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Electron Spin Resonance Evidence for Dissociative Electron Capture in γ-Irradiated Poly(vinyl chloride)–2-Methyltetrahydrofuran Glassy Solution

Y. J. Chung, S. Yamakawa, and V. Stannett*

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27607.

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ABSTRACT: In the radiolysis of poly(vinyl chloride) (PVC), the predominant process for formation of the primary PVC radical ($-CH_2\dot{C}H-$) has been widely assumed in the literature to be the homolysis of a C–Cl bond. We have found that PVC acts as an electron scavenger to produce the primary PVC radical in γ-irradiated PVC–MTHF glassy solution. Accordingly, it is proposed that dissociative electron capture plays an important role for the formation of the primary PVC radical in the present system. The primary PVC radical is characterized by an esr spectrum of eight equally spaced lines with an average separation of 21.7 G. The analysis of an esr spectrum obtained from the γ-irradiated PVC–MTHF glass has been facilitated by analyzing esr spectra obtained from γ-irradiated bulk 3-chloropentane and 3-chloropentane–MTHF glass.

In the radiolysis of poly(vinyl chloride) (PVC), the primary PVC radical ($-CH_2\dot{C}H-$) has been assumed[1] to be formed through the homolysis of a C–Cl bond. Dissociative electron capture which is a feasible alternative mechanism and has been established[2] as an important process in the radiolysis of alkyl chlorides, has not been considered in the case of PVC.

To assess the importance of dissociative electron capture in the case of PVC, we have carried out an electron scavenging experiment using PVC as an electron scavenger in 2-methyltetrahydrofuran (MTHF) glass at 77°K. MTHF glass is used in the present study since "trapped electrons" are known[3] to form in the γ-irradiated MTHF glass at low temperatures. Furthermore, MTHF is a solvent for PVC and has been found, in our laboratory, to form an excellent glassy solution of PVC at low temperatures. This paper reports esr evidence for dissociative electron capture by PVC during the γ irradiation of MTHF doped with PVC.

Experimental Section

An unplasticized commercial PVC (Sumilit SX-11, DP_n = 1100) supplied by the Sumitomo Chemical Co. was dissolved in tetrahydrofuran (Fisher Certified). After precipitating PVC from a tetrahydrofuran solution with methanol, PVC was washed in methanol, and dried *in vacuo* at room temperature. Eastman White Label MTHF (stabilized with hydroquinone) was distilled under vacuum from sodium and stored over sodium *in vacuo*. In the preparation of PVC–MTHF solution, a measured amount of MTHF was transferred into esr tubes (3-mm i.d), containing PVC, on a vacuum line. After sealing off *in vacuo*, the tubes were warmed at 318°K for 1 day to dissolve the PVC and then cooled down quickly to 77°K to form a rigid (glassy) solution. 3-Chloropentane was obtained from K & K Laboratories, Inc., and used without further purification. All samples used in the present esr studies were degassed to 10^{-5} mm and sealed off under vacuum. Esr tubes were made from Suprasil tubing supplied by Amersil, Inc., Hillside, N. J. γ Irradiation was carried out in a Gammacell 220 cobalt-60 source (Atomic Energy of Canada Ltd.); the dose rate of the source was 0.6 Mrad/hr. Total irradiation doses given to samples ranged from 0.3 to 1.5 Mrad in order to obtain suitably intense esr spectra. Esr spectra were recorded with an X-band spectrometer with 100-kHz field modulation (Japan Electron Optics Laboratory Co., Model JES-ME-1X).

Results and Discussion

A γ-irradiated MTHF glass at 77°K is colored blue.[3] The blue color disappears on exposure of the sample to visible light from a projector. The upper esr spectrum of Figure 1 shows an esr spectrum of the γ-irradiated MTHF recorded at 77°K in the dark. This esr spectrum consists of a very sharp singlet (g = 2.003) and a septet with an average hyperfine splitting (hfs) of 20 G. After recording the esr spectrum shown in the upper part of Figure 1, illumination of the sample *in situ* with visible light caused disappearance of the singlet as shown in the lower esr spectrum of Figure 1. The photobleachable singlet esr spectrum with line width between derivative maxima of 5 G becomes power saturated as the microwave power is raised. These results including the photobleaching, the esr line width and the power saturation of the singlet esr spectrum are characteristic of trapped electrons previously observed[4] in the γ-irradiated MTHF glass. Accordingly, the singlet esr spectrum is assigned to the trapped electron. The septet esr spectrum is analyzed into a quartet (hfs of 20 G) of doublets (hfs of 20 G) of doublets (hfs of 40 G). The determined hyperfine splittings are in good agreement with the reported[4] values of MTHF radical.

After γ irradiation at 77°K in the dark, the MTHF glass incorporating 3.5 mol % of PVC is colorless. Before exposing the γ-irradiated sample to visible light, an esr spectrum shown in Figure 2 was recorded at 77°K in the dark. It is analyzed into the nine equally spaced lines with an average separation of 19 G. On illuminating the γ-irradiated sample *in situ* with visible light for 30 min, the nine-line esr spectrum did not show any change, indicating that the singlet esr spectrum attributable to the trapped electron was not present in the nine-line esr spectrum. Thus, it is reasonable to assume PVC acts as an electron scavenger in the γ-irradiated MTHF glass. The nine-line esr spectrum can be analyzed into a doublet (hfs

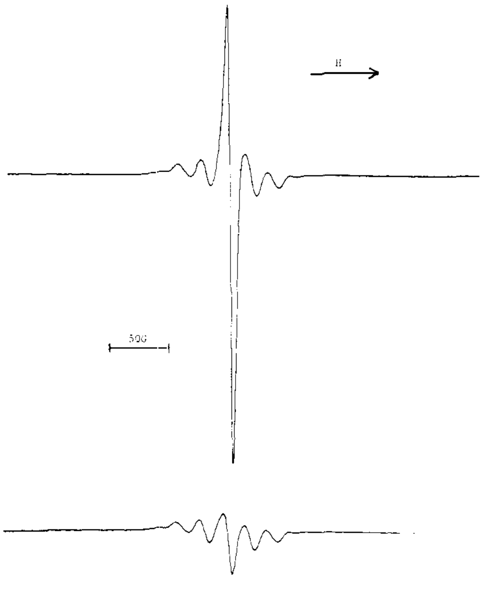

Figure 1. Esr spectra of γ-irradiated MTHF at 77°K. Upper and lower spectra were recorded at the same spectrometer gain settings before and after photobleaching, respectively. The microwave power was 0.1 mW. The irradiation dose was 0.3 Mrad.

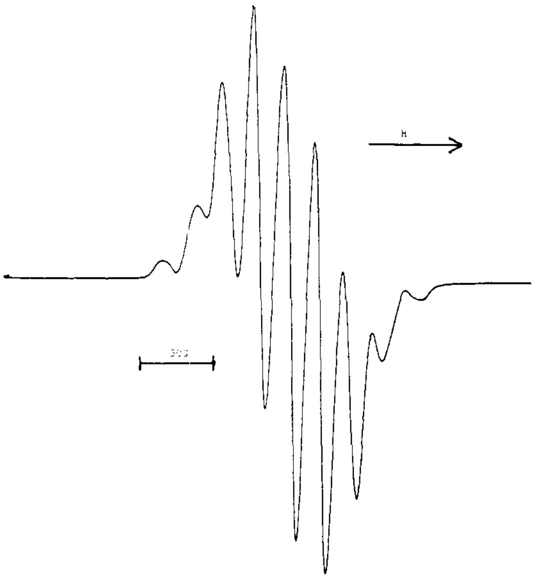

Figure 2. Esr spectrum of γ-irradiated PVC-MTHF glass at 77°K in the dark. The microwave power was 0.1 mW. The irradiation dose was 0.3 Mrad.

of 32 G) of triplets (hfs of 19 G) of triplets (hfs of 41 G). However, it is difficult to assign this spectrum to single radical produced in the present system since the doublet splitting of 32 G corresponds to the largest value of the hfs tensor of an α proton.[5] To facilitate interpretation of the nine-line esr spectrum, esr studies of γ-irradiated 3-chloropentane-MTHF glass, bulk 3-chloropentane, and bulk PVC have been carried out. The experimental conditions of these studies were similar to those used for the PVC–MTHF glass.

3-Chloropentane (1 mol %) incorporated into MTHF glass, after γ irradiation at 77°K, gives rise to similar esr results as those obtained from the γ-irradiated PVC–MTHF glassy solution. These results include an esr spectrum of nine equally spaced lines with an average separation of 19 G as shown in Figure 3 and the absence of the photobleaching effect on the nine-line esr spectrum. Consequently, 3-chloropentane is assumed to act as an electron scavenger in the γ-irradiated MTHF glass. As can be seen by comparing the esr spectra of Figures 2 and 3, there are remarkable similarities in the characteristic features of the esr spectra obtained from both γ-irradiated 3-chloropentane-MTHF and PVC–MTHF systems.

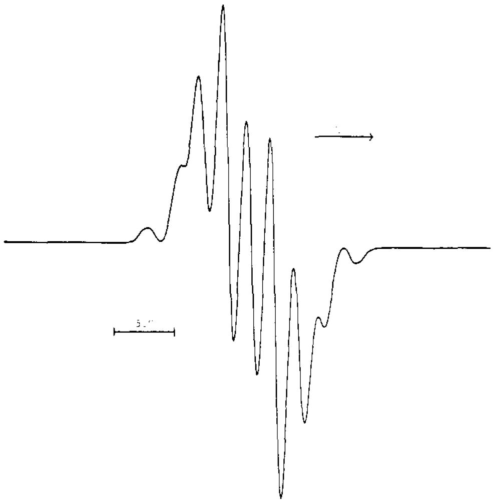

Figure 3. Esr spectrum of γ-irradiated 3-chloropentane-MTHF glass at 77°K in the dark. The microwave power was 0.1 mW. The irradiation dose was 0.3 Mrad.

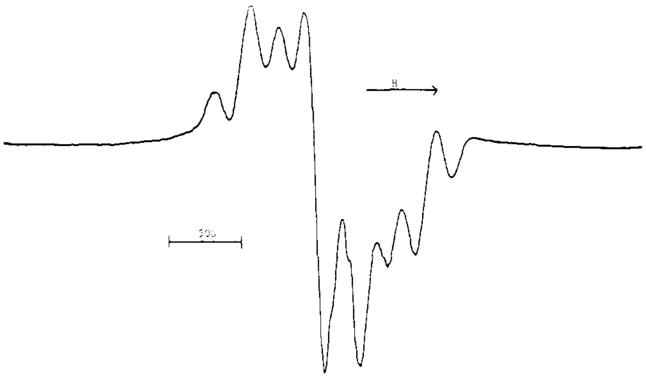

Figure 4. Esr spectrum of γ-irradiated bulk 3-chloropentane at 77°K in the dark. The microwave power was 0.1 mW. The irradiation dose was 0.6 Mrad.

An esr spectrum of γ-irradiated 3-chloropentane consists of eight equally spaced lines with an average separation of 21.7 G, as shown in Figure 4. This esr spectrum can be analyzed into a doublet (21.7 G) of triplets (21.7 G) of triplets (44 G). Consequently, the eight-line esr spectrum is assigned to the $CH_3CH_2\dot{C}HCH_2CH_3$ radical, assuming the hyperfine splittings for one set of two β protons are twice those for the other set of two β protons. The unequal interaction with β protons has been interpreted in terms of the variation in angle (θ) between the C_β–H_β bond and the p-orbital direction of the unpaired electron at C_α, projected to the C_α–C_β bond. For radicals of the type $R\dot{C}HR$, the contact hyperfine interaction of a β proton, $a_\beta(H)$ will vary[6] as $a_\beta(H) = A_0 + A_1 \cos^2\theta$ with $A_0 = 4.0$ G and $A_1 = 41.4$ G. By using this relationship, θ_1 for $a_\beta(H) = 44$ G and θ_2 for $a_\beta(H) = 21.7$ G are calculated to be 10 and 131°, respectively. When there are two β hydrogens on a β carbon, θ_2 is expected to be approximately equal to $\theta_1 + 120°$ because of the tetrahedral arrangement at the β carbon. This expectation has been satisfied in the present analysis, providing an internal check of the analysis. The hyperfine splitting of the doublet which is attributed to the nuclear hyperfine interaction with an α proton, is in good agreement with hfs of an α proton of a

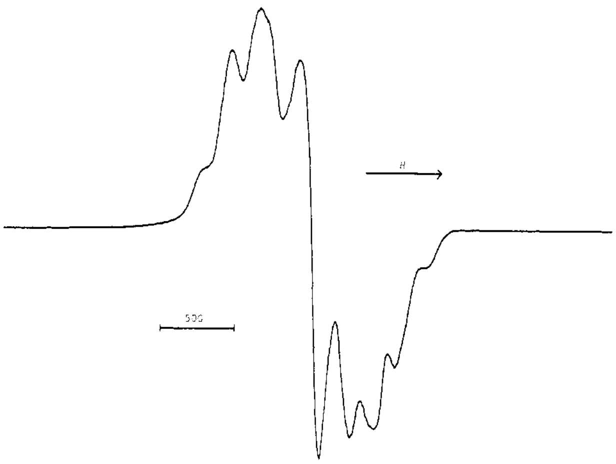

Figure 5. Esr spectrum of γ-irradiated bulk PVC at 77°K in the dark. The microwave power was 0.4 mW. The irradiation dose was 1.5 Mrads.

$R\dot{C}HR$ radical observed in a polycrystalline matrix. The hyperfine splittings of γ protons are not resolved since they are too small[7] (1 G or less in general).

An esr spectrum of a γ-irradiated bulk PVC is a poorly resolved eight-line spectrum with total spread of *ca.* 150 G as shown in Figure 5. It is similar to the esr spectrum which is observed in the γ-irradiated bulk 3-chloropentane and is assigned to the $CH_3CH_2\dot{C}HCH_2CH_3$ radical. By analogy, the eight-line esr spectrum observed in the case of bulk PVC can be reasonably assigned to the $-CH_2CHCH_2CHCl-$ radical since the contribution of a γ group to hfs of an esr spectrum observed in a solid-state matrix is negligible. This assignment is consistent with the fact that the esr results of the γ-irradiated PVC-MTHF glass are found to be very similar to those of the γ-irradiated 3-chloropentane-MTHF glass.

The coincidence of the two esr spectra of the nine equally spaced lines (total spread of 152 G) which were obtained from the γ-irradiated PVC-MTHF and 3-chloropentane-MTHF systems, suggests that the free radicals attributable to these spectra may be similar in nature as far as esr is concerned. *A priori,* free radicals which could have been produced in both systems include $-CH_2CClCH_2-$, $-CH_2CHCH_2-$, and MTHF radical. As discussed earlier, esr spectra of $-CH_2\dot{C}HCH_2-$ and MTHF radical consist of the eight equally spaced lines (total spread of 152 G) and the seven equally spaced lines (total spread of 120 G), respectively. However, an esr spectrum of the $-CH_2\dot{C}ClCH_2-$ radical has not been established to the best of our knowledge. By analogy with the esr spectrum of the $-CH_2\dot{C}HCH_2-$ radical, an esr spectrum of the $-CH_2\dot{C}ClCH_2-$ radical may be assumed to consist of a quartet (due to nuclear hyperfine interaction with a chlorine nucleus) of triplets (22 G) of triplets (44 G). A hfs of an α chlorine in a polycrystalline matrix is expected to be smaller than that of an α proton (*ca.* 20 G) in a polycrystalline matrix since the three principal components of the hyperfine tensor of an α chlorine are reported[8] to be 20.0, 6.4, and 10.0 G. Furthermore, a quartet (any hfs of an α chlorine) of triplets (22 G) of triplets (44 G) cannot give rise to an esr spectrum of the nine equally spaced lines with the total spread of 152 G. In contrast, the nine-line esr spectrum (total spread 152 G) can reasonably be constructed by superimposing the eight-line esr spectrum (total spread of 152 G) on the seven-line esr spectrum (total spread of 120 G) as shown in Figure 6, assuming that *g* values of the two spectra are the same. Consequently, the nine-line esr spectrum is interpreted as a composite spectra of $-CH_2\dot{C}HCH_2-$ and MTHF radicals. This interpretation is reasonable, since the $CH_3CH_2\dot{C}HCH_2CH_3(-CH_2\dot{C}HCH_2-)$, $-CH_2\dot{C}HCH_2CHCl-(-CH_2\dot{C}HCH_2-)$, and MTHF radical are observed in the γ-irradiated bulk 3-chloropentane, bulk PVC, and bulk MTHF, respectively.

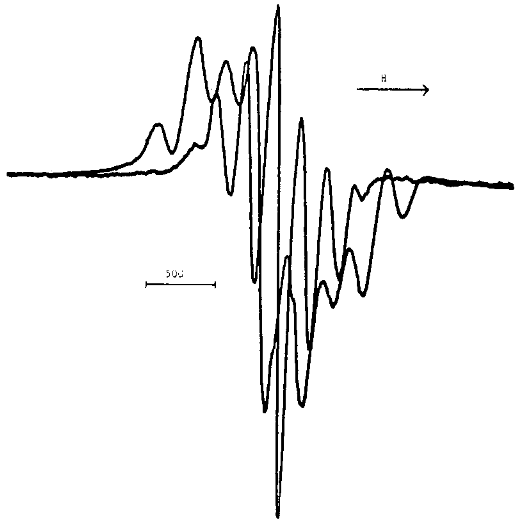

Figure 6. Esr spectrum of Figure 4 superimposed on the lower esr spectrum of Figure 1 recorded at higher spectrometer gain setting.

According to the esr results described here, 3-chloropentane and PVC act as electron scavengers to produce the $-CH_2\dot{C}HCH_2-$ radical in the γ-irradiated MTHF glass at 77°K. Since 3-chloropentane and PVC give rise to the same esr results, the discussion hereinafter is confined to the case of PVC for brevity. Two reasonable mechanisms for the formation of the primary PVC radical in the present system may be (1) homolysis following the geminate recombination, $(-CH_2CHCl-)\cdot^+ + e^- \rightarrow -CH_2\dot{C}H- + Cl\cdot$ and (2) dissociative electron capture, $-CH_2CHCl- + e^- \rightarrow -CH_2\dot{C}H- + Cl^-$. Since the concentration of the primary PVC radicals formed through the homolysis mechanism would be approximately proportional to the PVC concentration used, the contribution of homolysis to the total primary radical yield may be small. On the other hand, a significant yield of thermalized electrons (G value for trapped electrons of MTHF = 2.6) are generated from MTHF,[4] and these electrons are found to have been completely scavenged by PVC. In an electron-scavenging experiment using alkyl chloride as an electron scavenger, it has been shown[9] that alkyl chlorides undergo dissociative electron capture efficiently to produce the primary alkyl radical. Consequently, dissociative electron capture has been assumed[2] to be a major and selective process for electrons of thermal energy whenever the electron affinity of X in the molecule AX is greater than the bond dissociation energy, *D*(A-X). The electron affinity of a chlorine (83 kcal/mol)[10] atom is greater than the bond dissociation energy of a C-Cl bond in PVC which can be approximated as 73 kcal/mol according to the *D*(C-Cl) of isopropyl chloride.[11] Based on thermochemical considerations and the esr evidence obtained in the present study, it is proposed that in the radiolysis of PVC incorporated into MTHF glass, dissociative electron capture plays an important role for the formation of the primary PVC radical $(-CH_2\dot{C}H-)$ and the chloride ion. The chloride ion presumably reacts with a positive molecular ion, which is produced by ejection of an electron from a molecule as a consequence of interaction of γ rays with a molecule,[12] giving rise to formation of hydrogen chloride. A similar mechanism for HCl formation *via* dissociative electron capture has recently been verified[13] in a benzyl chloride-cyclohexane solution.

Based on the present results and discussion, it is tempting to assume that dissociative electron capture may be an important process in the radiolysis of bulk PVC. This possibility is presently under intensive study in these laboratories, and the results will be reported in the near future together with more detailed discussion of the mechanisms of radiolysis of bulk PVC.

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Spin-Label Investigation of Polyurethane Networks

Thomas Carl Ward* and Jeffrey T. Books

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061. *Received October 1, 1973*

ABSTRACT: Two types of polyurethane networks were examined using the spin-label technique. Nitroxide free radicals which are stable under moderate conditions were covalently attached to the network chains of amorphous polymers based on (1) poly(tetramethylene glycol), *p,p'*-diphenylmethane diisocyanate (MDI), trimethylolpropane, and (2) ethylene glycol, MDI, glycerine. Polymer (1) had very low "hard block" content, polymer (2) a very high content. Mechanical properties and differential thermal analysis measurements were made on polymer (1). Electron spin resonance spectra of the samples were obtained in the unstrained, strained, and swollen states. Large differences in the spectra were observed depending on chemical composition, temperature, and state of swelling. Transitions from "frozen" to "rapid motion" type of spectra occurred at 70° for polymer (1), at −10° for polymer (1) swollen to equilibrium, and were unobserved up to 150° for polymer (2). Since the nitroxide label was necessarily adjacent to MDI units, was present in very small concentrations, and experienced no alterations in environment as "soft segments" did, then it is suggested that the spin-label technique is a valuable tool for analyzing microstructure of pseudoamorphous systems.

This paper reports a multiple purpose study involving the paramagnetic labeling of an elastomeric polymer network. In the first phase the feasibility of chemically attaching a stable free radical to a cross-linked polymeric solid was examined. Then, the electron spin resonance (esr) spectra of such a labeled network under various thermodynamic and mechanical conditions were investigated. Finally, consideration was given to the kinds of structural information which might be obtained by a comparison of the spectral characteristics with the chemical composition, mechanical behavior, and thermal properties of the network.

Two types of polyurethane networks were used as the spin-label substrates. These were chosen to facilitate the spin-labeling chemistry and because of the inherent interest in the somewhat anomalous properties of "amorphous" polyurethanes. Both swollen and strained networks of one of the polyurethanes were investigated in addition to the dry material.

Although this study is not exhaustive at this time, some of the initial results are being reported here; indications are that, with cautions, networks may be investigated in a sensitive manner using spin labels.

Background Material and Preliminary Discussion

Spin Labels. With the development of a large series of nitroxide molecules of various shapes and reactivity has come steadily increasing interest in their *in situ* esr spectra as indicators of microscopic environments. Figure 1 shows a nitroxide derivative used in this study, with the free electron indicated. The stability of the nitroxide free radical even in moderately reactive conditions and the synthetic versatility it affords have made it a favorite structural probe for biological systems[1,2] heterogeneous aggregates[3] and, recently, for synthetic macromolecules.[4,5] Three-dimensional synthetic polymer networks have, however, not been studied using spin labels.

Some of the theory for interpreting esr spectra of nitroxide groups in viscous media has been developed.[5-12] Briefly, the esr spectrum of nitroxides in solution is a sharp triplet resulting from the hyperfine coupling of the unpaired electron with the three nuclear spin states of the nitrogen. The "isotropic" value of the hyperfine splitting constant is about 16 G for nitroxides of the Figure 1 type, and obtains when tumbling of the nitroxide group relative to the applied magnetic field is rapid. Figure 2 shows the esr derivative spectrum of 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl, an intermediate used in this work, in dilute chloroform solution and illustrates the characteristic sharp triplet of Lorentzian shapes.

Actually, both the g factor and hyperfine interaction tensors of nitroxides are anisotropic, and when the radical's motion with respect to the applied magnetic field is hindered then line broadening and shifts will occur. Spectral analysis becomes rather complex as extreme limiting of the radical's motion takes place. Rotational correlation times, τ_c, of less than 5×10^{-9} sec are required for use of the approximate equations previously devel-