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PHOTODEGRADATION OF POLYVINYLCHLORIDE

by

JOHN J. LIUTKUS

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Abstract

PHOTODEGRADATION OF POLYVINYLCHLORIDE

by

John J. Liutkus

Advisors: Professors Nan-Loh Yang and Howard Haubenstock

The behavior of polyvinylchloride (PVC) under ultraviolet irradiation was investigated by electron spin resonance spectroscopy (ESR). Various polymers of vinyl chloride were prepared to observe the effect of physiochemical properties on photodegradation, and to eliminate impurity effects often found on use of commercial samples. Polyvinylbromide and copolymers of vinyl chloride/vinyl bromide were also prepared as polymer analogs for PVC. In addition, low molecular weight halocarbons, and specifically deuterated samples were synthesized to aid in the analysis of ESR spectra.

It was determined that little new information could be gained from the poorly resolved ESR spectra obtained from irradiated polymer films and powders. Use of a polymer 'glass' system (solutions below T_m) markedly improved the resolution. Photodegradation of PVC glasses at liquid nitrogen temperature produced a sextet absorption in the ESR, which is attributed to the $-CH_2-\dot{C}H-CH_2-$ radical. A similar sextet was obtained for 3-chloropentane under the same conditions, and assigned to the $H_3C-CH_2-\dot{C}H-CH_2-CH_3$ radical. These radicals have never been identified by ESR in the degradation of the above compounds.

The effect of alpha deuteration on the observed spectra was negligible. This and other results led to the proposal of an isotopic exchange process between the radical and adjacent molecules.

On warming to $-110^{o}C$, the sextet converted to a quintet. This change suggested the assignment of another radical in the PVC photodegradation process, $-CH_2-\underset{\bullet}{C}Cl-CH_2-$.

Although allylic structures have often been proposed for PVC degradation, none could be detected in this work. However, an allylic radical was observed at $-145^{o}C$ ($H_2\dot{C}-CH=CH-CH_2-CH_3$) for 3-chloropentane irradiated by ultraviolet light at $-196^{o}C$.

ACKNOWLEDGEMENT

The author expresses gratitude to his parents, Stasys and Ona Liutkus, who constantly urged him to further his education. Sincere appreciation is extended to Drs. Nan-Loh Yang and Howard Haubenstock, without whose assistance this project could not have been completed.

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I. INTRODUCTION

Polyvinylchloride (PVC) is one of the most widely used thermoplastic materials because of its high chemical resistance, comparatively low cost, and wide variety of applications. In spite of these advantages, the even wider application of this polymer has been restricted by its low thermal and photochemical stability. The photochemical instability places a limit on the extent of outdoor applications that can be developed. Therefore, a knowledge of the photodegradation process in PVC would be highly desirable in protecting the material against light. In addition, the recent link between vinyl chloride (VC), a possible degradation product, and angiosarcoma, a form of cancer, has been established (1). This link has severely limited the use of PVC in the food packaging industry, and spurred efforts of researchers to re-evaluate their findings on degradation products of PVC.

Both ionizing and photodegradation of PVC have been shown to follow a similar radical chain mechanism (2) leading to a conjugated polyene and HCl as main degradation products (3). The reaction may be written:

$$-(CH_2-CHCl)_n- \xrightarrow{h\nu} -(CH=CH)_n- + nHCl$$

where n is usually 5-10 (3). However, no specific radical species has yet been identified as intermediate between the polymer and polyene. This has severely limited an understanding of the degradation mechanism.

On evaluating the literature of PVC degradation, two major problems were found to recur. Primarily, the use of commercial samples was widespread. Aside from inherent impurities, these materials varied widely in their polymerization and processing history. This made correlation of results quite difficult. In this work, PVC was prepared and characterized by the author. Therefore, comparisons can be drawn from among these polymers, which will have a broad spectrum of properties.

The second problem encountered in establishing the identity of initially formed PVC radicals was the lack of resolution in the low temperature ESR spectra. Low temperature studies are quite important, since initially formed radicals disappear on warming to room temperature (RT). The cause of poor resolution can be threefold. There may be more than one radical present, leading to overlap of ESR absorptions. Dipolar broadening is also probable, due to the inhomogenous environment of the unpaired electrons in the solid samples (low local mobility). Since the PVC samples that had been studied were in the form of powders or films, spin-spin broadening phenomena, caused by proximity of the free radicals, may also occur.

The last two effects can be minimized by using a PVC-solvent system (a glass) for the low temperature degradation. A polymer glass can be formed by solvating the chains, then rapidly freezing the solution, usually at liquid nitrogen temperature (LNT). This procedure allows the free radicals formed a more homogenous environment, and seperates them. The result is enhanced resolution in the ESR spectra.

This technique has only been employed once before for PVC (4) with inconclusive results. It has never been used for the UV degradation of PVC. The reason that so few researchers have used a glass system, for any polymer, was that the selection of solvent was most critical. Three main parameters must be considered: UV absorption; freezing point; and ESR absorption.

No perfect solvent system was found for these PVC-glasses, but results using tetrahydrofuran, p-dioxane, and tetrahydropyran were most encouraging. At LNT (-196°C), UV degraded PVC glasses exhibited a well resolved, symmetrical six line absorption in the ESR. The hyperfine splitting, ΔH, varied from 21-24G, but averaged 23G. This absorption has never been observed for irradiated PVC (UV or gamma ray) although its existence had been postulated (5). On warming to about -110°C, the sextet changed to a narrower (ΔH = 19G) and less intense five line absorption. Similar results were obtained for polyvinylbromide (PVB) and its copolymer with PVC (COP) when subjected to the same conditions. The analysis of the spectra will be presented in the Discussion.

Low molecular weight halocarbons, analogs of PVC, were prepared and irradiated under the same conditions as the polymer. The ESR spectra that resulted were very similar to those from PVC. As further evidence for the identity of radicals formed on irradiation, selectively deuterated PVC samples were prepared, as were deuterated PVC analogs. Surprisingly, the ESR spectra of irradiated deuterated samples were quite similar to the undeuterated ones. Since deuteration was performed to eliminate one or more absorptions in the spectra, the results were unexpected. However, an explanation of this phenomena could well be a proposed radical isotope exchange reaction that occurs even at LNT (6) (7) (8).

To correlate conformations of the PVC radical with its observed hyperfine splitting, computer simulation of the ESR spectra was employed. The resultant theoretical spectra closely resembled those from experiment. These studies strongly indicated that the methylenic protons were equivalent in the PVC radical at LNT, and that their dihedral angle to the p orbital of the unpaired electron was 30°. These results have provided strong evidence for the formation of $-CH_2-\underset{\bullet}{C}H-CH_2-$ as the radical formed on UV irradiation at LNT.

II. LITERATURE SURVEY

The degradation of PVC falls into five main categories: chemical; mechanical; thermal; ionizing; and photochemical. This survey will concern itself chiefly with photodegradation, but analogies drawn from thermal and ionizing degradation may be appropriate, since both take the form of a dehydrochlorination reaction which leads to a discolored polyene product. While photodegradation of PVC has been extensively studied, the mechanism of degradation has not been resolved, and the initiation step is especially elusive. No published data is available for PVB or COP in this area.

The earliest detailed investigations were performed by Kenyon (9), Druesdow (10), and Scarbrough (11) in 1953. Kenyon found that while a PVC analog, 2-chlorobutane, was stable to UV radiation down to 220 nm, PVC could be degraded by wavelengths as high as 300 nm. He proposed that the lower energy for PVC degradation was caused by the presence of carbonyl impurities in the commercial polymer. Druesdow was the first to suggest that PVC photodegradation followed a radical chain mechanism. He proposed that the mechanism involved a labile allylic chloride structure, $-CH=CH-CHCl-$, which led to dehydrochlorination of the polymer.

Scarbrough performed spectroscopic UV analyses on photodegraded PVC and concluded that the end product of this degradation involved a conjugated polyene structure, $-(CH=CH)-_n$.

In 1958, Bersch (12) reported five to six photodegradation products of PVC. These findings were refuted by Reinisch (13) in 1966 by use of a more sensitive mass spectrometer, 10^{-12} mole with 10^{-4} second scan time. He proposed that the only degradation product of PVC was HCl. Currently, the search for degradation products of PVC has intensified, since the presence of vinyl chloride (recently discovered to be carcinogenic) could severely limit many applications of the polymer.

Winkler (14) provided evidence for the radical chain degradation mechanism, observing that many good stabilizers for PVC also had the ability to interfere with radical chain reactions. He also suggested that labile sites in PVC may include tertiary structures and catalyst residues at polymer chain ends.

PVC has been irradiated by specific wavelengths in the range 200 to 340 nm. The purpose was to find a wavelength, and possibly a chromophore, most effective in its degradation (9) (13)(15) (16). Results varied widely, probably due to the many different types of PVC used. In addition, it was found that while pure PVC had no significant absorption above 260 nm, it could be degraded by UV radiation of much longer wavelengths.

PVC has also been irradiated under various atmospheres. The most significant conclusions can be drawn from O_2 (or air), N_2, and vacuum. Dehydrochlorination has been found to be about three times faster for PVC degraded under O_2 than the case for N_2 or under vacuum (17) (18). On UV irradiation, the initial effect of oxygen is to slow down further dehydrochlorination by reacting with the excited state of short polyene structures. However, the accumulation of reactive UV absorbers, such as peroxides and carbonyl groups, will eventually act to speed up the degradation process.

The definitive work on polyene structure and formation was performed by Mitani (3). He found that the average length of polyenes increased with increasing syndiotacticity of PVC, but that short polyenes (n=3-6) predominate in the degraded polymer. UV absorption bands (λ_{max}) for polyenes with n=3,4,5,6 are 285, 312, 329, and 345 nm respectively, progressing into the visible region for sequences of seven and above.

The ESR spectra of irradiated PVC measured at room temperature (RT) is a weak singlet, ΔH_{msl}=25G, regardless if the irradiation was at RT or LNT (19) (20) (21). This singlet has been thoroughly analyzed, and attributed to the polyenyl radical $-(CH{=}CH)_n-\dot{C}H-$. Larger values of n lead to a decrease in ΔH_{msl} due to an increased delocalization of the electron onto the conjugated system (22). On exposure to air, the ESR spectrum of the polyenyl radical changes to an unsymmetrical singlet with a high g-value, due to a peroxy radical (23) (24).

Little information is available on PVC photodegraded and measured at LNT (19) (20) (25). The available ESR spectra have overall widths of about 180 G, but are poorly resolved. The radical responsible for the absorption at LNT is probably the initial radical formed during PVC photodegradation. Its identification would be valuable in formulating a degradation mechanism and would also be a guide to selecting more effective stabilizers for the polymer. No such identification has yet been accomplished.

Commercially produced PVC exhibits a T_g of about 80°C (26). During processing, and often in use, it is subjected to elevated temperatures which can cause thermal degradation. This type of degradation for PVC is generally accepted as a two step process (27) (28). In the first stage, up to 400°C, dehydrochlorination is the chief reaction. The second stage, above 400°C, involves decomposition of the polymer to smaller molecules. Thermal studies are usually performed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The mechanism of this degradation is unknown, but since the product of the first stage dehydrochlorination involves a conjugated polyene radical (27), a free radical mechanism may be possible (29). Many attempts were made to identify the thermal degradation products of PVC, especially in the case of vinyl chloride. Results were found to vary widely. Dodson (30) reported only HCl as a degradation product.

Boettner (31) found fifty nine degradation products, including vinyl chloride. Therefore, the thermal degradation of PVC is still a matter of much controversy.

Degradation of PVC by ionizing radiation has been most widely employed. This was due to the ease of dehydrochlorination of PVC while subjected to such ionizing sources as cobalt-60, x-rays and electron beams. A dose of 50 Mrad of gamma radiation was found to have an effect on PVC similar to 5 hours of UV radiation (3.2×10^{15} quanta/cm^2/sec.) (17). However, this ease of degradation is coupled with non selectivity of bond cleavage. The energy associated with UV radiation in the 200 to 350 nm range is 150 to 50 Kcal/mole respectively. This energy is on the order of most organic bond strengths, usually leading to preferential cleavage of the weaker ones. Ionizing radiation is of much higher energy, 10^4-10^{10} Kcal/mole, causing bond scission at random. Ionizing radiation forms radicals in PVC at LNT (5)(43) and RT (22)(44). Since dehydrochlorination results, along with a polyene product, the degradation mechanism is assumed to be similar to that of photodegradation. However, the ESR spectra are more complex due to the probability of a variety of radicals formed by the ionizing radiation. Therefore, only the RT radicals have been identified (22) and ascribed to the same polyene radical found in the thermal and photodegradation studies.

III. ELECTRON SPIN RESONANCE

Since this research is primarily concerned with saturated alkyl radicals, the types of ESR interactions to be expected can be somewhat simplified. Several excellent references are available for general ESR theory (32)(33). The observed splittings were due to hydrogen or deuterium in the alpha or beta positions, and were presented as first derivative absorptions. Therefore, the peak of a normal absorption would correspond to the region of maximum slope on a first derivative ESR spectrum.

The simplest system is the hydrogen radical, a proton and an electron. The magnetic interaction between the electron and the nuclear spin of the proton gives rise to a doublet ESR absorption. This type of interaction is called hyperfine coupling and produces ESR spectra with hyperfine splitting (ΔH), measured in units of magnetic strength (gauss). In an applied external magnetic field, the magnetic moment of the proton has two possible orientations, +1/2 and -1/2, which affect the magnetic energy levels of the electron. The allowed transitions between these energy levels give rise to two absorptions in the ESR spectrum. In general, an electron interacting with a nucleus of spin=I will give rise to $2I + 1$ absorptions in the ESR.

Since the electron in a hydrogen radical is located in an s orbital, there is a possibility of finite electron spin density located directly at the nucleus. This is called Fermi contact interaction, and greatly affects the electron's transitions when the external field is applied. This interaction, along with the large magnetic moment of hydrogen gives it a hyperfine splitting larger than for any organic radical, 507 gauss.

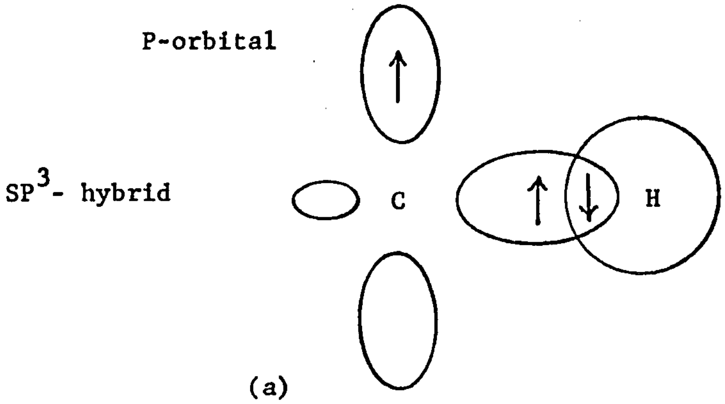
The deuterium radical has a nuclear spin of 1; this leads to a triplet absorption in the ESR. The magnetic moment of a deuteron is 15% that of a proton. Since magnetic moment is directly proportional to hyperfine splitting (34), the hyperfine splitting of a deuterium radical will be 507 x 0.15 or 77 gauss. When deuterium is substituted for hydrogen in a radical, the splitting caused by that hydrogen is also diminished by a factor of 0.15 and is usually too small to be detected. This substitution effectively 'erases' the splitting caused by that hydrogen.

In the case of alkyl radicals, the unpaired electron is localized in a p orbital on a carbon atom. Since carbon-12 has zero nuclear spin, it cannot affect absorptions in the ESR. The hyperfine splitting occurs by interaction of the unpaired electron with alpha or beta protons (gamma protons have a negligible contribution).

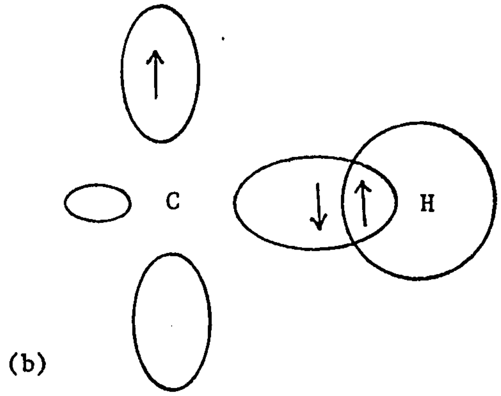
The alpha protons cause hyperfine splitting via spin polarization, an indirect interaction. Alkyl radicals are generally planar with the electron in the carbon's 2p orbital and the alpha proton(s) in the nodal plane of this orbital. No simple mixing with the hydrogen 1s orbital is possible, but indirect mixing does occur. With reference to a single C-H fragment (Figure 1), the electron in the carbon's sp^2 orbital may have either the same (A) or opposite (B) spin to the unpaired electron in the p orbital. If no electron were in this orbital, (A) and (B) would be equally probable. But, by analogy to Hund's rule, electrons enter equivalent orbitals with parallel spins, (A) is favored by lower energy over (B). Therefore, the 1s hydrogen orbital will have a net spin density, and can contribute to hyperfine splitting. Spin polarization from alpha protons is quantified by $\Delta H = Q\rho$ (35), where Q is a constant from theoretical considerations, and ρ is the unpaired spin density on the alpha carbon. Spin polarization effects vary little among alkyl radicals, and a fairly constant value for hyperfine splitting (21-23G) is observed.

For saturated alkyl radicals, the beta protons interact directly with the unpaired electron via hyperconjugation. The 2p orbital on the alpha car-

Figure 1. Spin Polarization



More Probable



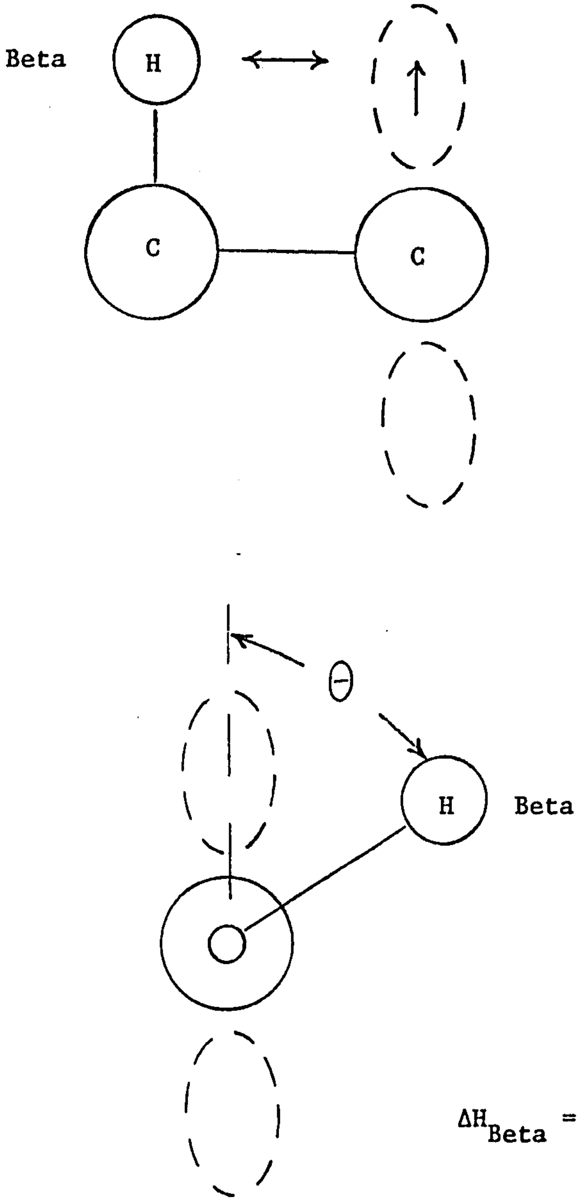
Less Probable

bon (bearing the unpaired electron) can overlap with the sp^3 hybrids on the beta carbon. This leads to delocalization of unpaired spin density into the beta hydrogen's 1s orbital (Figure 2). The hyperfine splitting caused by this overlap is strongly dependent on the dihedral angle Θ, between the alpha p orbital and the beta sp^3 hybrid. This effect has been quantified by Mc Connell (36): $\Delta H_\beta=(A+B \cos^2\Theta)\rho$, where A and B are experimentally derived constants, and ρ is the unpaired electron spin density on the alpha carbon.

If hyperconjugation were the sole mechanism for delocalization of spin density onto beta protons, then the hyperfine splitting should be zero when $\Theta=90^\circ$. However, in some cases (37), a small residual coupling in seen and this necessitates the use of the constant A. These two constants can vary signficantly from system to system: A=0-5G and B=40-50G (37)(38). As yet, no rule has been established regarding their use.

McConnell had assumed that ρ was equal to 1.00, with a variation of 0.01 to 0.10, for organic radicals. Therefore, he simplified the relationship to $A + B \cos^2\Theta$. This is the form that most researchers have employed in their calculations of hyperfine splitting. However, recent investigations, (35) have shown that the unpaired spin density on the alpha carbon can vary widely. For the methyl, ethyl, isopropyl, and t-butyl radicals, the respective spin densities are: 1.000; 0.919; 0.844; and 0.776. Use of these values in the original Mc Connell relationship will significantly alter the calculated hyperfine splitting of analagous radicals.

Figure 2. Hyperconjugation



$$\Delta H_{Beta} = (A + B\cos^2\theta)\rho$$

IV. PREPARATION OF POLYMERS

1. Materials

Vinyl chloride, 99.95%, and vinyl bromide, 99.84%, were obtained from Matheson Gas Co. (N.J.). Quoted impurities were (for vinyl chloride): acetylene 0-2 ppm; phenol 28-89 ppm; and water 0.002-0.01%. For vinyl bromide, the impurities were: phenol at 395 ppm and water at 150 ppm. The monomers were purified by bubbling through a 1% w/v KOH solution, and passing through a #4 mesh calcinated $CaCl_2$ drying tube (apparatus pre-flushed with nitrogen). AIBN (2,2'-azobis-(2-methylpropionitrile)) was supplied by Polysciences Inc. (N.J.) and purified by three recrystallizations from absolute ethanol. It absorbs strongly in the UV from 350 to 200 nm, and was stored in the dark under dessication at $-20^{o}C$. Uranyl nitrate, certified grade, was provided by Fisher Chemicals (N.J.). It absorbs moderately from 480 to 380 nm in the visible region and was stored in the dark at room temperature. Tetrahydrofuran, ultra high purity, was obtained from Burdick & Jackson Labs (Mich.), and was stored in the dark under nitrogen.

2. Polyvinylchloride

All PVC samples were prepared as powders in bulk using free radical photoinitiation. The vinyl chloride monomer was liquified directly into an evacuated borosilicate polymerization tube containing a micro magnetic stirrer and either AIBN or uranyl nitrate in absolute ethanol as initiators.

The AIBN/UV initiation was used for photopolymerization at temperatures of 50^{o}, 25^{o}, and $0^{o}C$ using a 200W Hg-Xe lamp. The AIBN initiator was not suitable for low temperature polymerization due to long induction times. Therefore, a uranyl nitrate/absolute ethanol initiation system with visible light source, 500W tungsten lamp, was used for polymerization at -78°C (45). This system was also used at higher polymerization temperatures for comparison with PVC samples prepared by AIBN/UV initiation.

Although it had been suggested (45) that the use of UV initiation might cause degradation during polymerization, no such evidence was found. The UV absorbance at 260 nm and the IR absorbance at 1630 cm^{-1}, indicative of unsaturated structures, were clear for the polymer films and solutions.

After liquification of the monomer was completed, the resultant solution, either with AIBN or uranyl nitrate in absolute ethanol, was degassed by freezing in liquid nitrogen and thawing at -78°C. Two types of vacuum systems were employed for degassing. The first used mechanical pumping along with a mercury diffusion pump (10^{-6}-10^{-5} torr). The second used mechanical pumping alone (10^{-4}-10^{-3} torr). Since no difference in polymers produced by either method could be determined spectroscopically, mechanical degassing was used for later preparations.

After degassing, the polymerization tubes were sealed under vacuum, and irradiated. Induction periods ranged from zero to two hours for polymerization temperatures of 50° and -78°C respectively. Since vinyl chloride is a poor solvent for PVC, after induction cloudiness occurred, and shortly thereafter a precipitate formed. The tube was then opened and unreacted vinyl chloride was vented in a hood. The polymer was washed thoroughly with absolute ethanol and distilled water to remove any traces of unreacted initiator.

Fifteen PVC samples were prepared via the above method, and stored under vacuum/dessication in the dark at RT. The most important variables were polymerization temperature and % conversion. Initiator concentration was not an important factor since chain transfer to monomer is the controlling factor in determining the molecular weight of the polymer (46). For PVC, a decrease in irradiation time will cause a decrease in % conversion. This will minimize branching since the branching mechanism involves chain transfer to polymer (45) (47). Conversions of less than 10% were shown to preclude branching in bulk polymerized vinyl chloride at -10^{o} to -30^{o}C (48). The polymers prepared in this work were kept below 10% conversion, allowing polymerization temperature to be the controlling factor for branching. Decreasing the polymerization temperature will decrease branching (47) (49), increase molecular weight (50), and increase crystallinity (51) (52).

The typical polymerization conditions (e.g. for PVC #14) were: 35 mg AIBN/45 ml VC; one hour of UV irradiation; and polymerization temperature 50^{o}C. Induction time was zero, and the yield was 3.5 grams or 8% conversion.

3. Polyvinylbromide

Polyvinylbromide was prepared in bulk using the same methods as for PVC. Polyvinylbromide is considerably less stable than PVC (53). Two samples prepared using AIBN/UV initiation were found to be degraded on polymerization (color: yellow-brown). Use of the uranyl nitrate/visible initiation eliminated degradation during polymerization. Unfortunately, the range of polymerization temperatures available was severely limited. Polyvinylbromide has been known to start degrading at 35^{o}C (54), and the long induction times (2-5 hours at RT) precluded polymerization at low temperatures.

The typical polymerization conditions (e.g. for PVB #4) were: 35 and VB; 0.4 g uranyl nitrate in 15 ml absolute ethanol; irradiation time 27 hours visible light; and polymerization temperature 25^{o}C. Induction time was five hours and yield was 9.8 grams or 20% conversion. In addition, since several previous PVB samples had degraded even under vacuum/dessication in the dark at RT, the polymers were stored in a dark dessicator at -20^{o}C.

4. Copolymers

Eleven copolymers of vinyl chloride-vinyl bromide were prepared in bulk using the same conditions as for preparation of PVC. Use of AIBN/UV initiation was found to degrade several of these copolymers, therefore later preparations employed the uranyl nitrate/visible light system. The ratio of VC/VB was varied from 1.5 to 10 (V/V). Since the copolymers with a high VB content exhibited poor stability at RT, later preparations used a higher VC/VB ratio.

The typical polymerization conditions (e.g. for Copolymer #11) were: 60 ml VC/6 ml VB; 0.75 g uranyl nitrate in 30 ml absolute ethanol; irradiation time 2 hours of 500W visible light; and polymerization time 25^{o}C. Induction time was one hour and yield was 3.1 g or 6% conversion. These copolymers were also stored in a dark dessicator at -20^{o}C.

5. Polymer Films

As previously mentioned, all the polymers precipitated from the monomers; after washing and drying under vacuum, they were in the form of white powders. Films were cast from 5% w/v solutions using tetrahydrofuran as solvent. Films from polymers prepared at low temperatures were brittle and translucent, indicating high crystallinity. The films from polymers prepared at higher temperatures (above 0°C) were clear and flexible. In addition, films of COP and PVB were more brittle than those of PVC prepared at corresponding temperatures. This suggests that substitution of a bromine for a chlorine increases the crystallinity of these polymers. Films were stored under the same conditions as their corresponding powders.

V. CHARACTERIZATION OF POLYMERS

1. Ultraviolet and Infrared Spectra

Ultraviolet spectra of polymer solutions, analogs, and solvents were obtained using a Cary-118 UV-visible spectrophotometer. These samples exhibited spectra similar to those of solid absorption filters; there was only a slight absorption before 'cut off' was reached. Therefore, a term analogous to 'cut off' will be used to describe the above spectra. The effective wavelength (λeff) will be defined as the wavelength at which 99% of the incident radiation is absorbed by the sample. Polymer solutions varied from 5 to 15% w/v; in this range λ eff was found to be constant. None of the polymer solutions showed significant absorbance above 260 nm. This indicated absence of carbonyl groups (λ_{max}=280nm) or short conjugated unsaturation (λmax=260-290 nm) due to degradation during polymerization.

The effective wavelength increased with increasing amount of carbon-bromine bonds in the polymer. Typical values were: 215 nm for PVC; 220 nm for COP; and 225-230 nm for PVB. Chloro analogs: 2-chloro-2-methylpropane; 1-chlorobutane; 3-chloropentane; and 1-chloropentane gave values similar to those for PVC, 215-220 nm. Bromo analogs, 1-bromooctadecane & 1-bromopentane showed the same λ eff as PVB. These results indicate that a greater amount of UV radiation will be absorbed by PVB; less by COP; and least by PVC.

Infrared was also used to detect carbonyl, conjugated, and allylic impurities. The carbonyl absorption (1725 cm^{-1}), conjugated unsaturation (1975-1950 cm^{-1}), and allylic absorption (1680-1600 cm^{-1}) were all absent in the spectra of the polymers. The four strongest absorptions for residual vinyl chloride appear at 1610, 1030, 910, and 720 cm^{-1} in the IR. No such bands were observed, indicating absence of the monomer in the polymer.

Quantitative tacticity was not determined for the polymers since, as will be noted later, the effect of this factor could not be readily correlated with degradation behavior. Isotactic methylenic groups in PVC absorb at 1434 cm^{-1}, while syndiotactic ones absorb at 1434 and 1428 cm^{-1} (55). Thus, absorptions at 1428 cm^{-1} can be used as a qualitative guide to the amount of syndiotacticity. All the PVC samples showed intense absorption at this wavelength, indicating a high degree of syndiotacticity. Reported values are listed as 54 to 77% for PVC polymerized at 50° to -75°C respectively (49).

The use of infrared to determine branch content in PVC was also attempted. While the procedure was complex and lengthy, it was found (Section VIII, 1, B) that no correlation of branching with degradation at LNT could be found. The method used (56) involved $LiAlH_4$ reduction of the polymer and construction of a calibration curve for compounds of known branch content. The reduced PVC's IR absorption at 1378 cm^{-1} (CH_3) and 1370 cm^{-1} (CH_2) were then compared to the calibration curve and branch content determined. Reported values ranged from 2.0 to 0 CH_3/1000 CH_2 for PVC samples prepared at 50° to -75°C respectively (49).

2. Thermal Analysis

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on representative polymers. DSC measures the energy difference supplied between an unreactive reference material and the sample, while maintaining a constant heating rate for both. TGA measures the weight loss of a sample as a function of temperature. Correlations between the two methods can give information on glass transition, degradation, and decomposition temperatures of a polymer.

The glass transition temperature (Tg) of PVC can vary widely, from 65° to 100°C, depending on polymerization temperature, 130° to -80°C respectively (57). Unfortunately, the deflection on a DSC curve that corresponds to Tg was slight for PVC, and could not be accurately determined for the various polymers.

The degradation of PVC involves a loss of HCl, which should produce a corresponding loss of weight in the polymer. Figures 3 and 4 show TGA's with a smooth weight loss curve for both PVC and PVB, corresponding to dehydrochlorination and dehydrobromination. The degradation temperature is taken as the point of maximum slope, and is 262° and 220°C respectively for the two polymers. Decomposition to low molecular weight compounds occur at higher temperatures, and is responsible for further weight loss. Figure 5 shows an endothermic DSC peak for PVC at 270°C, which compares favorably with the TGA degradation temperature. Two areas of decomposition are noted, one at 315° and another at 405°C.

A further use was made of TGA. A smooth transition, weight loss, indicates a steady rate of dehydrohalogenation, as was noted for PVC and PVB. If the prepared copolymer had random placement of monomers, a smooth transition should be observed. If, however, it were a block copolymer, two regions of degradation would be seen, one for dehydrobromination (at a lower temperature) and one for dehydrochlorination (at a higher temperature). A model for a block copolymer was prepared by physically mixing PVC and PVB (3/1, w/w). The TGA (Figure 6B) has two transitions, as expected. The copolymer (6A) shows only one transition, indicating random placement of the monomers.

3. Molecular Weight

Viscosity average molecular weights (M_v) were determined for representative polymers using a Cannon-Fenske capillary viscometer and cyclohexanone as solvent. Temperature was maintained at 25.00°C ($\pm$ 0.02°) by a Lauda K2/RD temperature bath. Timing and repeat readings were performed by a photoelectric attachment combined with an automatic recording viscometer. Five readings were used for each concentration: 0.25; 0.50; 0.75; and 1.00 g/dl.

Intrinsic viscosities were calculated using the graphical intercept method (46) and were determined to be 0.687, 0.655, and 0.104 (dl/g) for PVC #14, COP #11, and PVB #4 respectively. Use of the Mark-Houwink equation, $\{\eta\} = K\,M_v^a$, where $K = 2.4 \times 10^{-4}$ and $a = 0.77$ (58) allowed determination of M_v . The molecular weights were found to be: 31,000; 28,900; and 2,700 for PVC #14, COP #11, and PVB #4 respectively. Since polymerization temperatures for COP #11 and PVB #4 were the same, the large difference in molecular weights must be due to other factors. Recently, it has been suggested that vinyl bromide acts as a powerful chain transfer agent (53), thus limiting the molecular weight of PVB.

DU PONT INSTRUMENTS

SAMPLE: PVC # 14

SIZE 9.4 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2.0 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 0 mg.

RUN NO. DATE 6/21/74

OPERATOR J.L.

HEATING RATE 10 °C/min.

ATM. N_2

TIME CONSTANT 1.0 sec.

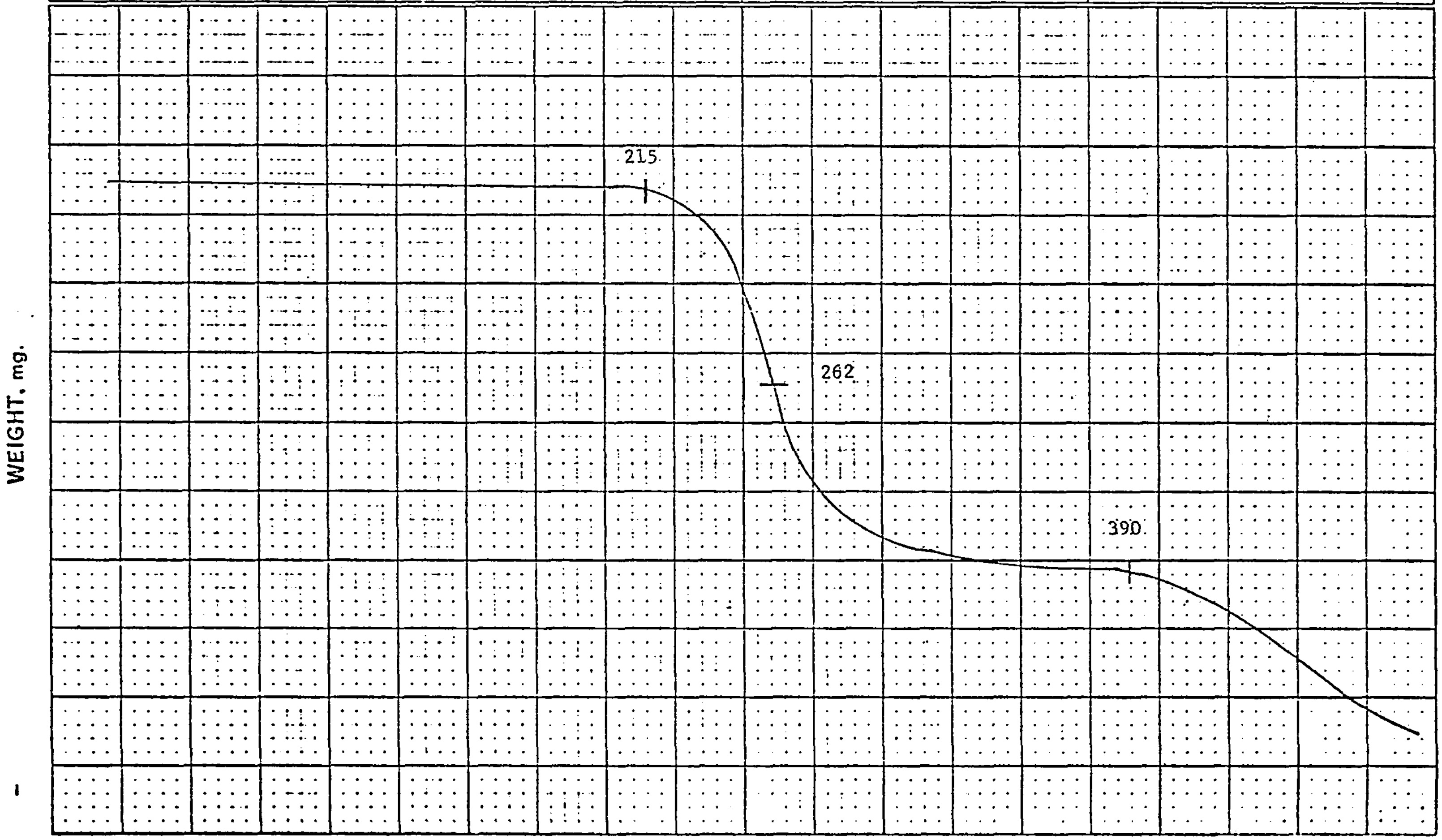


Figure 3. TGA of PVC

DU PONT INSTRUMENTS

SAMPLE: PVB # 3	**X-AXIS**	**Y-AXIS**	**RUN NO.** ____ **DATE** 6/26/74
	TEMP. SCALE 50 °C/inch	**SCALE** 2.0 mg./inch	**OPERATOR** J.L.
	SHIFT 0 inch	(SCALE SETTING X 2)	**HEATING RATE** 10 °C/min.
			ATM. N_2
SIZE 9.7 mg.	**TIME SCALE (ALT.)** ____	**SUPPRESSION** 0 mg.	**TIME CONSTANT** 1.0 sec.

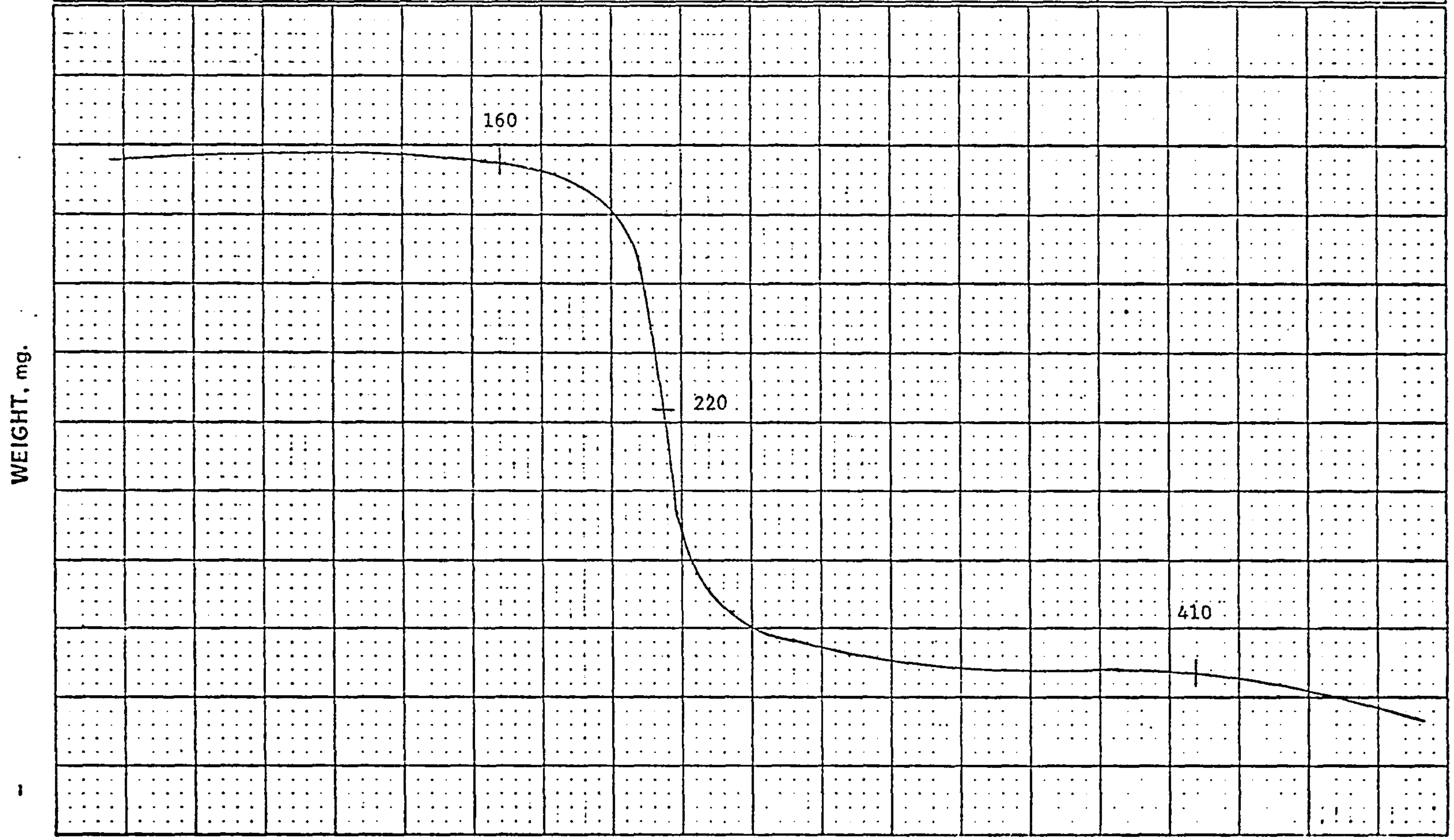
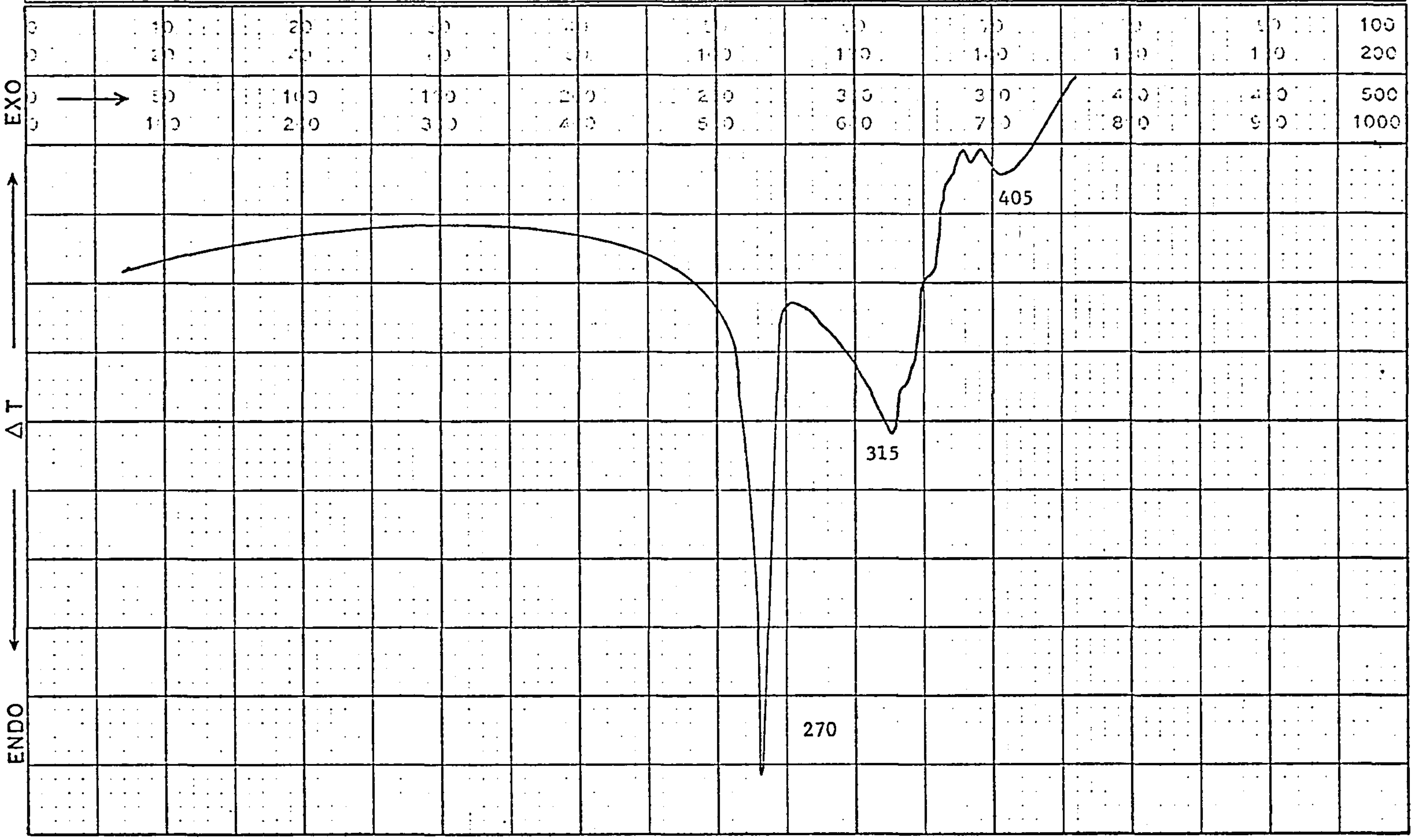


Figure 4. TGA of PVB

PART NO. 900304

INSTRUMENTS

SAMPLE:	SIZE 30 mg.	ATM. N_2, 0.3 MM	RUN NO.
PVC # 14	REF.	T ΔT	DATE 5/28/74
	PROG. MODE heat	SCALE 50 °C/IN. 0.2 °C/IN.	OPERATOR J.L.
ORIGIN:	RATE 20 °C/MIN., START 30 °C	SHIFT 0 IN. 0 IN.	BASE LINE SLOPE 0



SAMPLE:

RUN NO.:

Figure 5. DSC of PVC

DUPONT INSTRUMENTS

SAMPLE: (A) COP # 10 9.4 mg. (B) PVC # 14 + PVB # 3 7.5 mg. 2.8 mg. SIZE _____ mg.	X-AXIS TEMP. SCALE 50 °C/inch SHIFT 0 inch TIME SCALE (ALT.) _____	Y-AXIS SCALE 2.0 mg./inch (SCALE SETTING X 2) SUPPRESSION 0 mg.	RUN NO. ____ DATE 6/19/74 OPERATOR J.L. HEATING RATE 10 °C/min. ATM. N_2 TIME CONSTANT 1.0 sec.

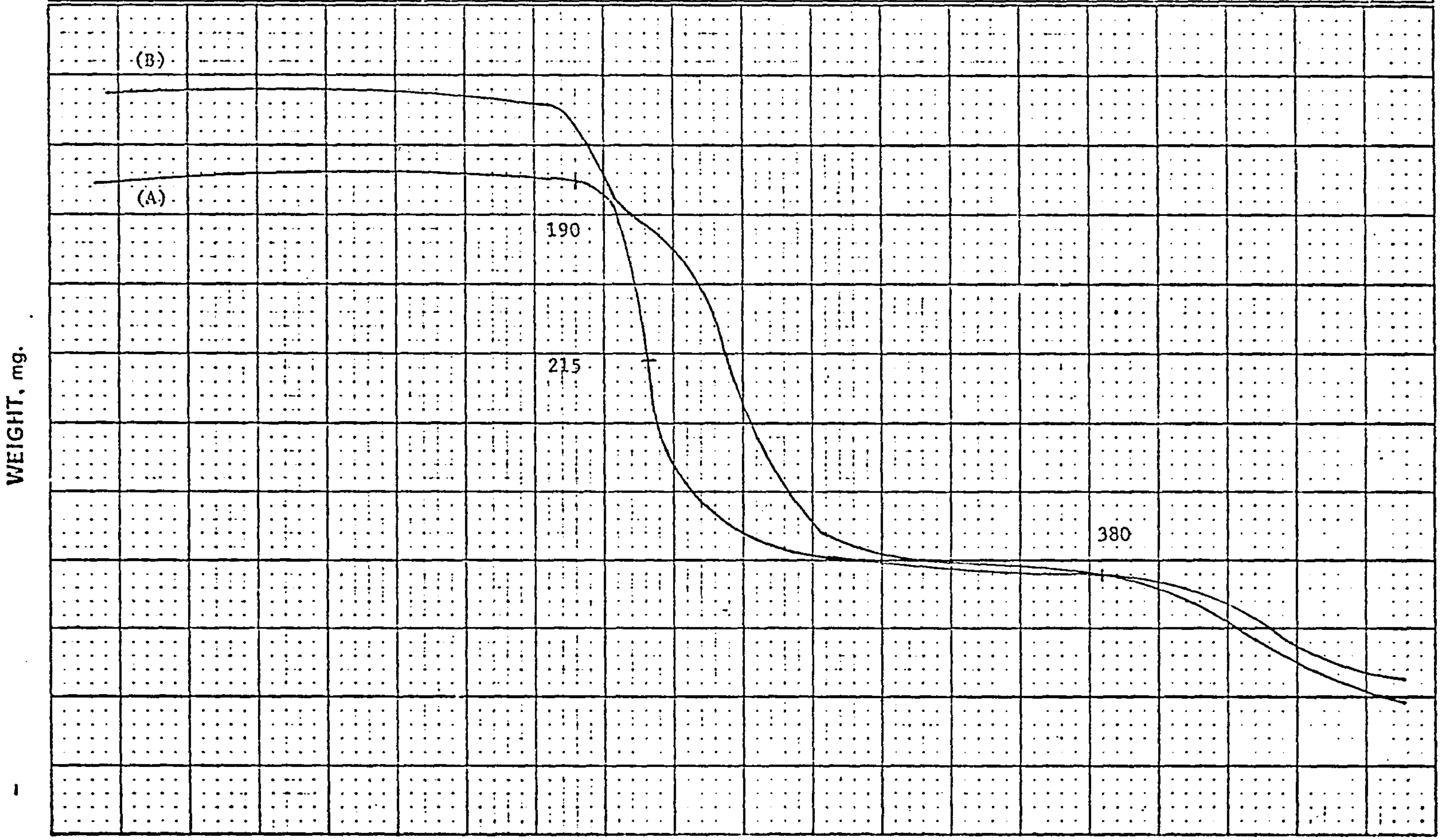


Figure 6. TGA of COP

VI. PREPARATION OF MODEL COMPOUNDS

1. Materials

Hexamethylphosphorictriamide (HMPT) was purchased from Aldrich Chemical Co. (N.J.). Lithium aluminum deuteride was obtained in 99^+% purity from Norell Chemicals (N.J.). Deuterium bromide, 99^+%, was provided by Merck Isotopes Inc. (Canada). Vinylidene chloride, 99.5%, was obtained from Tridom Chemicals (N.Y.), who also provided 1-chloropentane (ICP), 99^+%, which showed no extraneous bands in the IR, GC, or NMR. Instrumental analysis were determined using: Beckman IR-8 and IR-4260 Infrared spectrophotometers; Cary-118 UV-visible spectrophotometer; and JEOL-JNM-MH-100 NMR. Distillations were carried out with a spinning band column, Perkin Elmer Microstill-M131. Gas chromatographs of all products exhibited one peak in the Hewlett-Packard 750 Gas Chromatograph with a 1/8" x 12', 5% Carbowax 20M and 1/4" x 10', 10% Silicone Oil DC-200 columns.

2. 3-Chloropentane

This compound was prepared by the reaction of thionyl chloride on 3-pentanol. HMPT (caution: severe poison, suspected carcinogen) was used as a complexing agent to ensure total substitution at the 3 position (59). HMPT (50 ml, 0.26 moles) was introduced into a vessel cooled in an ice bath and fitted with a $CaCl_2$ drying tube. 3-pentanol (11 ml, 0.10 moles) and thionyl chloride (10 ml, 0.14 moles) were added dropwise, with vigorous stirring. The reaction mixture was warmed to room temperature and stirred for six hours. Water (150 ml, excess) was added and stirred an additional two hours. The organic layer was dried with magnesium sulfate and distilled. The middle fraction, b.p. 104^oC, was 6 ml or 50% yield.

3. 3d-3-chloropentane

This compound was prepared by reduction of 3-pentanone with lithium aluminum deuteride, followed by replacement of the resultant deuterated alcohol as described for the above procedure. All glassware was flamed and left in an oven (150°C) overnight to ensure dryness.

A solution of 3-pentanone (15ml, 0.14 moles) in 35 ml of anhydrous ethyl ether was added with vigorous stirring to 2 g (0.048 moles) of lithium aluminum deuteride in 50 ml of anhydrous ethyl ether. A magnetic stirrer was added, the vessel was sealed, fitted with a drying tube, and placed in an ice bath. After the exothermic reaction had subsided (ca. 1/2 hr), the reaction mixture was warmed to room temperature and stirred an additional two hours. The mixture was then hydrolized with water, followed by 100 ml of a 10% sulfuric acid solution. The organic layer was dried with magnesium sulfate and distilled. The fraction at b.p. 116°C was 14 ml or 95% yield of 3d-3-pentanol. Infrared carbon-deuterium bond absorptions showed bands at 4.66 and 4.78 microns (literature (60), 4.66 and 4.78 microns). Conversion of this alcohol to the corresponding chloride followed the same procedure as for 3-chloropentane. Distillation at 104°C yielded 7 ml or 40% of the 3d-3-chloropentane. Infrared showed a single absorption at 4.60 microns for the carbon-deuterium bond (literature (60), 4.55 microns). NMR indicated absence of splitting from the alpha hydrogen.

4. 1,1d_2-1-chloropentane

This analog was prepared by reduction of methyl valerate with lithium aluminum deuteride. The resultant 1,1d_2-1-pentanol was chlorinated in a manner similar to that for 3DCP. Similar precautions were taken to ensure anhydrous conditions in the glassware.

Methyl valerate (10 ml, 0.08 moles) in 50 ml of anhydrous ethyl ether were slowly added with vigorous stirring to 2 g (0.048 moles) of lithium aluminum deuteride in 50 ml of anhydrous ethyl ether. The reaction vessel was sealed, fitted with a drying tube and the mixture allowed to react for three hours at room temperature. The mixture was hydrolized with water, followed by 100 ml of a 10% sulfuric acid solution. The organic layer was dried and distilled. The fraction at 138°C was 8 ml or 95% yield of 1, 1 d_2-1-pentanol. Infrared absorptions for the carbon-deuterium bonds were observed at 4.58 and 4.80 microns (no literature values).

Conversion to chloride involved a procedure similar to that for 3 DCP, except reaction time was increased to six hours. Distillate at 108°C was 6 ml or 67% yield of 1, $1d_2$-1-chloropentane. Infrared analysis showed absence of carbonyl absorptions (5.80 microns) from residual methyl valerate, and absence of hydroxyl absorption (ca. 3.0 microns) from residual alcohol. Two carbon-deuterium absorptions were observed at 4.47 and 4.64 microns (no literature values). NMR confirmed absence of the alpha protons' triplet splitting (3.52 ppm).

5. PVC-alpha d_1

The alpha deuterated polymer was prepared via the following scheme:

$$H_2C{=}CCl_2 \xrightarrow[UV]{DBr} BrH_2C\text{-}CDCl_2 \xrightarrow{Zn} H_2C{=}CDCl \xrightarrow{AIBN/UV} \text{-}(CH_2\text{-}CDCl)_n\text{-}$$

A photochemical reactor (quartz) with a cold finger was supplied by Ace Glass Co. (N.J.) and used for the first reaction. U.V. irradiation was provided by an Oriel (N.J.) 200 W Hg-Xe lamp. The first two reactions were according to Francis and Leitch (61), the final one was a polymerization similar to those used for PVC. Extreme caution was observed due to the known carcinogeneity of vinyl chloride, and the unknown toxicity of the other intermediates.

A micro-magnetic stirrer and 50 ml of vinylidene chloride (excess) were added to the reactor. The system was flushed with D Br to eliminate air. The cold finger was fitted with a dry ice-hexane mixture, and stirring started. D Br was bubbled slowly through the vinylidene chloride, and irradiation started. After 6 ml (0.21 moles) of D Br had liquified in the reactor (a. 5 hours), the system was sealed and irradiation continued for an additional hour. The reactor was slowly allowed to reach room temperature, and unreacted D Br was vented (b.p. -67°C). The resultant 1 d_1-1, 1-dichloro-2-bromoethane (b.p. 134°C) was separated from unreacted vinylidene chloride (b.p. 32°C) via simple distillation. Yield was 6.5 g (0.036 moles) or 17%. NMR showed only a singlet (3.58 ppm) from the methylene protons. Absence of a triplet (5.44 ppm) confirmed deuteration at the chlorine bearing carbon.

A distilling flask was fitted with a dropping funnel and a water cooled reflux condenser. To this flask, 10 g of zinc (excess), fine mesh, and 40 ml of absolute ethanol were added. The condenser was attached to a polymerization tube and a mineral oil bubbler. The system was flushed with nitrogen and the polymerization tube immersed in a dry ice-hexane bath. The zinc-ethanol mixture was heated to boiling (78.5°C), and the deuterated ethyl halide (from the first step) was introduced dropwise with vigorous stirring. The evolved vinyl chloride-alpha d_1 (b.p. -14°C) condensed in the polymerization tube. Monomer evolution was tested by decoloration of a dilute aqueous permanganate solution. After the reaction ceased, the tube was stoppered; yield was 2 ml (0.032 moles) of the monomer, or 88%.

An evacuated IR gas cell was attached to the tube and filled with monomer. The following IR absorptions confirmed the presence of vinyl chloride-alpha d_1 (undeuterated vinyl chloride has no absorption in these regions), a strong band at 1100-1130 cm^{-1} and a moderate band at 2300-2320 cm^{-1} (62). Absence of undeuterated monomer was verified by following the shift of IR absorptions on alpha deuteration (63). These shifts were, from undeuterated to deuterated: 947 to 808; 1039 to 1100; 1377 to 1364; and 3079 to 2308 cm^{-1}. In addition, no extraneous bands were observed, indicating absence of impurities.

The polymerization procedure was the same as for PVC, with the following changes: 2 mg AIBN/2 ml VC-alpha d_1; two hours UV irradiation; temperature 0°C; and induction time 15 min. Yield was 0.2 g or 10% of PVC-alpha d_1.

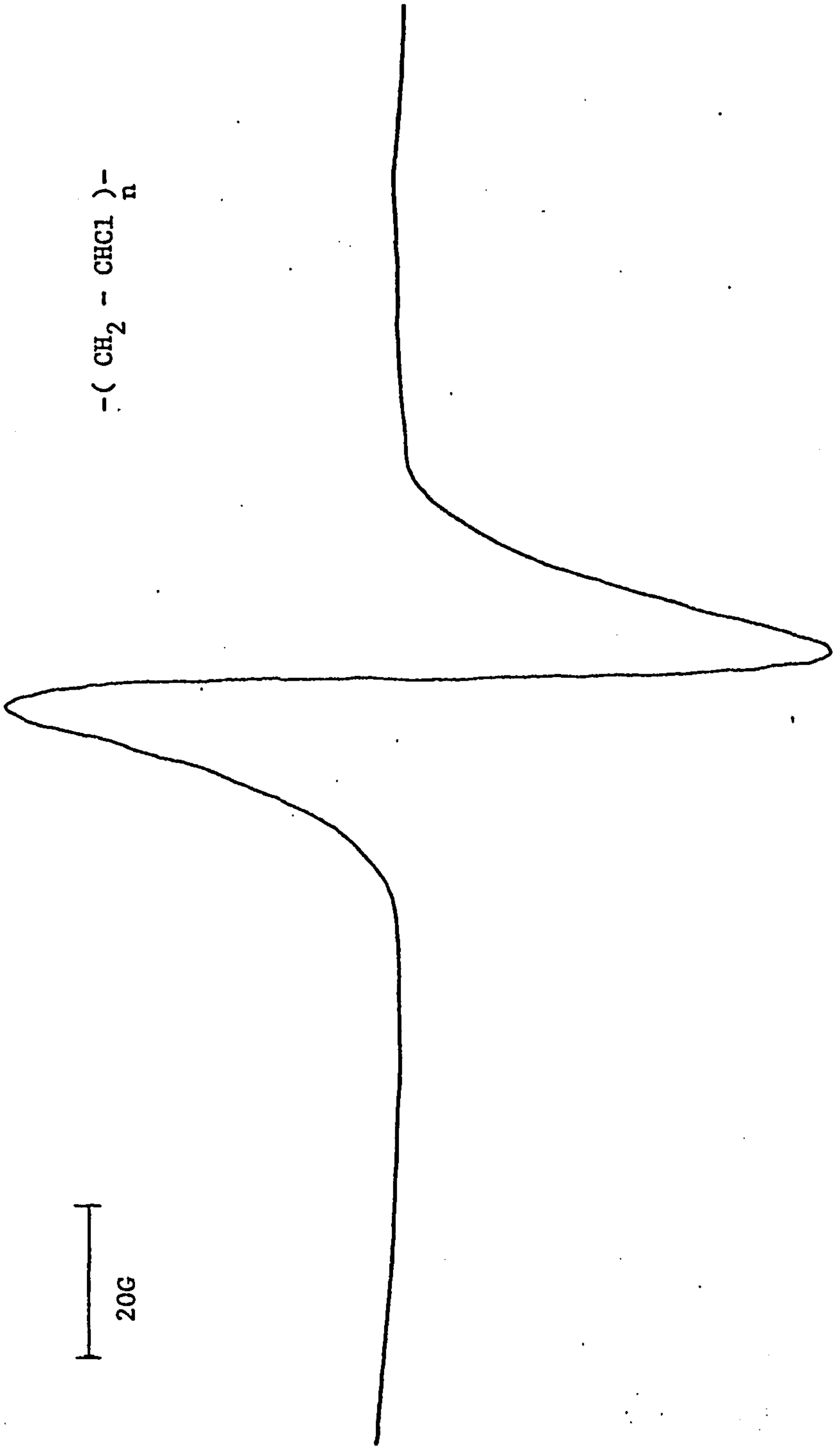
VII. ESR SPECTRA

1. Polymer Films and Powders

The prepared polymers were irradiated with either a 200 W Hg-Xe (ca. 1/2 hr) or a 1000 W Xe (ca. 5 min.) UV light source. ESR spectra were recorded using a JEOL Model JES-ME-3X ESR (N.J.) with accessories for liquid nitrogen (-196°C) and variable low temperature (-170°C to RT) measurements.

The unirradiated samples exhibited no absorption in the ESR, indicating absence of radicals that might have been trapped during polymerization. The polymers and copolymers exhibited only weak singlets, ΔH_{msl} = 10-20 G (msl = mean slope linewidth) on irradiation and measurement at room temperature (Figure 7). Irradiation of samples in air or under vacuum (10^{-6} torr) gave rise to identical singlets, but the spectra in air were more intense (Section II). This singlet has been widely recognized as due to the polyenyl radical $-(CH{=}CH)_n\dot{C}H-$ (19) (20) (21) where a longer conjugated sequence affords more delocalization to the unpaired electron, producing a narrower ESR line width. The length of these polyenes does not usually exceed n=15, and shorter polyenes predominate, giving average polyene lengths of n≈3-6 for degraded PVC (3). These structures gave rise to color changes in the photodegraded polymers. Clear PVC films and white powders turned yellow on irradiation at room temperature. The COP and PVB samples changed to red and dark brown respectively, indicating formation of longer polyene sequences. The COP and PVB samples were also found easier to degrade, since an exposure of 5-10 minutes (200 W UV) produced an absorption in the ESR comparable to 30 minutes irradiation of PVC. This result was as expected, since the carbon-bromine bonds in COP and PVB show stronger UV absorption than the carbon-chlorine bonds in PVC (Section V, 1.). In addition, the bond

Figure 7. ESR of UV Irradiated PVC Powder at RT



dissociation energy for a secondary carbon-bromine bond is 59 Kcal/mole, as compared to 73 Kcal/mole for a secondary carbon-chlorine bond. No references, however, were available on the photodegradation of the COP and PVB polymers.

After degradation of the PVC, COP, and PVB samples, the resulting polyene radicals were found to be stable for several days at RT. On termination of these radicals, polyenes were formed, and represent the end product of photodegradation at RT. The origin of this degradation is still in doubt, since intermediate radicals react too rapidly at this temperature. The first step in the identification of these radicals requires their immobilization. This was accomplished by irradiation and ESR measurement at LNT. The samples were then slowly allowed to approach RT in a variable temperature apparatus, and the changes in ESR absorptions were then observed. The polymers were irradiated under the same conditions as for RT, the results however were markedly different.

All of the PVC, COP, and PVB powder samples sealed under vacuum gave rise to a similar broad (overall width ca. 150 G) absorption in the ESR (Figure 8). This spectrum contained very little hyperfine structure. Films cast from THF, of the same powders, exhibited a possible six line absorption (Figure 9A) at LNT. The hyperfine splitting, ca. 25 G, was difficult to determine accurately due to considerable line overlap. The reason for the enhanced resolution of films in the ESR is not clear. It is possible that the randomly oriented crystalline regions in the powders can be re-oriented in a more ordered fashion during slow evaporation of the solvent in film formation.

Both films and powders, when sealed in air and irradiated at LNT gave rise to an asymmetric singlet in the ESR (Figure 9B). The characteristic shape and high g-value (2.015) of this singlet indicate that it is

Figure 8. ESR of UV Irradiated PVC Powder at LNT

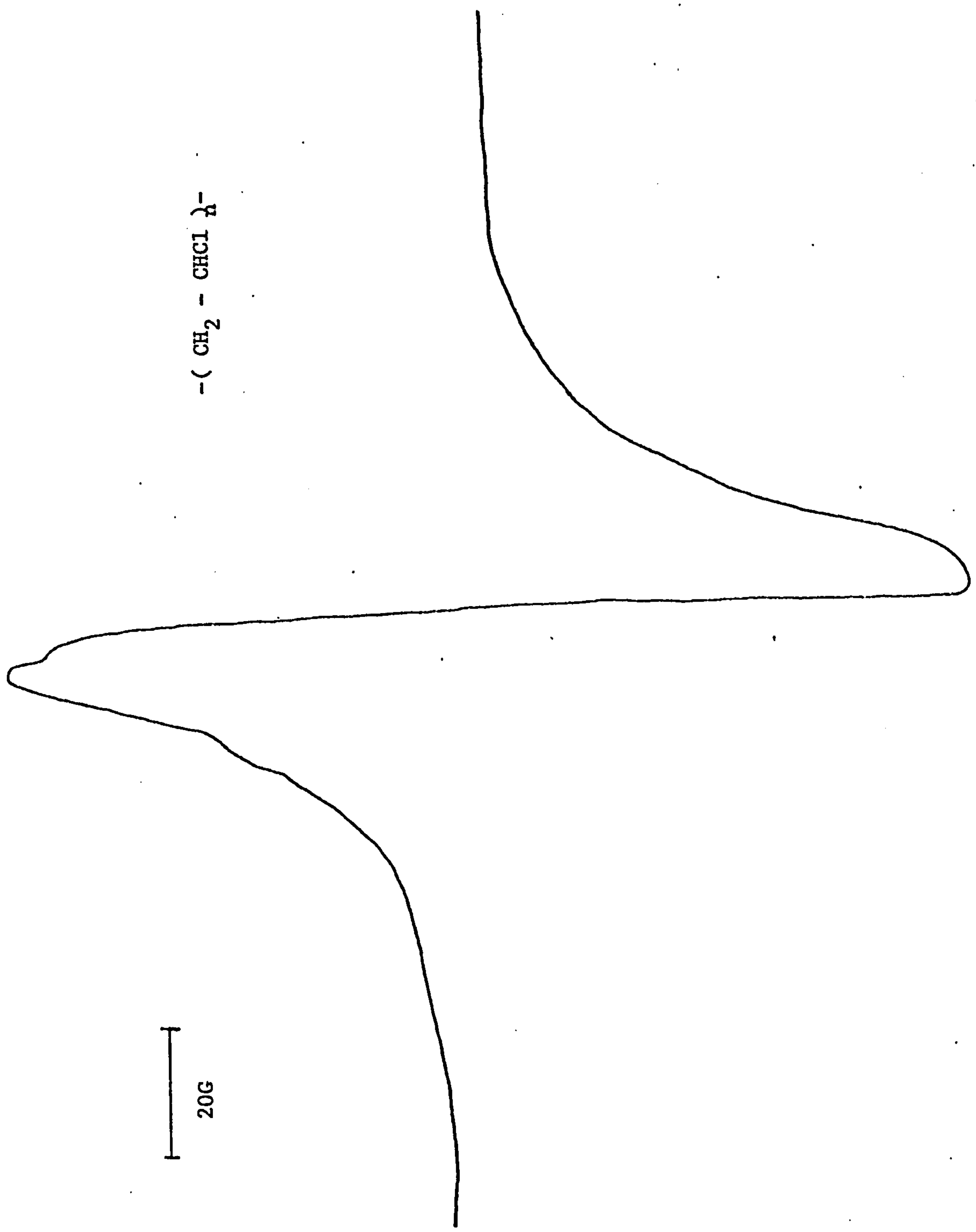
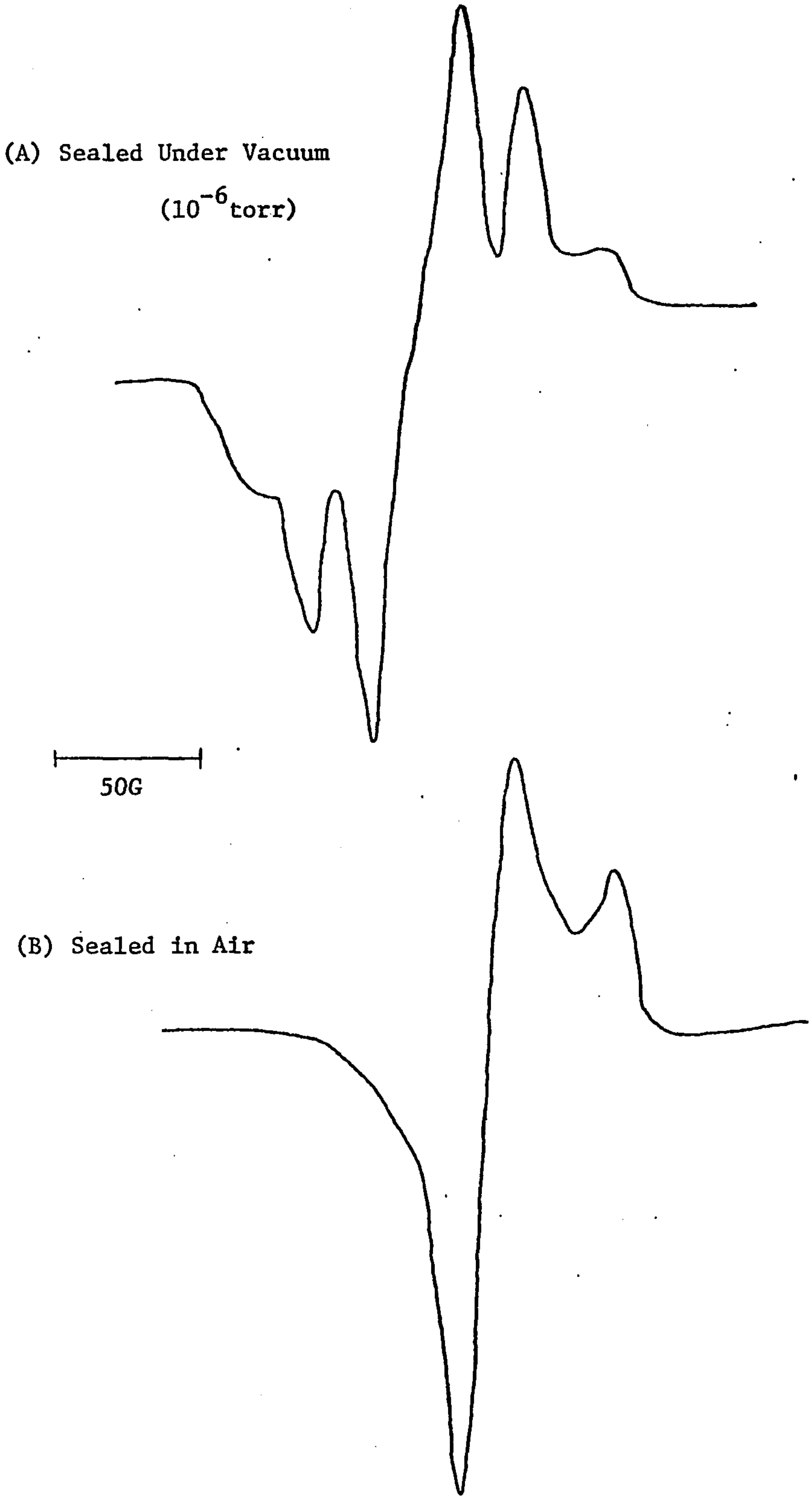


Figure 9. ESR of UV Irradiated PVC Films at LNT



due to a peroxy radical. This radical has frequently been associated with polymers irradiated in air (64). The reason that this peroxy absorption was not observed for samples irradiated in air at RT, is that the peroxy groups rapidly sensitize degradation of the PVC, COP, and PVB to the polyene radical.

On warming to RT, the spectra in Figures 8, 9A, and 9B all change irreversibly to the narrow singlet absorption attributed to a polyene radical (Figure 7). Little information can be obtained from the LNT spectra due to their inadequate hyperfine structure. The same problem of poor ESR resolution occurs throughout the literature of PVC degraded at LNT. As mentioned previously (Section I), the causes of poor resolution can be threefold.

If more than one radical is present at LNT, overlap of their ESR spectra would lead to broader absorptions. This effect would be most pronounced if the radicals had different g-values and/or hyperfine splittings. Radicals with different g-values should give rise to asymmetric spectra. The observed LNT spectra (under vacuum) appear symmetrical. However, there may still be radicals present with similar g-values, but different hyperfine splittings. If this were the case, other analyses should be performed (see Sect. VIII, 1., A.).

The second cause of unresolved ESR spectra may be due to dipolar broadening effects. Each dipole in a molecule produces a magnetic field at each of its neighbors. Thus, the total magnetic field experienced by the unpaired electron will include contributions from its neighbors, and will probably differ from the applied external field. Therefore, transitions will occur over a range of frequencies corresponding to the local field at each free radical.

A third cause for line broadening could be due to spin-spin coupling in the solid samples. Since the polymer chains are close together, there is a possibility that unpaired electrons may be formed in close proximity on adjacent chains. Each unpaired electron will then experience a magnetic moment from its neighbor and the applied magnetic field. This will create an effect analagous to dipolar broadening.

To minimize the second and third causes of line broadening, it was decided to use a polymer glass system for the PVC, COP, and PVB samples. The polymers were solvated, the resulting solution rapidly frozen in liquid nitrogen, and then irradiated. Solvating the polymer enhances local mobility in the chains. Rapid freezing will tend to yield an overall average conformation at LNT. This should give a more homogenous environment to the free radicals, thus minimizing dipolar broadening. In addition, since the polymer chains are now separated by solvent molecules, interaction of adjacent polymer radicals is minimal, as is spin-spin coupling. The first cause of unresolved ESR spectra, presence of more than one radical species, will be determined by use of g-values, power saturation, analysis of line intensity ratios, and variable temperature behavior of the ESR absorptions (Section VIII, 1., A.)

A PVC glass system has only been used once before (4) with inconclusive results. Difficulties could have arisen from the use of gamma irradiation, which can cause random cleavage in both polymer and solvent. This type of radiation frequently produces an intense, narrow ESR absorption due to free electrons ejected from the sample. The spectrum may have been further complicated by impurities from the commercially supplied PVC. A glass system has never been used for analysis of COP and PVB degradation.

2. Polymer Glasses at LNT

Since bond cleavage by UV radiation is more selective than gamma rays, and only pure, characterized polymers were used, the remaining problem was choice of a solvent system. Ideally, a solvent for the PVC, COP, and PVB glasses should meet three criteria: a relatively high melting point; no UV absorption; and no ESR absorption. In warming from LNT to RT, a high melting point is desirable, since once it is reached, the mobile radicals are free to terminate. The solvent should be clear in the UV region to allow maximum absorption of radiation by the polymer. The ESR of irradiated solvents should also be clear, since any absorption may interfere with that of the polymer.

No solvent was found that met these criteria, but three solvents were found to be close to ideal: tetrahydrofuran (THF); p-dioxane (DX); and tetrahydropyran (TP). THF was obtained as ultra high purity from Burdick and Jackson Labs (Mich.); DX as spectroquality grade from MC/B Inc. (N.J.); and TP as purum grade from Tridom Chemicals (N.Y.). The tetrahydropyran was the only solvent to exhibit UV absorption other than at λ eff. It was purified by passing through an activated alumina column, fractionally distilled from lithium aluminum hydride, and distilled from sodium. This treatment eliminated the extraneous UV absorptions. Effective wavelengths (Section V, 1.) and melting points were: 207 nm and $-108.5^{o}C$ for THF; 208 nm and $11.7^{o}C$ for DX; and 226 nm and $-45.0^{o}C$ for TP. No ESR literature was available for these solvents.

The solvents were placed in quartz ESR tubes, degassed three times by freezing and thawing, and sealed under vacuum (10^{-6} torr). They were then irradiated at LNT with a 1000 W Xe UV lamp for 30 min each. The resultant ESR spectra at that temperature are given in Figures 10, 11, and 12 for THF, DX, and TP respectively. The spectra are all similar, narrow singlets (ΔH_{msl} = 10-15 G) with some unresolved fine structure in the wings.

Figure 10. ESR of UV Irradiated THF at LNT

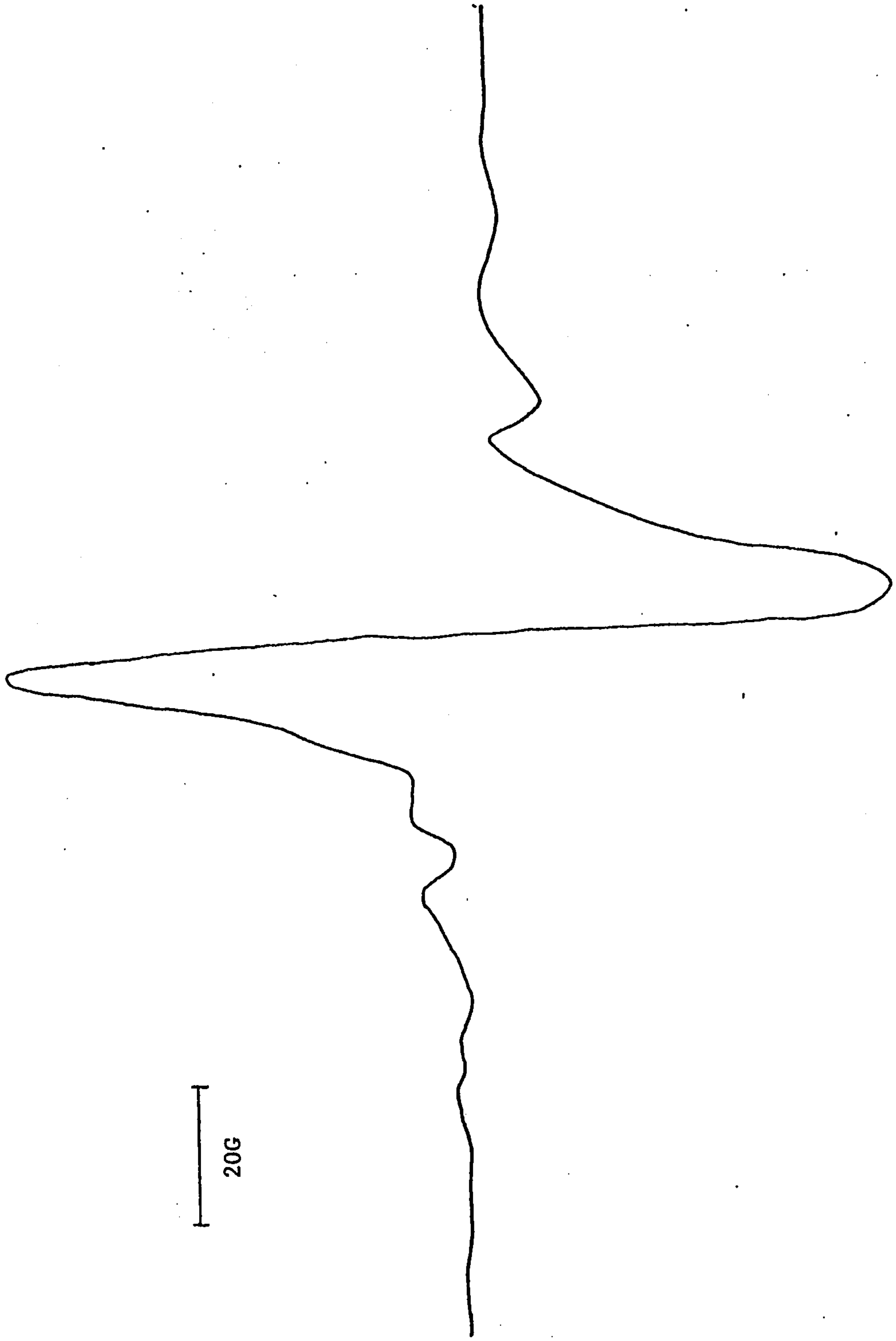


Figure 11. ESR of UV-Irradiated DX at LNT

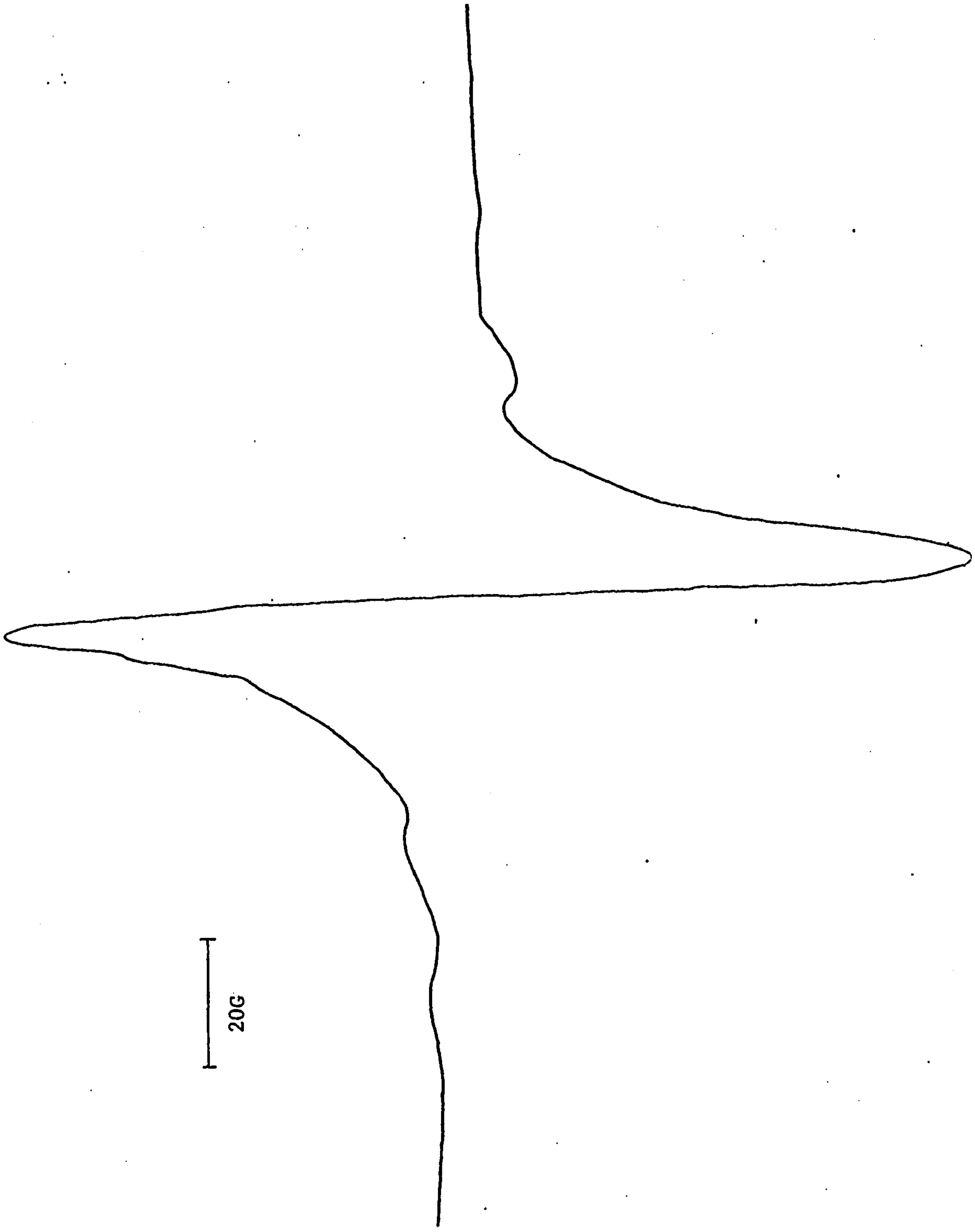
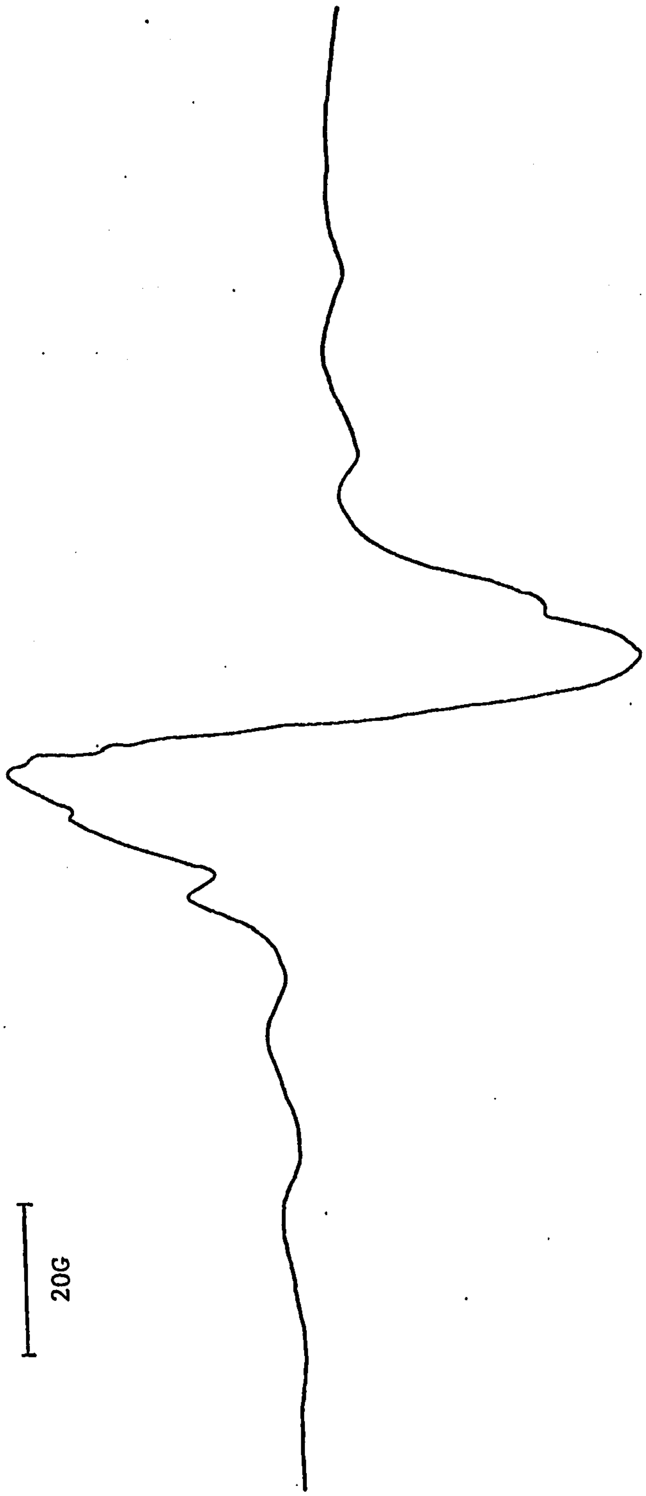


Figure 12. ESR of UV Irradiated TP at LNT



On warming to the melting point, the fine structure disappeared, and the singlet decreased in intensity. The identity of the radicals causing these absorptions could not be determined, but since the spectra are basically singlets, their interference in irradiated glasses should readily be noted.

PVC, COP, and PVB solutions (5-15%, w/v) were prepared from these solvents, degassed, sealed under vacuum (10^{-6} torr), and irradiated at the same conditions as the solvents. At LNT, the ESR of PVC and COP glasses were identical. Varying the solvent did affect the spectra slightly (Figures 13, 14 and 15). The glasses with THF, DX, and TP appear as similar six line absorptions in the ESR. There are interfering singlets in the THF and DX glasses, probably due to solvent radicals. The PVC/TP glass exhibits a well resolved sextet, with no interfering solvent radical. The spectra are all symmetrical, with a hyperfine splitting of 23 G, line intensity ratios of 1:4:9:9:4:1, and g-value of 2.0036 (reference DPPH). This spectrum has never been observed for PVC under any degradation conditions.

The glasses were clear before and after irradiation at LNT, indicating absence of polyenyl structures due to dehydrochlorination. On warming to RT, the PVC glasses became light yellow, and the COP glasses a light orange. These color changes indicate that the radical formed at LNT is a precursor to the polyene radical.

ESR spectra of PVB glasses irradiated and measured at LNT were similar to Figure 16, regardless of solvent used. In this case, traces of a sextet can be seen in the wings, but a broad singlet interferes with the central two lines. Before irradiation, the PVB glass was clear. On irradiation at LNT, the color changed to dark orange. Therefore, it is highly probable that the PVB has partially degraded, even at LNT, producing

Figure 13. ESR of UV Irradiated PVC/THF at LNT

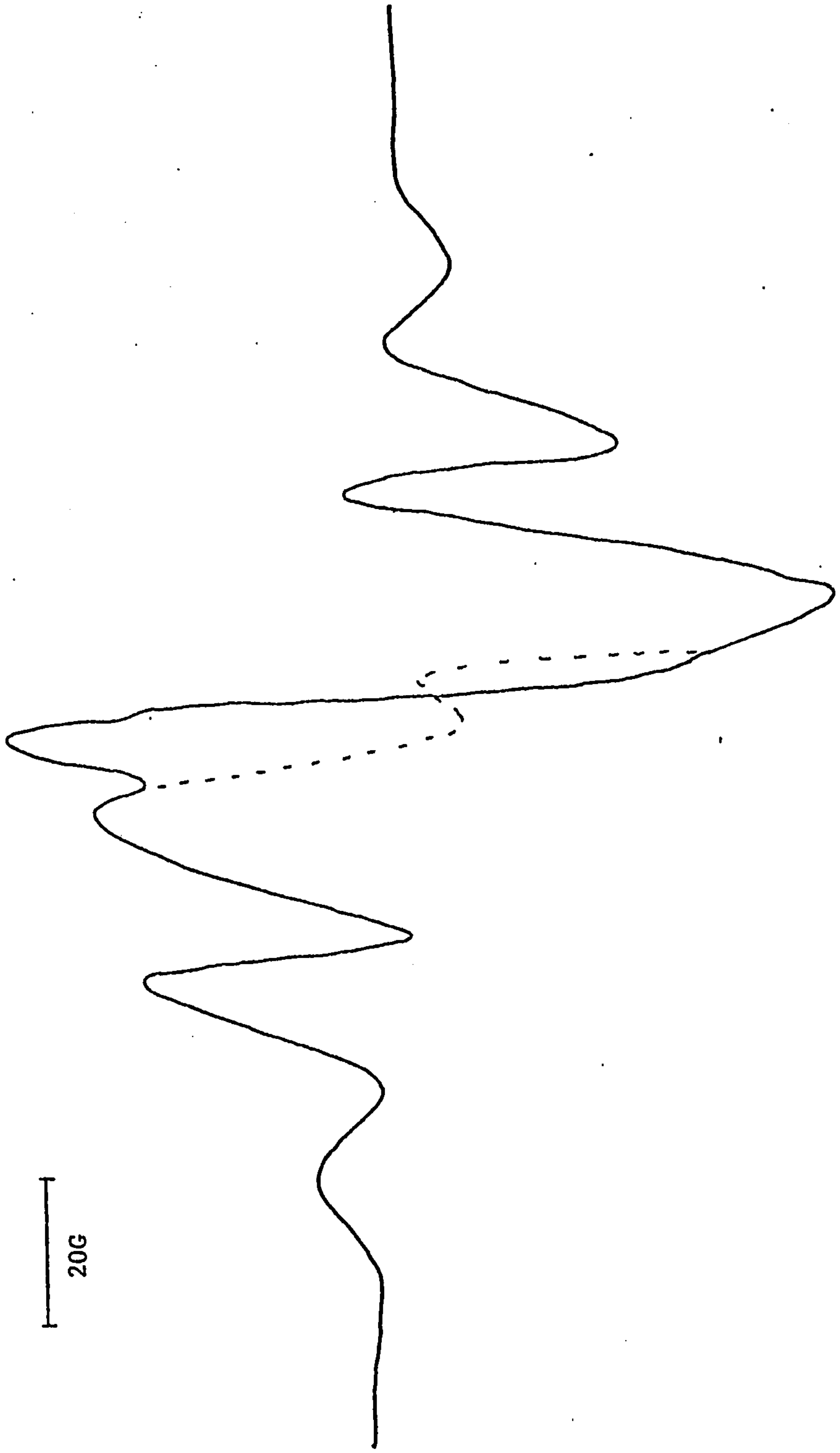


Figure 14. ESR of UV Irradiated PVC/DX at LNT

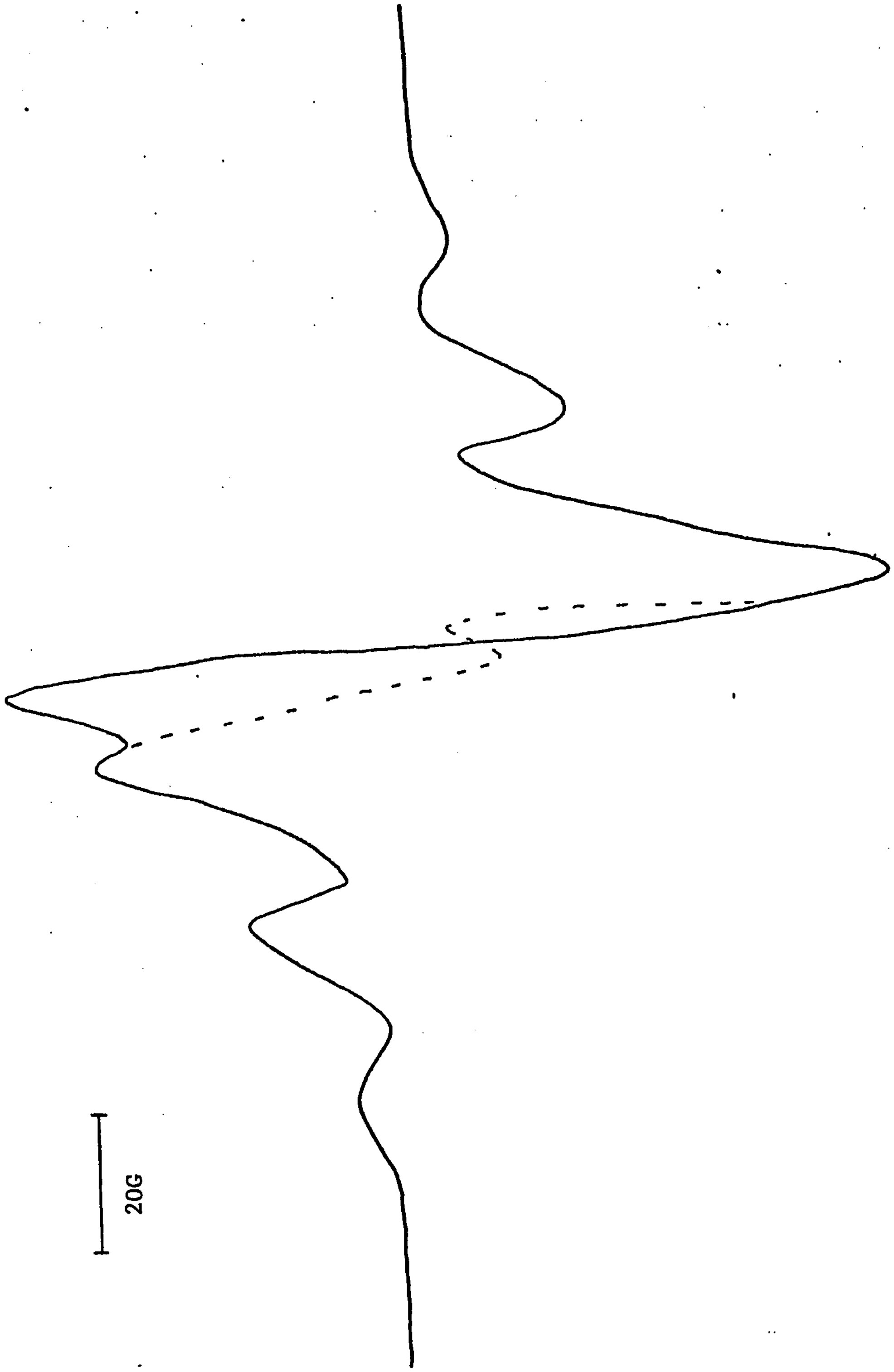


Figure 15. ESR of UV Irradiated PVC/TP at LNT

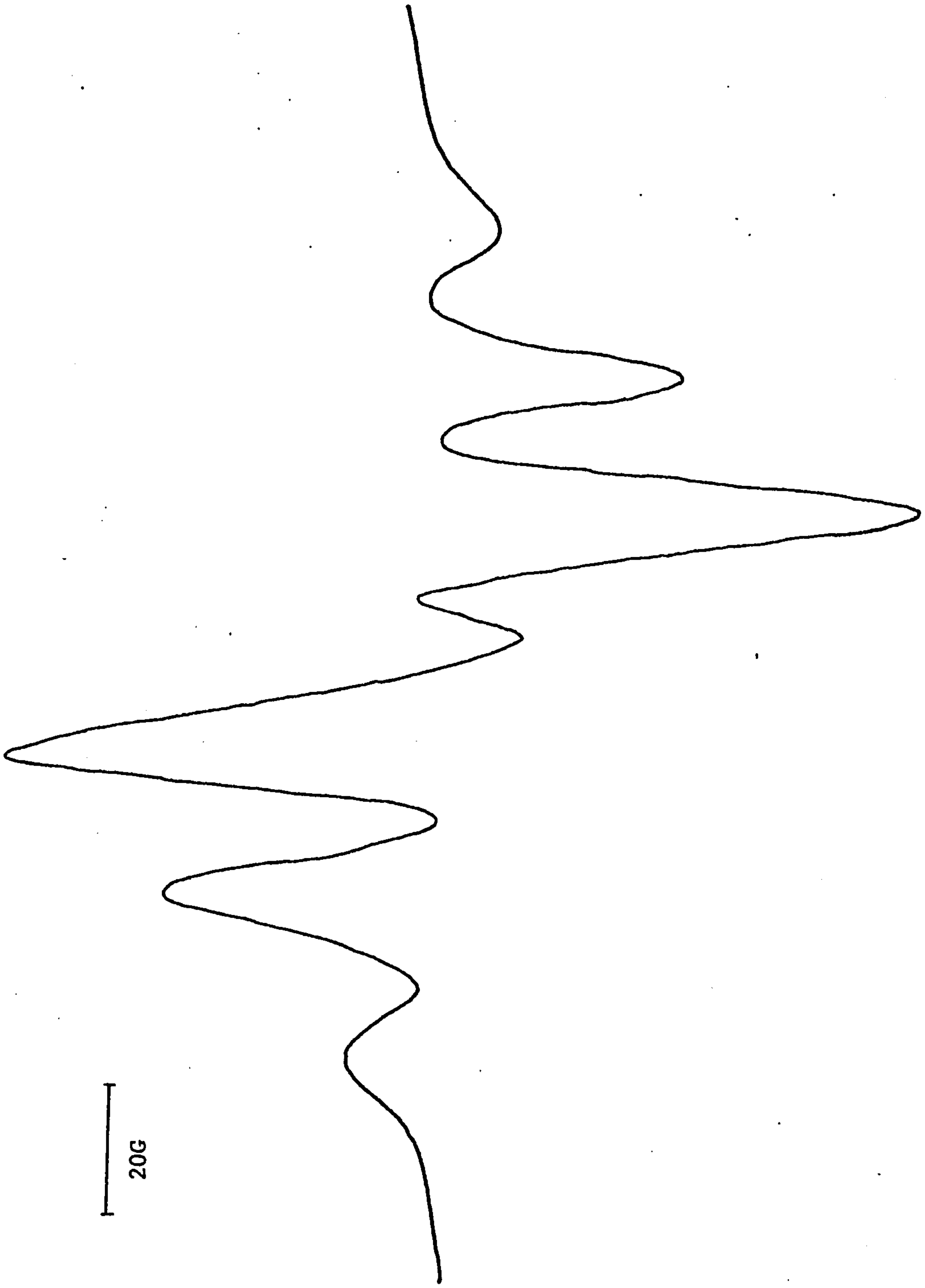
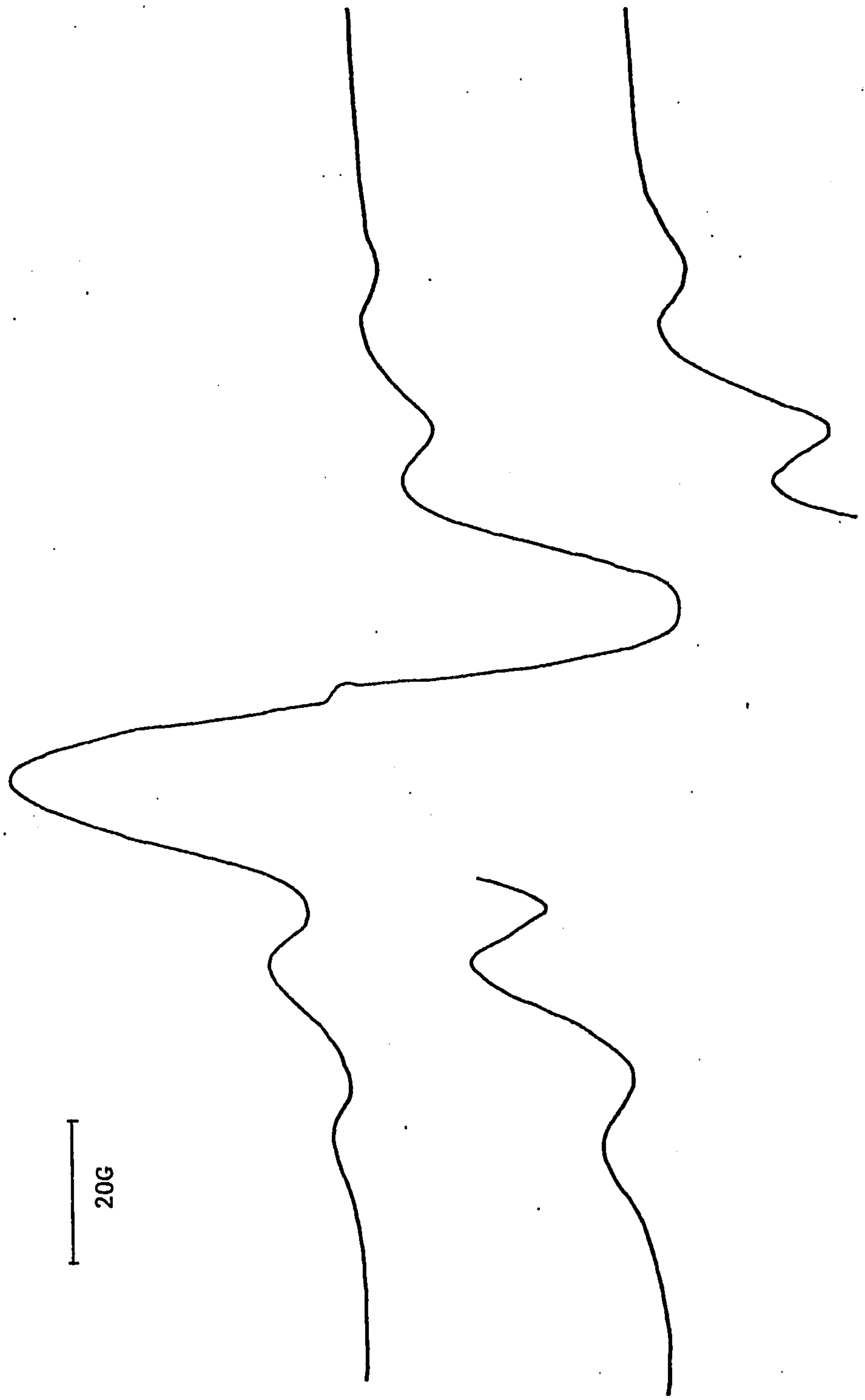


Figure 16. ESR of UV Irradiated PVB/TP at LNT



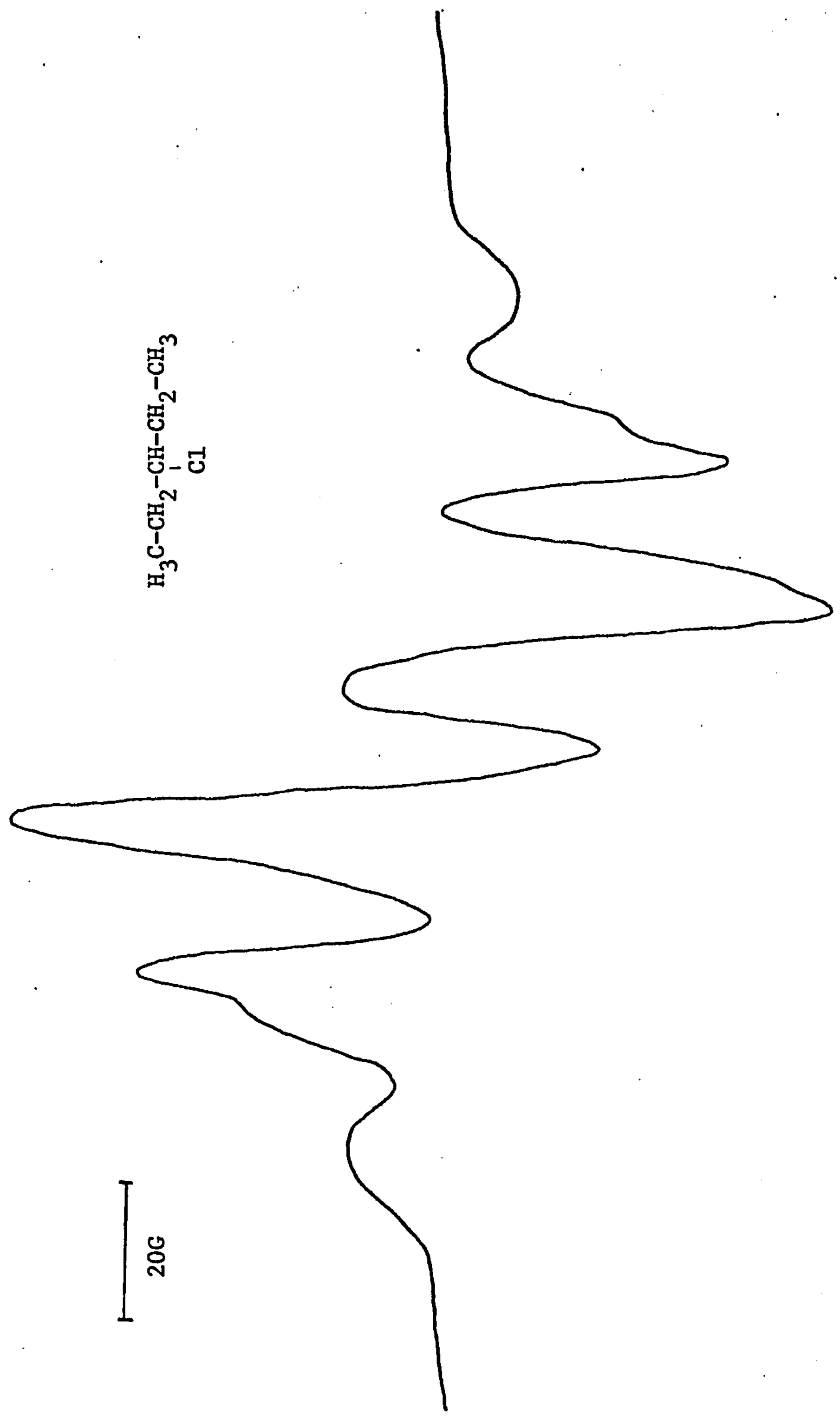
a singlet from the polyene radical. Since the dehydrobromination should not be extensive at LNT, the polyenes formed would be short, leading to a broader singlet absorption in the ESR. On warming to RT, the color changes to dark purple, indicating further degradation.

3. Analogs at LNT

The undeuterated analogs, 1-chloropentane (ICP) and 3-chloropentane (3CP) were degassed, sealed under vacuum (10^{-6} torr), and irradiated in the same manner as were the polymer glasses. Since these analogs were in liquid form at RT, no solvent was necessary to enhance resolution in the ESR. On freezing in liquid nitrogen, the highly mobile conformation should assume an average value, leading to homogenous radical environments. On irradiation, cleavage of the carbon-chlorine bond is expected in each. The 3CP should serve as a model to indicate carbon-chlorine cleavage in the main PVC chain. The ICP analog could be used to indicate formation of any primary radicals in PVC; from branch points, chain cleavage, etc. These analogs have never been used to study PVC degradation, and no ESR literature is available for them.

The ESR of 3CP irradiated and measured at INT is shown in Figure 17. The spectrum is almost identical to that of the PVC/TP glass. The hyperfine splitting, intensity ratio, and g-value are all the same. This result is not overly surprising, since carbon-chlorine cleavage was expected to be the major process in each, and both molecules can be considered as $R - CH_2 - CHCl - CH_2 - R$. Since this sextet was obtained without a solvent, a test was performed to examine the effect of TP on the signal. A 3CP/TP(1/1, v/v) solution was prepared and irradiated under identical conditions. The spectrum was essentially unchanged; intensity was a fraction lower and lines slightly broader. This result, coupled with that from the PVC/TP glass, indicates that tetrahydropyran, when used in a

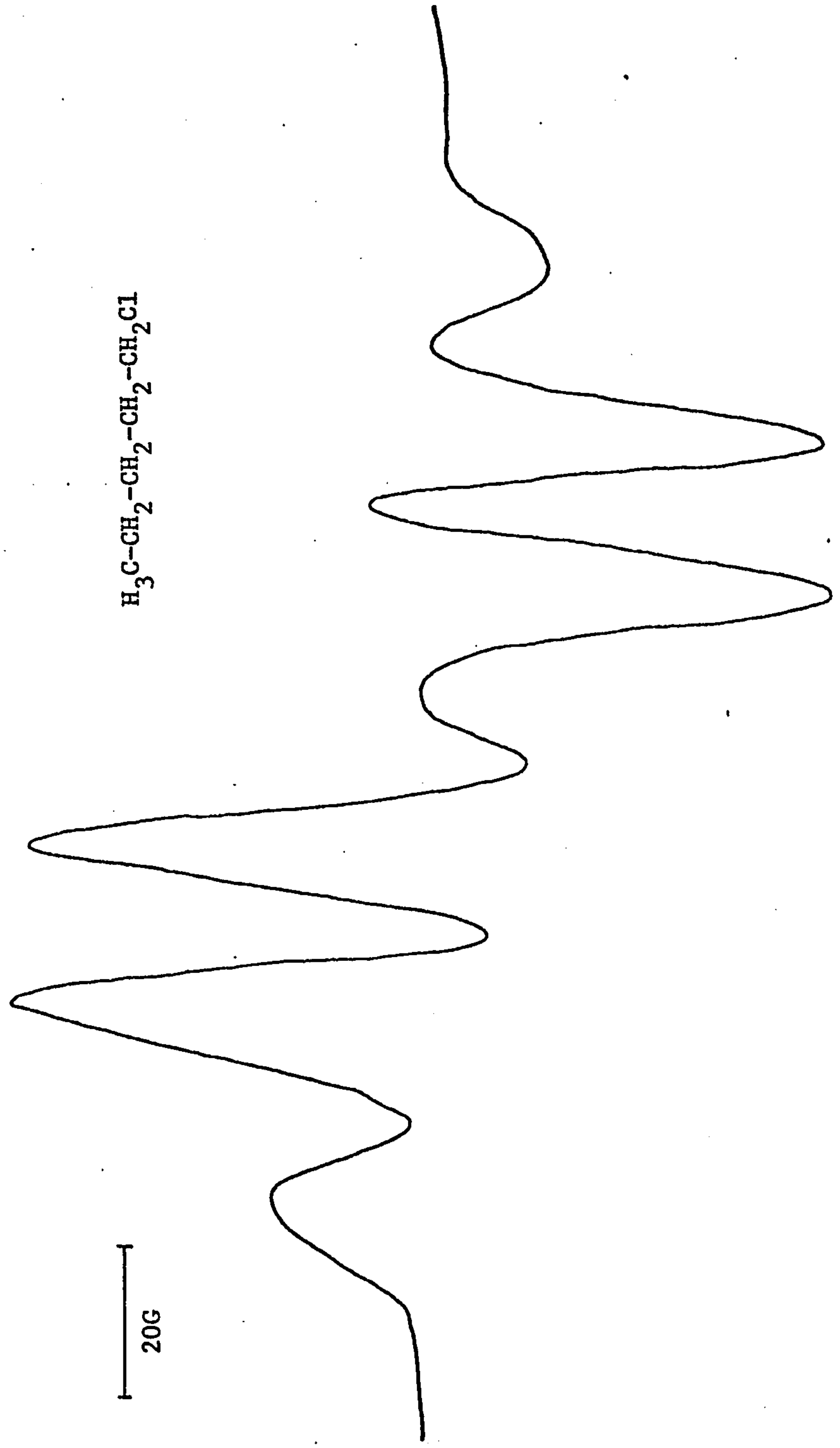
Figure 17. ESR of UV Irradiated 3CP at LNT



solution, is not susceptible to radical formation by UV light. The reason for this is not understood, but could involve PVC solvation processes, which are as yet unexplained.

The ICP analog, without solvent, also gave rise to a six line absorption (Figure 18). The hyperfine splitting and g-value are similar to that for 3CP, but the line intensity ratio is quite different, 1:4:4:4:4:1. This ratio is indicative of primary radicals and will be detailed later (Section VIII, 1., G.). Since this type of intensity ratio is not observed for the polymer glasses, no significant contribution from primary radicals is expected.

Figure 18. ESR of UV Irradiated 1CP at LNT



VIII. DISCUSSION

1. Analysis of ESR Spectra at LNT

A. Number of Radical Species

The ESR of PVC and COP glasses irradiated and measured at LNT were identical, regardless of polymerization conditions. PVC #14 (Section IV,2.) was chosen as representative of these glasses, and subsequent discussion will center on it along with the 3-chloropentane analog irradiated and measured in the same manner. This PVC should have the lowest molecular weight, least amount of crystallinity, and highest branch content, allowing for greater ease of solvation. The solubility of PVC #14 was limited to ca. 15% w/v due to gel formation in any of the solvents above that value. Gelation will limit degassing efficiency, and some air may be left in the sealed ESR tube. The oxygen will promote peroxide radical formation on irradiation at LNT, and this spectrum will overshadow that of the polymer radical. As mentioned earlier, the characteristic spectrum of the peroxy radical is readily detected. As the temperature increases, the peroxide will initiate degradation in the polymer, which is indicated by colored polyene formation at RT.

PVC glasses under vacuum gave rise to similar sextets, regardless of solvent. The glasses from THF and DX also showed the presence of a central singlet. This absorption has been tentatively assigned to a solvent radical, since the solvents alone exhibited similar singlets in the ESR. However, interfering singlets have often been noted on gamma irradiation of polymers, and ascribed to trapped electrons (65)(66)(67). Presence of these electrons can be discounted in the PVC/THF or PVC/DX glasses for the following reasons. Glasses with trapped electrons are dark blue in color, while all PVC glasses were clear on UV irradiation at LNT. Trapped electrons are photobleachable with visible light, and the UV light sources employed in this research had considerable output in the visible region. The electrons' ESR absorption has a ΔH_{msl} = 4-4.5 G, while the singlets observed for the PVC glasses had ΔH_{msl} = 10-20 G. In addition, UV radiation is associated with much less energy than gamma radiation, therefore ejection of an electron from an organic molecule (ionization) is not probable.

Four tests were performed to determine whether the sextet from 3CP and PVC glasses was due to a single radical species: g-value determination; power saturation; variable temperature behavior; and analysis of line intensity ratios.

The LNT spectra of the above samples appear as symmetrical absorptions centered at g=2.0036 ($\pm$0.0007). This indicates that if several different radicals are present, they must have the same or very similar g-values. This value indicates the position of an absoption in the ESR as a ratio of frequency to applied magnetic field. It is commonly determined by use of an external standard with a known g-value, such as DPPH (the diphenylpicrylhydrazyl radical). Unfortunately, the g-values of saturated organic radicals, with unpaired electron density on carbon, are similar, and close to the value for DPPH (g=2.0036). Therefore, the g-value measurement of the observed sextet can only indicate the presence of such a radical.

Power saturation of an ESR absorption can also be used to differentiate between radical species. At low power levels, more upward than downward transitions occur between the ground and excited states of the free radical. If high microwave power is applied to the system, the upward and downward transitions may become equally probable, leading to equal populations in both states. This effect would be observed in the

ESR as broadening and decrease of signal intensity. Different radicals show characteristic interactions with their environment, and therefore should saturate at various microwave powers. All original spectra were recorded at very low power levels, 0.1 mW, to avoid such saturation effects. When power was slowly increased to 60 mW, all absorption lines decreased in intensity and broadened proportionately. This result indicates absence of more than one radical species.

The observation of an ESR spectrum as it is warmed from LNT to RT can also give evidence to differentiate radicals. Radicals differ in reactivity, and therefore termination rates. When the PVC glass is warmed, a sudden decrease in intensity of certain lines would be an indication that one type of radical had terminated. No such decrease was observed.

A very useful technique for determination of radical species is an analysis of line intensity ratios. If an unpaired electron can interact with five equivalent protons, a sextet is expected, with a binomial intensity ratio of 1:5:10:10:5:1 (68). The intensity of an ESR absorption is determined by comparing the areas under each absorption. For Gaussian curves, the area of a first derivative absorption is proportional to: $I=Y'_{max}(\Delta H_{pp})^2$, where Y'_{max} is the peak to peak amplitude, and ΔH pp is the peak to peak width (69). Measurement of the intensity ratios for the 3CP and PVC glass spectra was hampered by some line overlap. The value obtained was 1:4:9:9:4:1, which compares favorably to the theoretical value for an unpaired electron coupled to five equivalent protons. Considering the parent molecules, the possibility of more than one radical containing five equivalent protons is remote. Therefore, this result, along with those from g-value determination, power saturation, and variable temperature studies, strongly suggest the presence of only one radical species present in the 3CP and PVC glasses at LNT.

B. Effect of Physiochemical Properties

Vinyl chloride was polymerized under a variety of conditions for the preparation of polymers with a range of branching, crystallinity, and molecular weight. The ESR spectra of all PVC glasses, however, exhibit the same six line absorption at LNT. This seems to indicate that the above properties are not involved in the degradation process of PVC.

Branching should incorporate weaker tertiary bonds in PVC, either carbon-hydrogen or carbon-chlorine. No determination has yet been made as to the preferential site of branching in PVC. A comparison of secondary and tertiary C-H bonds does show a lowered bond dissociation energy, 94 versus 90 Kcal/mole respectively. The dissociation energies for secondary and tertiary C-Cl bonds are not known accurately, but it is proposed that a tertiary carbon-chlorine bond may require even more energy for cleavage than a secondary one. The respective bond dissociation energies are 73 versus 75 Kcal/mole (70). Cleavage of the branch itself, though energetically possible, ca. 75 Kcal/mole, is improbable due to the bulky nature of the group. If cleaved at LNT, this group would be expected to remain in close proximity to the parent radical (cage effect) and would rapidly recombine. In addition, the evidence indicates only one radical species, the polymer radical, is responsible for the ESR spectrum at LNT. Therefore, the effect of branching may be minimal in providing initial sites for degradation.

However, it could be argued that radicals in a highly branched PVC should give rise to ESR spectra different from radicals in an unbranched polymer. Polyvinylchloride prepared at -78°C, containing no branches, was compared to PVC #14 prepared at 50°C and having the highest branch content (Section IV., 2.). Similar comparisons were made for polymers prepared with intermediate branch content. No differences were noted in the ESR spectra on irradiation and measurement at LNT. An explanation may be that while PVC #14 is regarded as highly branched, the number of branches are only four per thousand repeat units (49). Therefore, even if radicals are formed at (or near) these branch sites, their signal will be small compared to the greater probability of unbranched radicals.

The crystallinity of PVC can range from 10 to 80% for polymerization temperatures of 50^o to -78^oC respectively (57). However, comparisons between crystalline polymers was not possible in a glass system, since solvation destroys the crystalline regions. It is only known that the syndiotactic PVC sequences in solution form trans-trans conformations, separated by gauche-gauche units (71): $(TT)_x\ (GG)_1\ (TT)_y$. Syndiotacticity in PVC prepared at the above temperatures does not vary markedly, 54 to 77% respectively (49).

The molecular weight (M_v) of PVC #14 was found to be 31,000 from intrinsic viscosity measurements. Since this polymer was prepared at the highest temperature, it should have the lowest molecular weight. PVC prepared at -78^oC is expected to have the highest molecular weight, ca. 100,000. Aside from crystallinity and branch content, these polymers should differ only in number of end groups per unit weight of sample. Disproportionation reactions often terminate a growing PVC chain (57), resulting in unsaturated chain ends. These chain ends may be able to initiate degradation by providing labile allylic atoms for cleavage by UV., and will be discussed in the next section. The net effect of variable molecular weights is to provide correspondingly variable numbers of end groups. Since end group concentration is very low, the effect of molecular weight on degradation of PVC should be minimal.

Attempts were made to determine whether any other ESR absorption precedes the sextet observed at LNT. Of special interest was the detection of radicals from branch points or chain ends. The PVC glasses were irradiated in the ESR cavity, and growth of the signal was followed during irradiation. A very weak absorption was noted after a few minutes, but its identity could not be determined due to considerable noise at the limits of ESR sensitivity. On further irradiation, the sextet was observed, and increased in intensity as irradiation was continued. Therefore, a precursor to the sextet, if one exists, could not be determined at this time.

C. Effect of Crosslinking and End Groups

If crosslinking of PVC occurred during UV irradiation, the ESR spectrum at LNT should include contributions from crosslinked radicals. Powder samples of PVC, however, have been shown to form negligible crosslinks on UV irradiation (20). Since the polymer chains in a PVC glass are separated by solvent molecules, no crosslinking should occur. On warming to room temperature, no precipitate indicative of crosslink formation was observed in any of the irradiated PVC, COP, or PVB glasses. Therefore, the effect of crosslinking on the ESR spectra at LNT can be discounted.

Winkler (14) suggested that catalyst residues at PVC chain ends could be considered as labile sites for the initiation of degradation. Two types of initiator were used in this work, AIBN and uranyl nitrate (Section IV). Any unreacted initiator was removed from the polymer by thorough washing with absolute ethanol, followed by distilled water. Both initiators are highly soluble in ethanol. Neither UV nor IR spectra showed any traces of residual initiator in polymer films or solutions.

However, AIBN produces $\dot{R}CN$ radicals (where R is the isobutyl group) during photopolymerization. This cyano group is then incorporated into the ends of PVC chains. The RCN group was found (72) to absorb only in the vacuum UV (λ_{max} = 170 nm), and therefore should not be considered as a labile group on UV irradiation of 200 nm and above. The initiating radical formed on visible irradiation of uranyl nitrate is not known (45). A comparison of PVC samples prepared by the two different initiators was performed to determine if there was any effect on degradation at LNT. The ESR spectra were identical for the two systems. Therefore, uranyl nitrate end groups do not appear to effect the radicals formed on degradation of PVC at LNT.

In either case, polymerization was found to involve a significant amount of chain transfer to monomer:

$$-CH_2-\dot{C}HCl + CH_2=CHCl \longrightarrow -CH_2-CHCl_2 + CH_2=\dot{C}H$$

$$CH_2=\dot{C}H + CH_2=CHCl \longrightarrow CH_2=CH-CH_2-\dot{C}HCl \longrightarrow \text{Polymer}$$

On the average, only 0.19 to 0.40 initiator groups were found in each PVC molecule (57). Therefore, chain transfer to monomer is responsible for 60 to 81% of polymers produced. This type of initiation should provide a labile allylic group at the polymer chain end. Since termination of a growing PVC radical is mainly by disproportionation, allylic groups could be found at both ends of a PVC chain. The low bond dissociation energy of allylic chlorine, 58 Kcal/mole, and its

UV absorption, λ_{max} = 285 nm, would make this group favorable for initiation of degradation in PVC. This group is expected on disproportionation:

$-CHCl-CH_2-\dot{C}HCl + ClH\dot{C}-CH_2-CHCl- \longrightarrow -CHCl-CH_2-CH_2Cl + ClHC{=}CH-CHCl-$

but only on half of the terminated chain ends. Therefore, its concentration and effect on degradation would be minute. According to the previous chain transfer to monomer reaction, allylic hydrogens should be formed at the other chain end. The allyl hydrogen is more labile than a secondary hydrogen in the chain, 77 Kcal/mole versus 94 Kcal/mole, but it is not as labile as a secondary carbon-chlorine bond, 73 Kcal/mole. In addition, since allylic hydrogen groups only absorb in the vacuum UV, λ_{max} = 162 nm, they would not be expected to initiate degradation in PVC.

D. ESR of Polyethylene and Paraffins

Polyethylene irradiated with gamma rays at LNT has often exhibited a poorly resolved sextet absorption in the ESR (73) (74). It is remarkable that a similar spectrum can be caused by UV irradiation, even though polyethylene has no absorption in that region (75). The ESR spectra have been attributed to the $-CH_2-\underset{\bullet}{C}H-CH_2-$ radical. The only comment on the observed sextet is the assumption that the five protons in the radical are equivalent. Fessenden (76) did a thourough ESR study of paraffins irradiated by electron beams. He found that they all gave rise to a similar ten line absorption at RT (Figure 19). He assumed that the spectrum was due to four equivalent beta protons and a non-equivalent alpha proton interacting with the unpaired electron. The four beta protons should produce a quintet, which would be split into ten lines by the alpha proton. Therefore, the radical

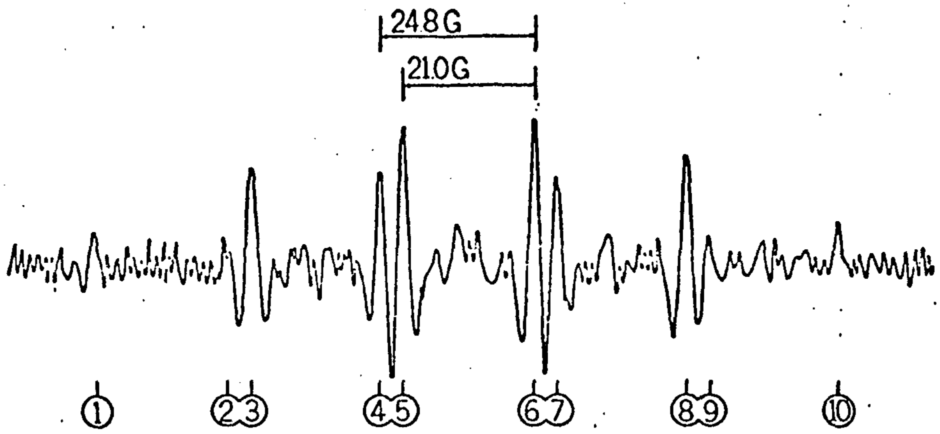


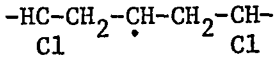
Figure 19. ESR of Electron Beam Irradiated Octadecane at RT (76) (Second Derivative Presentation)

$R-CH_2-\dot{C}H-CH_2-R$ was assigned to the ESR spectra of all the irradiated linear paraffins. It was experimentally determined that the hyperfine splitting was ca. 25 G for beta protons and 21 G for alpha protons. Unfortunately, he did not relate the dihedral angles of the beta protons with their observed hyperfine splitting. This could have provided valuable information as to the preferred conformation of the paraffin radicals.

It should be noted that the above spectra were obtained using liquid paraffins at room temperature in a flow system. This allows for high resolution in the ESR due to rapid averaging of local environments (increased homogeneity). If the same paraffins were irradiated and observed at LNT, the broadening effects mentioned earlier would occur. This would probably result in overlap of adjacent ESR absorptions (lines 2+3, 4+5, 6+7, and 8+9) in Figure 19.

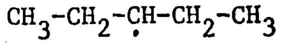
Therefore, the observed spectrum at LNT should be that of a sextet, possibly with some fine structure in the central four lines. This experiment was performed using highly purified pentane, but since it did not absorb in the UV, no resolvable signal could be detected in the ESR on UV irradiation and measurement at LNT.

Recently, a well resolved ESR spectrum of gamma irradiated polyethylene single crystals was obtained (77). There is definite evidence for overlapping absorptions in the central lines of Figure 20. When the 3-chloropentane spectrum (Figure 17) was observed at high sensitivity, similar overlaps could be observed in the central four lines (Figure 21). These results strongly indicate that the ESR spectra of polyethylene, 3-chloropentane, and probably PVC are actually unresolved ten line absorptions. Due to this observation, and previous results, the following radicals are proposed for PVC and 3CP on UV irradiation at LNT:



$-\underset{Cl}{HC}-CH_2-\underset{\bullet}{CH}-CH_2-\underset{Cl}{CH}-$

Radical I



$CH_3-CH_2-\underset{\bullet}{CH}-CH_2-CH_3$

Radical II

These radicals would be expected for the following reasons. Since the only UV chromophore in both PVC and 3CP is the carbon-chlorine bond, cleavage should occur at this site. The g-values indicate the presence of an organic radical with unpaired spin density localized on carbon. The intensity ratio of ESR lines indicates that the unpaired electron is interacting with five approximately equivalent protons. Similar spectra were observed for COP, PVB, polyethylene, and linear paraffins. And the spectra from PVC and 3CP were nearly identical.

Figure 20. ESR of Gamma Irradiated Polyethylene Single Crystals (77)

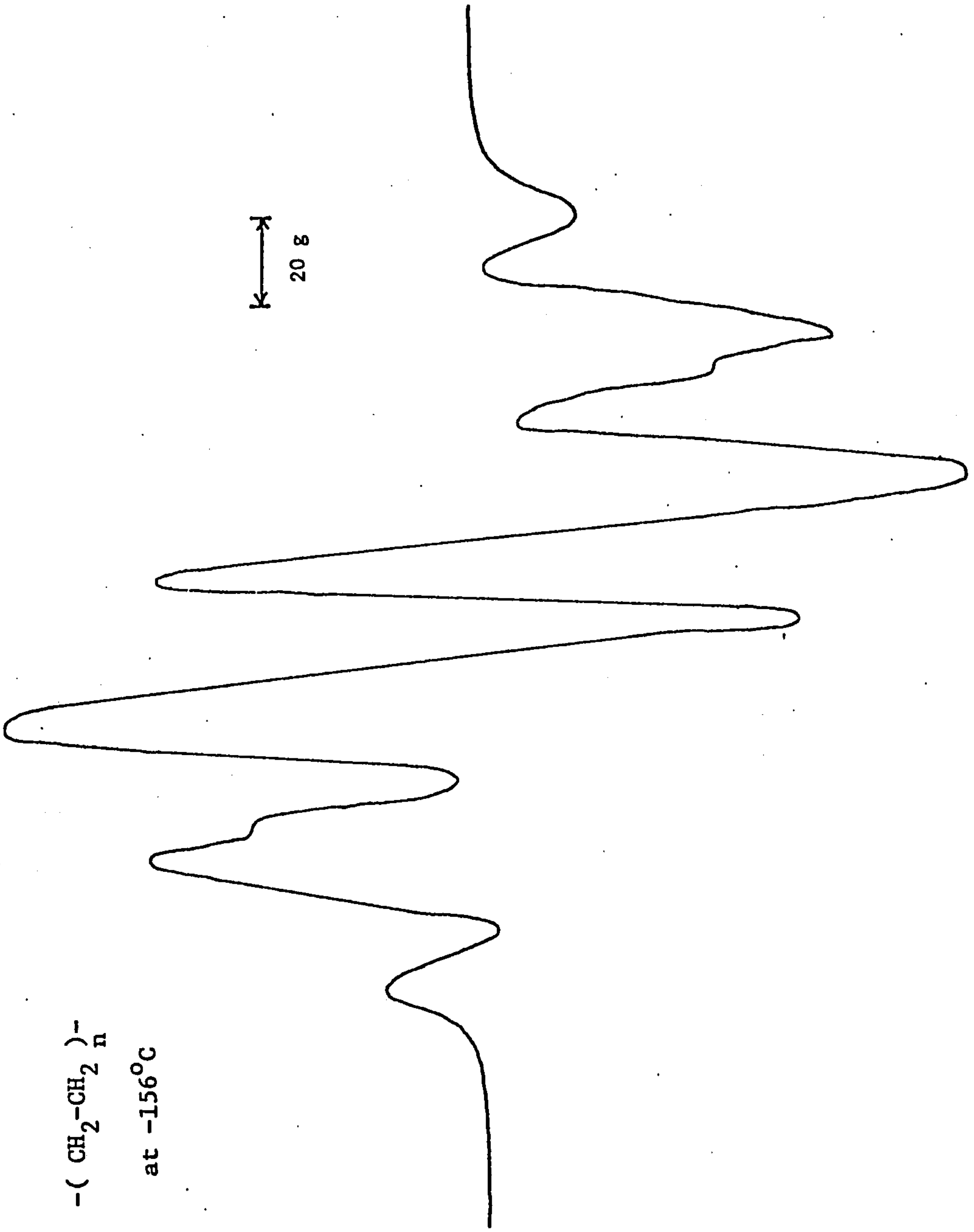
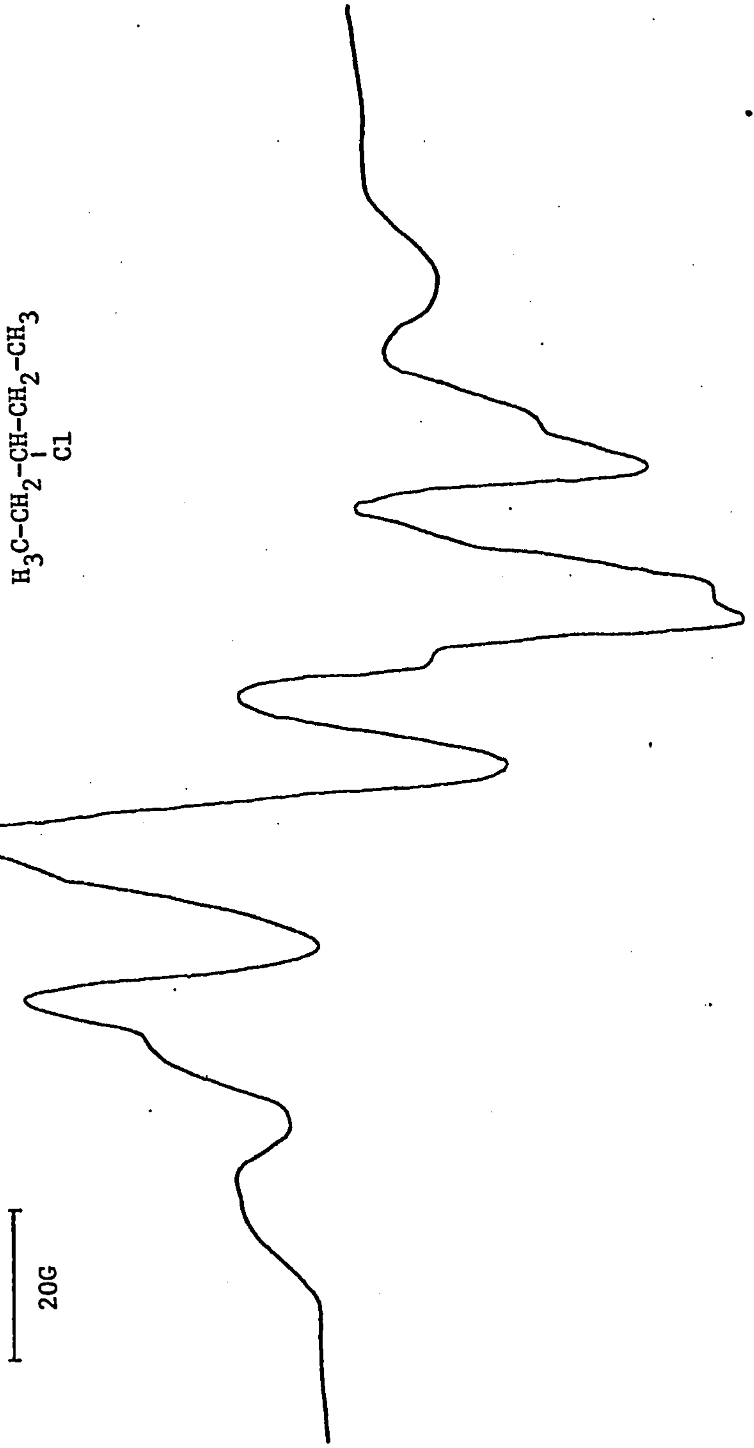


Figure 21. ESR of UV Irradiated 3CP at LNT (High Sensitivity)



E. Copolymer and Polyvinylbromide

The COP and PVB samples were prepared as polymer analogs of PVC. Cleavage of the carbon-halogen bond at LNT should result in the same radical for each of these polymers. Since secondary C-Cl and C-Br bond dissociation energies are 73 and 59 Kcal/mole respectively, a copolymer of vinyl chloride and vinyl bromide could be regarded as a PVC chain with weak points. As mentioned in Section IV-4, the feed ratio of VC/VB (v/v) was 10/1 for the majority of copolymers prepared. Since the reactivity ratio (in solution, at 40°C), r_1 =0.825 for VC and r_2 = 1.050 for VB (53), the copolymer composition should be 15 units of vinyl chloride for one unit of vinyl bromide. In addition, the values for r_1 and r_2 are close to one, indicating formation of a random copolymer, as had been proposed by the TGA analysis (Section V, 2.). Preferential scission is expected at the C-Br bond, but regardless whether this bond or the C-Cl one is cleaved, the resulting polymer radical would be the same. This is why all the COP glasses exhibited ESR spectra identical to the PVC glasses at LNT.

The PVB glasses produced an apparent sextet from the above radical, but with a broad overlapping singlet attributed to short polyene radicals (Figure 16). This implies that partial degration of the polymer has occurred, even at LNT. Polyene radicals were not observed for the PVC or COP glasses at LNT. Three factors may contribute to the greater ease of PVB degradation as compared to PVC and COP. While PVC contains C-Cl as its weakest link, and COP has one C-Br per 15 C-Cl bonds as its weakest link, the PVB chain contains only C-Br as its carbon-halogen bond. The molecular weight of PVB is 2,700, ca. one-tenth that of PVC or COP. This low value for M_v is due to the much higher chain transfer ability of vinyl bromide as compared to vinyl chloride (53). This low molecular weight provides PVB with about ten times the chain ends as PVC or COP. While the majority of chain ends were shown to be UV stable, a tenfold increase in the less stable groups would significantly effect the degradation of PVB. Polyvinylbromide is expected to contain a greater degree of syndiotacticity due to the very bulky bromine atom. This increased syndiotacticity will increase the amount of planar trans-trans units in solution. Since conjugated polyenes are planar due to resonance requirements, the higher degree of syndiotacticity of PVB should enhance their formation. While no photodegradation literature on PVB is available, the thermally degraded polymer has shown the presence of much longer polyene units, n=5-40, than PVC degraded at the same temperature, n=5=15 (78). These three factors should greatly lower the resistance of PVB to degradation. Thus it is not too surprising to see the polymer partially degraded at LNT.

F. The Chlorine Radical

When radical I or II (Section VIII, 1., D.) is formed, a chlorine (or bromine) radical should also be formed. This radical has never been observed by ESR in the liquid or solid phase, and could not be detected in this work. The expected spectrum of a Cl^{35} radical would consist of four triplets with equal intensity, each of the triplets being separated by 112 G (79). Since the natural abundance of Cl^{35} is only 75.4%, the spectrum would be complicated by an overlap of the Cl^{37} radical, which would comprise 24.6% of the total ESR absorption. The Cl^{37} radical would give a similar spectrum, though shifted slightly from that of the Cl^{35} due to the different magnetic moments of the nucleii.

The chlorine radical is well known to abstract hydrogen from alkanes at RT, since the energy required for the reaction is quite low, 0.7 Kcal/mole for secondary hydrogens (80). However, this abstraction may be considerably more difficult at LNT. If this reaction did occur in the 3CP and PVC glasses, there should be a new radical formed, equal in abundance to Radical I or II. Since only one radical species was found to be present in either the 3CP or PVC glasses, the abstraction of a hydrogen by chlorine must be minimal.

Two theories are currently used to explain the absence of a chlorine absorption in the ESR, spin lattice relaxation time and 'wall' deactivation. It was proposed that the spin-lattice relaxation time (T_1) of a chlorine radical is very short (81). The spin-lattice relaxation time can be explained by the following analogy.

If a spin system (Cl•) that has absorbed energy is thought of as having increased in temperature, then the spin-lattice relaxation time can be considered as the time it takes for the system to regain its equilibrium temperature with its surroundings. Therefore, the excited state of the unpaired electron on chlorine is thought to transfer energy rapidly to the surrounding molecules (lattice), making the transition between excited and ground states very quickly. If T_1 is the dominant relaxation process for chlorine, then the ESR line width is inversely proportional to it (33). This theory then assumes that since T_1 for Cl is very short, the line width of Cl absorptions in the ESR are broadened beyond detection. The chlorine radical was never observed for liquids or solids, but it has been observed in the gas state (82). The spin-lattice relaxation time for chlorine in the gas state should be much longer due to the scarcity of neighboring molecules. This longer T_1 would cause narrower lines which could then be detected by ESR.

It has also been proposed that the chlorine atoms can be deactivated by collisions with the walls of a reactor (83). Since the majority of UV radiation is absorbed by the surface of a PVC glass, adjacent to the quartz wall, this type of effect should be considered. The wall may be regarded as a neighboring molecule (mainly SiO_2), which can reduce the spin-lattice relaxation time of a chlorine radical, as mentioned above. Of more importance are the following possibilities (83):

$$Cl\cdot + Cl\cdot(W) \longrightarrow Cl_2 + W \qquad Cl\cdot + W \longrightarrow Cl\cdot W$$

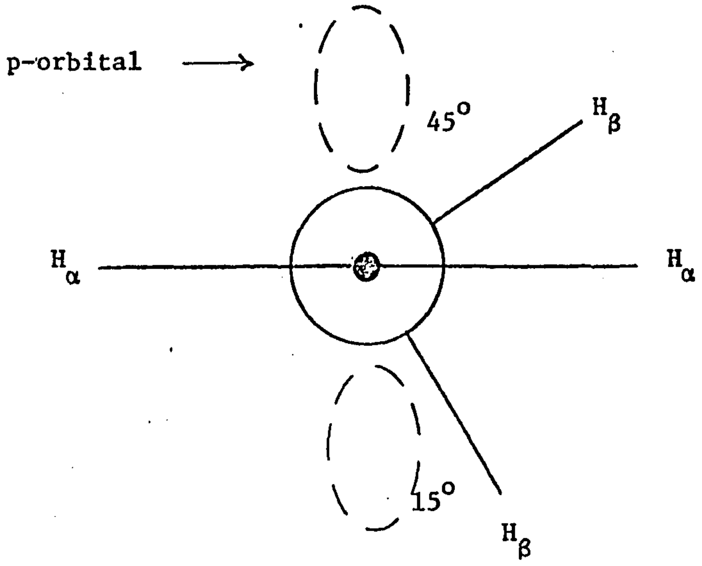
The first reaction assumes that one chlorine becomes adsorbed on the wall of a reactor, and a second chlorine radical can rapidly abstract the first, producing chlorine gas. Since this gas has not yet been determined as a degradation product of PVC, this reaction seems doubtful. The second reaction proposes that Cl· might become incorporated (possibly by a chemical bond) into the wall. This reaction may be significant because recently sand (SiO_2) has been shown to be an effective catalyst for the photochemical decomposition of carbon tetrachloride (84).

Attempts were made to study the effect of chlorine radicals on the degradation of PVC. This was performed by introducing chlorine gas into PVC glasses and analogs. Chlorine gas has a λ_{max} at 330 nm, and intense absorptions in the 250-200 nm range. Since the bond dissociation energy of Cl-Cl is only 58 Kcal/mole, it was expected that a large amount of additional chlorine radicals would be formed on UV irradiation of the samples at LNT. These additional chlorine radicals could possibly alter the ESR spectra. No such change was observed. This evidence may be interpreted in two ways. The additional chlorine radicals may have no effect on the degradation of PVC, and they were undetected due to the theories outlined above. Another possibility is that while the Cl-Cl bond is labile to UV radiation, the Cl atoms are quite bulky and very reactive. Therefore, when the bond is cleaved by UV at LNT, the atoms may rapidly recombine. This is probably the case, since when Cl_2 alone was irradiated and measured at LNT, no absorption could be detected in the ESR.

G. 1-Chloropentane

Irradiation of primary halocarbons has been shown to produce primary radicals by cleavage of the carbon-halogen bond (85) (86). In the UV irradiation of 1-chloropentane, this process should also occur, since a primary carbon-chlorine has a bond dissociation energy of 78 Kcal/mole as compared to 99 and 94 Kcal/mole for primary and secondary carbon-hydrogen bonds respectively. Therefore, ICP was used as an analog for the formation of primary radicals in PVC. Possible sites for these radicals could be at chain ends, at branch ends, or on cleavage of the polymer chain. While the spectra from ICP (Figure 18) and the PVC/TP glass (Figure 15) both appear as sextet absoprtions, the line intensity ratios are markedly different - 1:4:4:4:4:1 and 1:4:9:9:4:1 respectively. For ICP, the primary radical $R\text{-}CH_2\text{-}CH_2^{\bullet}$ is assumed to be in such a conformation that the dihedral angle of one beta proton is 15^o and the other is 45^o (Figure 22). Calculations for hyperfine splitting of the two beta protons, using the McConnell relationship with $\rho = 1.000$, yielded values of 24 and 46 G for the 45^o proton and 15^o proton respectively (37). However, since the spin density on an alpha carbon in a primary radical is actually 0.919 (35), the values should be lower,

Figure 22. Analysis of Primary Radical



Hyperfine Splitting

$$\text{Alpha-H} = Q\rho = (24.0)(0.919)^{**} = 22\text{G}$$

$$\text{Beta-H} = (A + B\cos^2\theta)\rho$$

$$\text{Beta-H}_{45} = 0 + 48^{*}\cos^2 45^\circ(0.919) = 22\text{G}$$

$$\text{Beta-H}_{15} = 0 + 48\cos^2 15^\circ(0.919) = 42\text{G}$$

$$(\ \text{Alpha-H} = \text{Beta-H}_{45} = \tfrac{1}{2}\ \text{Beta-H}_{15}\ )$$

* R.W. Fessenden, Adv. Rad. Chem., 2, 18 (1970)

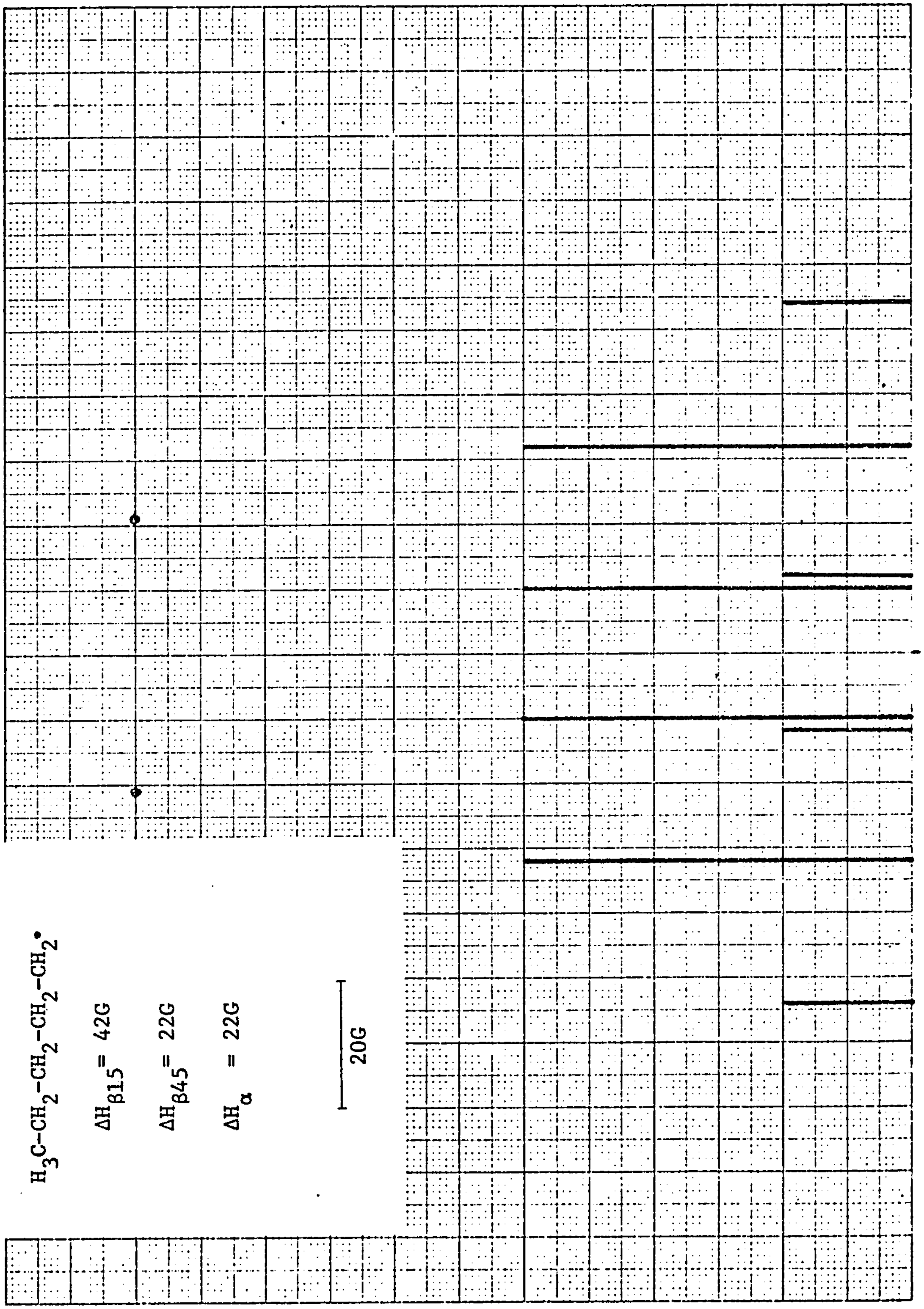
** S.Y. Pshezhetskii, et al., "EPR Of Free Radicals In Radiation Chemistry", Wiley & Sons, N.Y. 1974 i.e. 22 and 42 G. The alpha hydrogen's hyperfine splitting can be calculated from $\Delta H=Q\rho$ (Section III). For primary radicals, Q=24.0 and $\rho=0.919$ (35). Therefore, a value of 22 G for spin polarization of alpha protons is obtained.

Overall, there are three protons with equivalent splittings of 22 G, and one proton with almost twice that value, 42 G. This beta proton would produce a doublet of equally intense lines in the ESR; each of these two lines would then be split into a quartet with a binomial line intensity ratio of 1:3:3:1 by the other three protons. A simulated stick diagram is presented in Figure 23. It can be seen that due to line overlap, the observed spectrum would be that of a sextet. The theoretical line intensity ratio should be 1:3:4:4:3:1, which closely resembles that of the 1-chloropentane spectrum. This type of intensity ratio was not observed in the PVC glass spectra, therefore no significant amount of primary radicals is expected on irradiation of PVC at LNT.

H. Conformation and Computer Simulation

The conformation of the PVC radical formed at LNT has never been determined due to insufficient data on the hyperfine splitting of the beta protons. It will be assumed that the conformation of the 3-chloropentane radical is similar to that of the PVC radical, since their spectra are almost identical. The conformation of vinyl polymers, such as PVC, in solution could only be correlated with the amount of syndiotacticity in each. The characteristic chain conformation of vinyl syndiotactic sequences in solution has been shown by Morawetz (71) to consist chiefly of trans-trans groups, separated by gauche units: $\ldots (TT)_x (GG)_1 (TT)_y (GG)_1 (TT)_z \ldots$. Crescenzi (87) proposed a similar structure: (TT) (TT) (GG) (TT) (TT) ... (TT) (GG) (TT)... for

Figure 23. ESR Stick Spectrum of 1CP Radical at LNT



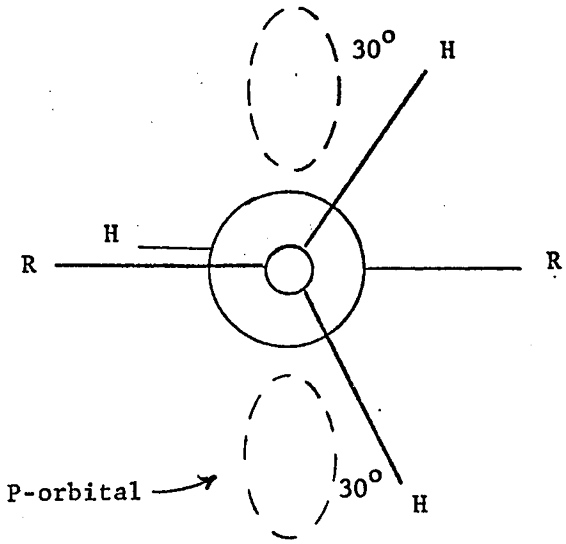
syndiotactic chains in solution. In addition, Corradini (87) calculated that the conformational internal energy of syndiotactic PVC was at a minimum for a (TTTT) sequence. The nature of conformational sequences in isotactic PVC has not been determined.

Since the prepared PVC samples had a high degree of syndiotacticity, 54-77% (Section V, 1.), it is expected that the trans planar groups should predominate for PVC in solution. On irradiation, the radical should be formed in one of the trans-trans sequences. If the proposed radical, $-CH_2-\dot{C}H-CH_2-$ is formed, it follows that the four beta protons must be equivalent from geometric considerations (Figure 24). There are only two dihedral angles that fulfill this requirement, $\Theta=60^o$ or 30^o. A dihedral angle of 60^o would not be in accord with the trans-planar sequence. Therefore, the dihedral angle must be 30^o.

This angle should be used in the McConnell relationship, along with appropriate values for A and B. The spin density on a saturated secondary carbon (the isopropyl radical) was found to be 0.844 (35). Therefore this value was used in the analysis of the analogous PVC radical. Thus, the hyperfine splitting of the beta protons was found to be 25.3 G. The previous equation, $\Delta H=Q\rho$, determined the amount of spin polarization for the alpha hydrogen. The values $Q=26.2$ and $\rho=0.844$ (for secondary alkyl radicals) gave 22G as the hyperfine splitting from the alpha hydrogen (Figure 25).

Therefore, due to the four equivalent beta protons, a quintet is expected, which should be split into ten lines by the alpha proton (Figure 26). This constructed spectrum can be applicable to either 3-chloropentane or PVC, the 'R' groups being CH_3 or polymer chains respectively. This spectrum appears quite similar to those found experi-

Figure 24. Conformation of PVC Radical



Micro

Macro

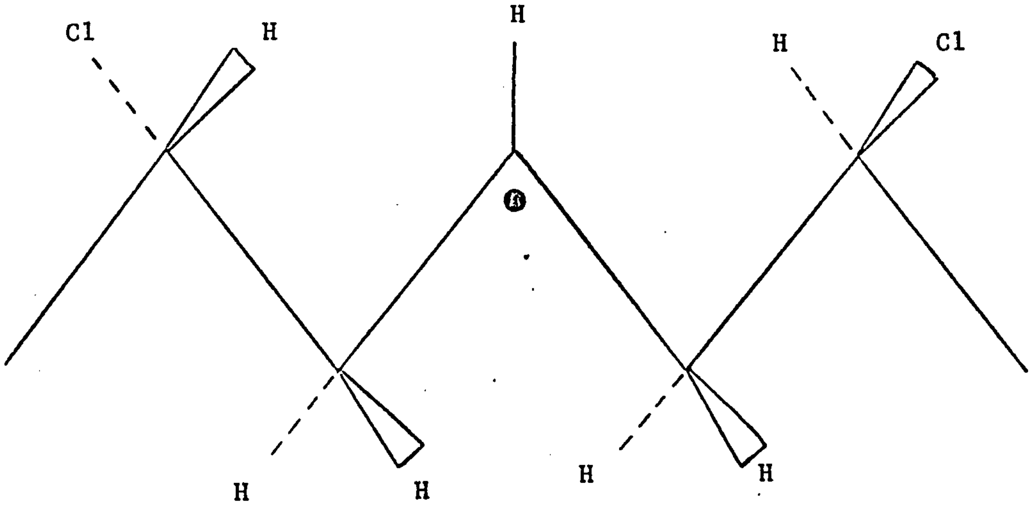


Figure 25. Calculation of Hyperfine Splitting for PVC Radical

$$\Delta H_{Beta} = (A + B\cos^2\theta)\,\rho$$

$\theta = 30^\circ$

$A = 0 - 5G$

$B = 40 - 50G^*$

$\rho = 0.776 - 1.000$ (for saturated alkyl radicals)**

Assume:

$A = 0$

$B = 40G$

$\rho = 0.844$ (value for 2° radical)

$$\Delta H_{Beta} = (0 + 40\cos^2 30^\circ)\,0.844$$
$$= 25.3G$$

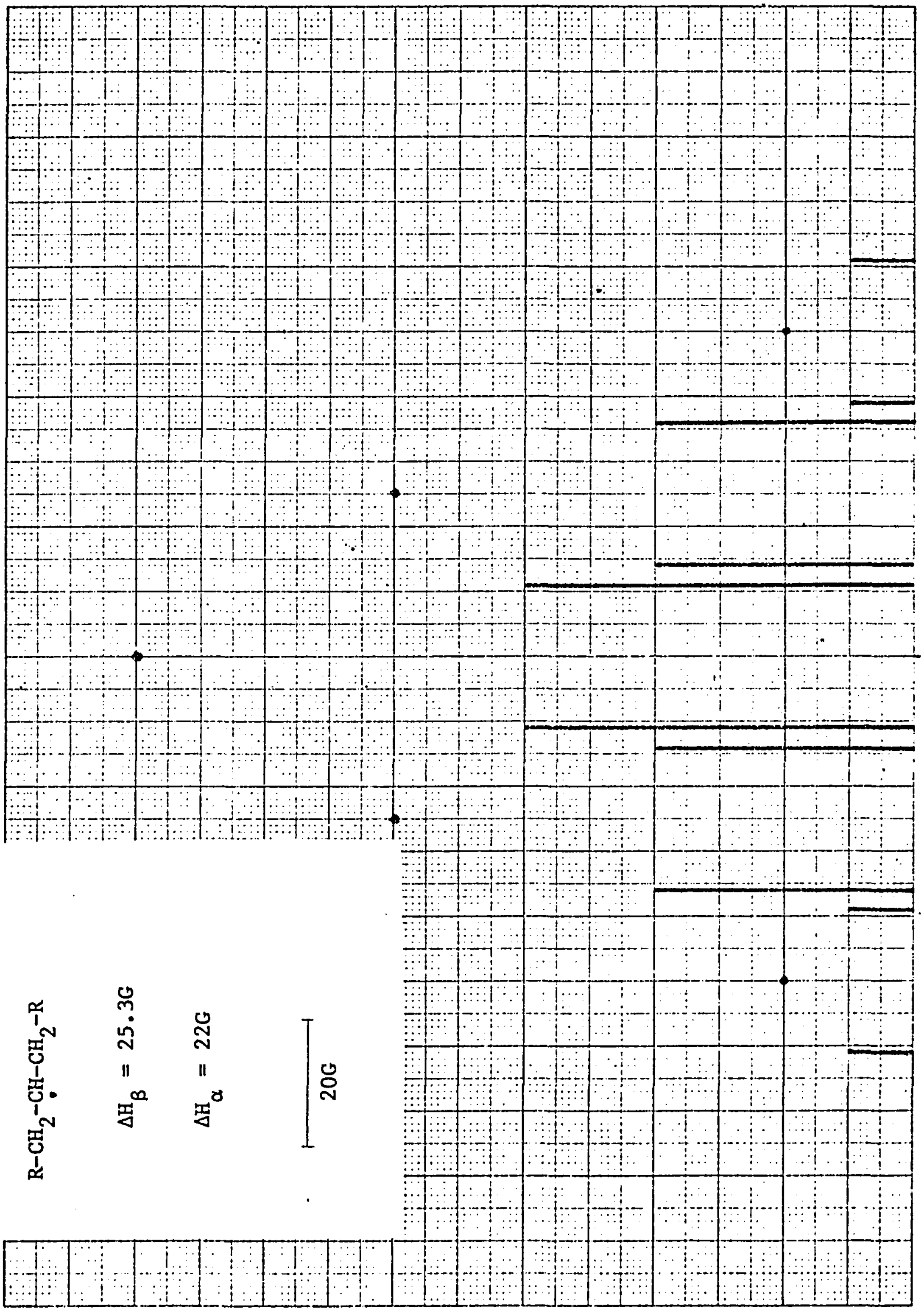
$$\Delta H_{Alpha} = Q\,\rho = (26.2)(0.844) = 22G$$

---

* R.W. Fessenden, Adv. Rad. Chem., 2, 18 (1970)

** S.Y. Pshezhetskii, et al., "EPR Of Free Radicals In Radiation Chemistry", Wiley & Sons, N.Y. 1974

Figure 26. ESR Stick Spectrum of PVC Radical at LNT



mentally by Fessenden (Figure 19). If this PVC radical could be observed in the liquid state, all ten lines would be visible. However, due to the broadening effects at LNT (Section VII, 1.), the central eight lines will overlap, and the spectrum would appear as a symmetrical sextet with a theoretical line intensity ratio of 1:5:10:10:5:1. The intermediate case, where only partial overlap of the central lines occurs, can be seen in the 3-chloropentane spectrum at high sensitivity (Figure 21). Fine structure in the central four lines is clearly evident.

A computer simulation was performed to observe the effect of variable line width on the first derivative of the calculated ESR spectrum Since dipolar interaction is the major contribution to line broadening, in the ESR spectrum of PVC radicals, a Gaussian line shape is expected for each of the ten absorptions. Therefore, each line was assigned a Gaussian curve, the variables being: relative amplitude (AMP); position in the spectrum (SHF); and line width (HAL). The resultant curves were then added, and the first derivative taken.

The equation for a first derivative Gaussian curve is (32):

$$Y'(H) = \frac{-2y_m \ln 2}{\frac{1}{2}\,\Delta H_{\frac{1}{2}}} \left(\frac{H - H_o}{\frac{1}{2}\,\Delta H_{\frac{1}{2}}}\right) \exp\left[-\left(\frac{H - H_o}{\frac{1}{2}\,\Delta H_{\frac{1}{2}}}\right)^2 \ln 2\right]$$

where: y_m is the relative amplitude of each line; $\Delta H_{1/2}$ is the line width at half the maximum amplitude; H_o is the reference position (origin); and H is the position of the abosorption. The relative amplitudes and line positions were as shown in Figure 26; the line width was varied from 4 to 24 G. This equation was normalized and transformed into a Fortran statement for an IBM 370/168 computer. The program and variables are given in Figure 27. The computed spectra were displayed

Figure 27. Fortran Statement for ESR Simulation

```
      DIMENSION Y(200,10),AMP(10),HAL(10),SHF(10)
      CALL TRAPS(0,0,5000)
    5 READ(5,*,END=999)N,(AMP(I),HAL(I),SHF(I),I=1,N)
      N2=N+2
      DO 10 II=1,200
      I=II-1
      Y(II,N+1)=0
      Y(II,N+2)=0
      DO 12 J=1,N
      A1=(SHF(J)-I)/HAL(J)
      A2=(SHF(J)+I)/HAL(J)
      E1=EXP(-A1*A1)
      E2=EXP(-A2*A2)Y(II,J)=AMP(J)*(E1+E2)
      Y(II,N+1)=Y(II,N+1)+Y(II,J)
      Y(II,N+2)=Y(II,N+2)+AMP(J)*2,*(A1*E1-A2*E2)
   12 CONTINUE
   10 CONTINUE
      WRITE(10,222)((I-1,Y(I,J),I=1,200),J=1,N2)
222   FORMAT(I6,E17.4)
      GO TO 5
  999 STOP
      END
$DATA
```

AMP	HAL_1	SHF
1	1	60
1	1	40
4	1	35
4	1	15
6	1	10

$HAL = 1/2\ \Delta H_{\frac{1}{2}}\ /\ (\ln 2)^{\frac{1}{2}}$

$HAL_2 = 4$

$HAL_3 = 12$

graphically by an IBM-1625 Plotter (90).

Figure 28 represents a well resolved spectrum (narrow line width) which could be obtained for PVC radicals with high local mobility in a homogenous environment. This spectrum is analogous to those from Fessenden's paraffins (Figure 19); ten lines can be clearly observed. As line broadening occurs, overlap of the central eight lines is noted (Figure 29). This computed spectrum can be compared with the one experimentally observed for 3-chloropentane (Figure 21). As can be seen in both, six lines are evident, with fine structure in the central four absorptions. Figure 30 represents the case for PVC glasses at LNT, broadening effects have transformed the observed spectrum to a sextet with no apparent fine structure. The computed hyperfine splitting is 23.8 G and the line intensity ratio is 1:5:10:10:5:1. These results offer further evidence for the proposed 3CP and PVC radicals, and support the contention that the observed sextet is actually an unresolved ten line absorption.

I. Effect of Deuteration

Deuteration of analogs and polymers should be a very useful tool in the analysis of their ESR spectra. The range of hyperfine splittings under consideration in this study is 22-26 G. Since the magnetic moment of a deuteron is 0.15 that of a proton, the splitting due to a deuteron will be 0.15 as much as a proton's, or ca. 3.5 G. The experimentally observed line widths are 21-26 G, therefore the hyperfine splitting caused by a deuteron would not be observed. The net effect of deuterium substitution would be to 'erase' the splitting caused by the replaced hydrogen.

Figure 28. Computer Simulated ESR Spectrum of PVC Radical (ΔH1/2 =2G)

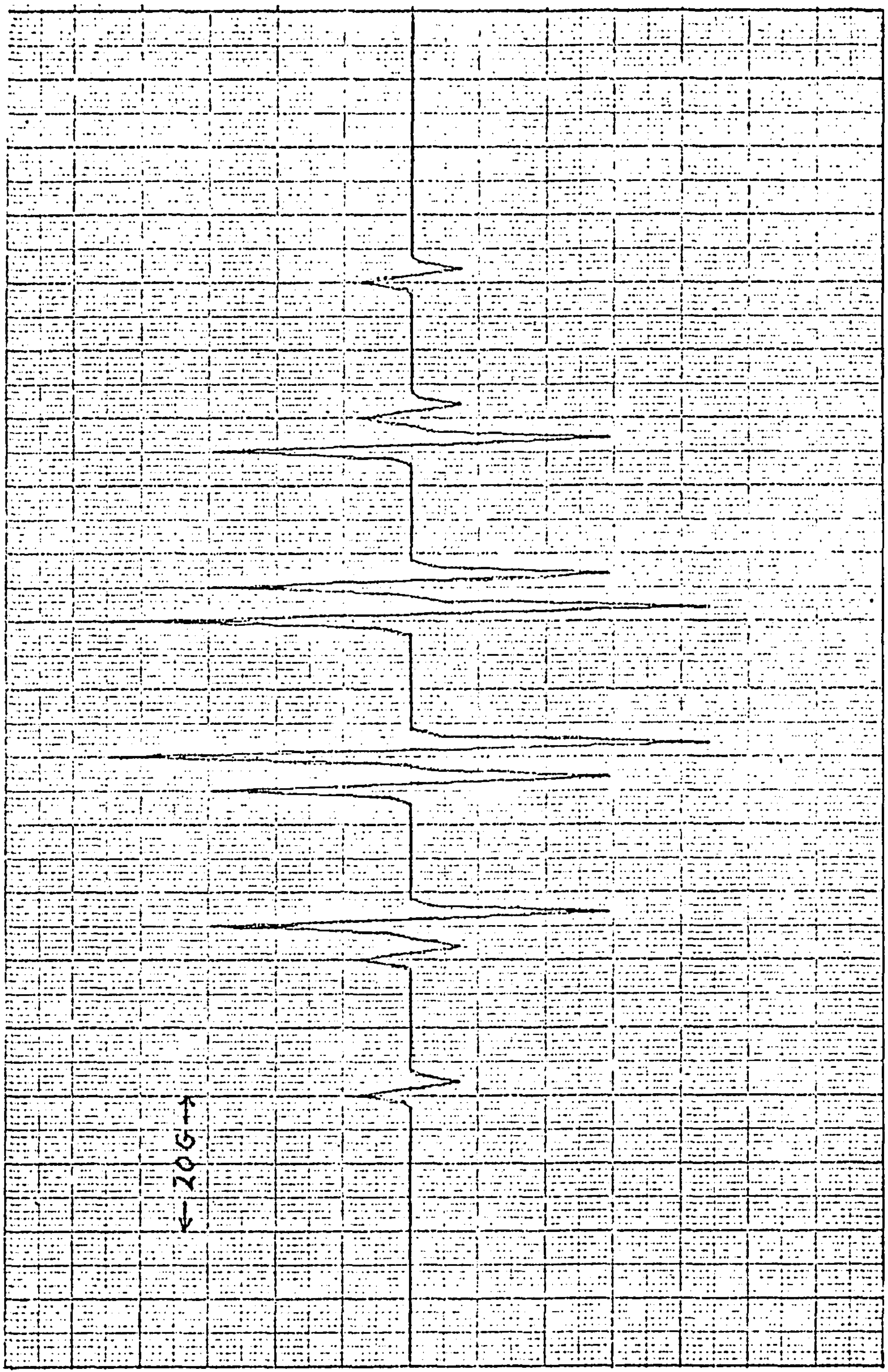


Figure 29. Computer Simulated ESR Spectrum of PVC Radical (ΔH1/2 = 8G)

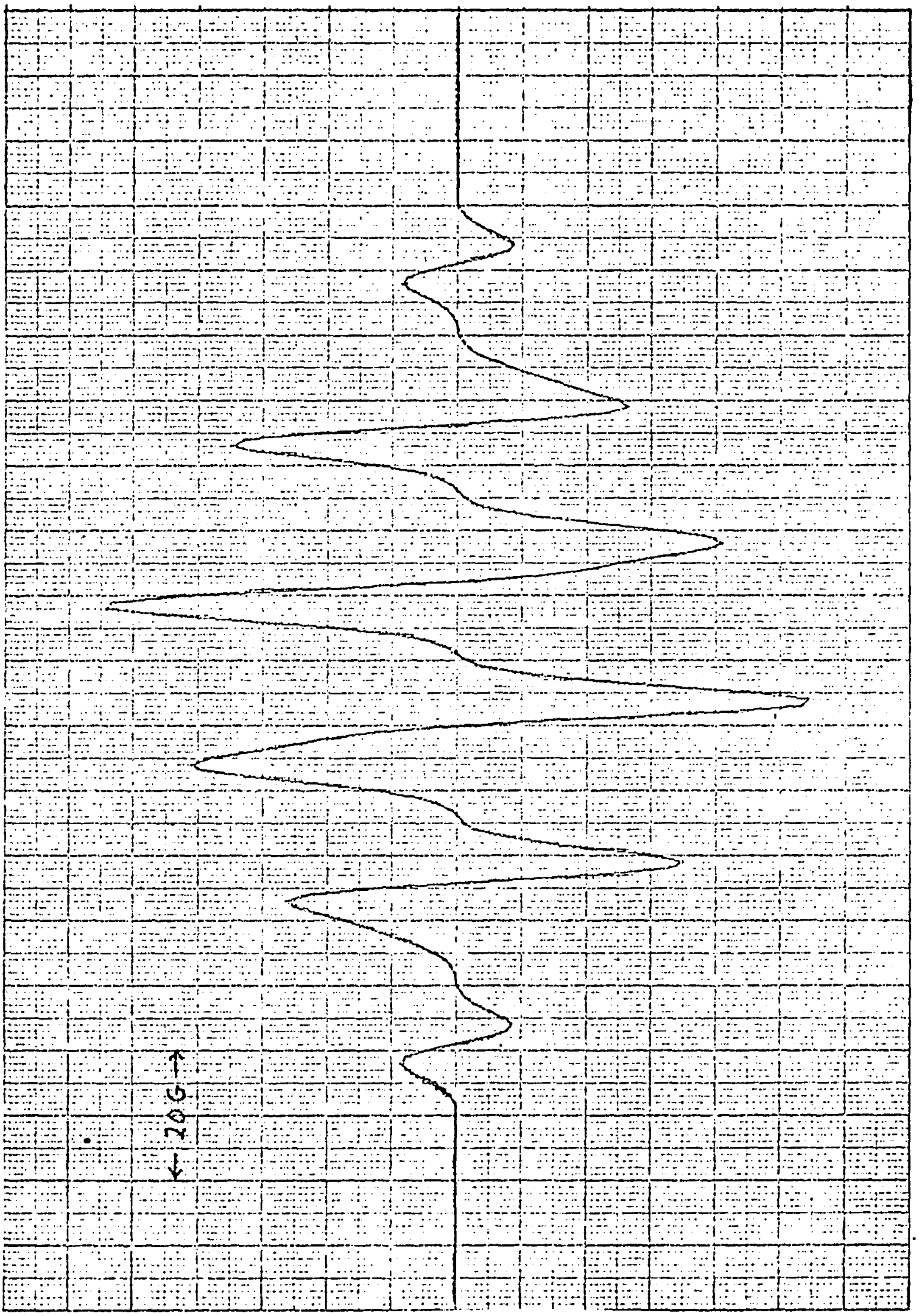
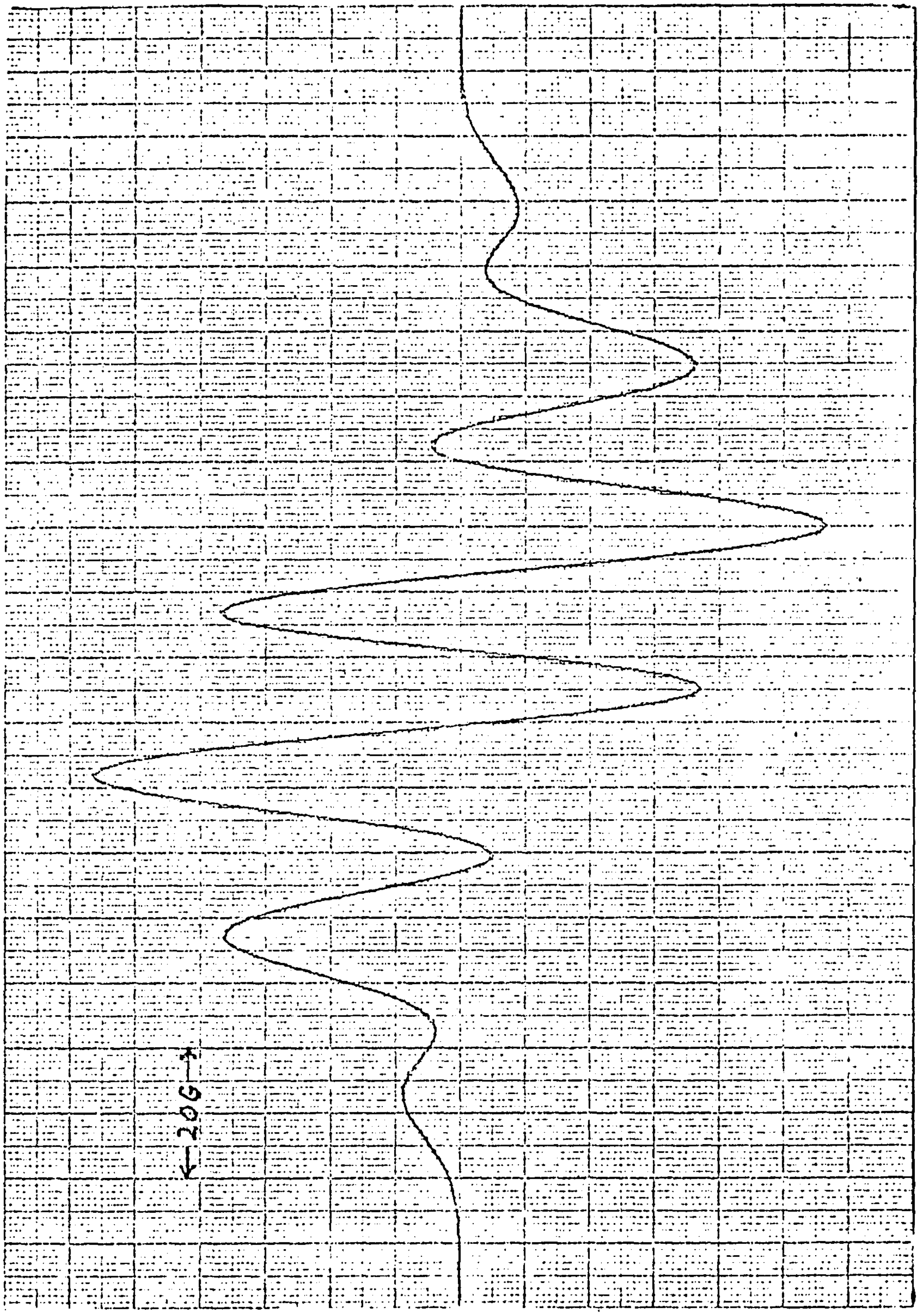


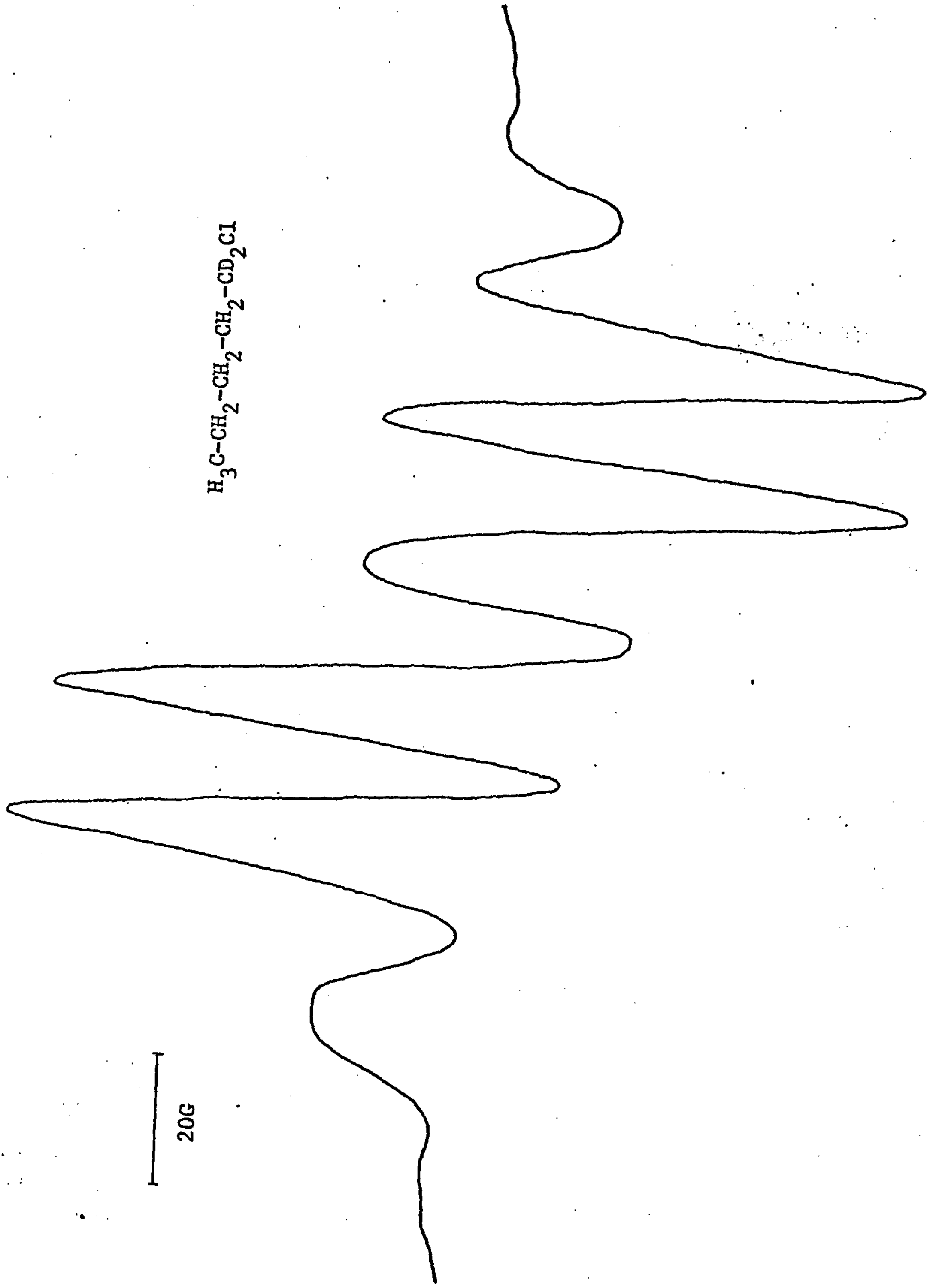
Figure 30. Computer Simulated ESR Spectrum of PVC Radical (ΔH 1/2 = 24G)



Two analogs and one polymer were prepared with deuterium specifically labeled in the alpha position (Section IV): 1, 1 d_2-1-chloropentane; 3d-3-chloropentane; and PVC - alpha d_1. These compounds were subjected to the same irradiation conditions as the undeuterated samples. No literature was available on the ESR behavior of these compounds, under any type of irradiation. Indeed, there were very few references on the ESR spectra of any deuterated radical. Since deuteration appears to be a useful technique in the analysis of ESR spectra, the scarcity of information was unexpected.

The 1-chloropentane had both alpha protons replaced by deuterons. Therefore, if the analysis of the undeuterated radical is correct, the only splitting observed from the alpha deuterated radical should be due to the beta protons. The 15° beta proton would produce a doublet absorption separated by 42 G. This doublet should then be split by the 45° proton to produce a quartet of equal line intensity, the hyperfine splitting being 20-22 G. On irradiation of 1, 1d_2-1-chloropentane, however, a sextet is observed in the ESR at LNT (Figure 31). This sextet is almost identical (except for a slight unidentified absorption in the wings) to the one obtained on irradiation of the undeuterated analog (Figure 18). This result is most surprising, since only the central four lines should be present. Since the observed spectrum is indicative of an undeuterated primary radical, it could be assumed that no carbon-chlorine cleavage had occurred in the deuterated analog, and that the radical had somehow formed at the other end of the molecule. This would be energetically unfavorable, since the bond dissociation energy for a primary carbon-hydrogen bond is 99 Kcal/mole, as compared to 78 Kcal/mole for a primary carbon-chlorine bond. In addition, the

Figure 31. ESR of 1DCP UV Irradiated at LNT



only chromophore in the molecule is the carbon-chlorine bond, which should cause cleavage at this site on UV irradiation.

In the 3d-3-chloropentane, the alpha proton has been replaced by a deuteron. Therefore, according to the analysis of the 3-chloropentane radical (Section VIII, 1., H.), only the hyperfine splitting caused by the four equivalent beta protons should be observed. A five line absorption is then expected on irradiation of this sample, the hyperfine splitting being 25 G. However, on irradiation of the deuterated compound, a sextet is again observed (Figure 32), with hyperfine splitting, line intensity ratio, and g-value similar to those from the undeuterated 3-chloropentane. The only noticeable difference is some fine structure in the outer two lines. The expected major change of sextet to quintet was not observed for the deuterated sample. This result is also surprising, especially since there is no possible radical site in 3d-3-chloropentane that could cause the observed sextet.

In PVC-alpha d_1, the alpha proton has been replaced by a deuteron. Since the analysis of the undeuterated PVC radical was the same as that of the 3-chloropentane radical, a quintet was also expected for the deuterated polymer. The irradiated PVC-alpha d_1/TP glass produced the ESR spectrum shown in Figure 33. This spectrum is again a six line absorption with the same characteristics as the ESR for the undeuterated PVC glasses. An unidentified singlet absorption is shown causing interference in the central lines of the spectrum. This singlet is not part of any quintet absorption, since the quintet should have an overall width of 4 x 25 G=100 G. The observed spectrum is characteristic of a sextet, 5 x 23 G=115 G, in width. This result is most unexpected, not only because it appears to negate carbon chlorine cleavage, but al-

Figure 32. ESR of UV Irradiated 3DCP at LNT

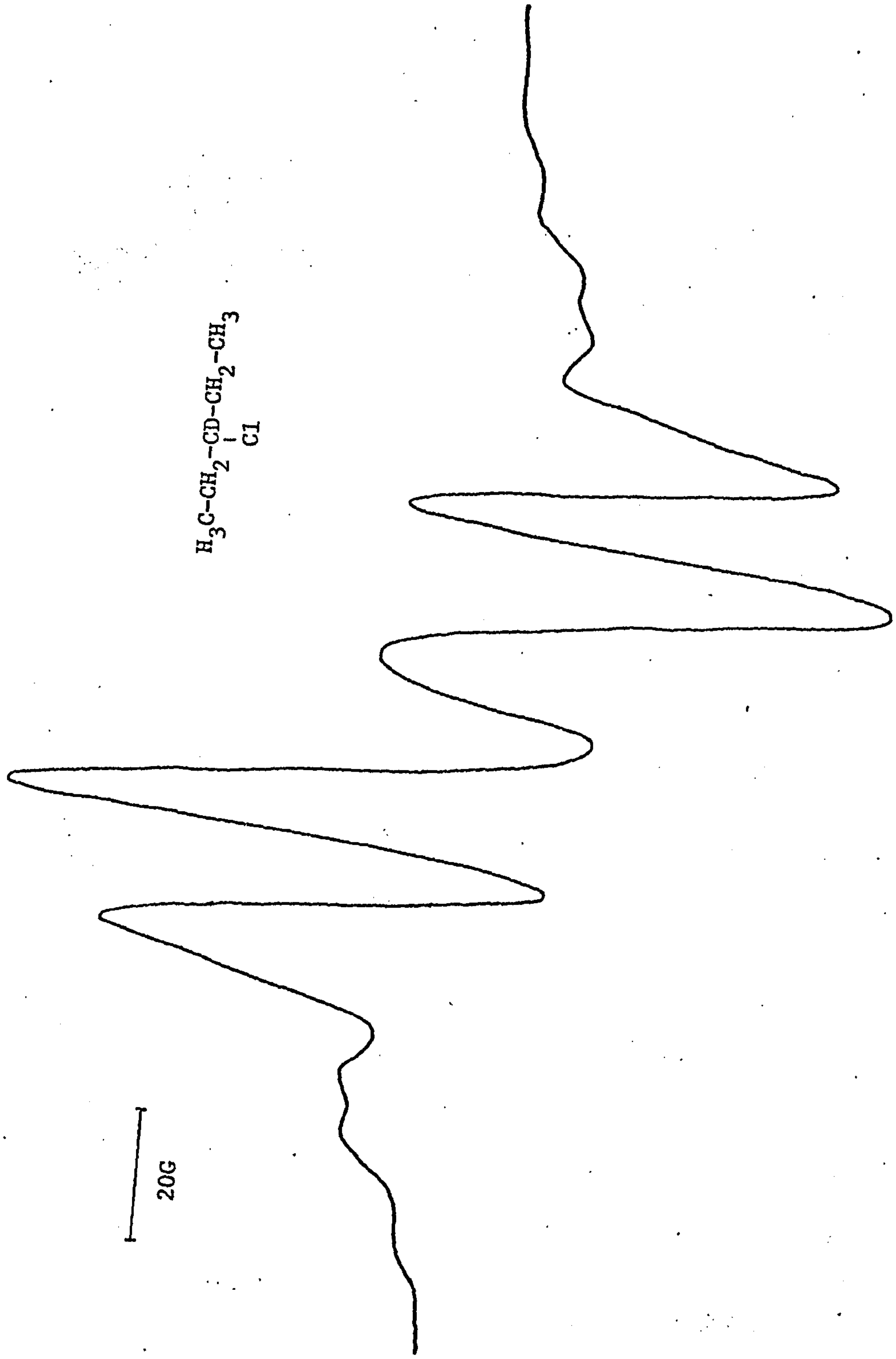
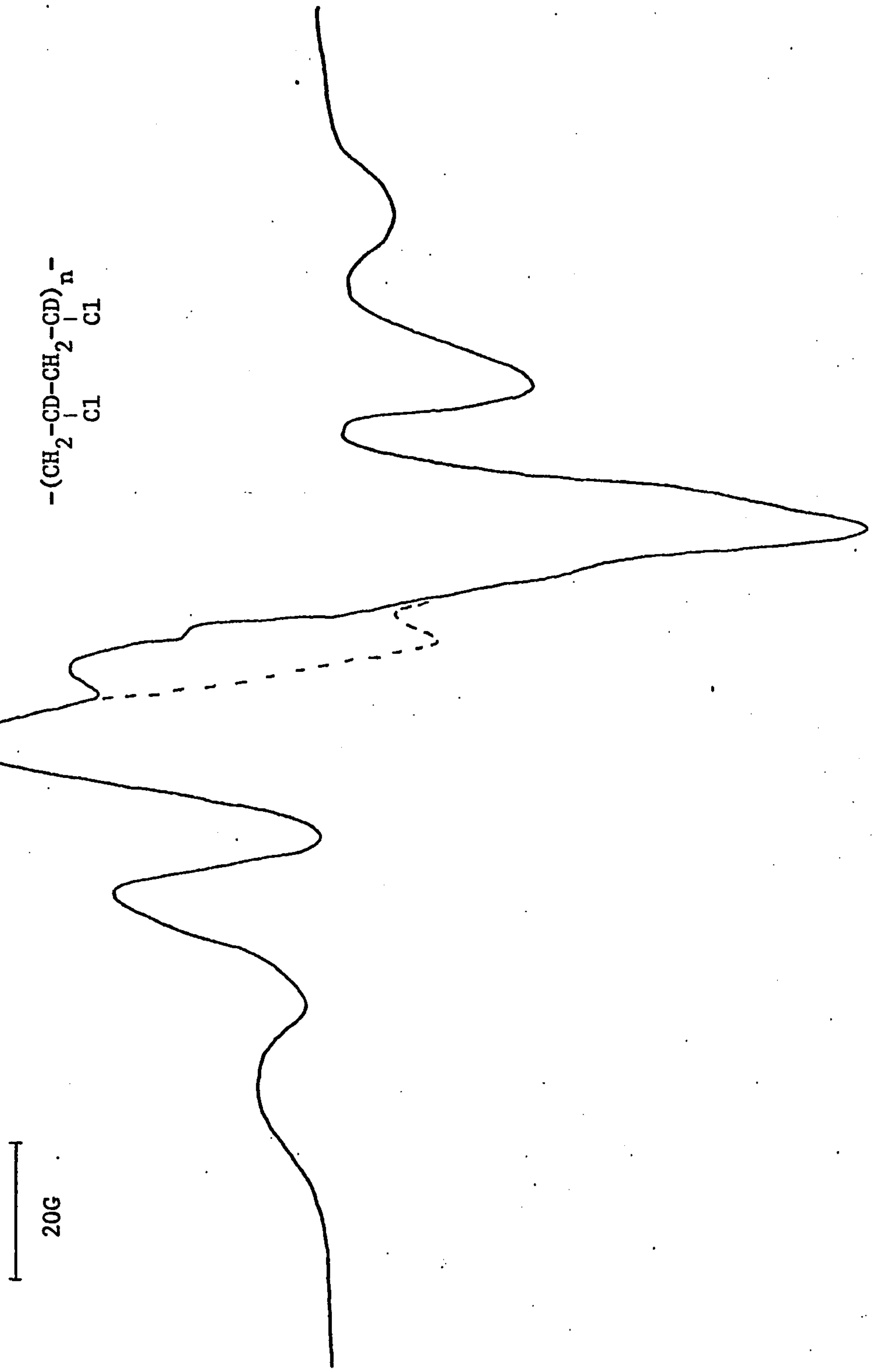


Figure 33. ESR of UV Irradiated PVC-αd_1/TP at LNT



so since there is no radical site in PVC-alpha d_1 that could produce such a sextet.

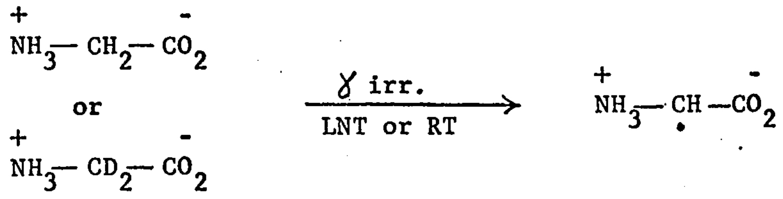
At first, it seemed that the assignment and analysis of radicals from 1-chloropentane, 3-chloropentane, and the PVC glasses were at fault. However, no radical in 3d-3-chloropentane or PVC-alpha d_1 could produce the observed ESR spectra, and it was highly unlikely that a radical would form at the opposite end of 1, 1 d_2-1-chloropentane. These results prompted a thorough search for effects of deuteration on the ESR spectra of any compound. In a review of ESR texts, only two were found that mentioned isotopic effects (33) (88). Weitz warned "In principle, selective deuteration *should* aid in the identification of organic radicals produced by ionizing radiation. However, in some cases, exchange of deuterons or protons with the host occurs after irradiation. In such cases, deuteration may result in misidentification of the radicals." (88).

For example, Weiner and Koski (89) irradiated various deuterated and undeuterated crystals of glycine ($\overset{+}{N}H_3\text{-}CH_2\text{-}C\overset{-}{O}_2$) with X-rays at LNT and RT. They found that the ESR spectra of alpha-deuterated glycine ($\overset{+}{N}H_3\text{-}CD_2\text{-}C\overset{-}{O}_2$) was virtually identical to that of the undeuterated sample. They postulated that since no change was observed in the ESR on alpha deuteration, the radical could not have been formed on the alpha carbon. However, subsequent investigations by Collins (91) and Morton (6) conclusively identified the radical formed on irradiation of glycine as $\overset{+}{N}H_3\text{-}\overset{\bullet}{C}H\text{-}C\overset{-}{O}_2$. The only way to rationalize the deuteration results required the assumption of a rapid hydrogen-deuterium exchange between the initially formed deuterated radical and adjacent host molecules, as proposed by Morton in Figure 34. The exchange is thought to occur between the alpha deuteron of the radical and a proton of the

Figure 34

HYDROGEN DEUTERIUM EXCHANGE
(GLYCINE)

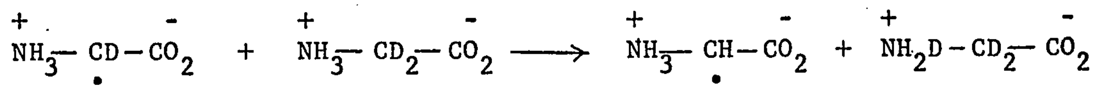
OBSERVED



$$\left.\begin{matrix}\overset{+}{NH_3}-CH_2-\overset{-}{CO_2}\\ \text{or}\\ \overset{+}{NH_3}-CD_2-\overset{-}{CO_2}\end{matrix}\right.\xrightarrow[\text{LNT or RT}]{\gamma\text{ irr.}}\overset{+}{NH_3}-\underset{\bullet}{CH}-\overset{-}{CO_2}$$

(R.F. Weiner and W.S. Koski, JACS, 85, 873, 1963)

PROPOSED



$$\overset{+}{NH_3}-\underset{\bullet}{CD}-\overset{-}{CO_2}+\overset{+}{NH_3}-CD_2-\overset{-}{CO_2}\longrightarrow\overset{+}{NH_3}-\underset{\bullet}{CH}-\overset{-}{CO_2}+\overset{+}{NH_2D}-CD_2-\overset{-}{CO_2}$$

(J.R. Morton, JACS, 86, 2325, 1964)

amine group. This exchange should be very rapid, even at LNT, since the ESR cannot detect the alpha deuterated radical.

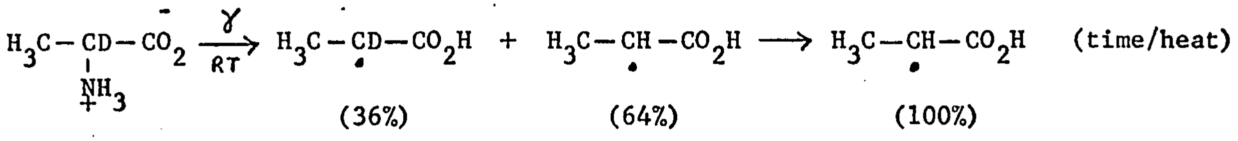
If this exchange did occur, it could be argued that a mixing of radical species is possible. Irradiation of the exchanged host, $D\overset{+}{N}H_2\text{-}CD_2\text{-}C\overset{-}{O}_2$, should produce an ESR spectrum different from the one observed for the $\overset{+}{N}H_3\text{-}\overset{\bullet}{C}H\text{-}C\overset{-}{O}_2$ radical. However, it was determined (92) that the radical concentration was 1/1000 that of the host. Therefore, any radical formed in the exchanged host would be undetected in the ESR. Unfortunately, no further studies on this phenomena have been reported since the original papers in 1963 and 1964.

The only current research into this isotopic exchange process is being undertaken by Miyagawa (Chairman, Department of Physics, University of Alabama). He has confirmed that on x-ray irradiation of alanine, the radical $CH_3\text{-}\overset{\bullet}{C}H\text{-}CO_2H$ is formed (93). However, immediately after irradiation of alpha deuterated alanine, a mixture of deuterated and undeuterated radicals are found in the ESR (94). The undeuterated radical predominates, and w/heat or time, total conversion to the undeuterated radical occurs (Figure 35). Miyagawa has proposed an exchange mechanism similar to Morton's, except that the exchange takes place between the alpha deuteron of the radical and the methyl protons of the host. This was confirmed by noting a nearly identical exchange process on irradiation of $CH_3\text{-}CD_2(\overset{+}{N}D_3)\text{-}C\overset{-}{O}_2$ (94). These results are shown spectroscopically in Figure 36. The second derivative presentation uses peaks as maxima of absorptions. The hyperfine splitting of the undeuterated radical is basically a quintet due to the unpaired electron interacting with four approximately equivalent protons. The splitting from the deuterated radical is a quartet due to interaction with methyl protons alone.

Figure 35

HYDROGEN DEUTERIUM EXCHANGE
(ALANINE)

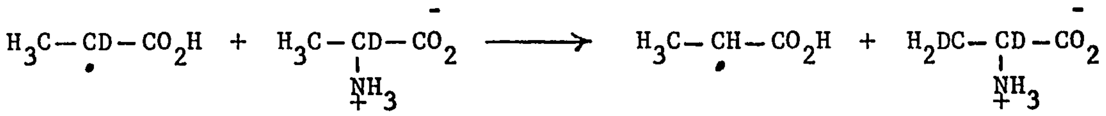
OBSERVED



$H_3C-\underset{\underset{+}{N}H_3}{\underset{|}{CD}}-\overset{-}{CO_2} \xrightarrow[RT]{\gamma} H_3C-\underset{\bullet}{CD}-CO_2H + H_3C-\underset{\bullet}{CH}-CO_2H \longrightarrow H_3C-\underset{\bullet}{CH}-CO_2H$ (time/heat)

(36%) (64%) (100%)

PROPOSED

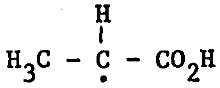


$H_3C-\underset{\bullet}{CD}-CO_2H + H_3C-\underset{\underset{+}{N}H_3}{\underset{|}{CD}}-\overset{-}{CO_2} \longrightarrow H_3C-\underset{\bullet}{CH}-CO_2H + H_2DC-\underset{\underset{+}{N}H_3}{\underset{|}{CD}}-\overset{-}{CO_2}$

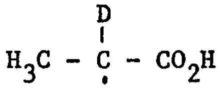
(K. Itoh and I. Miyagawa, J. Chem. Phys., 52(4), 1822 1970)

Figure 36. ESR Spectra of Irradiated Alanine*

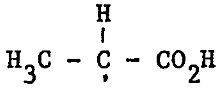
(Second Derivative Presentation)


$\mathrm{H_3C - \overset{H}{\underset{\bullet}{C}} - CO_2H}$

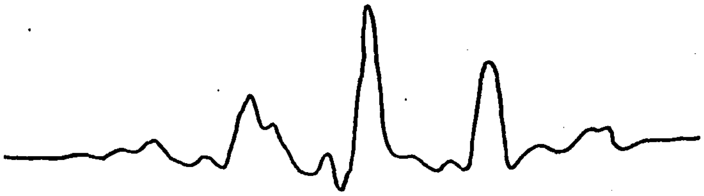
Undeuterated

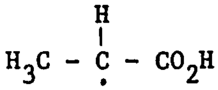

$\mathrm{H_3C - \overset{D}{\underset{\bullet}{C}} - CO_2H}$

and


$\mathrm{H_3C - \overset{H}{\underset{\bullet}{C}} - CO_2H}$

Alpha Deuterated




$\mathrm{H_3C - \overset{H}{\underset{\bullet}{C}} - CO_2H}$

Alpha Deuterated (w/ heat + time)

---

*I. Miyagawa (unpublished results)

Since the alpha deuteron exchanges preferentially with a methyl proton and not with the more labile amino protons, he further postulated that the nature of the chemical bond is not important in the exchange process. Observations were also made on partially deuterated alanine. The deuterium exchange ratio was found proportional to the substitution ratio of the alanine (95). This result indicates the absence of isotopic bond effects on the exchange process. No additional references for these unexplained phenomena are available. It is possible that researchers may have experienced isotopic exchange without having noted it as such. This is an important area for investigation, since the use of labeled compounds is becoming more common in ESR research.

Miyagawa's comments on the ESR spectra of the alpha deuterated samples in this research were invited. The reply, "I have no doubt about the H-D exchange in your case." was most heartening (6). The radicals from the alpha deuterated 1, 1 d_2-1-chloropentane and 3d-3-chloropentane can presumably undergo an isotopic exchange with adjacent molecules. The position of this exchange, if a preferential site exists, is in doubt. Since the PVC-alpha d_1 chains are separated by solvent molecules, it is not probable that an exchange can occur between adjacent chains. Therefore, the alpha deuterated radical may exchange with protons from the solvent. An attempt to test this theory using per-fluorinated cyclic ethers as solvents proved futile, since on fluorination, the ethers became non-solvents for PVC.

In retrospect, the analyses of radicals formed at LNT for 1-chloropentane, 3-chloropentane, and PVC were most likely correct, but deuterium labeling was not an effective method for their confirmation.

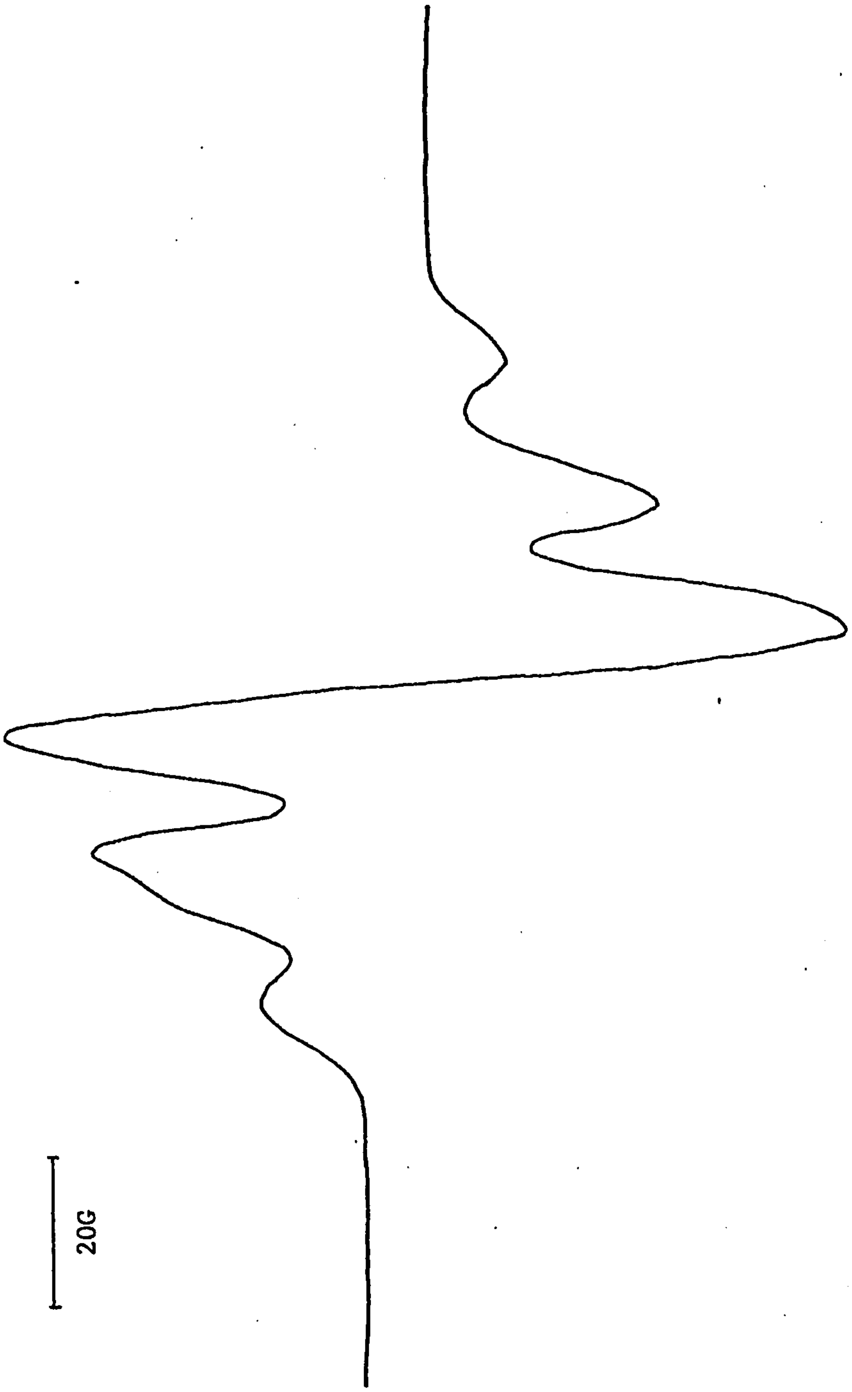
2. Analysis of ESR Spectra at Variable Temperatures

A. The Quintet Absorption

The variable temperature behavior of radicals formed in the analogs and polymer glasses was observed in the ESR on warming from LNT to the melting point. As temperature increased, the PVC/DX and PVC/TP spectra were found to narrow, accompanied by a loss of resolution. Their spectrum at -110°C became that of a broad absorption with no fine structure, ca. 90 G in width. In the PVC/THF glass at -110°C, a five line absorption was observed (Figure 37). Under the same conditions, tetrahydrofuran alone does not exhibit such an absorption. Its spectrum at -110°C was that of an unresolved seven line signal, with an irregular hyperfine splitting, 8-15 G. The ESR absorption from the PVC/THF glass had a hyperfine splitting of 19-21 G, and g-value of 2.0036. The line intensity ratio appears to increase as the center of the spectrum is approached (theoretical value 1:4:6:4:1), but interference from a central singlet, probably a solvent radical, did not permit quantification. However, it appears that this five line absorption is really a quintet.

This spectrum has never been reported in the degradation of PVC. It was determined that the spectral change of sextet at LNT (-196°C) to quintet at -110°C was not a conformational conversion, since on cooling from -110°C to LNT, the same quintet was observed. Therefore, a radical conversion must have occurred. It is probable that this quintet is unresolved in the PVC/DX and PVC/TP glasses, since the overall width of their broad absorption is ca. 90 G, while the width of the quintet is 4 x 20 = 80 G.

Figure 37. ESR Spectrum of PVC/THF at -110°C, UV Irradiated at LNT



With reference to the parent molecule, the most likely assignment for this spectrum is Radical III, $-CH_2-\underset{\bullet}{C}Cl-CH_2-$. This radical would produce a quintet if the beta hydrogens were equivalent. Butyagin (96) found that in polymer radicals of the type $-CH_2-\underset{\bullet}{C}X-CH_2-$, the methylene protons were equivalent. In addition, the contribution of an alpha chlorine to hyperfine splitting is listed as 2.8 G for aliphatic radicals (97). This splitting is too small to be observed in the spectrum, therefore, a quintet would be expected from the four equivalent beta protons. The dihedral angle could not be accurately calculated for this radical, since information on the spin density of the alpha carbon is unavailable. It is expected that the spin density in this case should be less than that for Radical I, since delocalization of the unpaired electron onto chlorine is possible. Fisher (97) found that as the electronegativity of the substituent (X) on the alpha carbon increased, the spin density decreased. This lower spin density in Radical III should produce a decrease in hyperfine splitting (as predicted by the McConnell relationship). This decrease was observed; for Radical I, the sextet is characterized by $\Delta H=23$ G, while Radical III has a $\Delta H=20$ G. Therefore it is possible that the dihedral angle is the same for both radicals, even though the observed splitting is different.

It is noteworthy that Radical III is more stable than Radical I. Kharash (98) found that radicals of the type $R-\underset{\bullet}{C}l-R$ were less reactive than the corresponding $R-\underset{\bullet}{C}H-R$ radical. This observation is in keeping with ESR results. On warming from LNT, the 'sextet' radicals terminate, and are replaced by 'quintet' radicals.

B. The Allylic Radical

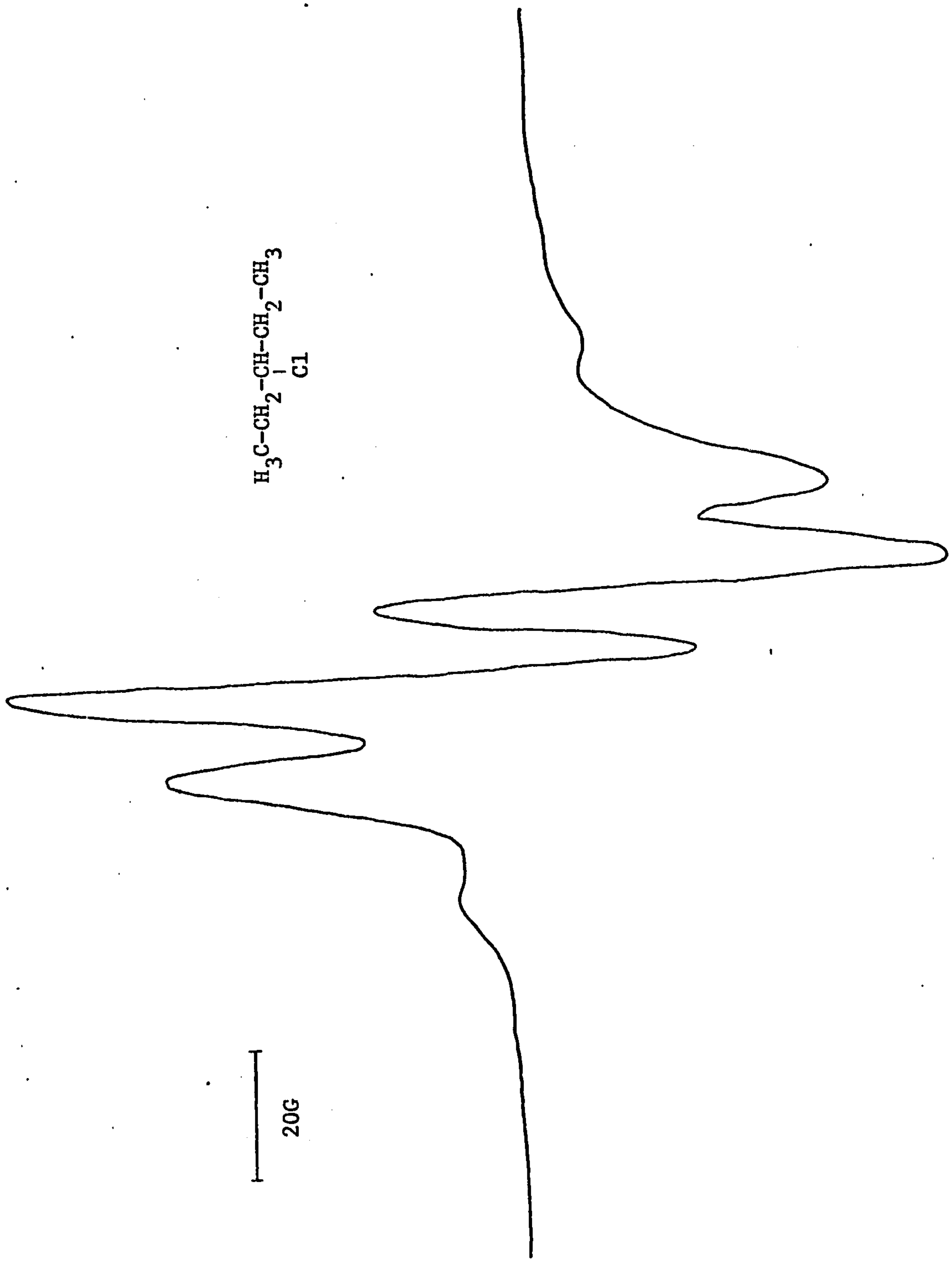
Most of the current mechanisms proposed for the photo, thermal, and ionizing degradation of PVC involve an intermediate allylic structure (99) (100). Only one partially resolved ESR spectrum has been obtained for an allyl radical in degraded PVC (101). The origin of this spectrum may be in doubt, since an unpurified commercial sample was used. This radical can have two resonance forms: $-CH_2-CH=CH-\dot{C}H-CH_2-$ and $-CH_2-\dot{C}H-CH=CH-CH_2-$. The interaction of the unpaired electron occurs mainly with the outer six protons, producing a septet absorption in the ESR, with a hyperfine splitting of 12-15 G (102). This value is small since the spin density on the two alpha carbons in the resonance structures was found to be 0.58 (35).

It should be noted that the proposed allylic radical in PVC was obtained at LNT using gamma irradiation. This radical would not be expected on UV irradiation since the 253.7 nm wavelength was found to be effective in converting the allyl to an alkyl radical (103):

$$-CH_2-CH_2-\dot{C}H-CH=CH- \xrightarrow{UV} -CH_2-\dot{C}H-CH_2-CH=CH-$$

However, once the UV radiation has ceased, and the sample is warmed from LNT to RT, the allylic radical may become involved in the degradation mechanism. This radical should directly precede formation of the polyene radical. Therefore, it would be expected in larger concentrations as room temperature is approached. Unfortunately, the only resolved PVC spectra at variable temperatures were obtained using THF as a solvent. Since this solvent melts at $-108.5^{\circ}C$, no determination of allylic radicals could be attempted above that temperature. It is also possible that allylic radicals were not observed in PVC because the dehydrochlorination can occur by molecular elimination of HCl, or

Figure 38. ESR Spectrum of 3CP at -145°C, UV Irradiated at LNT



another non-radical mechanism (104).

The variable temperature spectra of 3-chloropentane showed better resolution in the ESR than those for the PVC glasses. At -145°C, a possible six line absorption was observed (Figure 38) and attributed to the allylic radical, Radical IV:

$$\underset{1}{H_2\dot{C}}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{CH_2}-\underset{5}{CH_3} \longleftrightarrow H_2C=CH-\dot{C}H-CH_2-CH_3$$

Interaction of the unpaired electron with the five protons in the 1, 3, and 4 positions would produce six lines in the ESR. The outer two lines are overlapped, but the hyperfine splitting of the central four lines, 13G, is indicative of an allyl radical. In addition, this spectrum closely resembles the allylic radical spectrum formed on cleavage of the 1,4-poly(butadiene) chain (102).

IX. CONCLUSION

The photodegradation of PVC encompasses a wide area of research, with contributions from numerous sources. A thorough investigation of all the aspects of this topic would be well beyond the scope of this thesis. Therefore, it was decided to concentrate on a specific area, photodegradation at low temperatures. Relatively little research has been performed there, and the results were inconclusive.

Since a commonly cited initiator for this degradation was an impurity present in a commercial sample, it was deemed necessary to begin the research with highly purified and characterized polymers. These criteria applied to the seven analogs that were used, since their ESR spectra would be compared to those of PVC.

The ESR spectra of UV irradiated powders and films gave little new information as to the identity of radicals formed in PVC. It was impossible to ascertain the differences between PVC and its polymer analogs since their ESR spectra were all broad one line absorptions at LNT. The spectra of the low molecular weight analogs were found to be much better resolved under similar conditions. These observations and an analysis of broadening effects led to the use of a polymer glass system.

Comparisons were now possible between various physiochemically modified PVC samples, and between polymer analogs and low molecular weight halocarbons. These comparisons were instrumental in the assignment of a previously unidentified radical for the UV degradation of PVC at LNT: $-CH_2-\dot{C}H-CH_2-$. In addition, the determination of $H_3C-CH_2-\dot{C}H-CH_2-CH_3$ as the radical formed in 3-chloropentane has not been reported before.

Although branches and allylic end groups were found to have negligible effect on the ESR at LNT, this does not preclude their formation in small, undetectable quantities. Their radicals, along with the chlorine radical, are probably the cause for variations in the photodegradation behavior of PVC samples.

The calculated value of 30^o for the dihedral angle of the PVC radical at LNT was consistent with the commonly reported trans-planar structure of the polymer. Computer simulated ESR spectra using this value yielded a spectrum closely resembling the one found experimentally. In addition, this simulation, the fine structure of the 3-chloropentane spectrum, and the spectra from Fessenden's paraffins, gave strong evidence that the observed sextet was actually an unresolved ten line absorption.

The initial impact of the deuteration results was to contradict all previous evidence. Again, comparisons with analogs proved invaluable. It was unlikely that the analyses of the 1-chloropentane, 3-chloropentane, and PVC radical were all at fault, especially when no deuterated radical structure could explain the ESR spectra. Therefore, just as in Morton's and Miyagawa's studies, a radical isotope exchange must have occured.

It was expected that variable temperature ESR would detect an allylic radical in PVC, since this group is often assumed as a degradation intermediate. It is possible that such a radical does not exist, but more probable that it was not present in sufficient concentration at the limiting temperatures. However, a new radical was detected, $-CH_2-\dot{C}Cl-CH_2-$, and could be the predecessor of the allylic radical. While an allyl type radical was not expected in 3-chloropentane (on warming from LNT), one was observed, $H_2\dot{C}-CH=CH-CH_2-CH_3$. It was unfortunate that more information could not be gained from the variable temperature studies. Perhaps a more appropriate solvent system may resolve this problem.

Proposed photodegradation mechanisms for PVC are numerous. However, an accurate one reflecting experimental evidence is not possible at this time. Only the following scheme will be presented.

$$-(CH_2-CHCl)_n- \xrightarrow[\text{LNT}]{\text{UV}} -CH_2-\dot{C}H-CH_2- \quad + \quad Cl\cdot \ \underline{+} \ \text{(other initial radical)}$$

$$\xrightarrow{-110^{\circ}C} \text{(Radical I terminates, abstraction or coupling)}$$

$$+$$

$$-\ CH_2-\underset{\cdot}{C}Cl-CH_2-$$

$$\xrightarrow{\text{warming}} \text{(? allylic radical)} \quad \xrightarrow{\text{RT}} -(CH{=}CH)_n-\dot{C}H-$$

$$\xrightarrow{\text{time}} -(CH{=}CH)_n- \quad \text{(end product of degradation)}$$

The numerous gaps in this scheme indicate that the photodegradation mechanism for PVC is far from solved. However, it is hoped that this research has made a significant contribution to its eventual resolution.

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