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Identification of Free Radicals in the Photodegradation of Polystyrene and Its Homologs

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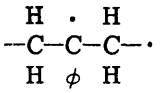
ABSTRACT

The photolysis of polystyrene and poly(α-methylstyrene) was studied by electron-spin-resonance (ESR) techniques using highly concentrated, glassy solutions of the polymers near liquid-nitrogen temperature. Care was taken to insure detection of the primary free-radical species. The use of poly(1-vinylnaphthalene) and polystyrene-2,3,4,5,6-d_5 verified that the primary free radical is located on the polymer chain and not the ring. The ESR spectra obtained for both polystyrene and poly(α-methylstyrene) are consistent with



Interpretation of the observed spectra is made on the basis of the stereochemistry of the polymer chain.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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IDENTIFICATION OF FREE RADICALS IN THE PHOTODEGRADATION OF POLYSTYRENE AND ITS HOMOLOGS

INTRODUCTION

Before any organic material can be effectively used for extended periods of time in the outdoors, it is necessary to understand the effects of environment upon its physical and chemical stability. The major source of environmental damage to organic systems, such as polymers and coatings, is photochemical degradation by sunlight. Damaging light can be divided into two categories: (a) those short wavelengths which produce electronically excited states when a photon interacts with a molecule, and (b) longer wavelengths which produce vibrationally excited (thermally excited) species. Photons in the former category are in the ultraviolet region of the spectrum (except in the case of dyes, where visible light may be photochemically active), while the latter are in the red and infrared region of the spectrum. The present work is concerned only with the interaction of polymer molecules with ultraviolet radiation, that is, degradation as a result of electronic excitation.

Many investigations of the effect of high-energy ionizing radiation on polymer systems have been undertaken. Reviews on this subject have been prepared by Chapiro (1) and Charlesby (2). The ultraviolet photolysis of polymers has been reviewed by Jellinek (3) and more recently by Fox (4). The photochemical processes which immediately follow the absorption of a photon are important in understanding the photodegradation of polymers. One of the more powerful techniques which may be used for the study of many of these primary processes is electron-spin-resonance (ESR) spectroscopy, which enables one to observe the free-radical species which are precursors to most degradation processes.

The ESR spectrum observed during the irradiation of polystyrene has been discussed in numerous papers (5-9). All of these papers indicate a triplet hyperfine structure with coupling constants ranging from 20 to 45 gauss. Most of the reported spectra indicate further hyperfine splitting of the main triplet signal. An ESR study of the free radicals produced during the irradiation of benzene and its derivatives has resulted in the proposal of a cyclohexadienyl-type radical species (10). More recent work (11) concerned with the reaction of hydrogen or deuterium atoms with a fibrous fluff of polystyrene, produced by freeze-drying benzene solutions of the polymer, has indicated that a cyclohexadienyl-type radical is responsible for the triplet signal. No direct evidence has been given which would indicate the source of the initial hydrogen atom which is required for the formation of the cyclohexadienyl-type radical in a polystyrene system.

Except for those studies performed on polymer fluffs (8,11), most of the samples used for ESR work have been bulk polymer, often of questionable purity. Although such samples are useful for connecting radiation effects to practical polymer problems, they do not lend themselves well to ESR techniques, where the radicals are best studied in an isolated, glassy matrix made from purified components. In such a system the magnetic resonance lines become narrowed, and the molecule tends to take on a geometrically stable conformation as the sample is cooled from a liquid at room temperature to a glass at lower temperatures. Many of the previous studies have been performed at room temperature, where molecular motion would afford little chance of observing any highly reactive prime free radical. In the present work the free radical is formed in a stabilizing glass matrix at reduced temperature and observed during irradiation, thus maximizing the possibility of seeing any short-lived primary species.

EXPERIMENTAL PROCEDURE

ESR spectra were recorded as the derivative on a Varian Model V-4500 x-band spectrometer. A transparent, quartz Dewar pipe was mounted within the microwave cavity of the spectrometer. The quartz was made ESR-signal-free by thorough annealing. This Dewar pipe was connected by a Styrofoam-insulated transfer tube to a 10-liter Dewar through a vapor-tight sealed top. The temperature of the sample within the Dewar pipe was regulated between room temperature and just above the boiling point of liquid nitrogen by a small resistor mounted near the bottom of the large Dewar. The heat output of the resistor, and hence the boiloff rate of the liquid nitrogen, was controlled by a variable transformer. The actual temperature of the sample was monitored with a thermocouple-potentiometer circuit. The microwave cavity was purged with dry, room-temperature nitrogen to reduce temperature fluctuations and prevent condensation of water vapor which would attenuate the microwave signal.

Samples were irradiated at the desired temperature within the microwave cavity of the spectrometer by a focused 250-watt mercury-xenon arc. The light output from the lamp passed through an optical filter which allowed only light of wavelengths longer than 2500A to be incident on the sample. Microwave power and modulation amplitude were adjusted to insure that the resulting signal was not artificially broadened.

The samples of polystyrene, poly(α-methylstyrene), and poly(1-vinylnaphthalene) were commercial research-grade polymers which were twice reprecipitated by adding a tetrahydrofuran solution of the polymer dropwise to a large excess of reagent-grade methanol. The polystyrene-2,3,4,5,6-d_5 was kindly supplied by Dr. Leo Wall of the National Bureau of Standards. This sample was also reprecipitated from tetrahydrofuran and methanol before use.

The tetrahydrofuran and dioxane used throughout this study were vacuum-distilled from lithium aluminum hydride. The 1-methyltetrahydrofuran was vacuum-distilled immediately before use.

Samples were prepared by filling a quartz ESR tube with the dry, powdered polymer and adding a few drops of the desired solvent. A very viscous solution of the polymer, resulted. At reduced temperatures this solution became a transparent glass suitable for ESR studies. A more dilute solution of the polymer in tetrahydrofuran formed an opaque, crystalline solid at liquid-nitrogen temperatures, which expanded upon warming, breaking the sample tube. The highly concentrated polymer solution used in this study can be more accurately described as plasticized polymer and at reduced temperature may be, on a molecular level, analogous to commercially used plastics.

RESULTS

The ESR spectrum of an ultraviolet-irradiated viscous solution of polystyrene in tetrahydrofuran at -185°C is shown in Fig. 1. It consists of seven lines with equal spacing of 18 to 19 gauss. Immediately after irradiation the intensity distribution appeared to be approximately 1:4:7:8:7:4:1. After several minutes of irradiation it was observed that a broad singlet of slightly higher g-value than the central peak of the multiplet began to grow into the ESR signal. Upon termination of irradiation this singlet signal continued to increase in intensity as the seven-line signal decreased (see Fig. 2). After 10 to 15 minutes in the dark following irradiation at liquid-nitrogen temperature, the original multiplet spectrum disappeared, leaving a broad singlet having no hyperfine structure (see Fig. 3). The change indicates the presence of two radical species. The radical responsible for the multiplet signal is probably the primary species, while the singlet is perhaps due to a second radical formed by the reaction of this primary species.

Fig. 1 – ESR spectrum of ultraviolet-irradiated polystyrene at -185°C in the g = 2 region of the spectrum.

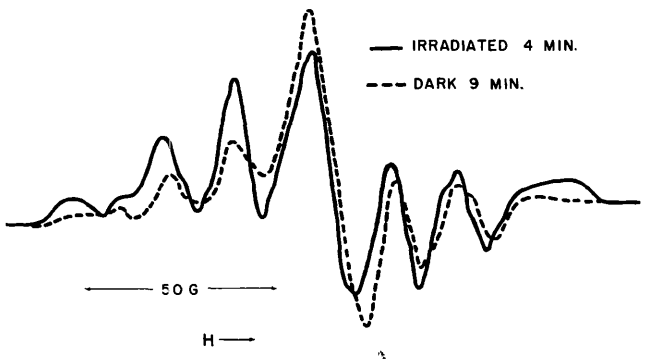


Fig. 2 – ESR spectra of ultraviolet-irradiated polystyrene at -185°C. Note the growth of a new central peak of slightly higher g-value as the original signal decreases in intensity.

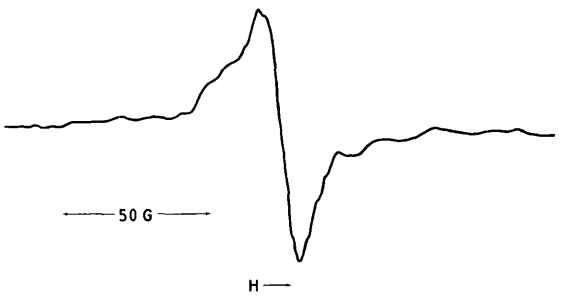


Fig. 3 – ESR spectrum of polystyrene at -100°C which was irradiated 6 minutes and left in the dark 10 minutes. Note the loss of the multiplet structure which was replaced by a broad singlet signal (see Figs. 1 and 2).

With the same experiment at successively higher temperatures, it was noted that appreciably less of the free radical was formed as the temperature increased, and no signal at all was observed above -155°C. The species observed is quite reactive in the environment in which it is formed, and the steady-state concentration of the free radical is too small for observation at higher temperatures where the matrix of the glass becomes less rigid.

Poly(1-vinylnaphthalene) and polystyrene-2,3,4,5,6-d_5 treated by the same photochemical and ESR techniques resulted in spectra identical to that of polystyrene. The use of either 1-methyltetrahydrofuran, dioxane, or styrene monomer as the solvent for samples of polystyrene yielded the same spectra as shown in Figs. 1 and 2. Solvent impurities or sensitization of the solvent by excited polymer molecules are therefore not the source of the free radical.

Ultraviolet irradiation at liquid-nitrogen temperature of a 10% solution of vacuum-distilled styrene monomer in a mixture of diethyl ether, isopentane, and ethyl alcohol (EPA) in a volume ratio of 5:5:2, respectively, resulted in a singlet ESR spectrum with a width of 14.7 gauss and having no hyperfine structure. Due to the difference in structure of the stabilizing matrix of EPA as compared to a viscous polymer solution, direct comparison of results is not possible.

The ESR spectrum of an ultraviolet-irradiated poly(α-methylstyrene) sample, prepared in the same manner as discussed above, is shown in Fig. 4. The spectrum consists of seven lines with a separation of 18 to 19 gauss and an intensity distribution of 1:3:3:2:3:3:1. As in the case of polystyrene, a central singlet of slightly higher g-value slowly grows into the multiplet signal and continues to grow in the dark as the multiplet decreases in intensity (see Fig. 5), strongly suggestive of primary and secondary species. To produce a signal of similar intensity, about 4 to 5 times as much radiation was required for polystyrene as for poly(α-methylstyrene).

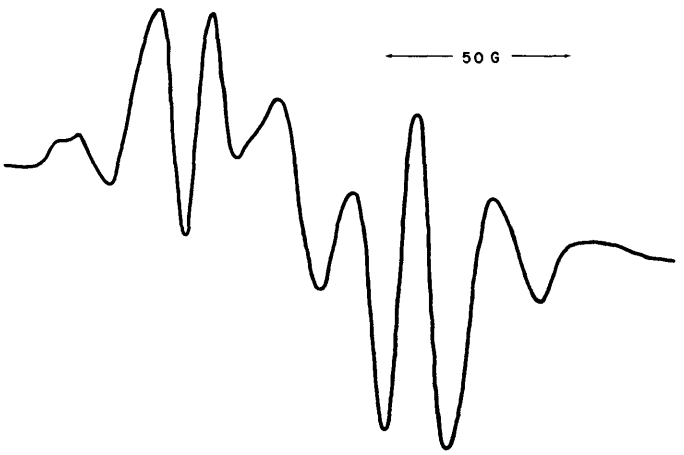


Fig. 4 – ESR spectrum of ultraviolet-irradiated poly(α-methylstyrene) at -185 C in the g = 2 region of the spectrum.

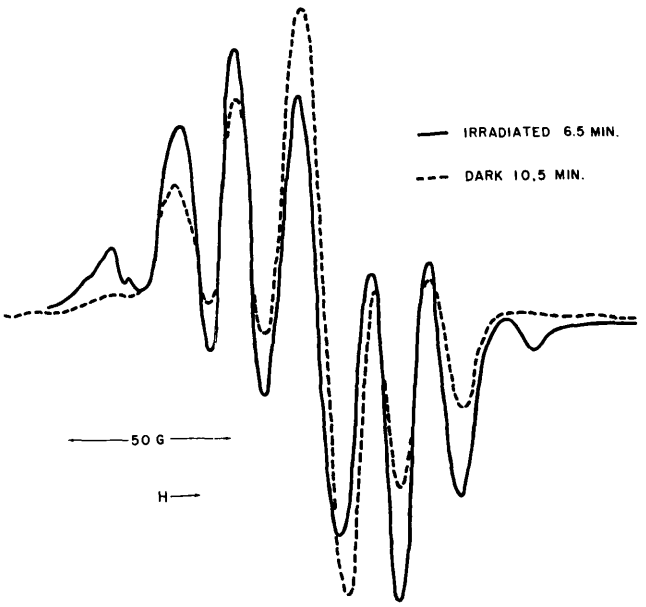


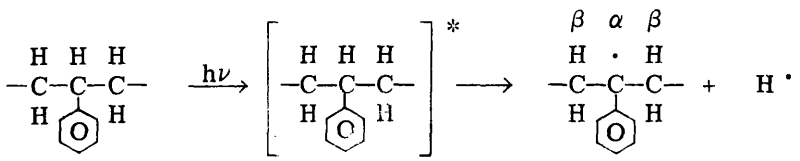
Fig. 5 – ESR spectra of ultraviolet-irradiated poly(α-methylstyrene). Note the growth of a new central peak of slightly higher g-value as the original signal decreases in intensity.

DISCUSSION

Interpretation of ESR Spectra

The observation that identical spectra are obtained for polystyrene, poly(1-vinylnaphthalene), and polystyrene-2,3,4,5,6-d_5 eliminates the possibility of the free-radical electron coupling with the protons of the benzene rings of polystyrene. Thus, the free-radical electron must be localized on the polymer-chain network and not the aromatic ring system. The coupling constants for both polystyrene and poly(α-methylstyrene) appear to be about 18 gauss as shown in Figs. 1 and 4. Since the coupling constant for α-protons of most alkyl radicals should be independent of other groups present on the carbon atom and is expected to be about 23 to 25 gauss (12,13), we can assume that there are no protons on the free-radical carbon atom in our polymer system. The similarity between the ESR spectra obtained for ultraviolet-irradiated polystyrene and poly(α-methylstyrene) strongly suggests a very similar and perhaps identical free radical for these two systems.

Considering all of the possible free-radical species which can be formed by breaking one C-H bond or one C-C bond in the polymer molecule and assuming that both fragments resulting from any chain scission should be observable, only one species is consistent with the observed results. This species is obtained by removing the methyl group in the case of poly(α-methylstyrene) or the H-atom on the carbon adjacent to the aromatic ring in the case of polystyrene. Thus, the photochemical reaction would be represented by



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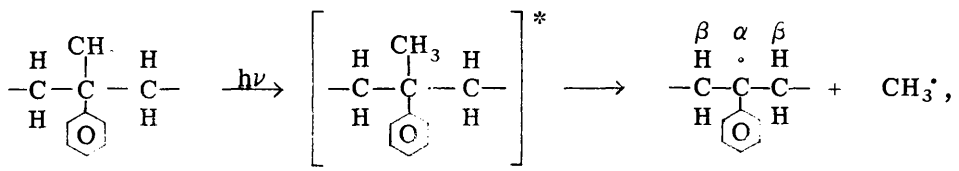

where the asterisk represents an electronically excited segment of the polymer. The hydrogen atom or methyl radical is free to react with another part of the same polymer molecule, a neighboring polymer molecule, or a solvent molecule. Since no methyl radical or hydrogen atom was observed, we must conclude that rapid reaction occurred, which is expected in such a highly concentrated solution.

The free electron on the above radical species should be capable of magnetically coupling with its neighboring four β-protons. The extent to which this electron couples depends on the conformation of the polymer unit. It has been suggested by Heller and McConnell (14) that the β-hyperfine coupling constants of most alkyl radicals can be approximately described by the cosine-square relationship

$$a_\beta = B + A \cos^2\theta,$$

where θ is the angle between the H–C–C plane and the axis of the p-orbital of the free electron (see Fig. 6). The values A and B have been estimated to be near 50 gauss and 0 gauss, respectively (13).

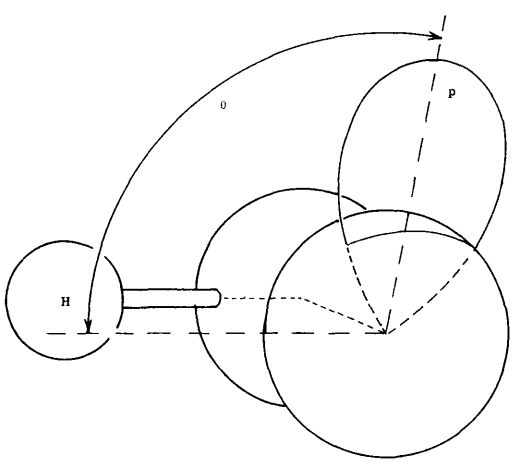

Fig. 6 – Model of free-radical segment showing the geometrical relationship between the orbital of the free-radical electron and the beta H-atom to which it is coupled.

The geometrical conformation which best fits the observed results for the case of poly(α-methylstyrene) is one in which the free electron couples equally with three protons with a_β = 17 to 19 gauss and with the fourth beta proton with a_β = 50 to 54 gauss. The resulting ESR signal for such a system is shown in Fig. 7.

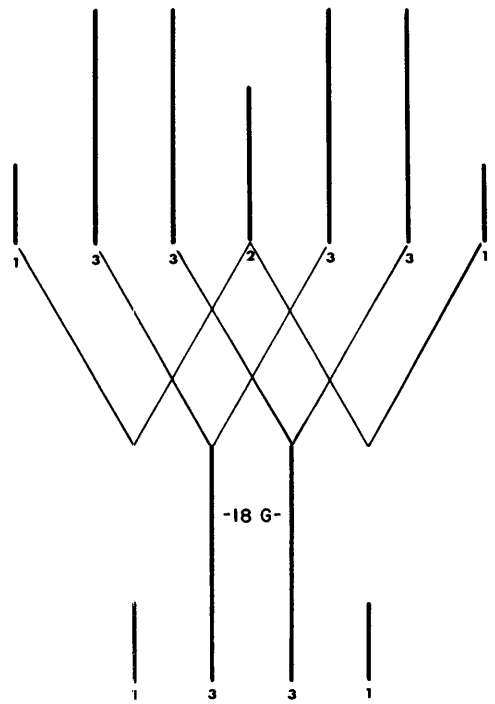

Fig. 7 – Proposed splitting diagram for poly(α-methylstyrene)

In the case of polystyrene no single system of four protons can be made consistent with the observed ESR spectrum shown in Fig. 1. If we assume the polymer chain to consist of two equally distributed (perhaps alternating) monomer-unit configurations, then the resulting ESR signal should appear as the sum of the signals from the two conformations. A system which is consistent with the observed results is one in which one of the polymer-unit configurations has all beta hydrogens equally coupled to the free electron with a_β = 18 gauss, and the second type of polymer unit has a configuration like that described above for poly(α-methylsytrene). The sum of the ESR signals arising from an equal distribution of free radicals of these two geometrical types is shown in Fig. 8.

Radical Conformations

Application of the above cosine-square law to these systems results in the assignment of an approximate geometrical configuration for the monomer units along the polymer chain. In the case of poly(α-methylstyrene), if we assume A to be near 50 gauss and B slightly larger than zero, the relationship predicts a conformation where θ_1, θ_2, and θ_3 = 60° (or 120°) while θ_4 = 180° (or 0°), the subscripts referring to the beta proton with which the electron is coupling. If the monomer unit repeats, the polymer chain takes on a spiral configuration. Construction of molecular models shows this configuration to be stable and one of several which is allowed after taking into account steric requirements of the methyl groups. Under the experimental conditions of highly concentrated solutions at low temperatures, such a tightly packed model would be most logical.

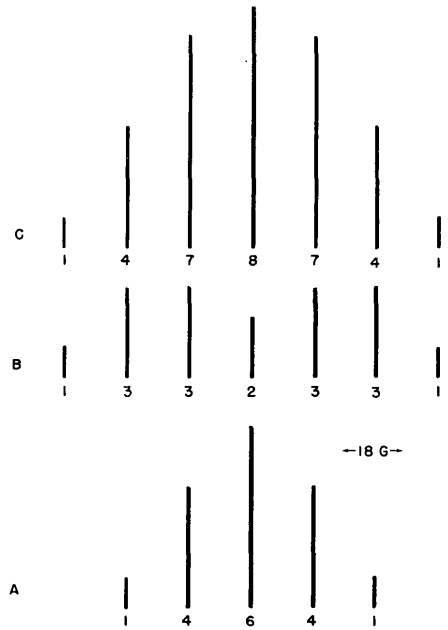

Fig. 8 – Proposed splitting diagram for polystyrene, consisting of the sum of two radical conformations.

In the case of polystyrene the cosine-square law predicts an alternating monomer-unit configuration – one as described above for poly(α-methylstyrene), and one with all θ values equal to 60° (or 120°). Again, construction of molecular models shows that this configuration is a sterically stable spiral.

The application of ESR techniques to the study of the absolute geometry of high polymers is unique and should be pursued further. The major drawbacks are the accurate identification of the free-radical species and the validity of the cosine-square law used in the above disscussion. Studies of free radicals at various temperatures could yield valuable information regarding the motion and phase changes of high-polymer molecules which could be applied to useful plastics at normal operating temperatures.

CONCLUSIONS

From the above discussion it can be concluded that the primary free radical produced upon the ultraviolet irradiation of highly concentrated, glassy solutions of polystyrene and poly(α-methylstyrene) is the species

$$\begin{array}{ccccc} & H & \cdot & H & \\ - & C & - & C & - \cdot \\ & H & \phi & H & \end{array}$$

The observation that an increase in the temperature of the glassy sample from -185° C to -155°C resulted in the disappearance of the ESR signal leads to the conclusion that the radical species reacts quite readily under these conditions. One of the reactions which it undergoes appears to result in the formation of a secondary species, the structure of

which is not yet known but may be closely related to the cyclohexadienyl-type radical as described by other workers (10,11). Upon application of the cosine-square law to the observed β-coupling constants, several stable spiral conformations of the polymer chain are found to be consistent with the data. The higher steady-state concentration after a given amount of untraviolet irradiation observed for poly(α-methylstyrene) as opposed to polystyrene is perhaps due to the greater ease of abstracting a methyl radical than a hydrogen atom as well as the protection afforded the radical by the steric hindrance of the remaining methyl groups along the chain.

If the same free radical is formed during the photolysis of poly(α-methylstyrene) and polystyrene at higher temperatures as was observed near liquid-nitrogen temperature, the difference in photolytic behavior of these polymers (4) at room temperature is most logically explained on the basis of steric interactions. The presence of methyl groups gamma to the free-radical electron in poly(α-methylstyrene) may sterically prevent cross-linking and might concomitantly induce strains which act to increase the efficiency of chain scission.

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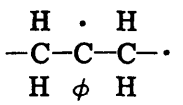

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Poly (1-vinylnaphthalene)						
Polystyrene-2,3,4,5,6-d_5						
Cosine-square law						
Steric hindrance						
Polymers						

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