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Degradation of β-Tritiated Polystyrene by Self-Irradiation

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SUMMARY

β-Tritiated polystyrene undergoes decomposition due to self-irradiation. The effects of irradiation in air and high vacuum at 25°C were studied and simultaneous chain scission and cross-linking were observed under both conditions. Analyses of gaseous products and polymer residues were carried out. Hydrogen was the only product of vacuum irradiation while water, formaldehyde, benzaldehyde, styrene and hydrogen were formed on irradiation in air. Possible mechanisms of degradation are discussed.

INTRODUCTION

Low energy β-emitting isotopes including ^{14}C and tritium have frequently been used in mechanistic studies of polymer systems. Such β-radiation is relatively strongly absorbed by many polymers and damage incurred by self-irradiation inevitably ensues. While studying reactions of tritiated polystyrenes, radiation damage was encountered and it seemed worthwhile to study the degradation processes in some detail, since comparatively little is known about the effects of this particular type of radiation on polymers.

EXPERIMENTAL

β-Tritiated styrene was prepared by the addition of tritiated water (total activity 10 mCi) to the Grignard reagent formed by the addition of β-bromostyrene to magnesium. After ether extraction the compound was purified by vacuum and molecular distillations and shown to be pure by gas chromatography. (Silicone rubber at 115°C.) It was then polymerized thermally to 18% conversion at 70°C under high vacuum conditions, and the polymer was isolated by precipitation from methanol. The osmometric molecular weight, determined at 30°C using toluene as solvent, was 324,000.

The β-activity of the polymer was determined by liquid scintillation counting, small weighed samples of the polymer being dissolved in toluene containing scintillants (p-terphenyl 2.5% and 2,2'-p-phenylene-bis(5-phenyloxazole) 0.15%). Allowance was made for quenching of fluorescence by the polymer, and a specific activity of 104 μCi/mg was obtained.

Studies were carried out at 25°C on polymer films (0.008 mm thick) so that the reactions could be followed readily by spectroscopic techniques. One set of films was exposed to air and another degassed and stored under high vacuum (10^{-6} mm Hg) in IR quartz cuvets fitted with stopcocks. These units could be placed in the sample holders in the UV and IR spectrometers, and it was thus possible to obtain instantaneous spectral changes without exposing the films to atmospheric oxygen. In this way the effects of β-irradiation and combined β-irradiation and oxygen could be separated.

RESULTS

The most obvious manifestation of radiation damage was a yellow coloration of the polymer. Ultraviolet and visible spectra of both samples were obtained at regular intervals, and although a general increase in absorbance over the entire spectral range was observed, absorption increases in the 2350 and 4400 Å regions were more pronounced. The results are shown in Figs. 1 and 2 in which increasing absorbances in these two regions are shown as a

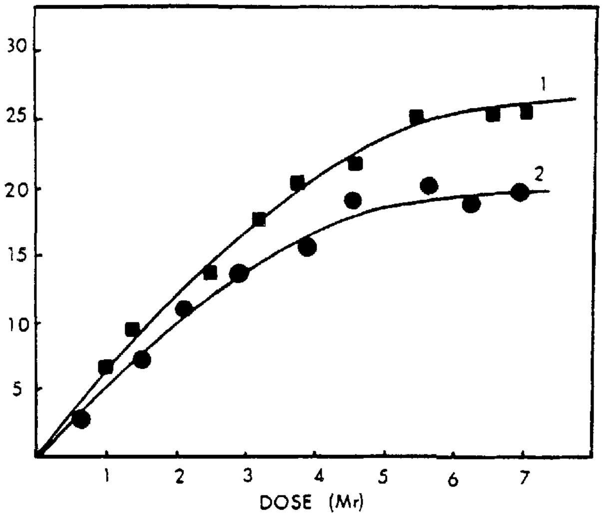


FIG. 1. Self-irradiation of β-tritiated polystyrene. Spectral changes at 2350 Å. Curve 1: Vacuum irradiation. Curve 2: Irradiation in air.

function of time of self-irradiation. The 4400 cm^{-1} absorption is due to coloration.

Infrared spectra were also recorded at regular intervals, the most significant changes appearing at 1740 cm^{-1} for the sample exposed to air and at 825 cm^{-1} for the vacuum-stored sample. The general characteristics of formation of the 1740 cm^{-1} band are shown in Fig. 3, which closely resembles Figs. 1 and 2. The 825 cm^{-1} absorbance was relatively small and appeared as a shoulder on the 840 cm^{-1} polystyrene band.

Mass spectrometric analyses were carried out on the gaseous products of β-self-irradiation. One film was exposed to air in a closed 1 liter bulb, the contents of which were sampled at monthly intervals and introduced into the mass spectrometer. Similar analyses were carried out on the vacuum-stored sample, the film being contained in a glass vessel which was connected directly to the mass spectrometer. The following products were detected: 1) by vacuum irradiation, hydrogen; and 2) by irradiation in air,

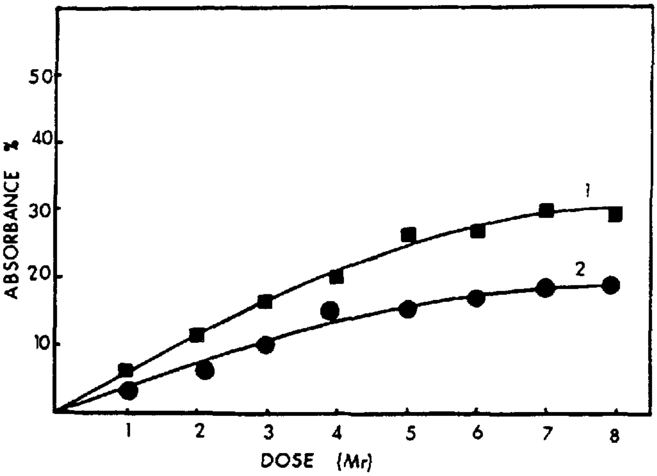


FIG. 2. Self-irradiation of β-tritiated polystyrene. Spectral changes at 4400 Å. Curve 1: Irradiation in air. Curve 2: Vacuum irradiation.

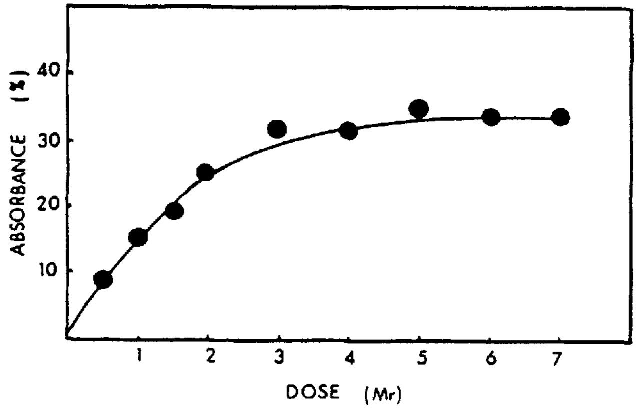


FIG. 3. Self-irradiation of β-tritiated polystyrene. Infrared absorption at 1740 cm^{-1}.

water, benzaldehyde, formaldehyde, styrene (trace), and hydrogen (trace).

Solubility tests showed that both samples underwent rapid cross-linking, indicated by the appearance of colored insoluble gel in the toluene solutions of the self-irradiated films. The insoluble gel was removed from the toluene solutions by centrifugation, and weights of both soluble and insoluble fractions were determined. The data were analyzed in terms of the Pinner-Charlesby equation [1].

$$(S + S^{1/2}) = \frac{\beta}{\alpha} + \frac{1}{\alpha \overline{P}_n D}$$

in which S is the soluble polymer fraction after absorption of dose, D, β is a constant proportional to the probability of chain scission, α is a constant proportional to the cross-linking probability, and $\overline{P}_n$ is the number-average degree of polymerization.

Doses were calculated (making the valid assumption that all the radiation energy was absorbed) from the Tolbert equation [2], i.e.,

$$F = \xi NE/M$$

in which F is the energy absorbed in rads, N is the number of disintegrations, E is the mean energy of the trituim β-particles (5,700 eV), M is the weight of the compound, and ξ is a constant (1.602×10^{-14} when M is in grams).

Plots of $(S + S^{1/2})$ vs. reciprocal doses are shown in Fig. 4, and it can be seen that vacuum irradiation leads to more cross-linking.

DISCUSSION

The experimental results are qualitatively similar to those obtained from studies of shortwave (2537 Å) UV irradiation of polystyrene [3]. However, the present system is potentially much more complex and it is consequently more difficult to deduce an unequivocal mechanism for the degradation. The following

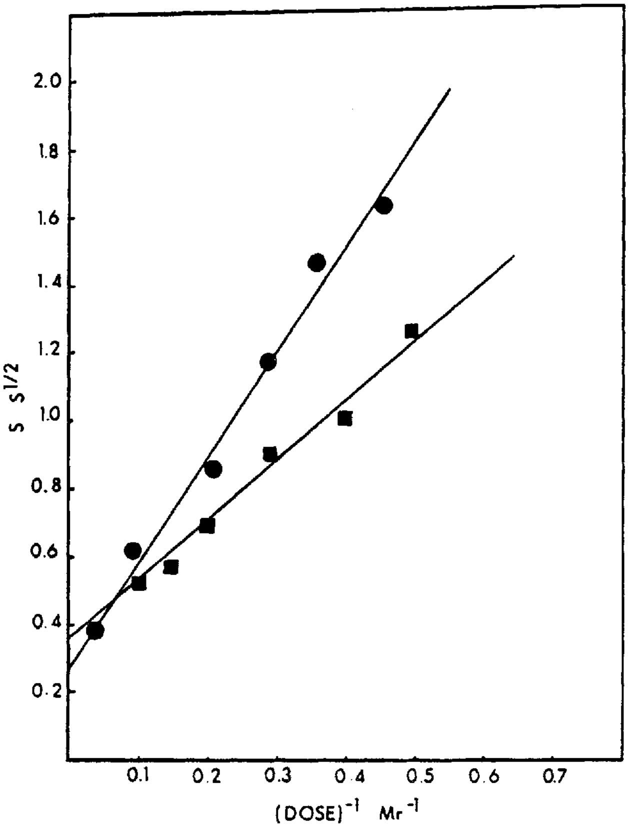


FIG. 4. Self-irradiation of β-tritiated polystyrene. Charlesby-Pinner plots: (●) vacuum irradiation, (■) irradiation in air.

discussion represents an attempt to account for the observed data in terms of known reactions of the polymer.

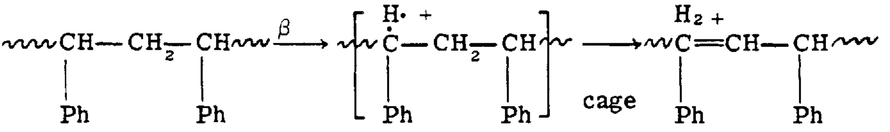
Degradation may be brought about by two primary processes: 1) Bond fission associated with the recoil of the polymer fragment following emission of the β-particles, and 2) Bond fission following the absorption of β-particles by the polymer.

Calculation of likely recoil energies using the data of Monk [4] shows that recoil processes will not contribute significantly to polymer degradation, the energy requirements being very unfavorable.

The initial interaction of the absorbed β-particles with the polymer will result in the formation of excited molecules which may decompose by either main- or side-chain bond fission, producing a variety of free radicals which may subsequently interact to form cross-links, or if oxygen is present react to produce oxygenated structures.

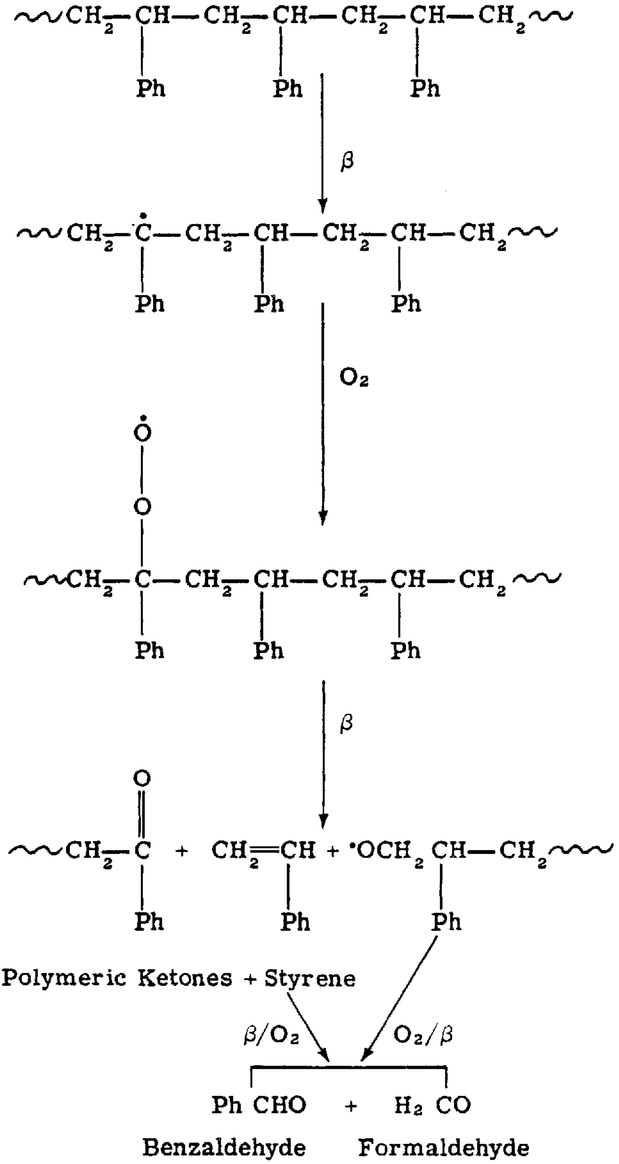
The linearity of the Charlesby-Pinner plot (Fig. 4) and the nonzero intercept on the $(S + S^{1/2})$ axis imply that simultaneous cross-linking occurs under both irradiation conditions.

Evolution of hydrogen, the only detectable product of vacuum irradiation, requires C—H bond fission and it seems probable, on account of a lower bond dissociation energy, that tertiary C—H bond fission will contribute a relatively large fraction of the hydrogen yield; undoubtedly hydrogen will also be lost from the pendant benzene rings and from the secondary C—H bonds; leaving radicals which can readily cross-link the chains. Hydrogen atoms will be formed in cages initially, and there is a probability that some hydrogen molecules are formed by abstraction of hydrogen atoms from adjacent carbon atoms, as in the scheme proposed by Weir [5]:



$$\sim\underset{\text{Ph}}{\text{CH}}-\text{CH}_2-\underset{\text{Ph}}{\text{CH}}\sim \xrightarrow{\beta} \left[\overset{\text{H}\cdot\;+}{\sim\underset{\text{Ph}}{\dot{\text{C}}}-\text{CH}_2-\underset{\text{Ph}}{\text{CH}}\sim}\right]_{\text{cage}} \longrightarrow \overset{\text{H}_2\;+}{\sim\underset{\text{Ph}}{\text{C}}=\text{CH}-\underset{\text{Ph}}{\text{CH}}\sim}$$

Absorption at 2350 Å (indicative of a double bond in conjugation with a benzene ring modifying the 2000 Å absorption band of benzene) and at 825 cm^{-1} (attributable to a trisubstituted olefin) can be reconciled with main-chain double bonds, and extended conjugation produced by a repetition of the process can lead to the observed coloration of the polymer. The remainder of the hydrogen is presumably formed by combination of two atoms in the presence of a third body. Hydrogen atoms will also add to benzene rings to give substituted phenyl radicals which will also participate in cross-linking reactions. Irradiation in oxygen involves further complications since the primary products of oxidation of the free radicals (oxygen acting as an efficient scavenger of the polymeric free radicals) can undergo radiolysis. The nature of the gaseous products suggests that the most important intermediates are peroxy radicals which decompose by a sequence analogous to that suggested by Marchal [6]:



Since hydrogen abstraction by the peroxy radical (to form the hydroperoxide) requires reorientation of the macromolecule [7], it is energetically unfavorable and radiation-induced peroxy radical decomposition preferentially occurs. It can be seen that random chain scission is concomitant with such decomposition. However, cross-linking involving oxygenated radicals is not precluded, and this is confirmed by the observance of the Charlesby-Pinner relationship (Fig. 4). The presence of oxygen does, however, decrease the extent of cross-linking. Styrene monomer is produced in this decomposition, but the actual amount detected was very small, presumably because it interacts with oxygen and other radicals to give the more abundant products benzaldehyde and formaldehyde.

The presence of polymeric ketone products is indicated by the 1740 cm^{-1} absorption [8] already attributed to such compounds. Water may be formed by a variety of reactions including those involving direct interaction of hydrogen atoms with oxygen.

Although the above scheme accounts qualitatively for the observed products, the quantitative interpretation of Figs. 1, 2, and 3 is considerably more difficult. It is possible that some sort of steady-state concentration of each of the groups or chromophores, e.g., carbonyl, is reached, the rate of formation being balanced by continuous radolytic decomposition. Alternatively, cross-linking of chains may inhibit both intra- and intermolecular interactions by making these geometrically unfavorable. The different extents of main chain unsaturation (Fig. 1) produced on irradiation in air and in vacuum can be explained in terms of diminished hydrogen abstraction, the oxygen rapidly reacting with the hydrogen atom.

The greater intensity of color produced on irradiation in air can be attributed to the presence of additional chromophores associated with oxidation reactions, e.g., carbonyls.

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