

On the Mechanism of Ionizing Radiation Damage in SBR Elastomers*†

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INTRODUCTION

The utilization of nuclear fission as a source of energy for the propulsion of naval vessels has imposed increasing demands on polymers used in the formulation of the rubberlike materials required for numerous shipboard applications. Commercially available polymers currently used for these purposes become embrittled, lose strength, and show an overall deterioration of desirable physical properties on being exposed to nuclear radiation energy. A comprehensive understanding of the reaction mechanism underlying these effects would be of inestimable value for devising methods to retard radiation damage. In this connection, it is generally known that changes in the physical properties of polymers are usually influenced by the extent to which crosslinking and chain scission reactions occur. The formation of infusible three-dimensional network structures in unvulcanized elastomers resulting from a predominance of crosslinking reactions is often considered desirable. The degree of crosslinking may be determined by measuring changes in the solubility and extent of swelling of the elastomer in organic solvents. When scission predominates over crosslinking reactions, the average molecular weight of the polymer decreases, with adverse effects on the mechanical and electrical properties of the material. The extent of elastomer chain cleavage is readily ascertained from the change in the viscosity of a dilute solution of the polymer.

The nature of the irradiated products formed during these crosslinking and chain scission reactions depends, in large measure, on the chemical

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environment in which their irradiation occurs. For example, it is known that the presence of oxygen will often accelerate and propagate the degradation of some polymers during exposure to ionizing radiation, while other polymers are unaffected. These radiation-induced chemical changes are measurable by infrared spectrophotometric techniques.

This paper presents the results of studies made to obtain information about the reaction mechanism underlying ionizing radiation damage of SBR elastomers, in order to develop criteria on which to base the preparation of vulcanizates with improved service-life. SBR was selected for investigation because of its extensive use in shipboard installations requiring elastomeric materials.

EXPERIMENTAL

Materials

A hot, nonpigmented SBR gum, having approximately 25% bound styrene and designated SBR-1000, was used in this study.

Irradiation

Toluene solutions containing approximately 1.0 and 2.0 g. of purified SBR per 100 ml. of solution were prepared as described in the literature.¹ Before being exposed to the ionizing radiation, the polymer solutions were centrifuged for 10 min. at approximately 20,000 rpm in a Spinco Model E ultracentrifuge, to remove microgel or foreign particles.

Aliquots of approximately 100 ml. of the polymer solutions were irradiated at 50°C. in sealed 31 × 215-mm. Pyrex tubes in a Co⁶⁰ source, at 1.2 Mrep./hr. The specimens were removed from the source at preselected time intervals corresponding to dosages of 1, 5, 10, 15, 50, and 100 Mrep. Equivalent volumes of toluene were similarly exposed to determine the effects of nuclear radiation on the solvent alone. No efforts were made to de-aerate

the samples before irradiation. The "Cobalt No. 35" underwater facility located at the Brookhaven National Laboratory, Upton, New York, was used as the radiation source.

RESULTS

Weight

Figure 1 shows the changes in weight of the solids content of the toluene solution of SBR-1000 irradiated in the range of 0-100 Mrep. These data are corrected for the solids content found in the same volume of toluene alone irradiated under identical conditions. It is apparent that, after an exposure of approximately 15 Mrep the increase in solids in the irradiated toluene solution varies inversely with the original polymer concentration, and directly with the radiation dose. The rate of increase is approximately 0.05% of total solids per megarep of gamma radiation. The radiation-

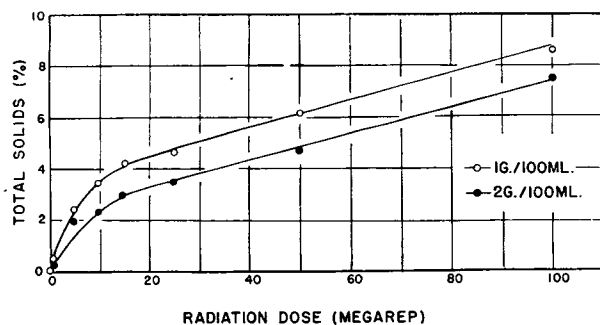


Fig. 1. Concentration (w/v) of SBR in toluene solutions vs. radiation dose.

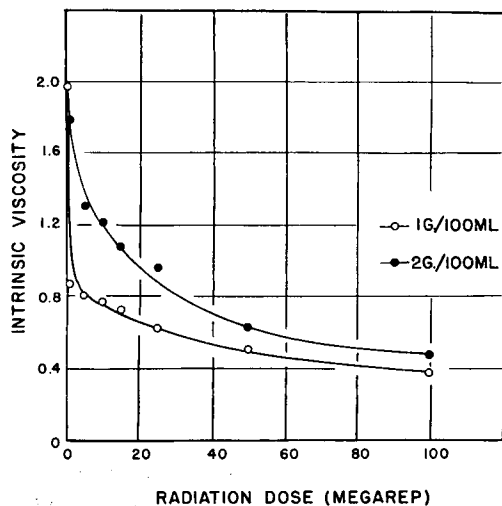


Fig. 2. Decrease in intrinsic viscosity of SBR-toluene solutions during irradiation.

induced weight increase of the polymer probably is due to polymer-solvent interaction.

Results of viscosity measurements of unirradiated and irradiated toluene solutions of SBR-1000 are presented in Figure 2. These data show that the intrinsic viscosity decreases quite rapidly initially and then more slowly as a minimal chain size is approached. In addition, these data indicate that the total drop in intrinsic viscosity is inversely proportional to the original polymer concentration.

The intrinsic viscosity of a polymer is proportional to the average molecular weight:

$$[\eta] = K\bar{M}^{-a} \quad (1)$$

where $[\eta]$ represents the intrinsic viscosity of a polymer solution having an average molecular weight \bar{M} , and K and a are constants whose values depend upon the polymer-solvent system.

The literature² shows that for the system SBR-toluene the intrinsic viscosity is proportional to the number-average molecular weight, \bar{M}_n , when K and a are 5.4×10^{-4} and 0.66, respectively.

Under the experimental conditions described SBR-1000 dissolved in toluene does not undergo crosslinking reactions. The number of main-chain scissions produced by irradiation can be determined therefore, from viscosity data, as follows

$$1/\bar{M}_v = 1/\bar{M}_v + (\bar{M}_n/\bar{M}_v)(N_A E_a)^{-1} R \quad (2)$$

where \bar{M}_v and \bar{M}_v are the viscosity-average molecular weights of the original elastomer and of the polymer at radiation dose R (e.v./g.), N_A is Avogadro's number, \bar{M}_n/\bar{M}_v is the ratio of the number-average to rise as average molecular weights, and E_a is the energy consumed per main-chain scission.

For a polymer having a "most probable" distribution,³ the ratio \bar{M}_n/\bar{M}_v is calculated as follows:⁴

$$\bar{M}_v/\bar{M}_n = \{(1+a)[\tau(1+a)]\}^{1/a} \quad (3)$$

where a is the constant given in eq. (1) and $\tau(1+a)$ is the gamma function of $(1+a)$. Thus for SBR-1000, a polymer that has a wide molecular weight distribution,⁵ \bar{M}_v is equal to 1.84 \bar{M}_n .

A plot of $10^6/\bar{M}_v$ as a function of R (Mrep) for irradiated SBR-1000 is given in Figure 3. These data show that the number of backbone scissions of the 1% (w/v) polymer solution is proportional to the radiation dose over the 0-100 Mrep range. The linearity of the plot shows that the chain scission occurs by a random-type reaction mecha-

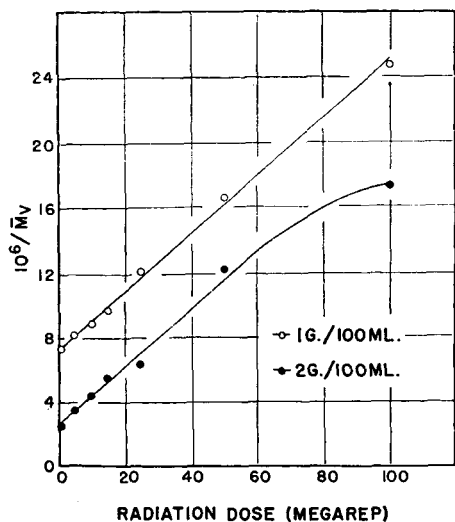


Fig. 3. Relation of degree of polymer chain scission to radiation dose.

nism. The 2% (w/v) elastomer solution, similarly treated, exhibits linearity only over a dose range of 0–50 Mreps, above which the rate of scission apparently falls off. The action of radiation energy on the solvent, with variations in the degree of polymer-solvent interaction or the concentration of polymeric residues in the solvent contributing to and complicating this, may account for the deviation from linearity. The similarity of the slopes of the linear portions of both curves indicates that, within the experimental limits used in this study, the rate of main-chain scission is independent of polymer concentration. The energy consumed per main-chain scission, calculated from the slope of the linear plot, is $E_d = 300$ e.v.

Alexander and Charlesby^{6,7} determined that, for a main-chain break a copolymer of isobutylene and 20% bound styrene requires an average of 32 e.v., as compared to 17–20 e.v. for polyisobutylene. If E_d values are used to compare the radiation stabilities of different polymeric materials, then SBR-1000 seems to offer much more resistance to radiation degradation than any of these other polymers. The findings reported herein are in agreement with those cited in the literature,⁸ which indicate that SBR vulcanizates are the most radiation-resistant of the commercially available synthetic elastomers.

Chemical Changes

Figure 4 shows the qualitative infrared spectra of films cast from unirradiated and irradiated toluene solutions of SBR-1000. It is apparent

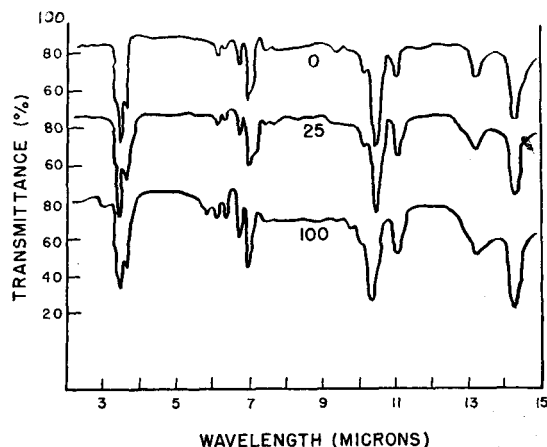


Fig. 4. Infrared spectra of untreated (0 Mrep) and treated (25 and 100 Mrep) SBR-1000.

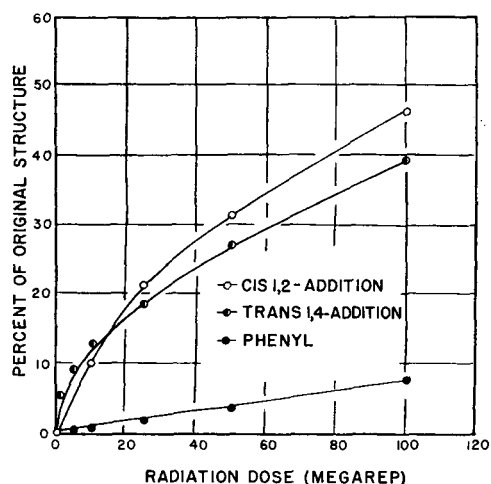


Fig. 5. Irradiation degradation of SBR-1000: percentage of original structures altered vs. dose.

from these spectra that the polymer undergoes no significant structural changes, during irradiation, except that small amounts of carbonyl and hydroxyl groups are formed, which are assumed to be products of interaction of the polymer with dissolved oxygen.

The results of quantitative determinations of the ratios of the absorbance of irradiated specimen films to that of a film of the original polymer (of the same thickness) are presented in Figure 5. These data show that the phenyl groups, and the *trans*-1,4- and *cis*-1,2-butadiene units, absorbing at 6.25, 10.35, and 10.98 μ , respectively, decrease in concentration with corresponding increases in irradiation dose. In addition, results indicate that the internal and external diene structures of the

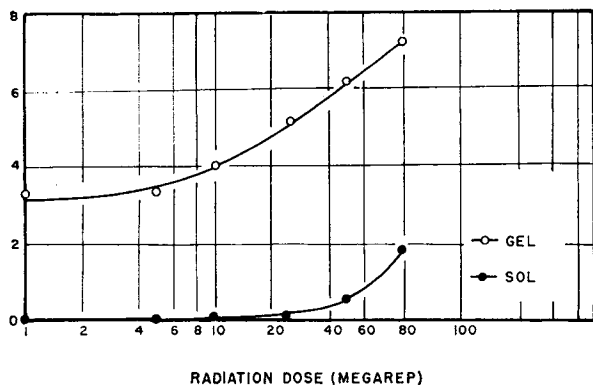


Fig. 6. Weight fractions of gel and sol of SBR-1000 in chloroform, vs. radiation dose. Ordinate: Weight of fractions, g.

polymer chain are degraded more rapidly by nuclear radiation than the phenyl rings of the styrene units. This may be due in part to the addition of phenyl rings to the polymer chain as a result of polymer-solvent interaction. The attack on the butadiene groups is not selective, however, since the external groups are degraded more rapidly than the internal units.

The internal and external diene units are known to be distributed randomly throughout the polymer chain. Since each of these diene groups exhibits a different degree of susceptibility to radiation damage, one would expect from these infrared data to find that the attack occurs by a random process. Evidence of such a random attack is given by viscometric data. Infrared measurements also show a decrease in the concentration of C—H links absorbing at 3.42μ with increase in the radiation dose.

Effects of Solvent

The effects of solvent on the nature of the polymer degradation were investigated by exposing chloroform solutions containing approximately 2.0 g. SBR-1000 per 100 ml. solution to gamma radiation over a range of 0–100 Mrep.

Visual examination of the irradiated specimens showed that the polymer solutions contained large quantities of gel. Figure 6 shows that the weight of gel formed during the irradiation process increased with the radiation dose. The weight of sol, on the other hand, dropped from the original 2 g./100 ml. to zero concentration at the 1 Mrep/dose, and then gradually increased again. It is evident from the zero sol fraction at 1 Mrep that, during irradiation of SBR in chloroform, the predominant process is one of rapid crosslinking rather

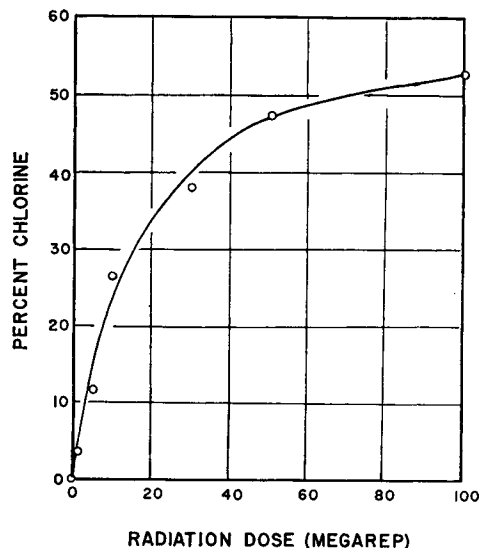


Fig. 7. Chlorine in gel fraction vs. radiation dose.

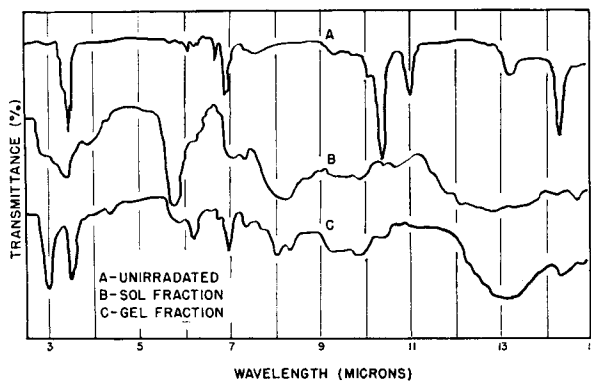


Fig. 8. Infrared spectra of untreated SBR-1000 and of sol and gel fractions irradiated to 100 Mrep.

than chain scission. The subsequent formation of soluble SBR from the gelled polymer indicates that on irradiation the crosslinked elastomer undergoes scission.

Evidence of the interaction of the polymer with chloroform is presented in Figure 7. These data show that on irradiation in chloroform the concentration of chlorinated structures bound on the gelled polymer increases with the radiation dose.

Figure 8 shows qualitative infrared spectra of unirradiated SBR-100 and of the gel and sol fractions of the polymer isolated from chloroform solution after an exposure of 100 Mrep. In general, the spectra of the sol and gel fractions appear to be similar. The spectra of the irradiated materials differ, however, from that of the original polymer. The *trans*-1,4 and *cis*-1,2 unsaturated groups found in the untreated polymer, absorbing at 10.35

and 10.98 μ , respectively, are almost nonexistent in their radiated fractions. The appearance of new broad bands in the 8–10 μ region and the broadening of the bands between 12 and 14 μ are indicative of the presence of chlorinated structures in the polymer molecule, substantiating the postulated polymer-solvent interaction. The development in the sol and gel fractions of hydroxyl and carbonyl groups absorbing at 2.90 and 5.83 μ , respectively, indicates that the polymer is oxidized as a result of irradiation of the oxygen originally dissolved in the solvent. Charlesby⁶ showed that the weight fraction of sol, S , formed during the random crosslinking and scission of polymer by ionizing radiation can be expressed as:

$$S = 1 - g = [1 + (\delta_R g / 2)]^{-2} \quad (4)$$

where g is the weight fraction of gel and δ_R is the number of crosslinked units per instantaneous primary weight-average molecule at a radiation dose R (e.v./g.). The relation of δ_R to δ , the number of crosslinked units per original primary weight-average molecule, is:

$$\delta = R/R_0^* = \delta_R/1 - (\beta/2\alpha)\delta_R \quad (5)$$

where β and α are the proportionality constants for scission and crosslinking, respectively. R_0^* is the theoretical radiation dose necessary to produce incipient gelation if the polymer does not undergo main-chain scission. Assuming proportionality between radiant energy absorption and the amount of crosslinking and main-chain scission, the ratio β/α can be determined by superimposing experimental data for S and R upon theoretical log-log plots of sol content versus crosslinking index. R_0^* is determined by measuring the distance moved along the S axis to give the best fit for β/α .

Figure 9 shows a log-log plot of the sol weight fraction as a function of R^{-1} . Comparison of these experimental data with theoretical curves given in the literature³ shows that β/α equals 0.09 and R_0^* , the theoretical dose producing incipient gelation if no main-chain scission occurs, is 6×10^{-3} Mrep.

The relation of R_0^* to the weight-average molecular weight of a primary molecule, \bar{M}_{w0} , is given by

$$R_0^* = a/\alpha\bar{M}_{w0} \quad (6)$$

where a is the weight of the basal mole. For SBR-1000, a basal mole is calculated to be 66.5 g. Thus α , the proportionality constant for crosslinking, is determined to be 2.1×10^{-2} .

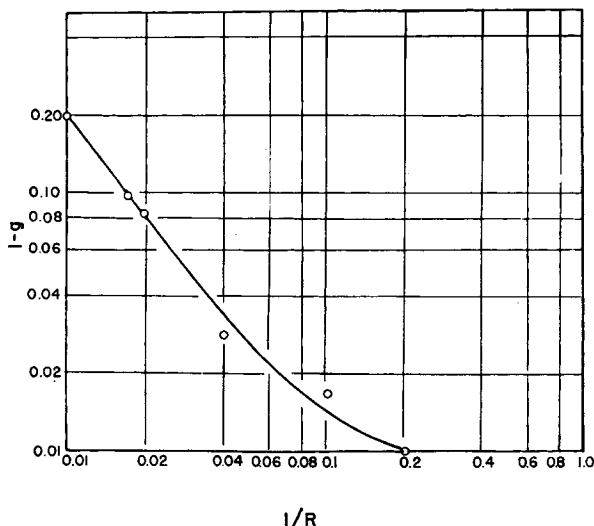


Fig. 9. Log-log plot of sol weight fraction vs. reciprocal of the radiation dose (Mrep⁻¹).

The critical radiation dose for gelation, if chain scission occurs, is given by:

$$R^* = \frac{a}{\alpha - (\beta/2)} \bar{M}_w^0 \quad (7)$$

From this equation, with the use of the values obtained for α and β/α , R^* is calculated to be 6.7×10^{-3} Mrep.

The critical radiation dose is also related to the energy dissipations for crosslinking, E_c , and for main-chain scission, E_d , by

$$R^* = \frac{\bar{M}_{w0}/N_A}{(1/E_c) - (1/2E_d)} \quad (8)$$

where N_A is Avogadro's number, 6.06×10^{23} .

Shultz⁹ showed that if backbone scission occurs at random in the crosslinked polymer, and if the number of new primary molecules is proportional to the dose, then the energy dissipation per main-chain fracture is given to a good approximation by

$$1/\delta_R = (1/\delta_0) + (R/2AE_d) \quad (9)$$

where δ_0 is the number of crosslinked units per original weight-average primary molecule, and A is the number of crosslinks produced per gram of sample.

Figure 10 shows a plot of $1/\delta_R$ versus R . The linearity of the plot indicates that the radiation-induced degradation of the polymer proceeds by a random mechanism. The intercept of the Y axis, δ_0 , is seen to equal 0.04^{-1} crosslinks per original

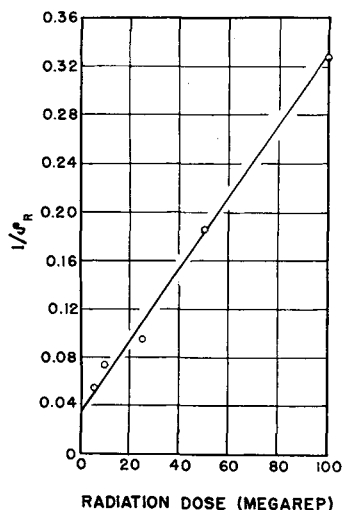


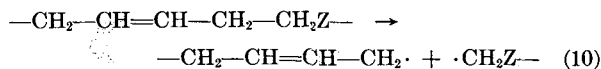
Fig. 10. Number of crosslinked units per instantaneous weight-average primary molecule as a function of radiation dose.

weight-average primary molecule. From the slope of the line $1/2AR_d$ and the original weight-average molecular weight M_{w0} , E_d is calculated to be 350 e.v. This is in the same range as the energy dissipated to produce backbone scission in SBR molecules irradiated in toluene. From eq. (8) E_c , the energy necessary to produce crosslinking, is calculated to be 3.3×10^{-1} e.v.

The low value of the energy required for crosslinking E_c when compared to the energy necessary for main-chain scission (E_d), very nicely accounts for the rapid crosslinking of SBR-1000 dissolved in chloroform. Apparently, after the polymer is crosslinked, additional radiation energy induces random scission reactions in the network. The dissipation energy E_d for backbone scission of the SBR-chloroform network is similar to that found for main-chain fracture of SBR dissolved in toluene.

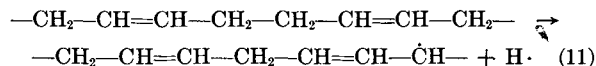
DISCUSSION

The literature¹⁰ indicates that the weakest C—C linkage in the polybutadiene chains is the interunit force β to the double bond. This suggests that the radiation-induced degradation of polymeric molecules composed of butadiene and styrene units is initiated as follows:

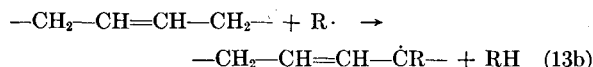
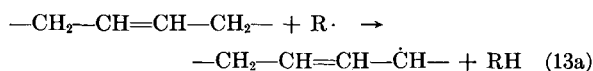
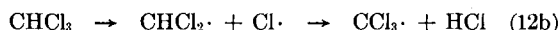
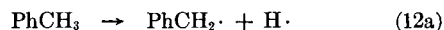


Where $-\text{CH}_2\text{Z}$ refers to *cis*-1,2- or *trans*-1,4-butadiene groups, or the styrene structure. Since

infrared analysis shows that aliphatic C—H linkages decrease with increasing radiation doses, the following initiation may also be considered:

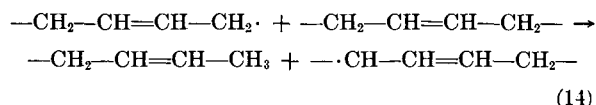


Similarly, activated structures may originate from the different butadiene and styrene units bonded to themselves or to each other. Initiation of attack on the polymer may occur also because of initial irradiation of the solvents followed by transfer of activity to the polymer chain:

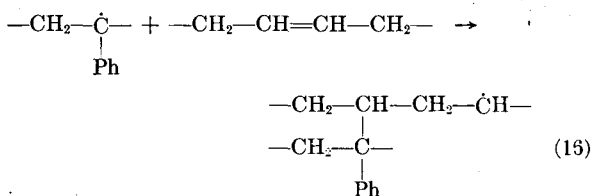
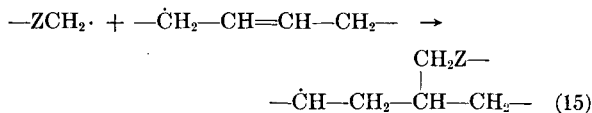


where $\text{R}\cdot$ represents $\text{PhCH}_2\cdot$, $\text{CCl}_3\cdot$, or $\text{H}\cdot$.

Reactions (10), (11), (13a), and (13b) may be propagated by intermolecular transfer processes such as



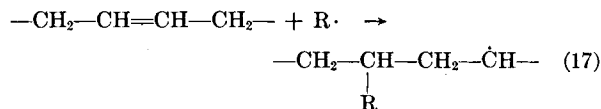
where the original chain is terminated and a new active site is produced, or



in which reactions branching or crosslinking occurs, with resultant loss of aliphatic unsaturation. The newly formed active sites are then available for interaction with other adjacent SBR chains. Reactions (15) and (16) may account, in part, for the loss of aliphatic double bonds shown by infrared data. Lawton and co-workers^{11,12} found that SBR gum is subject to crosslinking reactions when exposed to high-energy radiation. Such reactions may proceed along lines shown in eq. (16). Results presented herein indicate, however, that the nature of the irradiated products depends on the experimental conditions employed. In toluene, SBR

undergoes only backbone fracture, while in highly polar solvents, such as chloroform, crosslinking of SBR predominates over main-chain scission.

The observed decrease in aliphatic unsaturation may be accounted for also by a solvent interaction mechanism in which the activated structures produced in reactions (12a) and (12b) interact with SBR chains.

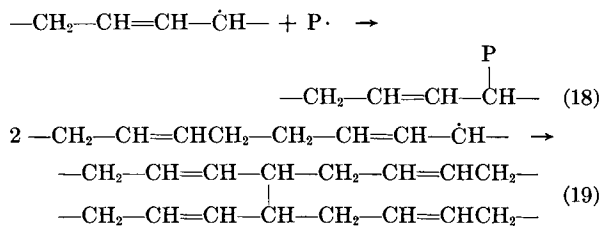


Since the polymer molecule contains an active site, reaction (17) also serves to propagate the radiation attack. If $\text{R}\cdot$ refers to active structures such as $\text{PhCH}_2\cdot$ or $\text{CCl}_3\cdot$, then (17) may also account for the progressive increase with radiation dose of the weight of solute obtained from the irradiated toluene and chloroform solutions.

Charlesby¹³ found that the radiation energy required to destroy a terminal double-bond structure on long-chain unsaturated compounds is only 60% of that needed to attack an internal double bond. These findings support the results presented herein, which indicate that the external *cis*-1,2-butadiene groups are degraded more rapidly by nuclear radiation than are the internal *trans*-1,4-butadiene units.

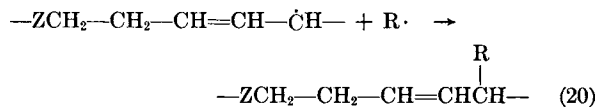
The recognized stabilizing effect of the phenyl structure on the polymer chain, due to its absorbing and dissipating the radiation energy without itself being deteriorated, is reflected in the moderate loss of such groups shown by infrared spectrophotometry. However, since experimental evidence indicates that toluene, under high-intensity nuclear radiation, interacts with the polymer, the net phenyl group concentration apparently includes structures due to polymer-solvent interaction as well as phenyl radicals in the styrene units of the original elastomer.

Termination of the reaction probably occurs when the polymer radicals are deactivated by such reactions as



wherein $\text{P}\cdot$ refers to an activated polymer chain such as $-\text{CH}_2-\text{CH}=\text{CH}-\dot{\text{C}}\text{H}_2$. Reactions (18)

and (19) yield branched and crosslinked polymers, respectively. The radiation reaction may also terminate because of solvent interactions:



Such reactions probably account also for the addition of chlorinated structures to the polymer chain during the irradiation of SBR in chloroform.

The end chemical effects of irradiation of SBR in toluene are seen to be entirely different from those produced by similar treatment of the polymer in chloroform. Chapiro and co-workers^{14,15} determined that the presence of aromatic rings in a monomer-solvent system subjected to gamma radiation results in a low efficiency of radical production, while electronegative groups such as the halogens tend to promote radical production. If this is true also for polymer-solvent systems, then it is reasonable to assume that the radiation attack on SBR proceeds by different mechanisms in toluene and in chloroform. The low efficiency of radical formation in a solvent such as toluene under ionizing radiation probably induces a preferential attack on the polymer chain along the lines shown in (10) and (11) rather than by the reactions shown in (13a) or (13b). The reaction probably is propagated as shown in (14), wherein the polymer undergoes backbone scission. To a small degree, propagation of the reaction may also be attributed to the polymer-solvent interaction given in (17). Termination of the process then apparently occurs as shown in (18), and to a lesser extent as in (20).

In the SBR-chloroform system, apparently the highly polar solvent is preferentially attacked by radiation energy as shown in (12b), and then the degradation of the polymer is initiated along lines given in (13a) or (13b), rather than as described in (10) or (11). The reaction probably is propagated along lines shown in (16), producing a gelled polymer containing active sites. Termination of the reaction probably occurs by a solvent interaction mechanism such as is given in (20), where $\text{R}\cdot$ represents active structures like $\text{CCl}_3\cdot$.

Infrared data show the presence of oxidation products in the crosslinked and chain-scissioned polymers. Oxidation most likely occurs when small quantities of oxygen dissolved in the solvents are converted by gamma radiation to ozone. The ozone then reacts with the polymer molecules, producing unstable intermediates that break down to hydroxyl and carbonyl structures. Apparently,

when all the dissolved oxygen molecules have been consumed, the oxidation reaction ceases, and therefore has little if any effect on the randomness of the radiation attack.

Radiation effects in solid SBR polymers were not studied in this investigation. Recent studies by several investigators¹⁶⁻¹⁸ have shown that polymers in solution undergo changes similar to those observed in solid state irradiations. Radiation deterioration of polymers in solution may result, however, from either indirect or direct action of radiation, or both. In the case of the original solid polymer it may be assumed that direct action is the primary mechanism of radiation attack. Where the elastomer is mixed with different compounding ingredients and then vulcanized, the material can, in a sense be considered a solid solution which on irradiation would be expected to be degraded by both direct and/or indirect action. The studies reported here show that the chemical changes that occur during their radiation depend primarily on environmental factors. It is quite probable that, if the irradiation of SBR vulcanizates proceeds by an indirect process, then the type of ingredients used in formulating the compound would also influence the nature of the chemical changes induced by gamma radiation. In any case, it has been shown in these studies that the radiation-induced main-chain scission or cross-linking of SBR proceeds by a random mechanism. Although the end chemical effects would apparently be different, vulcanizates of SBR treated in the solid state are also expected to be randomly attacked by high-energy radiation.

In a random type of degradation reaction, polymer chains of all molecular weights are equally susceptible to radiation damage. Therefore it seems highly improbable that the radiation stability of SBR could be improved by fractionation procedures. On the other hand it is quite possible that the attack on SBR elastomers may be inhibited to some extent by introducing, into the backbone or side chains, structures such as phenyl rings which can readily absorb and dissipate radiation energy without themselves, or neighboring groups, being appreciably affected. The literature¹⁹ indicates, however, that there is a limit to the number of phenyl rings which can influence the radiation stability of the polymer molecule; addition of phenyl rings above this limiting concentration would not necessarily produce a corresponding increase in the resistance of the elastomer to attack by gamma radiation.

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References

1. Delman, A. D., B. B. Simms, and A. R. Allison, *Anal. Chem.*, **26**, 1589 (1954).
2. Yanko, J. A., *J. Polymer Sci.*, **3**, 576 (1948).
3. Schultz, A. R., *J. Polymer Sci.*, **35**, 369 (1959).
4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
5. Delman, A. D., B. B. Simms, and A. E. Ruff, *J. Polymer Sci.*, **45**, 415 (1960).
6. Charlesby, A., *Proc. Roy. Soc. (London)*, **A230**, 136 (1955).
7. Alexander, P., and A. Charlesby, *Nature*, **173**, 578 (1954).
8. Broadway, N. J., M. A. Youtz, M. L. Zaring, and S. Palinchak, Radiation Effects Information Center Report No. 3, Battelle Memorial Institute, Columbus, Ohio, May 31, 1958.
9. Shultz, A. R., *J. Am. Chem. Soc.*, **80**, 1854 (1958).
10. Grassie, N., *Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956.
11. Lawton, E. J., A. M. Buche, and J. S. Balwit, *Nature*, **172**, 76 (1953).
12. Miller, A. A., E. J. Lawton, and J. S. Balwit, *J. Polymer Sci.*, **14**, 503 (1954).
13. Charlesby, A., *Radiation Research*, **2**, 96 (1955).
14. Prevot-Bernas, A., A. Chapiro, C. Cousin, Y. Landler, and M. Magat, *Discussions Faraday Soc.*, **12**, 98 (1952).
15. Chapiro, A., *J. Chem. Phys.*, **47**, 747, 764 (1950).
16. Alexander, P., and M. Fox, *Trans. Faraday Soc.*, **50**, 605 (1954).
17. Henglein, A., and M. Boysen, *Makromol. Chem.*, **20**, 83 (1956).
18. Alexander, P., and A. Charlesby, *J. Polymer Sci.*, **23**, 355 (1957).
19. Bartlett, P. D., *Experientia Supple.*, **7**, 275 (1957).

Synopsis

Studies were made to provide information for use in the development of SBR elastomers with improved resistance to attack by high energy radiation. Changes of molecular structure were investigated by viscometric techniques and by measuring gel content. Chemical changes were followed by use of infrared spectrophotometry. Results indicate that the polymer in toluene, when subjected to radiation doses in the range 0-100 Mrep, is randomly scissioned. When similarly treated in chloroform, the polymer is initially randomly crosslinked and then the newly formed elastomer network undergoes random scission. The nature of the end chemical changes is shown to depend on environmental factors. In the presence of a limited supply of oxygen, the polymer is partially oxidized. The oxidation reaction appears to have no influence, however, on the random nature of the degradation process. The external butadiene structures are shown to be attacked more rapidly than the internal groups. The phenyl rings of the styrene groups in the polymer molecules, on the other hand, are only moder-

ately affected in this respect. The results obtained in these solution studies are used to predict the effects of radiation damage to SBR vulcanizates.

Résumé

On a effectué des études pour obtenir des informations pouvant servir au développement des élastomères SBR possédant une résistance éprouvée à l'attaque des radiations de haute énergie. On a étudié les variations de structure moléculaire par des techniques viscométriques et des mesures de la quantité de gel. Les variations chimiques ont été suivies par spectrophotométrie infrarouge. Les résultats indiquent que lorsqu'on le soumet à des doses de radiation de radiation de l'ordre de 0 à 100 megarep, le polymère est scindé au hasard pour donner du toluène. Quand on le soumet à un traitement similaire dans le chloroforme, le polymère subit au début un pontage statistique et ensuite le réseau d'élastomère nouvellement formé subit une scission au hasard. On montre que les variations chimiques en fin d'irradiation dépendent des facteurs d'environnement. En présence d'une quantité limitée d'oxygène le polymère est partiellement oxydé. La réaction d'oxydation semble toutefois ne pas influencer la nature statistique du processus de dégradation. On montre que les structures butadiènes externes sont plus rapidement attaquées que les groupes internes. Les noyaux phényles des groupements styrènes dans les molécules de polymère ne sont, par ailleurs, que modérément affectés dans ces conditions. On utilise les résultats obtenus dans l'étude de

ces solutions pour prédire les effets des dommages dus aux radiations sur les vulcanisats SBR.

Zusammenfassung

Es wurden Untersuchungen durchgeführt, um brauchbare Informationen für die Entwicklung von SB-R-Elastomeren, die gegen hochenergetische Bestrahlung eine erhöhte Beständigkeit zeigen, zu erhalten. Änderungen der Molekularstruktur wurden durch Viskositäts- und Gelgehaltmessungen untersucht. Chemische Veränderungen wurden durch Infrarotspektrophotometrie verfolgt. Die Ergebnisse zeigen, dass bei einer Bestrahlung im Bereich von 0–100 Mrep in Toluol ein statistischer Abbau des Polymeren auftritt. Wird das Polymere ähnlich in Chloroform behandelt, wird es zuerst statistisch vernetzt und das neu gebildete Polymere anschliessend statistisch gespalten. Die Natur der endgültigen chemischen Veränderungen ist von milieubedingten Faktoren abhängig. In Gegenwart einer begrenzten Sauerstoffmenge wird das Polymere teilweise oxydiert. Die Oxydationsreaktion hat jedoch keinen Einfluss auf die statistische Natur des Abbauprozesses. Die äusseren Butadiengruppen werden rascher angegriffen als die inneren. Andererseits werden die Phenylringe der Styrolgruppen in dieser Hinsicht nur mässig beeinflusst. Die bei diesen Lösungsuntersuchungen erhaltenen Ergebnisse werden zur Vorhersage des schädigenden Bestrahlungseinflusses auf SB-R-Vulkanisate verwendet.

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