The Mechanism of Radiation Damage to Elastomers.   II.
Crosslinking and Antirad Action

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INTRODUCTION

Chain scission and crosslinking are the most important secondary events which result from the interaction of high energy radiation with polymers. Chain scission, particularly the effect of antirads on chain scission, was discussed in the first paper of this series.[1] Crosslinking is, however, equally important.

The mechanisms involved in crosslinking are not at all well understood.[2] It has been postulated that crosslinking may occur through combination of polymer radicals or through an addition of polymer radicals to unsaturation present in the polymer molecules. If the former mechanism predominates, the combination of secondary radicals will lead to tetrafunctional crosslinks, while the combination of a primary radical with a secondary radical will lead to a trifunctional crosslink. Similarly, radical addition to unsaturation can cause the formation of either tetra- or trifunctional crosslinks, depending upon the fate of the radical formed as the addition product.

These mechanisms are all merely speculative. Proof of their validity is lacking. The reality of crosslinking of some sort is not subject to doubt, however. It is evidenced by the increases in gel content, increases in modulus, and other similar property changes which polymers undergo during irradiation.

The present study was devoted to the changes in the high energy radiation-induced crosslinking caused by the presence of antirads (chemicals serving to reduce the deleterious property changes of polymers during irradiation). Once again, the major points of interest were *(1)* whether the antirads prevented crosslinking, *(2)* whether they were effective in the absence of oxygen or functioned rather, simply as antioxidants, and finally *(3)* whether the antirads differed only in degree of effectiveness or whether there were major qualitative differences among them.

The rate of development of crosslinks in elastomers containing various antirads was followed as a function of radiation dose. A carbon black-filled natural rubber stock was chosen as the control, since it had been used for the study of polymer scission by radiation and antirad protection against this scission in the preceding study. The antirads were chosen as before, from those showing maximum antirad effectiveness in an empirical study by Born[3] and those having structural variations of interest.

EXPERIMENTAL PROCEDURES

The same recipe was used as that in the study of radiation-induced chain scission, except that the curing ingredients were eliminated:

	Parts by weight
Natural rubber	100
Phenyl-2-naphthylamine	1
EPC carbon black	50

To this control recipe were added five parts of one of the following nine antirads: *(1)* N-phenyl-N'-o-tolylethylenediamine (FLX), *(2)* N-cyclohexyl-N'-phenyl-p-phenylenediamine (Antiox 4010), *(3)* 6 - phenyl - 2,2,4 - trimethyl - 1,2 - dihydroquinoline (Santoflex B), *(4)* N,N'-dioctyl-p-phenylenediamine (UOP-88), *(5)* 2-naphthylamine, *(6)* 1,4-naphthoquinone, *(7)* phenylhydroquinone, *(8)* 2-naphthol, and *(9)* a mixture of 35% N,N'-diphenyl-p-phenylenediamine and 65% phenyl-1-naphthylamine (Akroflex C).

Once again comparisons of antirad effectiveness are not possible, since in some of these compounds the solubility limit of the antirads in the rubber was exceeded. Mechanistic conclusions remain unaffected, however.

All of the materials were added to the rubber on a mill held at a mill roll temperature of 160°F. The mixture was milled for 15 min. before being sheeted off. Sheets of 0.025 in. thickness were

molded at 212°F. for 10 min. between cellophane sheets.

Each of the sheets was cut into strips 0.25 in. wide and approximately 1.35 in. long. After removal of cellophane, each of the strips was placed in a small open test tube if the irradiations were to be performed in air. Samples destined for vacuum irradiation were sealed into small glass ampules after being evacuated at a pressure of less than 10^{-6} mm. Hg for 16 hr. or more. Calculation of the diffusion rate of oxygen through these samples and past experimental evidence have proven this treatment to be adequate, even on a conservative basis, to remove any oxygen effects.

The samples were irradiated in the B. F. Goodrich Gamma Facility. The dose rates varied from 5.2×10^4 to 7.3×10^4 r/hr., and the time to complete the irradiations desired ranged from 6 to 49 days. The dosages were determined by glass slide dosimetry at each sample position.[4] The glass slides were placed in the same holders (test tube or glass capsules) as were the samples in order to compensate for any shielding effect of the holders. The experiments were conducted at room temperature.

The irradiated samples were removed from their holders and their lengths were measured. They were then allowed to swell for 24 hr. in benzene containing 0.1% of phenyl-2-naphthylamine. After blotting the samples dry, their swollen length was measured. It had been previously demonstrated that samples treated in this fashion swell isotropically.

The molecular weight between crosslinks M_c was calculated from the equation:[5]

$$M_c = \frac{-\rho V_1 [1 - 2(M_c/M)] [v_{2m}^{1/3} - (v_{2m}/2)]}{[\ln (1 - v_{2m}) + v_{2m} + \chi v_{2m}^2]}$$

where

$$v_{2m} = \frac{(f\rho_T/\rho)}{[(L/L_0)^3 - 1 + (f\rho_T/\rho)]}$$

and where ρ is the density of the polymer (= 0.93), f is the weight fraction polymer in the compounded stock, ρ_T is the density of the compounded stock (= 1.11), V_1 is the molar volume of the solvent (= 89.32), M is the primary chain molecular weight, χ is the solvent-polymer parameter (= 0.44), and L_0 and L are the original and swollen sample lengths, respectively.

The corrective term for end groups $[1 - 2 (M_c/M)]$ was neglected in this work due to the difficulty in obtaining accurate measurements of M in a carbon black-filled elastomer. The effect of this correction is not great since in most cases $M_c \ll M$. No correction was made for any sol which might be present. Previous experience indicated that the amount of sol would be negligible.

As Moore and Watson[6] pointed out in their studies relating to the measurement of crosslink density, the swelling technique gives a measure of all effective crosslinks. These may include not only the conventional chemical crosslinks, but also effective crosslinks caused by chain entanglement or crosslinks resulting from polymer-filler interactions.

RESULTS AND DISCUSSIONS

The type of results obtained is illustrated in Figure 1, where the reciprocal of the molecular weight between crosslinks is shown as a function of
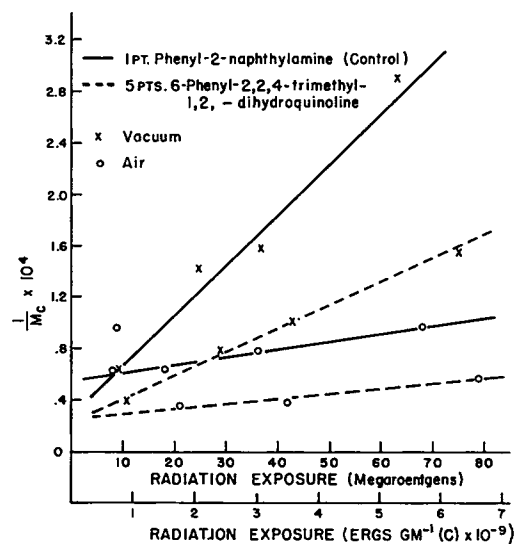

Fig. 1. Changes in crosslink level during irradiation of carbon black-loaded natural rubber.

radiation dosage R for the control and the stock containing 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline. The radiation dosage has been expressed both in terms of megaroentgens exposure and ergs per gram of carbon exposed to the same radiation flux, since a general agreement as to acceptable terminology has not yet been reached.

The slope of the linear portion of these curves was then measured to obtain the rates of crosslinking expressed as the crosslink density change per megaroentgen exposure $[1/M_c R]$. These

may be readily converted to crosslink yield G_x by the equation

$$G_x = [1/M_cR] \ (N/2) \ (6.58 \times 10^{-17})$$

In this equation, N is Avogadro's number. The conversion factor of 6.58×10^{19} e.v./g. absorption of energy, which is taken as being equivalent to 1 megaroentgen exposure, was used as described in the preceding paper.[1]

The crosslink yield is given in Table I. Charlesby[7] has reported G values for crosslinking in unfilled natural rubber stocks irradiated in vacuum ranging from 1.1 by elastic modulus to 1.7 by swelling in decane. Although the black-loaded system studied here is certainly not directly comparable to Charlesby's unfilled stocks, the values for G_x are similar.

It is immediately apparent that all of the antirads studied decrease the yield of crosslinks by a factor of approximately two in the absence of oxygen. Electron paramagnetic resonance measurements have proven directly the presence of considerable numbers of free radicals in polymeric systems during irradiations.[8,9] Analogy to simple chemical reactions involving free radical dimerization leads us to presume that crosslinking may occur in the same fashion. However, the ease of free radical addition to olefinic unsaturation means that this must also be considered as a potential crosslinking reaction. In any event, any reaction leading to a decrease in the concentration of free radicals would presumably decrease the rate of crosslinking.

We may postulate that the antirads may react with polymeric free radicals in the following fashion:

$$R \cdot + ARH \longrightarrow RH + AR \cdot \quad (\text{stable}) \quad (1)$$
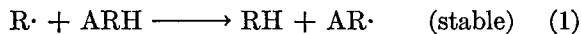
Here ARH refers to an antirad molecule containing a labile hydrogen. The antirad free radial may stabilize itself by dimerization with a similar radical or by rearrangement mechanisms. This mechanism is supported by recent studies by Shelton[10] of the relative antioxidant properties of conventional antioxidants as compared to those in which deuterium replaced the labile hydrogen atoms. The less labile deuterium gave less oxidation protection than the hydrogen substituted material. Since oxidation is also a free-radical process, it seems logical to assume that the labile hydrogen neutralization of the polymeric free radical is also an important step in antirad action.

TABLE I
The Effect of Antirads on Crosslink Yields

Antirad (5 pphr)	G, events/100 e.v. (crosslinks) in	
	Vacuum	Air
None (1 pphr phenyl-2-naphthyl-amine)	1.9	0.29
N-Phenyl-N'-o-tolylethylenediamine	1.1	0.28
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	1.3	0.33
6-Phenyl-2,2,4-trimethyl-1,2-di-hydroquinoline	0.83	0.19
N,N'-Dioctyl-p-phenylenediamine	0.87	0.12
2-Naphthylamine	0.87	0.30
1,4-Naphthoquinone	1.1	0.48
Phenylhydroquinone	1.1	0.46
2-Naphthol	1.1	0.24
N,N'-Diphenyl-p-phenylenedi-amine (35%) + phenyl-1-naph-thylamine (65%)	0.97	0.27

Irradiation in air with no antirads present resulted in a reduction in crosslinking yield. Here the same number of polymer radicals should be formed, but the rapid reaction

$$R \cdot + O_2 \longrightarrow RO_2 \cdot \quad (2)$$

should play a predominant role. This should lead to a decrease in the concentration of $R \cdot$ radicals to a level below that developed in an irradiation in a vacuum and thus to a decreased rate of crosslinking. Apparently the $RO_2 \cdot$ is not an active participant in crosslinking reactions; rather, its presence leads predominantly to chain scission, as was shown in our earlier paper.[1]

If antirads are now introduced to the oxygen-containing system, we may postulate the simultaneous occurrence of two different types of reactions. First, the antirad may act as in the vacuum to further decrease the $R \cdot$ concentration and thus decrease the rate of crosslinking. On the other hand, the antirad itself may be oxidized, thus reducing the local concentrations of oxygen and inhibiting reaction (2). At the same time, the antirad itself would be inactivated by its oxidation, and consequently reaction (1) would also be decreased. The combination of these reactions would increase the concentration of $R \cdot$ radicals and consequently the rate of crosslinking. Thus, antirads may either increase or decrease the rate of crosslinking, depending on relative rates of reaction.

Examples of the first type of reaction, crosslink inhibition. may be seen in compounds containing

the antirads N,N'-dioctyl-p-phenylenediamine or 6 - phenyl - 2,2,4 - trimethyl - 1,2, - dihydroquinoline. The second type of behavior, crosslink acceleration, is shown by compounds containing the antirads 1,2-naphthoquinone or phenylhydroquinone.

All of these mechanisms are speculative and are quite likely to be too simple to explain these reactions when they are understood in detail. For the present, however, they do stand as one mechanistic explanation for the observed facts.

These observations are qualitatively similar to those Turner,[11] who studied the effect of additives on gum natural rubber, and those of Prober,[12] who conducted a similar study on polyethylene.

It is informative to compare the crosslinking yields obtained here to the scission yields which we reported earlier.[1] The ratio of G (scission) to G (crosslinking) is shown in Table II. It should be pointed out that the scission yields in the absence of air were determined from measurements at stress relaxation conducted under nitrogen. Other work in this laboratory, however, has demonstrated the equivalence of nitrogen and vacuum environments.

Table II shows that the scission-to-crosslinking ratios range from 45 to 4.3 in air and from 2.3 to 0.92 in vacuum. This may at first seem unusual when it is recalled that Charlesby,[13] studying irradiated, unfilled natural rubber, and others studying similar systems report ratios which are

less than 0.1. An essential difference should be stressed, however.

In our earlier paper,[1] the point was stressed that stress relaxation measures all chain scissions in which the broken chain ends migrate away from each other under the applied stress before they reunite. We must however consider what happens to these broken chain ends. First of all, they may be tied back into the polymer substrate by combination with other free radical ends or by addition to unsaturated sites along the polymer chains. These we will term transient chain scissions. On the other hand, the broken chain ends may be stabilized by oxidation, hydrogen abstraction, disproportionation, or reaction with various other substances present. These we will term permanent chain scissions. Measurements based on gel formation such as those of Charlesby really measure only permanent chain scission.

The present work, when compared to the work of Charlesby and others, indicates that temporary chain scission is greater than permanent chain scission by a factor of 10 to 100. The vast majority of the stressed chains broken by radiation induced reaction must reunite after relaxation.

CONCLUSIONS

All of the antirads studied serve to decrease the rate of crosslinking of carbon black loaded natural rubber during irradiation in a vacuum. Oxygen also serves very effectively as an antirad toward crosslinking. In air, some antirads enhance this protective effect of oxygen; others serve actually to increase the rate of crosslinking.
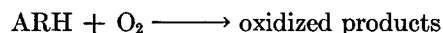
Mechanisms sufficient but not necessary to explain these observations are presented. They involve reactions of the antirads with polymer radicals, viz.:

$$R\cdot + ARH \longrightarrow RH + AR\cdot \quad \text{(stable)}$$

reactions of oxygen with polymer radicals, viz.:

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
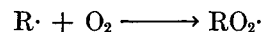
and reactions of oxygen with antirads, viz.:

$$ARH + O_2 \longrightarrow \text{oxidized products}$$

The ratio of scissions to crosslinks range from 45 to 4.3 in air and 2.3 to 0.92 in vacuum. The sol-gel measurements of other workers show, however, that most (90–99%) of these scissions are only temporary chain breaks which are rapidly reformed.

TABLE II
The Effect of Antirads on the Ratio of Scission to Crosslink Yields

Antirad (5 pphr)	Ratio of G (scission)/ G (crosslinking)	
	No air	Air
None (1 pphr Phenyl-2-naphthylamine)	1.4	45
N-Phenyl-N'-o-tolylethylenediamine	1.6	15
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	0.92	4.3
6-Phenyl-2,4-trimethyl-1,2-dihydroquinoline	2.3	22
N,N'-Dioctyl-p-phenylenediamine	1.7	42
2-Naphthylamine	1.8	19
1,4-Naphthoquinone	1.8	12
Phenylhydroquinone	2.0	12
2-Naphthol	1.2	17
N,N'-Diphenyl-p-phenylenediamine (35%) + phenyl-1-naphthylamine (65%)	1.4	14

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Synopsis

The effect of antirads (compounds added to reduce changes of polymer properties during irradiation) on the crosslink yields in black-loaded natural rubber stocks during gamma irradiation has been measured. The crosslink yields were determined by swelling techniques. Antirads decrease the crosslink yields if oxygen is absent. Oxygen alone effectively decreases crosslink yields. In the presence of oxygen some antirads further decrease crosslink yields, while others increase crosslink yields by their presence. These results may be explained in terms of competitive reactions between R. radicals, the antirad, and oxygen. Evaluation of the ratios of crosslink yields and scission yields indicate that most of the scission is temporary in nature, the chain breaks being reformed rapidly.

Résumé

On a mesuré l'effet des antirads sur le taux de pontage dans des échantillons de caoutchouc naturel chargés de noir soumis à irradiation gamma. Le taux de pontage a été mesuré par les techniques d'écoulement. Les antirads diminuent le taux de pontage si l'oxygène est absent; l'oxygène seul diminue également ce taux. En présence d'oxygène quelques antirads diminuent le taux de pontage, tandis que d'autres l'augmentent. Ces résultats peuvent être expliqués sur la base de réactions compétitives entre radicaux R·, antiradicaux et oxygène. L'évaluation du rapport des taux de pontage aux taux de scission, montre que la plupart de ces derniers sont momentanément en cause lors de la rupture de chaîne, qui est rapidement reformée.

Zusammenfassung

Der Einfluss von Strahlungsschutzmitteln auf die Vernetzungsausbeute bei der γ-Bestrahlung von russgefülltem Naturkautschuk wurde gemessen. Die Vernetzungsausbeute wurde durch Quellungsmessungen bestimmt. In Abwesenheit von Sauerstoff setzen die Schutzstoffe die Vernetzungsausbeute herab. Sauerstoff allein gibt eine wirksame Herabsetzung der Vernetzungsausbeute. In Gegenwart von Sauerstoff liefern einige Schutzstoffe eine weitere Herabsetzung der Vernetzungsausbeute, während andere durch ihre Gegenwart die Vernetzungsausbeute erhöhen. Diese Ergebnisse können durch die Annahme von kompetitiven Reaktionen zwischen R·-Radikalen, Schutzstoff und Sauerstoff erklärt werden. Die Ermittlung des Verhältnisses zwischen Vernetzungsausbeute und Kettenspaltungsausbeute lässt erkennen, dass die letztere zum grössten Teil nur ein temporärer Effekt ist, da die Bruchstellen rasch reformiert werden.