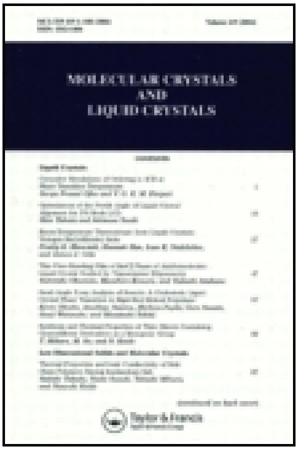

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ESR of Radicals Produced in Co^{60} Gamma-Irradiated Polystyrene‡

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Abstract—The ESR spectra of radicals produced in Co^{60} γ-irradiated polystyrene have been studied for doses ranging from 1 to 700 megarads. At least three distinct radical species are observed to occur in this dose range. The observed 100 electron volt yield of radicals for 25 °C radiolysis is 0.102 ± 0.005 and is approximately $\frac{1}{4}$ of the previously reported value. The observed spectrum of the species produced at low doses has been previously reported and interpreted as the disubstituted benzyl radical. The yield for this radical is estimated to be 0.09 per 100 electron volts. The second species, giving a single broad line at $g = 2.002$, formed with a yield of 0.012, is the most thermally stable species and may involve a crosslink center. This yield is in good agreement with the additional crosslink yield reported to occur when the polymer is heated above the glass transition temperature before exposure to oxygen following vacuum radiolysis. A third radical species is observed at intermediate doses (> 5 Mrad) and is attributed to the chain radical formed by loss of a beta hydrogen. The observed yield of this radical is < 0.002 per 100 electron volts deposited. All three species are observed to decay isothermally at temperatures greater than about 55 °C with the crosslink species having the greatest stability and the beta radical the least. Exposure to oxygen causes the irreversible bleaching of all three species with the same rate. These data are interpreted in terms of the mechanisms of crosslinking, scission and post-irradiative oxidation of polystyrene.

Introduction

Several previous investigations of radical production by Co^{60} gamma radiolysis in bulk polystyrene have been performed,[1,2,3] and the postulated radical structures related to permanent radiation chemical changes in the bulk material.[3] The earlier studies reported the observation of a signal composed of three hyperfine components with

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maximum splittings of 34[1] to 40[2] gauss and a radical yield, 0.2 per 100 eV. Florin, Wall and Brown[3] later observed a triplet spectrum and reported a maximum splitting of 95 gauss and a yield of 0.015 but concluded the spectra were in " reasonable agreement " with those of earlier investigators. The dose levels used in these two studies differed by an order of magnitude.

This investigation shows that at low doses radical spectra with the splittings reported by Abraham and Whiffen[2] and interpreted as disubstituted benzyl radicals do appear and that as the dose is increased, this spectrum gradually changes to that observed by Florin, Wall and Brown[3] and later interpreted as arising from a cyclohexadienyl radical.[4,5]

It is also shown that long range energy migration and trapping[6] is involved in the production and in the distruction of the benzyl radical. When the polymer chain is short, compared to mean migration lengths, end group radicals are formed exclusively.

Experimental

The polystyrene used in this investigation was obtained from the Sinclair-Koppers Company in the form of small spheres less than approximately 0.5 mm in diameter. This material was screened and the fraction 0.3–0.4 mm diameter used without purification. This polystyrene was placed in 4 mm o.d. fused quartz sample tubes to a depth of 3 to 4 cm and evacuated to less than 0.1 mm Hg for a period of 4 hours before sealing. During the last hour prior to sealing, the sample tubes were heated on a water bath to ≈ 70 °C and this temperature was maintained during seal-off. Irradiations were performed in a 20,000 Curie cobalt-60 source giving a dose rate of approximately 10^6 r/hr at the highest station. All irradiations were performed at ambient irradiation cell temperature of 30 °C and were observed at 25 °C.

Following irradiation, the top 3 cm of each sample tube was annealed at a red heat for about one minute with the remainder of the tube containing the sample immersed in liquid nitrogen to prevent carbonization of any gaseous products. This treatment effectively removes any signal imparted to the fused quartz during radiolysis.

These samples were then analyzed using a Varian V-4500 E.P.R.

spectrometer system equipped with a 100 KHz modulation-detection system.

Spectroscopic splitting factors were measured relative to the quartz color center taken as 2.000 at the peak in the absorption spectrum. Radical yields were measured by comparison of the double integral spectra with benzene solutions of 1, 1-diphenyl-2-picryl hydrazyl in the same sample tubes.

Results

SPECTRA

Figure 1 shows the progression of the observed spectra from low to high doses. At doses below 10^7 rads the spectra are essentially identical with those observed by Schneider[1] and Abraham and Whiffen,[2] exhibiting three lines which may arise from hyperfine interaction with two nearly equivalent protons or from a single transition having an anisotropic spectroscopic splitting factor with maximum assymetry.[7] In order to test which of these possibilities obtains, a segment of $\frac{1}{4}''$ diameter polystyrene rod was extended to approximately 10 times its original length while heated to slightly above 100 °C, cooled, and irradiated after evacuation. Under these conditions, a partial orientation of the polymer chains is expected and if the observed structure does result from an anisotropic spectroscopic splitting factor, the relative magnitude of the components should change from the purely random case. The spectrum obtained from the partially oriented rod was identical to that from the spherical samples. This result strongly favors the hyperfine structure origin of the observed spectral shape. Irradiated polyethylene oriented in this fashion shows distinct spectral differences from non-oriented samples.[8]

In samples irradiated to doses from 10^7 to 5×10^7 the changes are characterized by a loss of the three line character in the central region and a growth of two new lines with substructure in the wings of the absorption. The spectrum obtained above 3×10^7 is consistent with that found by Florin, Wall and Brown[3] in gamma irradiated bulk polystyrene. Experiments with various irradiated deutero styrenes[3] and with polystyrene fluffs bombarded with protons and deuterons[4,5,9] have established that the species

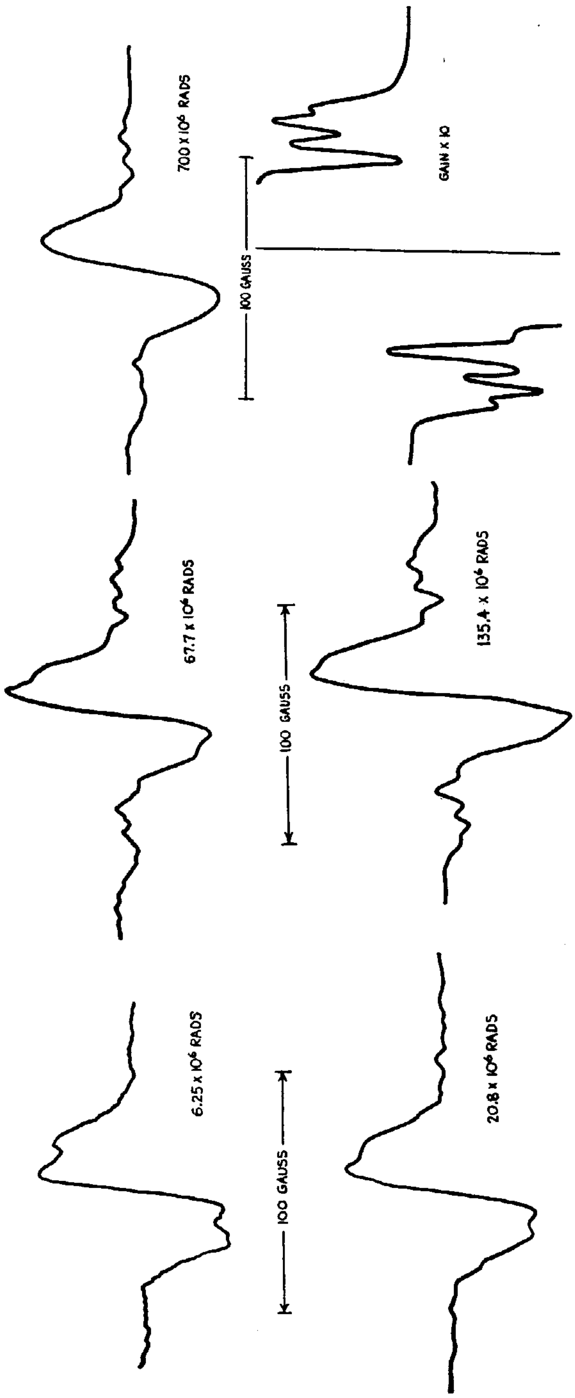


Figure 1. Variation of spectra with dose.

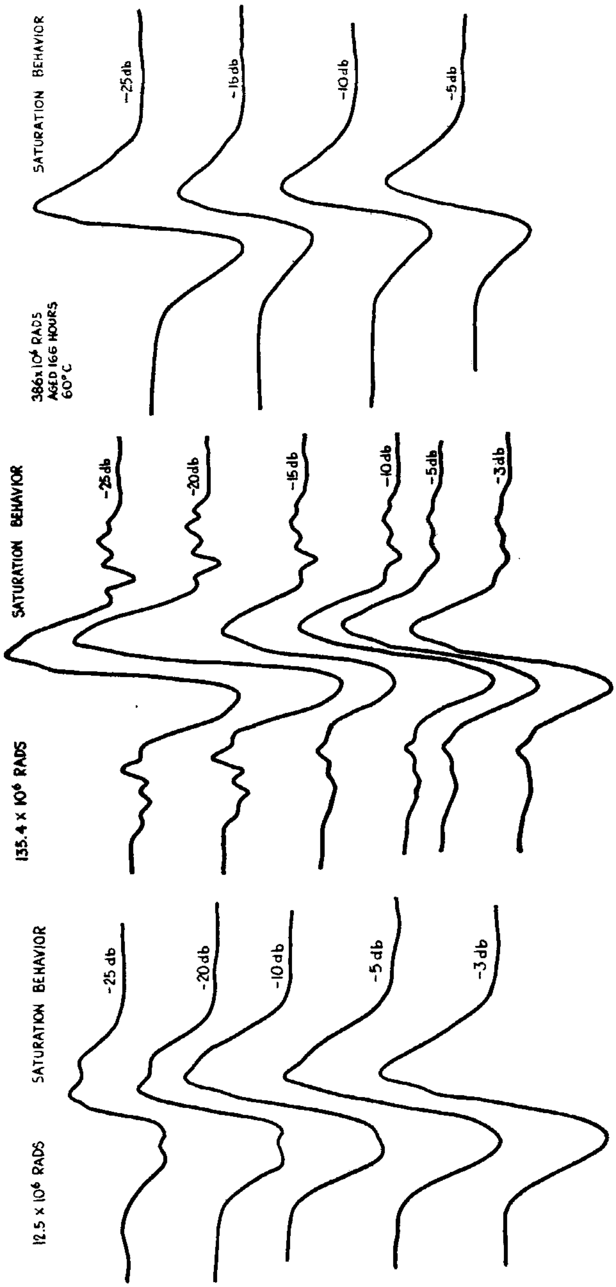


Figure 2. Power saturation behavior.

responsible for this additional signal is most likely a substituted cyclohexadienyl radical.

For doses greater than about 5×10^7 rads the central region of the spectrum is seen to increase in intensity relative to the outer lines and become more symmetrical. This must result from the continued growth of a third specie and a gradual saturation of the concentrations of the first two.

Figure 2 shows the behavior of the spectra subjected to power saturation for low dose, high dose, and thermally aged high dose species. In the low dose range, the loss of the triplet character of the absorption without increase in breadth in the wings of the signal may indicate the presence of more than one radical contributing to the signal, even at relatively low doses, which saturates at higher powers than the signal from specie One. The same behavior is observed in the saturation behavior of the spectrum obtained at high doses and to a lesser extent for the thermally aged sample.

Table 1 summarizes the spectral data.

TABLE 1

Spectral data	This work	Previous obs.
g (outer components low dose)	= 2.0023 ± 0.0003	
g (center line low dose)	= 2.002 ± 0.0003	
g (high dose)	= 2.0023 ± 0.0003	
DH (low dose outer lines)	= 40.0 ± 1 gauss,	34^a, 40^b
Line width (low dose)	= 16.0 ± 1 gauss,	17^a, 20^b
DH max (high dose)	= 120.0 ± 5 gauss,	$(100)^c$
Line width (center high dose)	= 21.5 ± 1 gauss,	19^c
$DH_{1,2,3}$ (outer components)	= 6.25, 8.75, 6.25 gauss	

[a]. Taken from reference 1.
[b]. Taken from reference 2.
[c]. Taken from reference 3.

THERMAL AGING

Thermal aging of the irradiated samples was carried out at 60 °C and the nature of the spectral changes observed. Figure 3 compares the high dose and low dose spectrum changes. In both instances the central line intensity decays less rapidly than the structured portion of the spectrum implying that the specie contributing to this line is

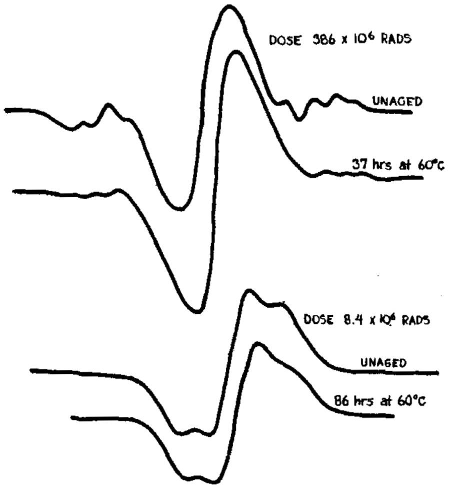


Figure 3. Changes in spectra on annealing at 60 °C.

thermally the most stable. If the assignment for the structures of species One and Two is correct, it is difficult to imagine an efficient mechanism for radical migration on a single chain and therefore disappearance by bimolecular recombination should be governed by the properties of the polymer chain rather than by the radicals themselves. As is indicated by Fig. 4, after times of about 100 minutes

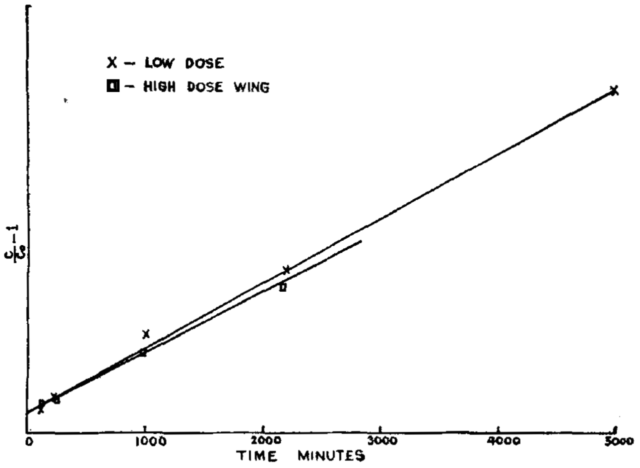


Figure 4. Thermal decay of radicals.

the decay of the low dose specie and the specie contributing to the wings of the high dose signal are approximately second order with the same rate constant.

Production of Radicals

The production of radicals was monitored by the intensity of the central signal at constant instrumental parameters and the data, summarized in Fig. 5, indicate three regions of radical production corresponding to the three species identified by spectral changes. These data indicate a concentration saturation of specie One at doses greater than about 12 Mrads and a saturation of specie Two at doses greater than 200 Mrads. No concentration saturation of the third moiety appears at doses below the highest obtained, 700 Mrads. One hundred eV yields were estimated at two dose levels, 12.51 Mrads and 135.4 Mrads. The measured yields were 0.064 and 0.013, respectively. Using the plots of Fig. 5, initial 100 eV yields for each

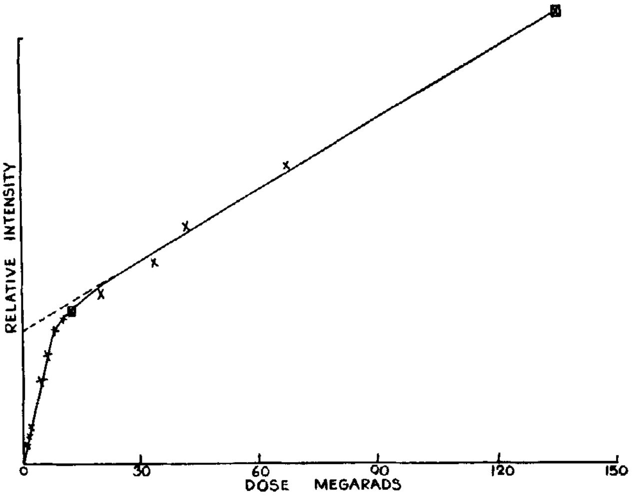


Figure 5a. Radical production. (a) Low dose.

of the three species were estimated to be 0.085, 0.009, and 0.001. The apparent yield at 61.5 Mrads is estimated to be 0.019 which is in good agreement with the previously measured value of 0.015.[3]

Table 2 summarizes these data.

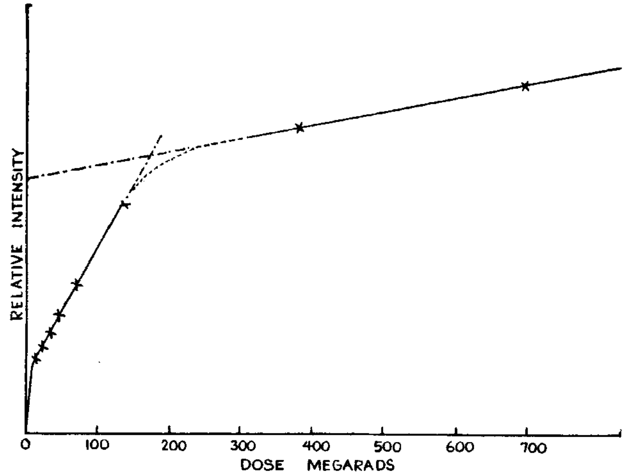


Figure 5b. Radical production (b) High dose.

TABLE 2

Radical	100 eV yield	Dose at saturation	Saturation conc.
1	0.085	8.5×10^6 rad	7.9×10^{-4} molal
2	0.009	170×10^6	1.35×10^{-3} molal
3	0.001	$>700 \times 10^6$	—

Discussion

The E.S.R. spectra observed in this work are assignable to at least three species formed with various yields and saturating at different values of total dose. The spectrum appearing at low doses is similar to that observed both by Schneider[1] and by Abraham and Whiffen[2] and is a distinct specie from that observed by Florin, *et al.*[3] The chain orientation experiment strongly indicates that the structure is in fact due to hyperfine interaction primarily with two protons and the line width due to lesser interaction with other non-equivalent protons. Chemically the most likely radical to account for this spectrum is that formed from loss of an α chain hydrogen. The observed spectrum is not inconsistent with this structure and experiments with deuterated styrenes could establish this conclusively.

From the data on thermal decay of both high and low dose spectra, it is difficult to justify the concentration saturation of this moiety as resulting from thermal decay or from bimolecular reaction with any of the other metastable radicals observed.

It is, however, possible that the concentration saturation occurs by destruction of the moiety as a primary act of the energy deposition. Recent studies have shown that molecules such as anthracene and naphthalene are capable of scavenging energy deposited radiolytically in polystyrene and that this deposited energy migrates over considerable distances in the polystyrene chain[6] (in the order of 200 Å or about 65 monomer units).

Assuming that the destruction of the radicals occurs from localization of the same migrating energy species which produces triplets in anthracene and naphthalene, and using the data from references 6 and 10, we calculate a molal concentration at which the production of triplets in anthracene is equal to initial production of radicals of specie One to be 1.43×10^{-3} molal. This compares quite favorably with the observed saturation concentration of 0.79×10^{-3} molal.

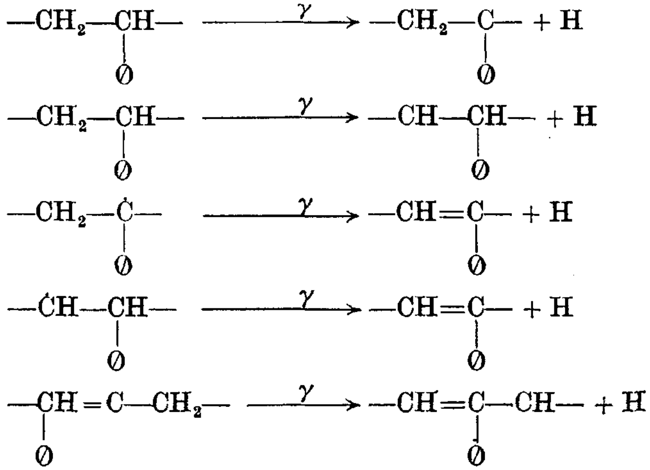
A sample of polystyrene with a number average molecular weight of 2080, about 20 monomer units in length, was irradiated to about 10^7 rads. None of the species observed in the high molecular weight material was observed here. Instead, the spectrum can be attributed to terminal formyl radicals exclusively. Since oxygen was excluded from these samples, we conclude that these radicals arise from decomposition of end groups containing polymerization catalyst. This confirms the participation of long range energy migration in the production as well as the decay of radicals in polystyrene.

The nature of the radical responsible for the second spectra has been well established, from studies on deuterated polystyrenes,[3,5] and hydrogen atom and deuterium atom bombardment of polystyrenes,[4,5,9] to be a cyclohexadienyl radical formed by hydrogen atom addition to the phenyl rings. Our second spectra are in good agreement with these observations, but do show some structure in the outer line positions not seen in the spectra from reference 9. This additional structure may be due either to a fourth species contributing in this region or to an increase in specificity of addition to the rings in the bulk polystyrene not shown by the atom bombardment of the fluffs. The first of these possibilities is the more likely and a radical formed by loss of β hydrogen from the chain can indeed be invoked to account for intensity in these regions.

Similar calculations to those for specie One for the radiation chemical destruction of specie Two led to a saturation concentration of 0.15×10^{-3} molal, nearly a factor of 10 lower than the measured value at saturation. It is then possible that destruction of the second species occurs by an entirely different process or that this radical is much less effective in trapping the migrating energy. The postulated structure for radical specie Two seems to favor the first of these possibilities rather than the latter.

The third major radical specie, contributing to the central region of the spectrum predominantly at high doses, and appearing exclusively following prolonged annealing at 60 °C, shows no features which allow interpretation of its structure. We can infer from its superior temperature stability that it may be associated with a crosslink site stearically stabilized or with a resonance stabilized form. The proposed energy migration and destruction of benzyl radicals probably proceeds to form an α–β disubstituted styrene entity in the polymer chain which can serve to localize the radiation chemical energy giving a preferred site for further damage. This process can lead to formation of conjugated unsaturation in the chain backbone of the polymer and polyenyl radicals which are expected to show only a single line in the solid.

From these observations the following set of reactions summarizes the primary chemical events resulting from radiolysis:



$$1.\quad \text{—CH}_2\text{—}\underset{\emptyset}{\text{CH}}\text{—} \xrightarrow{\gamma} \text{—CH}_2\text{—}\underset{\emptyset}{\text{C}}\text{—} + \text{H}$$

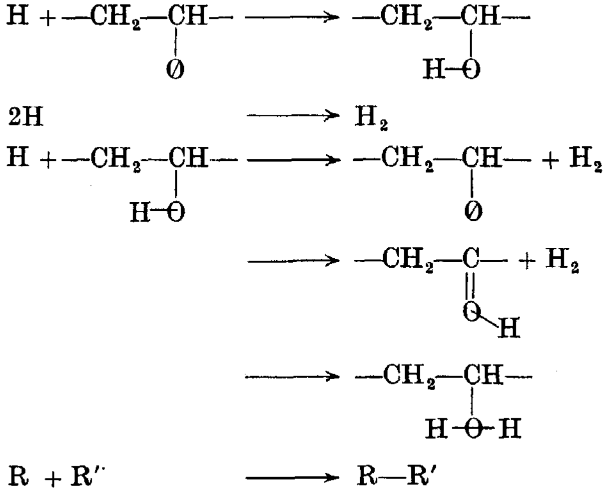
$$2.\quad \text{—CH}_2\text{—}\underset{\emptyset}{\text{CH}}\text{—} \xrightarrow{\gamma} \text{—CH—}\underset{\emptyset}{\text{CH}}\text{—} + \text{H}$$

$$3.\quad \text{—CH}_2\text{—}\underset{\emptyset}{\dot{\text{C}}}\text{—} \xrightarrow{\gamma} \text{—CH}{=}\underset{\emptyset}{\text{C}}\text{—} + \text{H}$$

$$4.\quad \text{—}\dot{\text{C}}\text{H—}\underset{\emptyset}{\text{CH}}\text{—} \xrightarrow{\gamma} \text{—CH}{=}\underset{\emptyset}{\text{C}}\text{—} + \text{H}$$

$$5.\quad \text{—}\underset{\emptyset}{\text{CH}}{=}\text{C—CH}_2\text{—} \xrightarrow{\gamma} \text{—CH}{=}\underset{\emptyset}{\text{C}}\text{—CH—} + \text{H}$$

The following thermal reactions lead to the formation of additional species:



6. $H + -CH_2-\underset{\phi}{CH}- \longrightarrow -CH_2-\underset{H-\phi}{CH}-$

7. $2H \longrightarrow H_2$

8(a). $H + -CH_2-\underset{H-\phi}{CH}- \longrightarrow -CH_2-\underset{\phi}{CH}- + H_2$

(b). $\longrightarrow -CH_2-\underset{\overset{\|}{\phi\text{-}H}}{C}- + H_2$

(c). $\longrightarrow -CH_2-\underset{H-\phi-H}{CH}-$

9. $R + R' \longrightarrow R-R'$

The lower yield of cyclohexadienyl radicals than benzyl radicals implies that the cyclohexadienyl radicals, even at low concentration, compete quite favorably (reaction 8) for hydrogen atoms with the phenyl rings (reaction 6).

Since the rate of addition of thermal hydrogen atoms to phenyl rings is quite low,[9] it is expected that the distribution of radicals from this reaction will be nearly homogeneous. From the observed rate of bimolecular decay at 60 °C for these species, we conclude that crosslinking in polystyrene does not primarily result from this source. Hot hydrogen atom addition may, however, proceed with a much higher rate and give closely spaced radical pairs. These would decay with high rate unimolecularly to give crosslinks and only a few radicals from this reaction would survive at room temperature. Some evidence for this conclusion exists in the early part of the thermal decay at 60 °C. A small portion of both cyclohexadienyl and benzyl radicals decays initially with greater rate than that observed at later times (see Fig. 4). If this situation obtains, the initial yield of benzyl radicals would, in fact, be the sum of our observed yield, 0.085/100 eV, and the measured crosslinking yield, 0.034/100 eV[11] or 0.119/100 eV. The ratio of hot H atom reaction to thermalization is 0.034/0.085 = 0.4.

POST IRRADIATION OXIDATION

Samples of unannealed low dose and annealed high dose material were exposed to air while monitoring the central region of the spectrum. In both cases the E.S.R. signal decayed rapidly and identically with time. After about 20 minutes of oxidation the signal was no longer detectable. Films of polystyrene, cast from benzene solution of the polystyrene spheres, approximately 0.004 cm in thickness, were irradiated in air, and their ultraviolet spectra examined. A band appears at 330 mμ with an intensity corresponding to a product $Gx\epsilon = 945$ cm^{-1}. Aromatic and unsaturated ketones have bands in the region between 310 and 330 mμ and saturated ketones below 300 mμ. These bands typically have extinction coefficients in the range 15–300 cm^{-1}. One hundred eV yields from 65–3.15 depending on specific choice of structure are suggested from our data. A maximum yield of $\approx 0.2/100$ eV is expected if each radical gives rise to a single carbonyl following oxidation. The observed band intensity strongly favors a chain mechanism for these oxidation reactions.

Conclusions

This investigation has established the existence of at least three distinct radical species involved in the radiolysis of polystyrene. The concentration of each specie was found to maximize at different doses, thus accounting for the inconsistencies between previous studies.

It has also been established that long range energy migration is intimately involved in the primary process of radical formation in this polymer and in the destruction of this primary species at higher doses. This exciton-like entity appears to be confined to a single polymer chain and, for short chains, to be trapped at chain ends preferentially.

In addition, it has been demonstrated that irradiation induced oxidation involves radicals and proceeds by a chain mechanism.

Acknowledgments

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