Electron Spin Resonance Investigations of Radicals and Trapped Electrons in γ-Irradiated 3,4-Polyisoprene and 1,2-Polybutadiene

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ABSTRACT: Radical formation during the radiolysis of 3,4-polyisoprene (3,4-PI) and 1,2-polybutadiene (1,2-PB) has been investigated by esr. In both polymers alkyl and allyl radicals are observed. Alkyl radicals are formed by a cross-linking reaction and are only stable at low temperatures. Allyl radicals are formed by hydrogen abstraction from the main chain. They could be observed even at temperatures up to 0°. The adsorption of 3,4-PI and 1,2-PB on silicagel leads to resolution enhanced esr spectra. The reason for the lower line width is a reduction of the dipole–dipole interactions which is achieved by the formation of a thin polymer layer. In the esr spectrum of 3,4-PI a singlet with a line width of $\Delta H_{\mathrm{ms}} = 11$ G is observed. Because of the infrared bleaching and the low microwave power saturation it is assigned to trapped electrons. The trapping depends on the physical structure of the polymer.

The radiolysis of 1,4-polybutadiene and 1,4-polyisoprene has been studied thoroughly in many investigations. Iimura, *et al.*,[1] showed by esr measurements of γ-irradiated *cis*-polyisoprene and natural rubber that allyl radicals were formed by chain scission and hydrogen abstraction. Novikov, *et al.*,[2] got evidence for an ionic cross-linking mechanism in γ-irradiated 1,4-PB from their thermoluminescence, photoconductivity, and optical absorption measurements. In contrast to these investigations little work has been done on the radiolysis of 3,4-polyisoprene (3,4-PI) and 1,2-polybutadiene (1,2-PB). The recent investigations of Katzer,[3] Raven,[4] and Kaufmann[5] into the γ radiolysis of 3,4-PI and 1,2-PB have shown that in these polymers a radiation-induced cyclization occurs in a cationic chain reaction. In order to elucidate the radiolysis of 3,4-PI and 1,2-PB, we studied radicals and electrons trapped in the polymer matrix at low temperatures by means of esr spectroscopy. Because of the poor resolution of esr spectra of polymer radicals due to dipole–dipole broadening, it was sometimes difficult to make an accurate assessment of the spectra. For a reduction of the line broadening interactions we made measurements with thin polymer layers adsorbed on silicagel.

Experimental Section

The preparation of the polymers has been described by Raven[4] and Kaufmann.[5]

Silicagel for esr measurements lower than 230 mesh was obtained from Merck. It was degassed for 60–70 hr at 450° and a final pressure of 10^{-5} Torr. The polymers to adsorb on silicagel were solvated in *n*-hexane and benzene. The solvents were of spectroscopic purity ("Uvasol") and were dried over $\mathrm{CaH_2}$ and Na. The polymer solutions were added to known amounts of silicagel excluding oxygen and afterwards the solvent was removed by means of a rotary evaporator. The samples were sealed off in quartz tubes under a vacuum of 10^{-5} Torr and irradiated with $^{60}\mathrm{Co}$ γ-rays at −196° in the dark (dose rate 6.4×10^{15} eV/(g/sec)).

Esr spectra were obtained at various temperatures using a Varian V-4502 ESR spectrometer equipped with a dual sample cavity. The concentration of radicals was measured by comparison with the standard sample 0.1% "pitch in KCl" (Varian). Photobleaching was achieved with the filtered light from a tungsten lamp. The microwave power level was measured by means of γ-irradiated glycylglycine as an esr microwave power comparison standard. This method has been described by Copeland.[6]

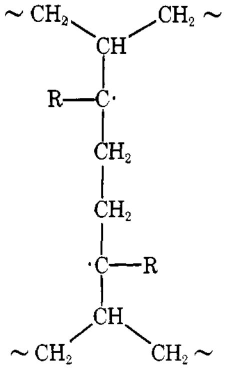
Results and Discussion

Esr Spectra of 3,4-Polyisoprene (3,4-PI) and 1,2-Polybutadiene (1,2-PB). The esr spectrum of 3,4-PI γ irradiated and recorded at −196° is composed of a singlet in the center and a septet with a splitting of 23 G (Figure 1, top). After heating the sample to −50°, the spectrum changed to a septet with a splitting of 15 G (Figure 1, bottom). Due to the broad line width the two outermost lines are not resolved, but the line intensities are in good agreement with the binomial coefficients for six equivalent protons. Two lines of the central part of the latter spectrum are also visible at $T = -196°$ (arrows in Figure 1, top) indicating the presence of two different radicals at low temperatures.

The esr spectrum of 1,2-PB γ irradiated and measured at $T = -196°$ is very poorly resolved and shows a nearly structurless broad singlet. Only by annealing the sample at 0° could a hyperfine structure be achieved (Figure 2, top). The spectrum consists of a septet with a splitting of 16 G which corresponds to the septet of 3,4-PI observed at higher temperatures as well. The difference spectrum of two samples tempered at −140 and −70° exhibits a quintet of lines separated by about 27 G (Figure 2, bottom).

The septet with 23 G hyperfine splitting (hfs) for 3,4-PI and the quintet of 27 G hfs for 1,2-PB are due to alkyl radicals trapped in the polymer matrix at low temperature. These radicals cannot be explained by chain scission or scission of the side chain. The only explanation for their appearance is a radical formed by cross-linking. This is in agreement with the mechanism for cross-link formation proposed by Raven[4] and Kaufmann.[5]

Radical 1 with six β protons in the case of 3,4-PI and one α proton and three β protons for 1,2-PB explains the observed quintet and septet. Certainly the coupling of the unpaired spin with the α protons and the different β protons in these alkyl radicals should not be identical. Secondary alkyl radicals in long chain saturated hydrocarbons are



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3,4-PI, $R = \mathrm{CH_3}$

1,2-PB, $R = \mathrm{H}$

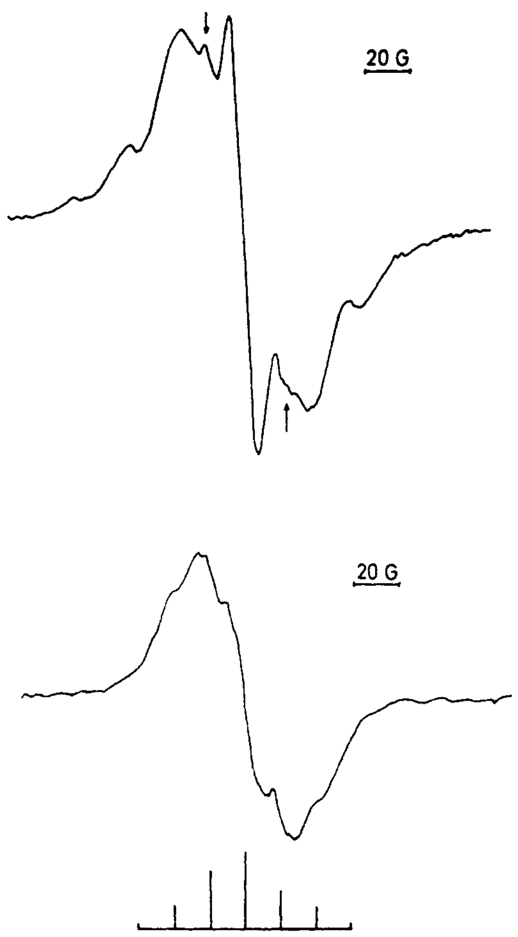
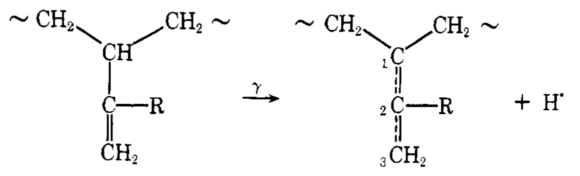


Figure 1. Esr spectra of 3,4-PI irradiated at −196°, dose 6.9 × 10^{19} eV/g: (top) mesured at −196° immediately after irradiation; (bottom) measured at −196° after warming to −50°.

comparable to the alkyl radical with R = H. In these radicals the difference between the hyperfine constant of the α and β protons is 3.8 G.[7] There are further examples of alkyl radicals showing only small differences in splitting of α and β protons.[8] Taking into account the large line width (~15 G) the differences in the splitting of α and β protons are not resolved and α and β protons appear nearly equivalent in our spectra.

The esr septets with 15 and 16 G hfs, respectively, are assigned to allyl-type radicals. They are formed predominantly by hydrogen-atom abstraction from the main chain.



Because of the low spin density at C_2 and the broad line width of the polymer radicals the observed allyl spectra contain no hfs with either the proton or the methyl group bonded to C_2. Analogous to the alkyl radical the differences in the splitting of α and β protons in the allyl radical are not resolved.

So in both cases there is an interaction of the unpaired spin with two α protons and four β protons which lead to a seven-line spectrum.

In the radiolysis of 3,4-PI and 1,2-PB alkyl and allyl radicals are created simultaneously at low temperature. Upon warming the samples the alkyl radicals decay rapidly. This decay corresponds to about 40% of the total radical concentration.

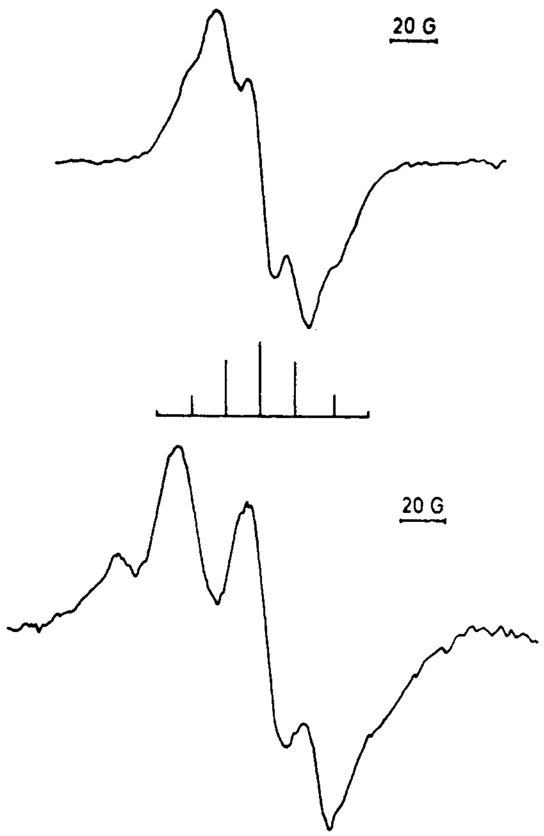


Figure 2. Esr spectra of 1,2-PB irradiated at −196°, dose 24.3 × 10^{19} eV/g: (top) measured at 0°; (bottom) difference spectrum of two 1,2-PB samples tempered at −140 and −70°.

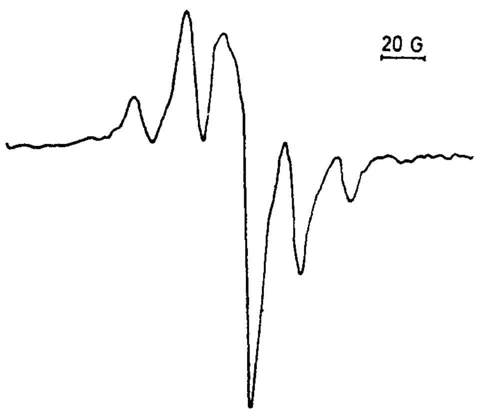


Figure 3. Esr spectrum of 3,4-PI adsorbed on silicagel irradiated and measured at −196°, dose 6.2 ×10^{19} eV/g.

Esr Spectra of 3,4-PI and 1,2-PB Adsorbed on Silicagel. Because of the poor resolution polymer spectra identification of the radicals was only possible in some cases with the help of the integrated line intensities. To improve the resolution a reduction of the line broadening interactions was necessary. It turned out that the adsorption of a polymer layer on silicagel has a line narrowing effect on the esr spectra of the adsorbed polymers.

γ-Irradiated 3,4-PI adsorbed on silicagel (T = −196°) shows a well-resolved alkyl septet (radical 1) with the same coupling parameter as 3,4-PI irradiated in bulk (Figure 3). The original line width of 15 G is halved to 7.5 G in the adsorbed state. The sample fraction of PI was 10% by weight. Lower weight portions of the polymer proved to be disad-

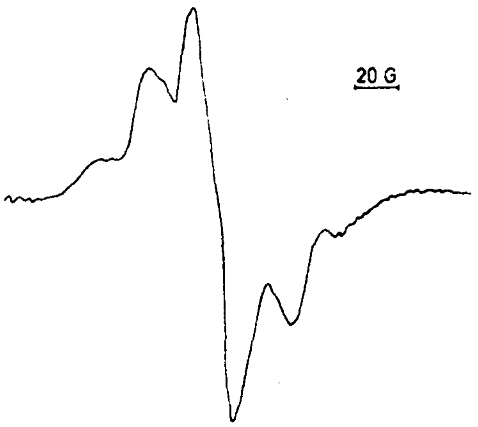


Figure 4. Esr spectrum of 1,2-PB adsorbed on silicagel irradiated and measured at −196°, dose 6.2×10^{10} eV/g.

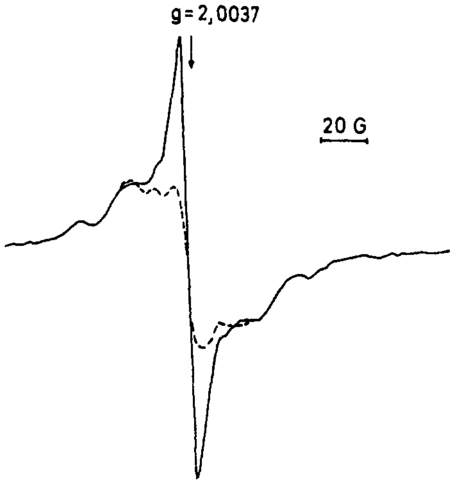


Figure 5. Esr spectrum of 3,4-PI stored below the glass transition temperature (storage temperature −18°) before irradiation; irradiation and measurement at −196°, dose 7.5×10^{19} eV/g: (——) immediately after γ irradiation; (- - -) after bleaching with infrared light of the wavelengths 800 nm $\leq \lambda \leq$ 1500 nm.

vantageous because of the increasing intensity of the silicagel signal.

The esr spectrum of 1,2-PB (10% by weight) adsorbed on silicagel is shown in Figure 4. It is an alkyl quintet with a splitting of 25 G. This corresponds to the quintet of 1,2-PB irradiated in bulk, which could only be obtained by the substraction method. The line width has been reduced from 20 G to 11 G.

Though the interaction between the adsorbate and silicagel is important for the stabilization of ions and radicals,[9] there should be no effect on the resolution. The reason for the line narrowing process in the adsorbed state is a reduction of the dipole–dipole interaction which is obtained by the distribution of the polymer molecules over the great surface of the adsorbents. The formation of a polymer layer with only few molecule dimensions leads to a strong spatial separation and therefore a reduction of the dipole–dipole interaction of the electron spins is achieved. An inverse effect is observed after γ irradiation of both polymers in bulk; at higher doses the resolution of the esr spectra of 1,2-PB and 3,4-PI worsens because of the increasing density of radicals.

Trapped Electrons in 3,4-PI. Depending on the pretreatment and therefore on the physical structure of the polymer samples a singlet of varying intensity and a line width of ΔH_{ms} = 11 G is superimposed on the radical spectra of 3,4-PI (Figure 5). The largest signal intensities (G(R) = 0.25) have been observed with polymer samples prepared by dry freezing and stored below the glass transition temperature (T_g). T_g of 3,4-PI is about 0° and was determined by radical decay measurements. This is in agreement with the results of Kaufmann based on the temperature dependence of the radiation induced double bond loss in 3,4-PI.[5] The singlet intensity in 3,4-PI stored above the glass transition temperature before γ irradiation was either very low or not observable ($G \leq 0.1$).

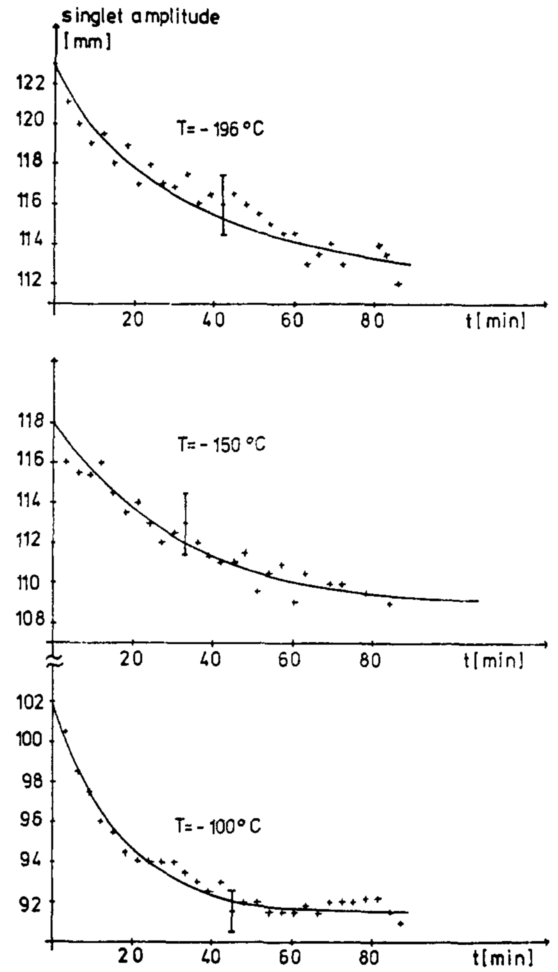


Figure 6. Isothermal decay of trapped electrons in 3,4-PI at various temperatures.

The singlet is optically bleachable with near-infrared light (λ >800 nm) (Figure 5), but the spectrum is not affected by illumination with visible light.

The saturation of the amplitude of the esr singlet in 3,4-PI with increasing microwave power shows that the maximum signal amplitude occurs at a power level of 0.06 mW.

The singlet is thermally relatively stable. Raising the temperature above −150°, there is a continous decay of the singlet amplitude; above −40° it is no longer detectable. Figure 6 shows the isothermal decay over an 90-min time interval at the temperatures −196, −150, and −100°. For this purpose after removal from the γ source the samples were kept 12 min at −196°. Afterwards they were heated within 3 min to the appropriate temperatures and the isothermal decay was measured. For each temperature independent samples were used and the initial concentrations of trapped electrons differ to some extent. All decay curves are characterized by a nearly exponential decay and only at T = −196° there is no approach to an asymptotic value during the observation interval.

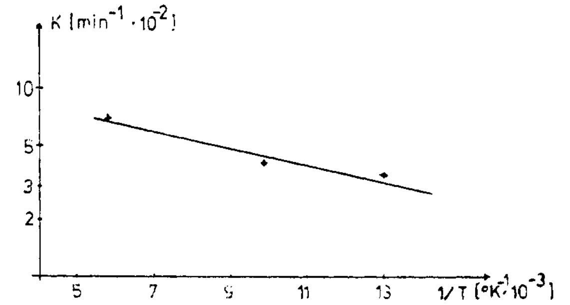


Figure 7. Arrhenius plot of the measured rate constants for the thermal decay of trapped electrons in 3,4-PI.

Chart I

Temp, °C	k, min^{-1}
−196	0.034
−150	0.040
−100	0.070

The decay curves were tested for first-order kinetics using the Guggenheim method[10] as it was done by Keyser[11] who measured the thermal decay of an esr singlet in polyethylene which was due to trapped electrons. The relationship between A_t, the singlet amplitude at time t, and the time t for a first-order process is given by

$$A_t - A_{t+\Delta} = (A_0 - A_\infty)(1 - \exp(-k\Delta)) \exp(-kt)$$

where k is the first-order rate constant, A_0 and A_∞ are singlet amplitudes at zero and infinite times, and Δ is a fixed increment of time. The decay curves exhibit a linear relationship between ln $(A_t - A_{t+\Delta})$ and the time t with the rate constants in Chart I. From an Arrhenius plot (Figure 7) of these rate constants one obtains an activation energy E_a = 0.2 kcal/mol, assuming the relationship $k = A \exp(-E_a/RT)$.

The addition of electron scavengers such as pyrene, anthracene, and biphenyl had no influence on the singlet intensity in 3,4-PI.

From the features of the esr singlet in 3,4-PI especially, the photobleaching with infrared light indicates that the esr singlet is due to trapped electrons in the polymer. Furthermore, the relatively low microwave power saturation of 0.06 mW is further evidence for the presence of a weak interacting paramagnetic species such as trapped electrons. Typical values of socalled "physical" trapped electrons in polyethylene as they were reported by Keyser[11] are 3 G for the singlet line width and 0.004 mW power level for microwave saturation. The higher values of power saturation and line width indicate that in 3,4-PI the trapped electrons are more strongly coupled to their environment than in the case of polyethylene. On the other hand, a chemical electron trap (*i.e.*, anions) is unlikely because of the infrared bleaching and the structure-dependent occurrence of the esr singlet. As already pointed out electrons are preferrably trapped in samples prepared and stored at temperatures below the glass transition point. Keyser reported that in polyethylene the trapped electron yields depend on the crystallinity of the polymer and therefore the trapping site is likely to be in the crystalline regions of the polymer. A structure-dependent trapping of electrons in β-irradiated polystyrene has been observed by Witt[12] as well.

The fact that trapped electrons are not affected by the presence of electron scavengers seems to be evidence for a preferred electron trap in crystalline parts of the polymer, as additives go only into amorphous regions.

The isothermal decay at different temperatures was found to be a first-order process and the decay constants fit an Arrhenius plot. Therefore we obtain a single value for the thermal activation energy of trapped electrons in 3,4-PI (0.2 kcal/mol). This can only be explained by a uniform depth of all electron traps. A similar value for trapped species has been obtained by Charlesby and Partridge[13] by thermoluminescence measurements of polyethylene. In contrast to our results Keyser found the isothermal decay of trapped electrons in polyethylene to be of composite first order which is attributed to different activation energies (3.20–5.16 kcal/mol) for various populations of trapped electrons.

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