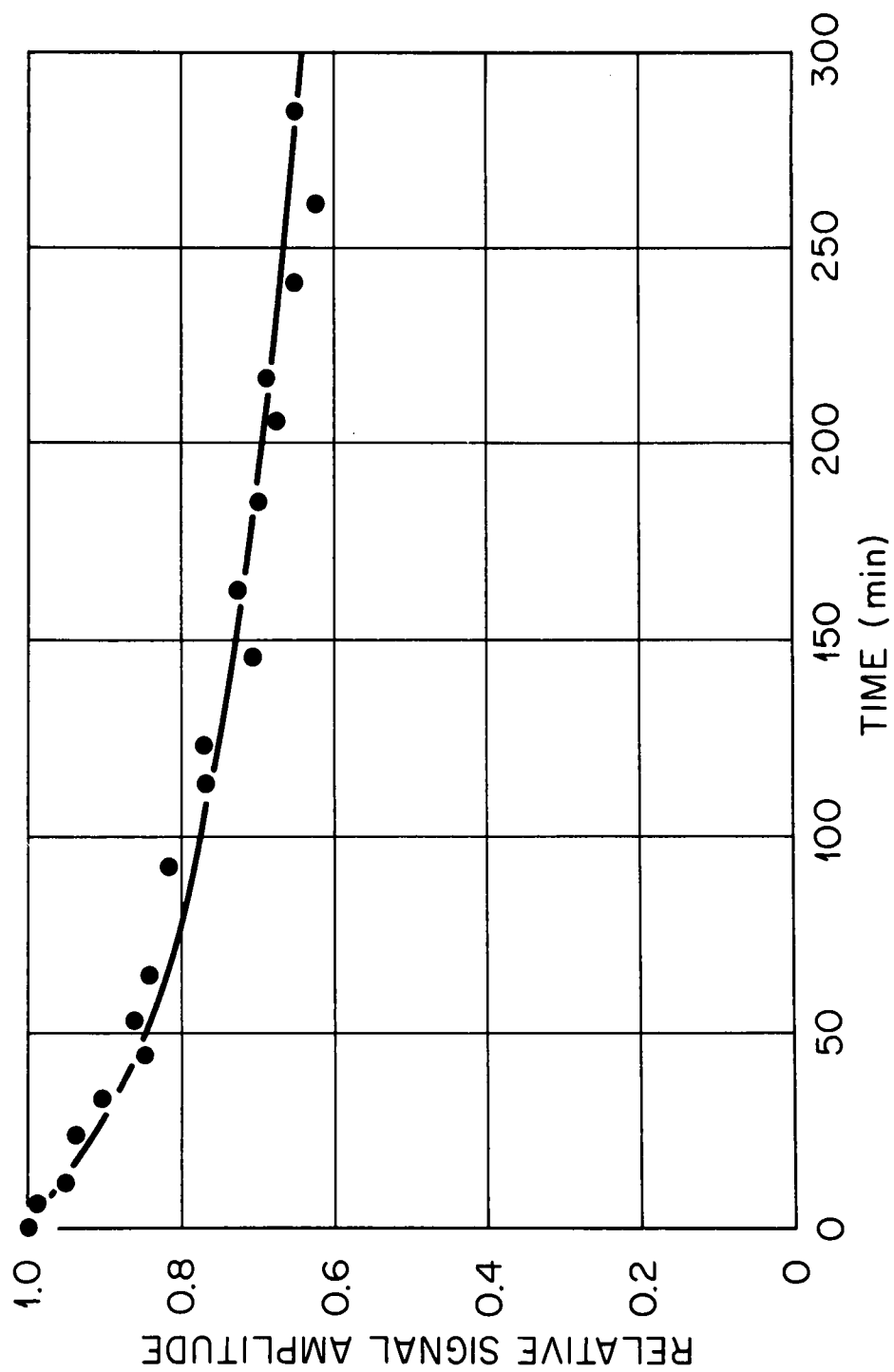


Figure 32. Thermal decay of trapped electrons in γ -irradiated n-hexatriacontane at 77°K.

TABLE VI

EFFECT OF n-ALKANE ADDITIVES ON TRAPPED ELECTRON CONCENTRATION AND ESR LINEWIDTH IN γ -IRRADIATED n-HEXATRIACONTANE^a

Concentration of Additive (mole percent)	Trapped Electron Concentration (electrons/g)	ΔH_{ms}^b (gauss)
None	1.8×10^{16}	3.6
1% dotriacontane	2.0×10^{16}	3.3
10% dotriacontane	2.3×10^{16}	2.8
1% octacosane	3.1×10^{16}	3.0
3% octacosane	3.2×10^{16}	2.8
10% octacosane	3.0×10^{16}	2.5
3% tetracosane	1.7×10^{16}	3.6

^aSamples irradiated to a dose of 3×10^{19} ev g⁻¹ at 77°K.

^bPeak-to-peak linewidth of trapped electron ESR singlet.

slight enhancement of trapped electron concentration and a significant reduction in the linewidth of the trapped electron ESR singlet. The effects are more dramatic when n-octacosane is the additive. The resulting trapped electron concentrations are nearly double that in additive-free hexatriacontane and the increased yield does not appear to be dependent on octacosane concentration. Moreover, ΔH_{ms} for the trapped electron singlet decreases from 3.6 gauss in additive-free hexatriacontane to 2.5 gauss when 10 mole percent octacosane is added. On the other hand, adding 3 mole percent n-tetracosane appears to have no effect. Trapped electron concentration and ΔH_{ms} are the same as in additive-free hexatriacontane in this instance.

CHAPTER V

DISCUSSION OF THE RESULTS

A. Introduction

The implications of the results from the experimental investigations on electron trapping in hydrocarbon polymers are explored in this chapter. The assignment of the narrow singlet appearing in the ESR spectra of irradiated polymers to trapped electrons is discussed. Previous reports of ESR spectra from trapped electrons in polymers are also discussed in the light of this assignment. An effect of crystallinity on the yields of trapped electrons is noted and the possibility of electron trapping in voids is explored. A phenomenological model to account for the thermal stability of the trapped electron in Marlex 6050 polyethylene is proposed and the chapter concludes with some discussion of the possible influence of free radicals on trapped electron yields.

B. Assignment of the Narrow ESR Singlet to Trapped Electrons

The narrow singlet appearing at $g = 2.0023 \pm 0.0002$ in the ESR spectra of the various polymers examined in this work has been assigned in the previous chapter to an electron trapped in the polymer matrix. This assignment rests entirely on the similarity of the singlet in the ESR spectra of the polymers, with respect to both photobleaching and power saturation behavior, to the corresponding ESR line from trapped electrons in rigid alkane glasses following γ -irradiation. The evidence for associating the singlet in the ESR spectra of alkane glasses with trapped

electrons has been discussed in depth in Chapter I. The assignment in this latter instance seems quite secure.

Before comparing the ESR observations in polymers with those in alkane glasses, it is worthwhile to first explore the possibility that the singlet might result from either a free radical or from some impurity effect. A singlet has been reported in the ESR spectra of polyethylene subjected to very large radiation doses and has been assigned to a polyenyl free radical of the type $-\text{CH}_2(\text{CH}=\text{CH})_n\dot{\text{C}}\text{H}-\text{CH}_2$.⁷⁴ This singlet can only be observed at doses above 2×10^{22} ev g^{-1} . Its linewidth is $\Delta H_{\text{ms}} = 26$ gauss and it is thermally stable even at 150°C . This behavior is clearly not in accord with that of the singlet observed in the present investigation; ΔH_{ms} for the singlet in Marlex 6050 polyethylene is 3.4 gauss, it may be observed at doses below 10^{18} ev g^{-1} , and it undergoes appreciable thermal decay at temperatures only slightly above -196°C . Thus, a polyenyl free radical cannot be responsible for the singlet observed in this study.

In fact, a number of features of the narrow ESR singlet are not in accord with the characteristics of ESR spectra from free radicals in polymers. The singlet linewidths are significantly narrower than is typical of polymeric free radicals. The singlet is quite susceptible to microwave power saturation whereas polymeric free radicals are much more resistant to saturation. For example, the singlet in Marlex 6050 displays a maximum in its saturation curve at $4\mu\text{W}$ (Figure 13, p 92). The underlying alkyl free radical is not appreciably saturated even at the relatively high power level of $100\mu\text{W}$. Finally, the singlet is readily removed by exposing the sample to infrared light. Typical polymeric free radicals are not affected by infrared light. All these differences

indicate that some species other than a free radical is responsible for the narrow singlet.

The likelihood that the singlet arises as a result of electron capture by a polymer molecule can be discounted. Saturated hydrocarbon polymers do not possess an electron affinity nor do suitable low-lying orbitals exist to accommodate the electron. That the singlet results from electron capture by some impurity in the polymer is also improbable. The amplitudes of the singlet observed in this study were always greatest when care was taken either to exclude impurities or to reduce the impurity content. Thus in linear polyethylene, the yield of the species responsible for the singlet was diminished in the presence of impurities such as antioxidants. Moreover, in the hydrogenated polyethylene sample, the singlet was only observed after rigorous effort to reduce the impurity content. Finally, both the linewidth and amplitude of the singlet from irradiated isotactic polypropylene were the same in samples received from two different manufacturers. If the singlet results from an impurity effect, this equivalence would seem to require that the nature and concentration of the impurity be the same in both polypropylene samples. In view of the fact that they were obtained from different sources, this seems unlikely.

Turning now to a comparison of the ESR singlet observed in the case of polymers with that from trapped electrons in alkane glasses, a number of close similarities are immediately evident. In both instances, the singlet is narrow; $\Delta H_{ms} = 4.0 \pm 0.2$ gauss in a variety of alkane glasses⁶³ and ranges from 2.6 ± 0.2 gauss for isotactic poly(4-methylpentene-1) up to 3.4 ± 0.2 gauss for polyethylene. In both polymers and alkane glasses,

the singlet is readily photobleached by near infrared light of $\lambda > 1000$ nm. Moreover, the singlet in both types of materials is very susceptible to microwave power saturation. The maximum in the saturation curve for the ESR singlet in Marlex 6050 polyethylene occurs at $4 \mu\text{W}$ for a modulation frequency of 200 Hz (Figure 13, p 92). For comparison purposes, a typical alkane glass such as 3-methylhexane displays a corresponding maximum of $25 \mu\text{W}$.⁶⁵

Thus, despite small differences in linewidth and saturation effects, the gross features and behavior of the ESR singlet in polymers are entirely analogous to those of the trapped electron singlet in alkane glasses. In view of this overall correspondence, the assignment of the singlet in polymers to electrons physically trapped in the polymer matrix can be made with confidence. The term physically trapped electron is used here in precisely the same context as employed in Chapter I in the discussion of the nature of the trapped electron in alkane glasses. A physically trapped electron is to be regarded as an electron localized in the matrix such that it is bound to no single molecule and does not reside entirely within the molecular orbitals of surrounding molecules. It is therefore, of itself, a distinct chemical entity and is to be distinguished from a chemically trapped electron. A chemically trapped electron is one which is chemically bound to a molecule of the medium and which resides entirely within the molecular orbitals of that particular molecule.

To the author's knowledge, the only previous report of an ESR spectrum attributed to trapped electrons in a saturated hydrocarbon polymer is by Alfimov, Nikolskii, and Buben.⁷⁸ These authors reported that the

ESR spectrum of polyethylene after γ -irradiation at 77°K consisted of a singlet superimposed on a broad free radical spectrum. Furthermore, the singlet could be removed by photobleaching the sample. The singlet observed by the Russian workers, however, is readily distinguished on the basis of linewidth from that observed in the present work. The linewidth of the trapped electron singlet from both Marlex 6050 and Alathon 1414 polyethylenes is 3.4 ± 0.2 gauss (Figure 5, p 69 and Figure 19, p 107, respectively). In the work of Alfimov et al., the singlet is much broader, $\Delta H_{ms} \sim 20$ gauss, as judged by the fact that the resolution of the two center lines in the underlying free radical signal is totally obscured in the spectrum obtained prior to photobleaching.

The Russian workers suggested that the singlet they observed resulted from an electron "captured in a trap," but the nature of the trap (chemical or physical) was not specified. A broad line in the center of the spectrum could well be the result of unresolved hyperfine structure from some paramagnetic species produced by electron capture, i.e., a chemically trapped electron. Indeed, the Russian workers also report that radiolysis of polyethylene containing benzene yielded an ESR spectrum containing a broad line. Such a result is in accord with the idea of chemical trapping of the electron by aromatic impurities.

C. Some Speculation on the Nature of the Electron Trap in Saturated Hydrocarbon Polymers

In the preceding section, the evidence has been discussed for assigning the narrow singlet in the ESR spectra of irradiated polymers to an electron trapped and physically localized as a distinct chemical entity within the polymer matrix. The question then naturally arises as

to what can be said regarding the nature of the trap itself. Such a question is not an easy one to answer. In principle, the answer might be forthcoming from a knowledge of the hyperfine interaction of the trapped electron with surrounding magnetic nuclei. Such an approach has been particularly fruitful in the study of the F-center in alkali halide crystals.⁶ In the case of polymers, however, the lack of resolved hyperfine structure in the ESR spectrum of the trapped electron prohibits this method of attack from being employed.

In view of the overall similarity between the trapped electron observed in polymers and that in alkane glasses, it seems reasonable to suppose that the environment of the trapped electron in the two cases might exhibit certain similarities as well. As has been discussed in some detail in Chapter I, the generally accepted model for describing the electron trap in glassy alkane systems considers the electron to be trapped in pre-existing voids of molecular dimensions which are frozen into the matrix. The electron derives its stability from the lower energy state available to it when localized in a void. It therefore seems advantageous to approach the problem of electron trapping in polymers within the framework of the void concept and to examine the similarities and differences between the behavior of trapped electrons in both polymers and alkane glasses within this context.

In terms of a void model, the results on polymers imply electron trapping in a void that is larger than in alkane glasses. This conclusion follows from three lines of evidence. First, the linewidths of the trapped electron singlet observed in polymers are in all instances somewhat narrower than the value of 4.0 ± 0.2 gauss⁶³ found for alkane glasses.

If the linewidth is due mainly to unresolved hyperfine interaction between the trapped electron and surrounding protons in the void boundary, then increasing the radius of the void would be expected to weaken the hyperfine interaction and lead to the smaller linewidths observed. A similar conclusion is reached from a comparison of spin-lattice relaxation times. At comparable conditions of radiation dose and modulation frequency, $T_1 = 3 \times 10^{-3}$ sec for the trapped electron in a typical alkane glass⁶⁵ whereas in this study, T_1 was found to be $\geq 2 \times 10^{-2}$ sec in Marlex 6050 polyethylene. Thus T_1 in polyethylene is at least an order of magnitude greater than in alkane glasses. Since T_1 can be regarded as a measure of the strength of the interaction of a trapped electron with its environment, a large T_1 implying a weak interaction, it is evident that the trapped electron in polyethylene is more weakly coupled to its environment than is the case for trapped electrons in alkane glasses so that this result can also be understood naively in terms of a larger void in polymers than in the glasses. Finally, the apparent shift to lower energy of the optical absorption band from the trapped electron in poly(4-methylpentene-1) relative to the corresponding bands in alkane glasses is also of interest in this connection. If a simple "particle in a box" description can be applied to an electron in a void, then the red shift of the absorption band in poly(4-methylpentene-1) implies a larger void in polymers since the optical transition energy decreases with increasing void radius.⁶⁶

As pointed out in Chapter I, a major factor suggesting that electron trapping in rigid organic glasses occurs in voids is the effect of crystallinity on trapped electron yields. Amorphous, glassy systems

would be expected to possess a significant number of voids as a result of their disordered structure. Hence electron trapping in such systems should be a facile process compared to electron trapping in crystalline systems which, because of their well-ordered structure, possess relatively few voids. Therefore, it is of interest to examine the effect of crystallinity on trapped electron yields in polymers. Table VII compares both the initial $G(e_t^-)$ and the maximum trapped electron concentration observed in the various polymers studied in this investigation with the degree of crystallinity of the polymers. Estimates of the degree of crystallinity are based on the conventional assumption that the polymer consists of both crystalline and amorphous phases.¹⁰⁵

It is evident from the data in Table VII that the ability of a polymer to trap electrons is strongly correlated with its crystallinity. Polymers of the highest crystallinity, Marlex 6050 polyethylene and isotactic polypropylene, exhibit the greatest concentration of trapped electrons at the maximum in the concentration versus dose curve and also the highest values of $G(e_t^-)$. Polymers of intermediate crystallinity such as Alathon 1414 and poly(4-methylpentene-1) display intermediate trapped electron yields. Finally, in non-crystalline polymers such as atactic polypropylene and polyisobutylene, the trapped electron yield is either vanishingly small or else non-existent.

This correlation of the trapped electron yield with crystallinity strongly implies that the trapping site is associated with crystalline regions in the polymer. Such an effect of crystallinity is quite opposite to that observed in the majority of work on electron trapping in low-molecular weight systems where, in both frozen alcohols³⁴ and in

TABLE VII

EFFECT OF CRYSTALLINITY ON TRAPPED ELECTRON YIELDS IN γ -IRRADIATED HYDROCARBON POLYMERS

Polymer	Percent Crystallinity	Initial $G(e_t^-)^a$ (electrons/100 ev)	Maximum Observable Concentration of Trapped Electrons ^b (electrons/g)
Marlex 6050 polyethylene	$\sim 82^c$	0.46	4.6×10^{16}
Alathon 1414 polyethylene	$\sim 45^c$	0.12	---
Isotactic polypropylene	$\sim 70^d$	0.17	1.5×10^{16}
Atactic polypropylene	0	< 0.02	---
Isotactic poly(4-methylpentene-1)	$\sim 40^d$	0.08	0.5×10^{16}
Polyisobutylene	0	0	---

^aDetermined from plot of trapped electron concentration versus dose as described in Chapter IV.^bMaximum in the concentration versus dose curve as described in Chapter IV.^cCalculated value based on specific volume equations of R. Chiang and P. J. Flory, J. Am. Chem. Soc., **83**, 2857 (1961) and the densities given in Table II, p 42.^dManufacturer's estimate.

several glassy alkane systems,⁶³ trapped electron yields are severely diminished by any tendency toward crystallinity in the sample. While at first sight the observation that the trapping site in polymers is associated with crystalline regions would appear to be in conflict with the concept of electron trapping in voids, current views regard the crystalline state of polymers as being characterized by a large number of defects including those of the void type.¹⁰⁶

Present knowledge regarding the morphology of the crystalline state of bulk-crystallized polymers (i.e., crystallized by cooling from the melt) has been strongly influenced by the discovery¹⁰⁷ in 1957 that well defined single crystals of polyethylene could be grown from solution. The shape of a typical polyethylene single crystal as revealed by electron microscopy is that of a flat, diamond-shaped lamella some 100 Å thick and with lateral dimensions of the order of some 100 microns. Electron diffraction patterns of individual lamellae have shown that the molecular chains are oriented with their axes perpendicular to the lamellar plane. Since typical polymer molecules are several thousand angstroms long and the thickness of a lamella is only about 100 Å, the conclusion¹⁰⁷ is that the polymer chains are folded back and forth within the crystal with a fold period of some 100 Å, i.e., the lamellar thickness. Crystallization of a variety of polymers from solution into this type of folded-chain structure has now been observed and the phenomenon appears to be quite general.

The available evidence now indicates that bulk-crystallized polymers are also composed of crystal lamellae of the folded-chain type¹⁰⁶ although, in the bulk solid, these may be somewhat modified. In bulk

polymers, the crystal lamellae are oriented in a radially symmetric array known as a spherulite. The lamellae radiate outward from the center of the spherulite such that the axes of the polymer chains in the lamellae are oriented perpendicular to the spherulite radius. Since the folded-chain lamellae are the building blocks of the overall crystalline structure in bulk-crystallized polymers, it is of interest to examine their morphology in more detail.

Single crystals of polymers are much less perfect than are those of low-molecular weight materials. This fact follows primarily from density considerations. Single crystals of linear polyethylene exhibit densities ranging from 0.96 to 0.98 g cc⁻¹ whereas the density computed from x-ray data for a perfect crystal is 1.00 g cc⁻¹.¹⁰⁸ While there is some controversy over the origin of this density anomaly,¹⁰⁹ it has been suggested¹¹⁰ that it might arise from incorporation of some 2-4% voids of zero density in the crystal. While voids might be associated with a number of different types of crystal defects, a particularly attractive possibility is that of a partial row-vacancy resulting from a chain end which does not extend completely through the crystal lattice.¹¹⁰ This type of void or defect is depicted schematically in part A of Figure 33. To account for 4% voids in terms of this defect, it has been pointed out¹¹⁰ that, for a typical polyethylene molecule which makes about 30-40 folds of some 100 -CH₂- units each, it is only necessary to assume that the end of the molecule extends on the average about halfway through the crystal leaving the remaining lattice positions void. This concept of a row-vacancy defect, or void, has been used to explain certain features of mechanical relaxation phenomena in polymers as well as effects resulting from annealing of single crystals.¹¹¹

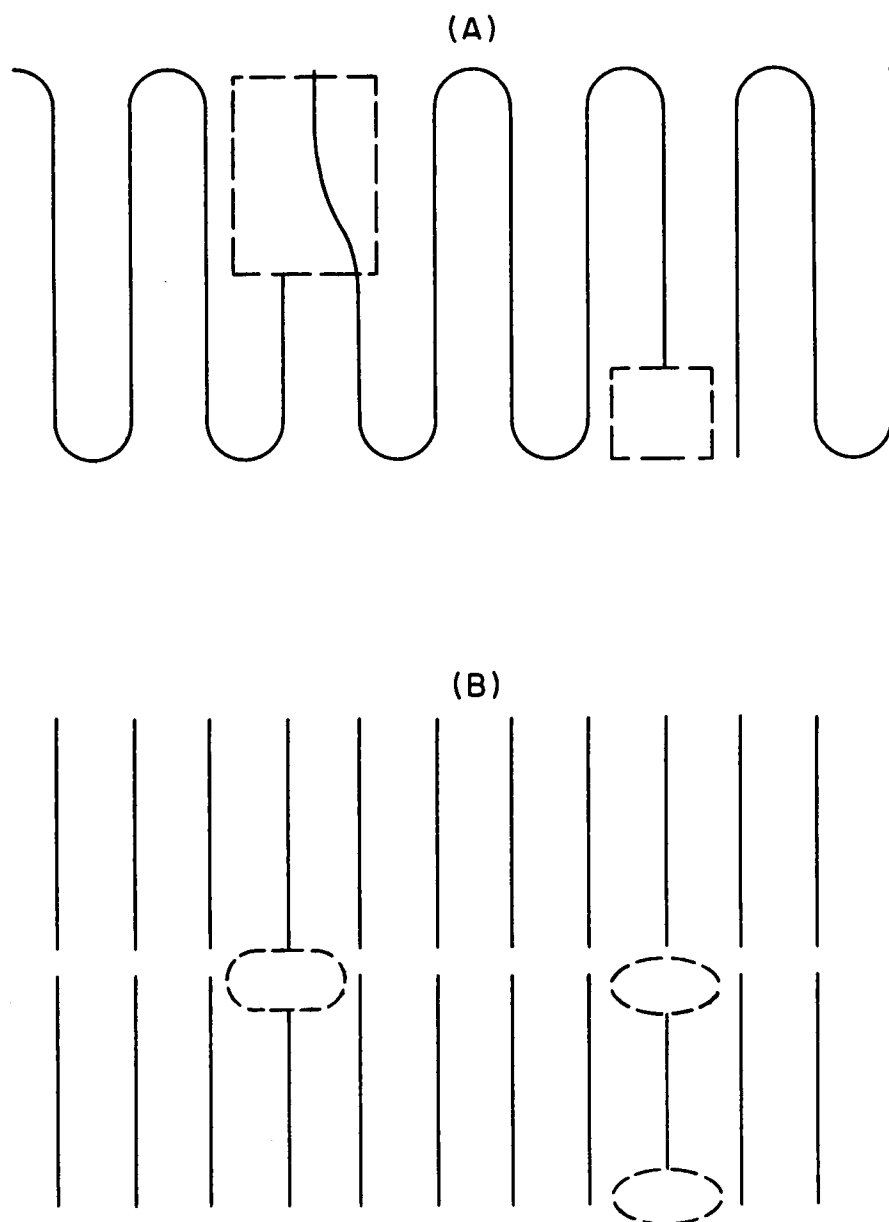


Figure 33. Schematic representation of row-vacancy defects in folded-chain polyethylene crystals (A) and in hexatriacontane.

Dotted lines indicate defect regions. In (A), the solid line represents a polyethylene chain. In (B), two layers of hexatriacontane molecules are represented by the solid lines.

This somewhat abbreviated discussion of the crystalline morphology of polymers has been directed toward demonstrating that significant numbers of defects of the void type are believed to occur in crystalline polymers. Hence, the evidence that the electron trap is associated with crystalline regions in the polymer is not inconsistent with the concept of trapping in a void. Whether the trap is specifically a void of the row-vacancy type is admittedly a highly speculative matter. Some support for this possibility does derive, however, from the experiments involving n-hexatriacontane.

The linewidth and thermal decay at 77°K of the trapped electron singlet in n-hexatriacontane are very similar to those in Marlex 6050 polyethylene, a fact which suggests that the mode of electron trapping is similar in both instances. n-Hexatriacontane crystallizes in the form of sheets composed of layers of molecules in an extended chain configuration.¹¹² The chain axis is perpendicular to the plane of each layer so that the resulting structure is quite similar to that of polyethylene crystals. The only essential difference is that in the case of n-hexatriacontane, the top and bottom surfaces of each layer are formed by the ends of the molecule whereas for polyethylene, these surfaces are formed by folds in the polymer chain.

These considerations suggest that it might be possible to manufacture row-vacancy defects in n-hexatriacontane by the simple expedient of doping the material prior to crystallization with small amounts of shorter chain n-alkanes. Assuming that the short chain material is incorporated into the host lattice in normal fashion, the resulting structure would be expected to appear as indicated schematically in part B of

Figure 33 (p 143) where the induced row-vacancy defects are indicated by dotted lines.

If an electron can be trapped in a void associated with a row-vacancy defect, then two effects should be observed upon irradiation of a hexatriacontane sample containing shorter chain alkanes. First, the trapped electron yield should increase since voids have been effectively built into the sample. Second, the linewidth of the trapped electron singlet should decrease as the chain length of the additive decreases since the size of the void increases with decreasing chain length of the additive. This latter prediction rests, of course, on the assumption that the major cause of line broadening results from unresolved hyperfine interaction as previously discussed.

These predictions in fact tend to be borne out by the data of Table VI (p 130). When n-dotriacontane is the additive, the trapped electron yield is enhanced by some 20% and ΔH_{ms} is less than in additive-free hexatriacontane. Adding n-octacosane enhances the yield by nearly a factor of two and the linewidth is reduced even more than in the case of n-dotriacontane at comparable concentrations. The decrease in ΔH_{ms} with increasing additive concentration is plausibly interpreted as resulting from an increasing probability of side-by-side juxtaposition of additive molecules with increasing concentration, thereby leading to a larger void. Why the enhancement of trapped electron yield is independent of additive concentration and why this enhancement is less in the case of n-dotriacontane than when n-octacosane is the additive is not clear, however.

As previously noted, the interpretation of these effects in terms of electron trapping in a row-vacancy defect rests on the assumption that the short chain additive is incorporated into the host lattice. This assumption appears to be valid so long as the host and additive molecules are not too greatly disparate in chain length. Thus Nechitailo et al.¹¹³ find that mixtures of $n\text{-C}_{30}\text{H}_{62}$ in $n\text{-hexatriacontane}$ form solid solutions and so $n\text{-C}_{32}\text{H}_{66}$, and quite likely $n\text{-C}_{28}\text{H}_{58}$ as well, would also be expected to do so. These same authors also examined mixtures of $n\text{-C}_{20}\text{H}_{42}$ in $n\text{-C}_{30}\text{H}_{62}$ and found that, in this instance, only a mixture of discrete $\text{C}_{20}\text{H}_{42}$ and $\text{C}_{30}\text{H}_{62}$ crystals resulted. Here the chain lengths are substantially different. In regard to this latter observation, it is of interest to note that no linewidth or yield effects were evident when $n\text{-tetracosane}$ was added to hexatriacontane (Table VI, p 130). Such a result is in accord with the idea of crystallization into individual components in this system.

The possibility that impurities in the additive might be responsible for the linewidth and yield effects in the doped hexatriacontane samples needs to be examined. Reference to Table III (p 46) reveals that dotriacontane and octacosane are the least pure of the alkane samples and it is just these materials that produce the linewidth and yield effects. Furthermore, although the yield of trapped electrons in dotriacontane is nearly the same as that in additive-free hexatriacontane, the yield in $n\text{-octacosane}$ is very much lower. It is difficult, though, to see how an impurity which serves to inhibit the trapping of electrons in $n\text{-octacosane}$ could also serve to enhance the yield when this material is added in small amounts to $n\text{-hexatriacontane}$. Therefore, it does not

seem likely that impurities are responsible for the linewidth and yield effects observed in doped hexatriacontane.

Thus, many of the features of trapped electrons in n-hexatriacontane samples doped with shorter chain n-alkanes are explainable in terms of electron trapping in voids associated with row-vacancy defects. Since it is difficult to prepare long chain alkanes free of small amounts of shorter chain homologues, it seems quite conceivable that this mode of electron trapping may also be responsible for the fact that trapped electrons are observed in "pure" hexatriacontane, dotriacontane, etc. A similar conjecture also applies to a recent observation of trapped electrons in n-nonane, decane, and hexadecane.⁶⁸

The intent of this section has been to explore the possibility that electron trapping in voids, which is thought to be the mode of trapping in low molecular weight glassy systems, also occurs in polymers and in long chain n-alkanes. The overall similarity in spectral features of the trapped electron singlet in both polymers and alkane glasses suggests that this may indeed be the case. In terms of the void concept, the experimental results demand that the void be larger in polymers than in alkane glasses and, moreover, that it be associated with crystalline regions in the polymer. A specific type of void, namely a row-vacancy defect, has been suggested as the trapping site and, while admittedly highly speculative, this suggestion does derive support from the effects of short chain additives on trapped electron linewidths and yields in n-hexatriacontane.

On the other hand, one observation which does not seem to be in accord with the idea of trapping in a void is the evident inability of

amorphous polymers such as polyisobutylene and atactic polypropylene to trap significant numbers of electrons. High concentrations of voids certainly ought to occur in these materials owing to their disordered structure and one would expect a correspondingly high yield of trapped electrons. Such is not the case. It may well be that in order for an electron to be trapped in a void, the molecules forming the void boundary may be required to undergo some type of spatial displacement in order for the electron to be accommodated in the void. Indeed, some support for this idea follows from recent experiments involving pulse radiolysis of alkane glasses. The optical absorption band of the trapped electron is not observed immediately after the radiation pulse but requires some 10^{-7} sec to "grow in."¹¹⁴ This time lag may represent the time taken for motional reorganization of the void boundary to occur. If this is the case, then whatever molecular displacements are required to trap the electron would be expected to occur more rapidly and more easily in the case of alkane glasses than in polymers simply on the basis of mobility considerations. The mobility of a segment of a polymer chain is much lower than that of a small molecule.

Of course, if this line of reasoning is adopted to explain the failure of amorphous polymers to trap electrons, then one would need to postulate that voids in crystalline regions of polymers are already pre-formed, so to speak, such that relatively little if any molecular reorganization is required to trap the electron. The final word on the nature of the electron trap in polymeric systems is obviously yet to come and clearly, much more work on this problem is needed before definite conclusions can be reached. Hyperfine interaction of the trapped electron with surrounding

protons might possibly be resolved using ENDOR techniques. Such information could have an important bearing on this problem.

D. Thermal Decay of Trapped Electrons in Marlex 6050 Polyethylene

The results of several experiments in which the thermal decay of trapped electrons was investigated in Marlex 6050 polyethylene have been presented in Section B-5 of Chapter IV. The decay of the trapped electrons was seen to be complex and to depend on the manner in which the experiment was carried out. In one approach (see Figure 9, p 82), the temperature of a polyethylene sample was raised in 10° steps from 77°K to 127°K and the decay followed for about two hours at each of the temperatures 77° , 87° , 97° , 107° , 117° , and 127°K . The decay at each temperature was found to proceed by first-order kinetics with rate constants given in Table V (p 87). Furthermore, 16% of the original number of electrons appeared to decay each time the temperature was stepped upward by 10° . These considerations suggest that there are populations of trapped electrons relatively stable toward thermal decay until the temperature is raised to a point where they become vulnerable. Thus 16% of the electrons decay on standing at 77°K , 16% more decay on raising the temperature to 87°K , another 16% decay when the temperature is raised to 97°K , and so on. For convenience in the discussion to follow, the initial trapped electron concentration will be divided into six fractions each consisting of 16% of the initial concentration. That fraction vulnerable to decay at 77°K will be referred to as the 77° population, the fraction decaying at 87°K will be called the 87° population, and so on.

In a second series of experiments represented by the data of Figure 12 (p 90), the thermal decay of the trapped electron was studied isothermally for up to six hours at temperatures of 77°, 98°, and 118°K. In contrast to the stepwise warm-up experiment, the decay at 98°K and 118°K does not occur by a first-order process nor, for that matter, does it correspond to any simple kinetic order. Moreover, there is still a slow decay evident at long times which is not yet accounted for in terms of the simple picture of populations of electrons of varying thermal stability inferred from the results of the stepwise warm-up experiment.

Analysis of the 77°K data in Figure 12 (p 90) by the Guggenheim method indicates that in this instance, the decay over the initial two hour period does proceed by first-order kinetics with a rate constant virtually the same as that observed in the stepwise warm-up experiment also at 77°K. This observation suggests that the decay curves in Figure 12 may in fact represent composites of the decay of the 77° through 127° trapped electron populations, these populations decaying not necessarily with the rate constants derived from the stepwise warm-up experiment, but with rate constants characteristic of the actual temperature at which the decay takes place.

Proceeding on this assumption, the 77°K curve in Figure 12 (p 90) is interpreted as being the sum of the following decay processes: (1) a relatively rapid decay of the 16% of the trapped electrons comprising the 77°K population with a first-order rate constant given in Table V (p 87), and (2) a much slower decay of the 16% of trapped electrons comprising the 87° population. This latter decay is governed not by the rate constant given in Table V for the 87° fraction, but by a smaller

one corresponding to the fact that in this instance the decay occurs at 77°K and not 87°K. On this basis, the first-order contribution from the 77° population can be subtracted from the 77°K curve in Figure 12 (p 90). The decay curve remaining after this subtraction process is attributed to the 87° fraction and from it, a half-life of 400 min can be derived for decay of the 87° population at 77°K. This derivation assumes that 16% of the initial concentration of trapped electrons observed immediately after irradiation comprises the 87° population. From the value for the half-life of the 87° population, a first-order rate constant of $1.7 \times 10^{-3} \text{ min}^{-1}$ can be calculated for decay of the 87° population at 77°K. This value is to be compared with $k = 2.5 \times 10^{-2} \text{ min}^{-1}$ observed for the decay of the 87° population at 87°K in the stepwise warm-up experiment (Figure 9, p 82, and Table V, p 87).

From these two rate constants, a value of the activation energy for decay of the 87° population may be derived on the assumption that the rate constants are represented by the usual Arrhenius form:

$$k = A e^{-E_a/RT} \quad (5-1)$$

In Equation (5-1), k is the rate constant, A a frequency factor, E_a the activation energy, R the gas constant in $\text{cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$, and T the absolute temperature. Since two equations of the form of (5-1) result for the two values of k at 77 and 87°K, the value $E_a = 3.58 \text{ kcal/mole}$ is readily obtained assuming that A is temperature independent. Moreover, using this value of E_a for the 87° population, it is also possible to calculate activation energies for decay of the remaining populations of electrons if it is assumed that the frequency factor, A , is the same for

all populations. For example, E_a for the 77° population may be obtained from the equation

$$\frac{k_{77}}{k_{87}} = \frac{e^{-E_a/77R}}{e^{-3.58 \times 10^3/87R}} \quad (5-2)$$

where k_{77} and k_{87} are the first-order rate constants for thermal decay of the 77° and 87° populations at these same respective temperatures. These rate constants are tabulated in Table V (p 87). Activation energies for decay of the various populations obtained in this manner are given in Table VIII.

Knowing the activation energies, it is a simple matter to calculate first-order rate constants for thermal decay of any given trapped electron population at any temperature of interest from the Arrhenius expression. For example, k at 77°K for the 77° population is known to be $2.1 \times 10^{-2} \text{ min}^{-1}$ from Table V (p 87) and suppose k for this same population is desired at 117°K . This value may be found from the equation

$$k_{\text{at } 117^\circ} = 2.1 \times 10^{-2} \exp \left[\frac{3.2 \times 10^3}{R} \left(\frac{1}{117^\circ} - \frac{1}{77^\circ} \right) \right] \quad (5-3)$$

where A has again been taken as temperature independent. Values of k obtained in this fashion for the decay of the various populations at temperatures of interest are given in Table IX.

From the rate constants in Table IX, it is possible to synthesize trapped electron decay curves at any temperature of interest. For example, isothermal decay at 77°K results from the 77° population decaying with a rate constant of $2.1 \times 10^{-2} \text{ min}^{-1}$ and the 87° population with a rate constant of $1.7 \times 10^{-3} \text{ min}^{-1}$. The decay of the remaining populations is too slow at 77°K to make a measurable contribution at least over

TABLE VIII
ACTIVATION ENERGIES FOR THERMAL DECAY OF THE VARIOUS
TRAPPED ELECTRON POPULATIONS

Trapped Electron Population	Activation Energy (kcal/mole)
77° population	3.20
87° population	3.58
97° population	3.92
107° population	4.32
117° population	4.77
127° population	5.16

TABLE IX

RATE CONSTANTS FOR THERMAL DECAY OF THE DIFFERENT TRAPPED ELECTRON POPULATIONS AT VARIOUS TEMPERATURES

Electron Population	First Order Rate Constant, k (in min ⁻¹) for decay at					
	77°K	87°K	97°K	107°K	117°K	127°K
77° population	2.1 x 10 ⁻²	---	1.5	---	25.7	---
87° population	1.7 x 10 ⁻³	2.5 x 10 ⁻²	2.1 x 10 ⁻¹	---	4.9	---
97° population	2.0 x 10 ⁻⁴	---	3.7 x 10 ⁻²	---	0.97	---
107° population	---	---	4.4 x 10 ⁻³	3.6 x 10 ⁻²	0.20	---
117° population	---	---	4.5 x 10 ⁻⁴	---	3.0 x 10 ⁻²	---
127° population	---	---	---	---	5.5 x 10 ⁻³	3.3 x 10 ⁻²

a six hour interval. Likewise, curves for decay at 97°K and 117°K can be constructed by simply adding the contributions of the various trapped electron populations as reflected by the rate constant values in Table IX. In each instance, each population is assumed to consist of 16% of the initial number of trapped electrons observed immediately after irradiation. The trapped electron decay curves calculated on this basis are plotted as the solid lines in Figure 34. Experimental data from Figure 12 (p 90) are also plotted in Figure 34 for purposes of comparison. The agreement is seen to be quite satisfactory.

Thus, it is possible to account for the features of the thermal decay of the trapped electron in Marlex 6050 polyethylene in terms of a simple model consisting of various populations of trapped electrons which exhibit varying stability toward decay. This varying stability is governed by the different activation energies for decay. In this connection, it is of interest to note that the optical absorption band maximum in alkane glasses ($\lambda_{\text{max}} \sim 1650 \text{ nm}$)⁶³ corresponds to an energy of some 17 kcal/mole. Although the band maximum for trapped electrons in poly-(4-methylpentene-1) appears to be shifted to somewhat lower energies than this, it does not seem likely that the shift is so extensive that the band maximum corresponds to an energy very much lower than 17 kcal/mole. This value is significantly greater than the activation energies derived for thermal decay of trapped electrons in polyethylene which lie in the range of 3-5 kcal/mole (see Table VIII, p 153). Thus the decay of trapped electrons in polyethylene by thermal activation does not appear to involve the upper state reached in the optical transition. An activation energy of some 3-5 kcal/mole is not inconsistent with some type of

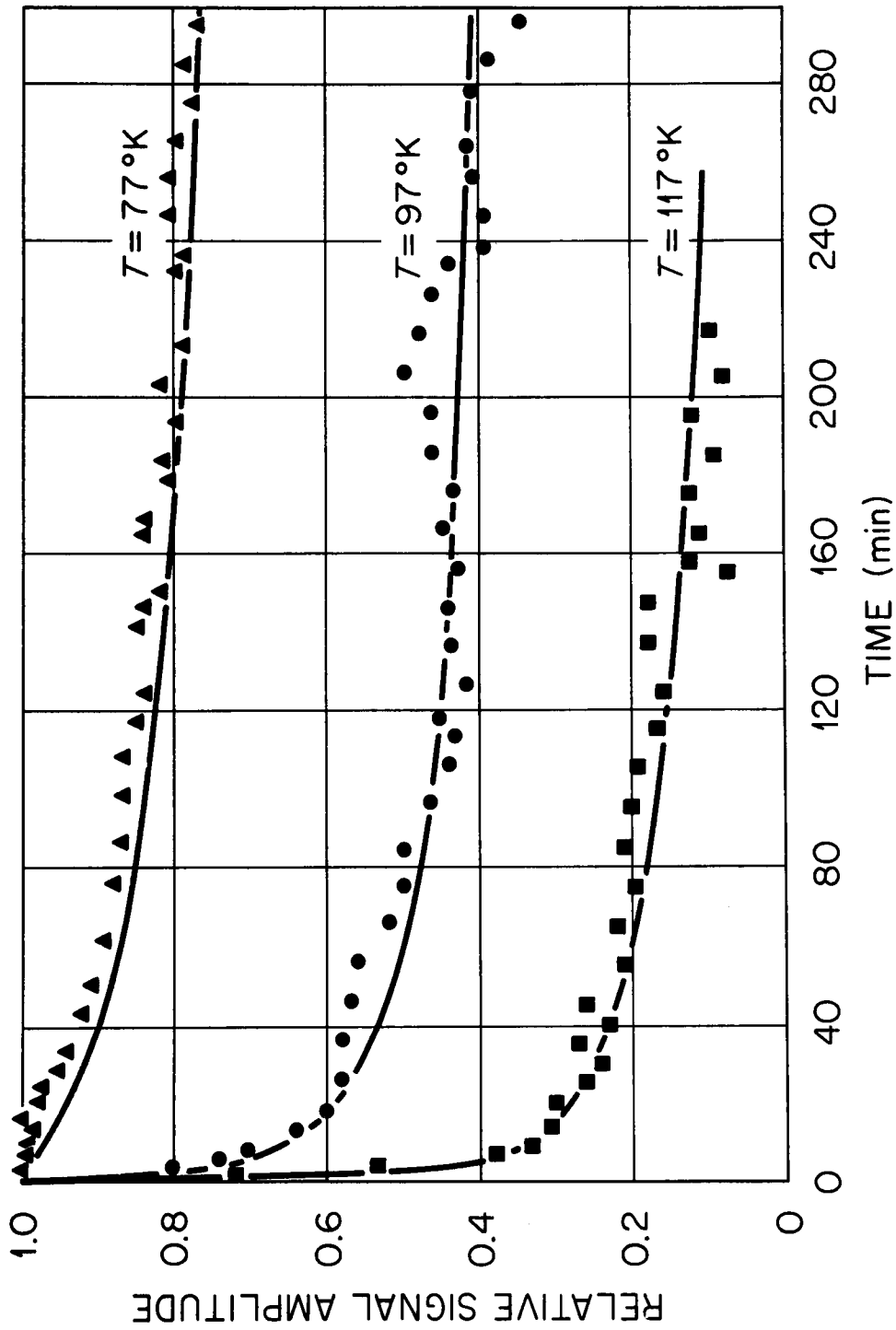


Figure 34. Comparison of calculated thermal decay with experimental results for the thermal decay of trapped electrons in Marlex 6050 polyethylene

Lines, calculated as described in the text; points, experimental data.

rotation about a C-C bond. Hence it is possible that the thermal decay results from some kind of molecular motion involving the surrounding environment of the trapped electron which causes the electron to become mobile. In this connection, the frequency factor, A, for the decay of the trapped electron in polyethylene has a value of 10^5 sec^{-1} . Such a value is reasonable for a complicated motion of a polymer chain. Bond vibrations correspond to frequencies of the order of 10^{13} sec^{-1} and rotations to 10^{11} sec^{-1} . Therefore a more complicated motion, perhaps of a torsional type, would be expected to take place at lower frequencies.

E. Influence of Free Radicals on Trapped Electron Yields

The results of several experiments designed to explore the possibility that free radicals produced by irradiation may influence trapped electron yields in polyethylene have been summarized in Section B-4 of Chapter IV. These experiments basically involved an initial irradiation of the sample followed by a photobleaching treatment to remove trapped electrons. The free radical concentration produced as a result of the initial irradiation was then adjusted either by means of a second irradiation, which produced additional free radicals, or by thermal annealing followed by a second irradiation. The thermal annealing treatment destroys free radicals produced by the first irradiation so that by varying the length of the annealing treatment in combination with the second irradiation, any desired free radical concentration can be produced. As a result of these experiments, it was noted that the yield of trapped electrons following the second irradiation was directly correlated with the concentration of free radicals, the trapped electron yield decreasing with increasing free radical concentration.

This correlation of trapped electron yield with free radical concentration implies that free radicals may scavenge electrons. Such a scavenging process can occur by two routes:



In these reactions, $R\cdot$ represents an alkyl free radical and R^- a carbanion resulting from electron capture by the free radical. The symbol (e_t^-) stands for a trapped electron and (e_m^-) for a mobile electron, i.e., an electron prior to being trapped. It has been pointed out¹¹⁵ that reactions of the type indicated by Equations (5-4) and (5-5) can be expected to be exothermic by about one ev or more as judged by analogy with the electron affinity of a methyl radical.

Experimental support for carbanion formation by either of reactions (5-4) and (5-5) has recently been obtained by Willard and co-workers.¹¹⁶ These authors observe an optical absorption in the neighborhood of 375 nm in γ -irradiated 3-methylpentane glass which they attribute to a carbanion formed as a result of electron capture by a 3-methylpentyl radical. Photobleaching of the trapped electron optical band in this matrix ($\lambda_{\max} \sim 1600$ nm) with light of $\lambda = 1400$ nm eliminates the optical band associated with trapped electrons and enhances the 375 nm absorption. Subsequent photobleaching with light of 375 nm wavelength reduces the intensity of the 375 nm absorption and restores a portion of the trapped electrons.

It thus appears that the presence of free radicals can influence trapped electron yields as a result of the scavenging processes

represented by reactions (5-4) and (5-5). In fact reaction (5-5) provides a means to account for the rather curious decrease in trapped electron concentration observed in polyethylene, the isotactic forms of polypropylene and poly(4-methylpentene-1), and n-hexatriacontane at high irradiation doses. A similar decrease has also been observed in alkane glasses so the effect seems to be quite general. (A previous suggestion⁹⁸ that the decrease in trapped electron concentration in alkane glasses results from reaction of hydrogen atoms with trapped electrons to form hydride ions has now been shown to be untenable.¹¹⁶)

On the assumptions (1) that the matrix contains only a limited number of trapping sites and (2) that a carbanion formed by reaction (5-5) occupies the trap in such a manner that further trapping is precluded on the basis of coulombic repulsion, then reaction (5-5) would be expected to become competitive with the trapping of electrons at irradiation doses large enough to generate significant numbers of free radicals. Further increase in irradiation dose should result in the competition being heavily in favor of reaction (5-5) and the trapped electron concentration should then decrease. It is well to note, however, that for this to happen, it is necessary to postulate either that free radicals have sufficient mobility in solid polymers so as to enable them to encounter trapped electrons, or else that the mechanism of energy deposition in the material is such that free radicals are formed in close proximity to electrons which have already been trapped. The former situation seems unlikely in view of the fact that free radicals in the polymers studied here are thermally stable at 77°K. Finally, it should be pointed out that reaction (5-4) cannot lead to a decrease in trapped electron

concentration at high doses. The competition in this instance is for electrons which have not yet been trapped so that when the dose is sufficiently large that all (e_m^-) are scavenged by $R\cdot$, the trapped electron concentration will have reached a plateau independent of dose.

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PUBLICATIONS RESULTING FROM THIS DISSERTATION

1. Characterization of Trapped Electrons in γ -Irradiated Hydrocarbon Polymers by Electron Spin Resonance and Optical Absorption Spectroscopy (with Ff. Williams), J. Phys. Chem., 73, 1623 (1969).
2. Trapped Electrons in γ -Irradiated Polyethylene Identified by Electron Spin Resonance Spectroscopy (with K. Tsuji and Ff. Williams), Macromolecules, 1, 289 (1968).
3. Trapped Electrons in γ -Irradiated Polyethylene and Hydrocarbon Glasses (with J. Lin, K. Tsuji, and Ff. Williams), Polymer Preprints, 9, 277 (1968).