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NUCLEAR RADIATION RESISTANT POLYMERS AND POLYMERIC COMPOUNDS

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FOREWORD

This report was prepared by the B. F. Goodrich Company, Research Center, Brecksville, Ohio, under Project No. 1448 "ANP Airframe and General Support," Task No. 73032, "Radiation Tolerant Elastomers and Polymers," to USAF Contract No. AF 33(616)-6442. This is the sixth annual report, designated Part VI. The work was administered under the direction of the Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio, with Mr. Warren R. Griffin as project engineer.

Said report covers work conducted from 1 April 1959 to 31 March 1960. The text was compiled by Mr. John W. Born from individual summary reports of the technical men who conducted the separate phases of research. Their names appear above the sections in the text with which they were directly concerned.

Under a contract such as this, the technical men directly responsible for the research phases benefit in great measure from being members of the larger Research Center team. They draw on the varied training and in some cases greater experience of their associates. Since it is not feasible to name all such personnel here, general appreciation is expressed. In particular, the authors wish to acknowledge the important contributions of Dr. W. L. Semon and Dr. E. B. Newton as technical advisors under the research program.

Several analytical services research groups have been of assistance: namely, the Infrared Analytical Section, the Light Scattering Analytical Section, the Chemical Analytical Section, the Rubber Compounding Section, the Physical Testing Section, and the Engineering Design Section. The Materials Testing Reactor Gamma Facility of the National Reactor Testing Station has provided valuable irradiation services.

Finally, recognition is respectfully given to the personnel of the Elastomers Section of the Materials Central who monitor and assist in the fulfillment of this contract.

ABSTRACT

This research includes the following: fundamental studies of radiation energy transfer and of the mechanisms of radiation damage in high polymers; the selection, design, and synthesis of special new monomers to produce new high polymers with outstanding inherent radiation resistance and heat stability; polymerization of said monomers, identification of the resulting polymers, and evaluation of their radiation and heat stabilities; applied studies of the effect of gamma irradiation in air at room temperature on the compression set properties of various rubber compounds, with and without potential antirads present; and static and semi-dynamic radiation testing of "O" rings with attempts to protect the military-approved rubber compounds against radiation damage with antirads.

The work which is reported includes fundamental, basic, and applied research. The results are stated briefly in the summary which follows.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

J. M. KELBLE, Acting Chief
Elastomers and Coatings Branch
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Materials Central

SUMMARY

Elastomers and rubber products have critical applications in nuclear-propelled vehicles. The goal of this entire work is to minimize radiation damage and so extend the service life of rubber end-items. Five lines of attack are being pursued to reach that goal.

Studies of fundamental mechanisms of radiation damage and its inhibition are in progress to guide the design of organic high polymers with superior radiation stability as well as improved antirads. Radiation energy transfer via cis-trans isomerization of polybutadiene proceeds by collisional or direct excitation of the π electrons of the double bond in the solid state. Although the latter excitation occurs in the solution state, it is less important than excitation resulting from collisions of the second kind with excited solvent molecules. Polybutadiene approaches a radiostationary cis/trans ratio of 20/80 in the unsensitized case in contrast to a thermodynamic equilibrium ratio of 8/92 in the sensitized case. The unsensitized isomerization takes place via an excited state of the polymer double bond, whereas the sensitized reaction involves the formation of a transitory free radical adduct. It is concluded that radiation-induced unsensitized isomerization of polybutadiene does not involve free radicals but results instead from energy transfer processes exclusively. Inhibition of isomerization by additives thus appears to involve quenching of excited states.

The design of special monomers to produce radiation-resistant polymers involved study of the influence of the number of aromatic substituents and of their distance from the main chain on polymer radiation stability. The preparation of the first year's monomers is three-fourths completed. Purity data and full instructions for synthesis are given for each of the monomers, which are designed to produce homologous and analogous series of polymer structures.

Two of the latter polymers have been synthesized and evaluated for radiation stability: namely, poly (phenyl acrylate) and poly (phenyl methacrylate). The former underwent predominant crosslinking, having a G (x) = 0.054 and a β/α = 0.48 compared to 0.37 and 0.20, respectively, for poly (ethyl acrylate). The poly (phenyl methacrylate) underwent predominant chain scission, having a G (s) = 0.48 $\pm$ 0.11 compared to approximately 1.67 for poly (methyl methacrylate) (52). Polymerization of the eight remaining monomers and evaluation of their polymers is expected to provide the experimental basis for deriving correlations between polymer molecular structure and radiation stability. One plastic polymer, poly (N-vinyl carbazole) has proved twice as resistant as polystyrene to radiation-induced crosslinking. Copolymerization of N-vinyl carbazole with acrylates has produced elastomers with promising radiation stabilities. In addition, a 90/10 ethyl acrylate-maleic anhydride copolymer series with various aromatic amine substituents indicated that radiation stability increases with increasing resonance energy of the substituents.

Measurements of compression set during irradiation have shown both that increasing the state of cure improves resistance to radiation-induced set and that antirads significantly decrease such set in certain rubber compounds. Natural rubber compounds showed no protection; Hycar 1001 and Hycar 1011 were most protected; and Neoprene GN, SBR 1500/1501, and Hypalon 20 stocks were intermediate in their

response to the potential antirads. Initial studies indicate that the type of curative may influence radiation-induced set. A mathematical expression is being developed to relate radiation-induced compression set to radiation dose.

Applied radiation testing of "O" ring seals has begun as the second end-item study. Stress-strain, hardness, compression set, and volume swell measurements of four base compounds and three antirad variations of each are to be made after radiation exposures from 5×10^8 to 1×10^{10} ergs/gram (C). In addition, measurements of compression set during irradiation are scheduled as a further preliminary to eventual dynamic testing. This study will indicate what additional radiation resistance the potential antirads can impart to actual "O" rings.

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SECTION 1

INTRODUCTION

The probability of nuclear propulsion of aircraft, missiles, and eventually spacecraft poses a great many engineering problems. One of the principal considerations is the effect of penetrating nuclear radiation on the physical and mechanical properties of the materials of construction. Early research made it apparent that organic high polymers constitute one of the groups of materials most sensitive to radiation damage. Since each added pound of vehicle weight costs a high premium in propulsion efficiency, radiation shielding must be minimized. Elastomers, the substantial basis of rubber compounds, are organic high polymers. The principal immediate effects of high energy radiation on such materials are ionization, excitation, and transmutation. All of the important radiation-induced processes ensue from these effects. The critical results are changes in molecular structure which alter the physical properties and service performance of the polymers. Thus, the essential goals of this contract are to learn by what mechanisms such changes take place, to define the limits of use for rubber materials subjected to irradiation, and to markedly improve the radiation resistance of elastomers and rubber compounds.

This report is Part VI of a consecutive series dealing with efforts to define, understand, and inhibit radiation-induced deterioration of such materials. Part I comprised a broad survey of radiation effects on over 200 rubber compounds as a function of elastomer, curing system, reinforcing agent, antioxidant, antiozonant, and inert filler (1). It provided the basis for more specific, directed research and resulted in the discovery of inhibitors of radiation damage, which were named antirads. Part II concerned an extensive screening program based on natural rubber to select superior antirads (2). That work also involved dynamic testing of irradiated samples of ASTM rubber compounds plus preliminary efforts to relate molecular structure of the elastomer to radiation-induced changes in physical properties. Part III reported the extension and completion of the research of Part II and laid the experimental foundations for the radiation testing of aircraft rubber end-items such as tires, hose, "O" ring seals, fuel cells, and wire insulation (3). The results emphasized the need for both more basic studies and more end-item testing.

Part IV saw the beginning of fundamental studies of the mode of radiant energy transfer in high polymers and the effect of molecular weight, molecular weight distribution, and variations in copolymer composition on radiation resistance (4). Also included were successful attempts to protect textile cords from radiation damage with antirads. Other investigations included determination of the effectiveness of antirads in elastomers other than natural rubber, environmental studies on

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practical rubber compounds, and radiation testing of actual aircraft tires. The work described in Part V completed the latter four studies from Part IV (5). In addition, a study of radiation-induced compression set was begun which quickly showed that this property, perhaps more than any other, will be a limiting factor in gasket, hose, and seal applications. Fundamental studies of energy transfer and structural effects further emphasized the need for the synthesis of new elastomers having superior inherent radiation resistance.

This technical summary (Part VI) reports an important transition in radiation effects research on elastomers and rubber compounds. During the current contract period the emphasis shifted decisively from the earlier survey, screening, and development of radiation-resistant rubber compounds. The present effort centers mainly on the synthesis and subsequent development of new monomers and polymers, especially elastomers, which will inherently possess outstanding radiation resistance and thermal stability. The concept and development of radiation damage inhibitors ("antirads"), first formulated for rubbers by this organization under U.S. Air Force contract, has provided the bridge from the previous to the present research. Concurrent applied research includes the development of rubber compounds with improved resistance to compression set during nuclear irradiation and of radiation-resistant "O" ring compounds.

This summary therefore covers two main categories, basic and applied research. It involves five lines of investigation: namely, determination of mechanisms of radiation effects and their inhibition; the design, selection, and synthesis of monomers to produce polymers with superior radiation resistance and heat stability; polymerization of the monomers and the chemical characterization and evaluation of radiation and heat stabilities of the polymers; compounding research to develop rubbers with improved resistance to radiation-induced compression set, one of the most critical mechanical service properties; and modification of approved "O" ring rubber compounds and "O" ring testing to improve radiation service performance.

SECTION 2

BASIC RESEARCH

2.1 Mechanisms of Radiation Damage and Protection

(This research was conducted and reported by M. A. Golub)

2.1.1 Introduction

The principal effort this year in connection with mechanisms of radiation damage and protection was devoted to an extensive study of the γ-ray induced cis-trans isomerization of polybutadiene in solution and in the solid state, in the absence of a sensitizer. A manuscript describing this work and substantially the same as this section of the Technical Report has been submitted to the Journal of the American Chemical Society as Part III in our continuing study of radiation chemistry mechanisms.

The analogous isomerization of polybutadiene in benzene, sensitized by bromine atoms or thiyl radicals, was described in two previous papers (6, 7). The existence of an "unsensitized" isomerization in solution, that is, where no particular sensitizer was deliberately added to the polybutadiene prior to γ-irradiation, was briefly mentioned there. It was also pointed out (6) that no evidence had yet been found for an analogous isomerization of the pure polymer in the solid state, although such a reaction might be expected on the basis of possible direct excitation of the polymer molecules, and hence also, the π electrons of the double bonds, through impact with the energetic electrons generated by the γ-rays. Since the unsensitized isomerization of polybutadiene was considered to be a potentially very useful reaction for investigating energy transfer processes in irradiated polymers, it appeared desirable to re-examine the solid state irradiation of polybutadiene and at the same time obtain further data on the unsensitized isomerization in solution.

Recently it has been found that the pure polybutadiene can indeed undergo isomerization on γ-irradiation in the solid state, but the rate is only about an eighth of that in the unsensitized solution case which is itself very slow in comparison with the sensitized isomerizations considered previously. Nevertheless, the unsensitized isomerization, in solution or in the solid state, turns out to be a highly efficient non-chain reaction when viewed from the standpoint of energy utilization. Furthermore, both these unsensitized isomerizations, starting from either the all-cis or all-trans polybutadiene, approach a radiostationary state in which the cis/trans ratio is about 20/80, in contrast to the thermodynamic equilibrium value of about 8/92 obtained in the sensitized isomerizations. This clearly indicated a fundamental difference between the mechanisms of the sensitized and unsensitized isomerizations, quite apart from the role of the sensitizer itself. The present work is therefore likewise concerned with elucidating this difference, which is presumably due to the sensitized isomerization proceeding through a

transitory radical adduct whereas the unsensitized isomerization must involve an excited state of the polymer double bond.

The solution isomerization has to be carried out in an aromatic solvent, such as benzene or toluene, since aliphatic, cyclo-aliphatic or other solvents for polybutadiene nearly always cause the polymer to gel on exposure to γ-rays, thus making it impossible to recover the polymer in a form suitable for infrared analysis. The solid state work, on the other hand, is very conveniently carried out with thin polymer films which can be examined by infrared before and after irradiation, despite any amount of crosslinking which might develop in the solid polymer.

In addition to isomerization, considerable phenylation of the polymer takes place during γ-irradiation in benzene or toluene, but this does not affect the isomerization kinetics although it does complicate the infrared analysis. This complication arises because the attached phenyl groups absorb in the same range of the infrared as do the cis double bonds, so that it is difficult or impossible to calculate the cis/trans ratio in the irradiated polymers, especially at the higher doses where the phenylation is quite pronounced. In order to perform some definitive isomerizations in benzene solution without this complication, a few experiments were also carried out in benzene-d_6, inasmuch as the deuterio-phenyl groups formed from this solvent absorb at much higher wavelengths in the infrared than the ordinary phenyls and so do not interfere with the cis/trans determination.

2.1.2 Experimentation

Two polybutadiene samples were used in this work, one having the monomer units arranged in a nearly all-cis configuration (CB) and the other in a nearly all-trans configuration (TB). The polymers were prepared by stereospecific polymerization techniques to a viscosity average molecular weight of around 400,000 for the cis polymer and around 150,000 for the trans polymer. The structures of the polybutadienes, as determined by infrared analysis, consisted of approximately 95% cis-1,4 and 2% trans-1,4 units in CB, and about 95% trans-1,4 and 2% cis-1,4 units in TB, with the remaining unsaturation in either polymer made up of vinyl groups resulting from 1,2-addition polymerization. Since the 1,2 units were not involved in the isomerization, only the percentage of the total 1,4 polymerization units having the cis (or trans) configuration, or, alternatively, the cis/trans ratio, in the polymer before and after irradiation was required. The cis/trans ratios of CB and TB were thus taken to be 98/2 and 2/98, respectively.

Benzene solutions of CB, with and without antioxidant, and of TB, without antioxidant, were prepared for γ-irradiation to a polymer concentration of about 10 g./l. The cis polymer, containing about 1% by weight of antioxidant when received, was dissolved in benzene, the resulting solution filtered to remove small amounts of insoluble material, diluted to the appropriate concentration and used as such for the antioxidant-containing CB stock solution. To portions of this solution methanol was added, precipitating the polymer, which was then washed with further alcohol, vacuum-dried and redissolved in benzene to give a stock solution of purified CB free of antioxidant. The TB polymer, which also contained antioxidant originally, was dissolved in boiling hexane and then allowed to crystallize out of solution on standing at -20°C. The purified TB was then dissolved

in benzene to the required concentration to make up a stock solution of this polymer. Several additional solutions of CB were prepared at various concentrations in benzene up to about 18 g./l. in order to consider the effect of polymer concentration on the rate of isomerization. Solutions of CB in toluene, m-xylene, ethyl benzene and tetralin were also used in this work. In addition, some experiments were carried out with solutions of CB and TB in benzene-d_6, which avoided the infrared difficulties encountered with ordinary benzene and thus afforded a rather definitive estimate of the cis/trans ratio of the radiostationary state. The solvents were all commercially available C.P. materials; the benzene-d_6 was purchased from Merck and Co., Ltd., Montreal, Canada.

In the solution isomerization case, portions of the stock solutions were placed in ordinary screwcap glass bottles and irradiated in air at room temperature. Aliquots of the irradiated solutions were withdrawn after receiving the desired doses, and the polymers contained therein analyzed for cis/trans ratio by means of infrared absorption spectra run on thin films cast from these solutions. In the solid state case, polymer films were prepared directly from the stock solutions onto rock salt plates, the spectra of the polymers then run, after which the plates were sealed in glass cells in vacuo and irradiated to a series of doses at room temperature. Following each successive irradiation period, the salt plates were removed from the cells, the spectra of the irradiated polymers obtained, and the plates then re-sealed in vacuo for further irradiation until integrated doses in excess of about 3×10^{10} ergs/gram (C) were received.

The irradiations were performed in either of two Co^{60} γ-ray sources having radiation fluxes initially of about 7×10^6 and 1.3×10^7 ergs/gram (C) hr., with the latter intensity later increased to about 3.8×10^7 ergs/gram (C) hr. In this way, it was possible to investigate the effect of dose rate on the kinetics of the unsensitized isomerizations.

The infrared spectra were obtained in the 2-15μ range with a Perkin-Elmer Model 21 spectrophotometer equipped with NaCl optics. The analysis for the cis/trans ratio in the polybutadienes was based on the characteristic absorption bands for the cis and trans double bonds at 13.6 and 10.35μ, respectively. The method for calculating this ratio was described in the previous paper (7). Typical infrared spectra for a high cis and a high trans polybutadiene were presented in the first paper of this series (6) and need not be repeated in detail here. Apart from showing some phenylation and occasionally a small amount of oxidation, the polymer spectra obtained from CB and TB in the solution case were similar to those considered previously, while the spectra obtained for the polymers in the solid state case were practically identical to those of the corresponding unirradiated polymers, except for changes in the cis and trans content. However, the infrared absorption due to phenylation is of definite interest and this is shown in Figure 1 for typical cases involving CB and TB irradiated to various doses in benzene. The strong band at 14.4μ and the weaker one at 13.3μ (not yet evident in A) indicate the presence of monosubstituted phenyl groups attached to the polymer chain and are strictly analogous to the absorption bands found in the polystyrene spectrum at these same wavelengths (8). The origin of the intense peak at 13.6μ (also not evident in A but very clear in B and D) in the spectra of the phenylated polymers is not known, but it might arise from two phenyl groups attached to the same carbon atom alpha to the

double bond. At any rate, it appears not to be due to phenyl groups added across the double bonds. At relatively low doses, the extent of phenylation in CB is slight, and the interference of the phenyl peaks with the cis band located in the 13-15 μ region can be practically ignored; at higher levels of phenylation, on the other hand, it is evidently quite difficult to estimate the absorption due to the cis structure itself. This difficulty is especially pronounced in the case of TB where just a small amount of phenylation overlaps considerably any cis structure which might have been formed during γ-irradiation. Consequently, work in benzene or toluene was generally confined to CB at fairly low doses (less than $3\text{-}4\times10^9$ ergs/gram (C)), while benzene-d_6 solutions of CB and TB were used up to quite high doses. Unfortunately, it has not been possible to estimate the degree of phenylation with any accuracy and so no effort has been made here to consider the kinetics of this particular reaction.

The solution irradiations had to be carried out in air since the polymer usually commenced to gel after a dose of about $1\text{-}2\times10^9$ ergs/gram (C) when irradiated in nitrogen or other inert atmosphere. Furthermore, even in air irradiations, it was necessary to work at polymer concentrations less than about 20 g./l. in order to avoid rapid crosslinking which set in at the higher concentrations. Although the molecular weight of the polymers in dilute solution dropped somewhat on irradiation in air, the infrared spectra of the recovered polymers were generally quite acceptable. In the absence of antioxidant, some oxidation of the polymer occurred, but neither it nor phenylation nor chain scission affected the rate of the solution isomerization. The solid state isomerizations were carried out in vacuo as a convenient way to work in the absence of oxygen which has a strong oxidative effect on thin polymer films, leading to very poor spectra. Since the antioxidant had a marked inhibiting effect on the solid state isomerization, such work was confined to the antioxidant-free stock solutions. A detailed study of the mechanism of this inhibition by various antioxidants and the so-called antirads is contemplated.

2.1.3 Statement of Results

Representative kinetic data for the γ-ray induced unsensitized isomerization of CB and TB in solution and in the solid state are assembled in Table I. The first order rate constants, $\underline{k}$ and $\underline{k}'$, representing the forward and reverse processes, respectively, of the radiochemical isomerization reaction were calculated using

$$\underline{\text{cis}} \underset{\underline{k}'}{\overset{\underline{k}}{\rightleftharpoons}} \underline{\text{trans}} \qquad (1)$$

the expressions

$$\underline{k} = \frac{-2.303\,\underline{K}}{(1+\underline{K})} \times \frac{d \log (1 - \underline{x}/\underline{x}_e)}{d\underline{R}} \qquad (2)$$

$$k' = \frac{-2.303}{(1 + K)} \times \frac{d \log (1 - y/y_e)}{dR} \qquad (3)$$

K is the equilibrium constant for reaction 1, x is the per cent cis changed into trans after a radiation dose R, and x_e is the maximum per cent cis which can be converted in this reaction, starting with CB, while y and y_e are the corresponding amounts of trans which can be changed into cis, starting with TB. Since the cis/trans ratios of CB and TB were initially 98/2 and 2/98, respectively, and approached the radiostationary value of about 20/80, K was assumed to be 4.0, and x_e and y_e were taken to be 78% and 18%, respectively. The logarithmic terms in the above expressions were determined from the slopes of the various kinetic plots obtained, similar to those depicted in Figure 2.

The constant K for the radiostationary equilibrium could not be directly determined very accurately owing to the very long irradiation period required to reach this equilibrium in the solution case and the prohibitively long one required in the solid state case. In either situation, the infrared spectra become indistinct as the irradiation is carried to extremely high doses. Instead, K was estimated as being equal to 4.0 since TB on irradiation in benzene-d_6 appeared to approach asymptotically a cis content of around 20%, while the CB isomerization also tended towards this same cis content, but the ultimate cis/trans ratio was not actually attained from either direction. However, since $K = k/k'$, K could be estimated alternatively from the kinetic data for CB and TB isomerization in benzene-d_6 (see Table I). A value of about 4.5 was thus indicated for K which corresponds to a cis/trans ratio of around 18/82, in close agreement with the value of 20/80 assumed above for the radiostationary state. A similar but somewhat less reliable value could also be obtained for K from the kinetics of the solid state isomerization. The data do not warrant a more precise statement about the equilibrium cis/trans ratio in reaction 1, and the treatment here is no less rigorous for having selected 20/80 as the value for this ratio.

As seen in Figure 2, the data for CB in benzene at relatively low doses are completely compatible with those obtained in benzene-d_6, so that the latter solvent could be regarded, at least from the standpoint of promoting the isomerization of polybutadiene, as fully equivalent to ordinary benzene. No evidence was found for any isotope effect in the rates of isomerization in these two solvents. The hexadeuteriobenzene, of course, has the indispensable feature of enabling the solution isomerization work to be extended to very large doses and still provide polymers with readily analyzable infrared spectra, but the high cost of this solvent limited its use here to only a few definitive experiments needed to determine the cis/trans ratio of the radiostationary state. The abundant and inexpensive ordinary benzene, on the other hand, which was a most effective solvent for the isomerization to occur in, was employed freely for doses up to about 3×10^9 ergs/gram (C). At higher doses, phenylation of CB becomes serious enough that the calculated cis/trans ratios turn out to be greater than they should be, and this is illustrated by the dotted line in Figure 2. As mentioned above, because of the very pronounced phenylation problems encountered with the use of benzene solutions of TB, even at quite low doses, work with this polymer was confined to solutions in benzene-d_6.

The effects of such variables on the isomerization kinetics as nature of the solvent, polymer concentration, presence or absence of antioxidant, and intensity of γ-radiation are all shown in Table I. Of the various aromatic solvents considered in this work, not all of which are indicated in this table, benzene and toluene were found to be the most effective, with nearly equal ability, in promoting the solution isomerizations. m-Xylene and ethylbenzene are seen to be less effective in this respect, having rate constants about two-thirds as large as those of benzene and toluene, while tetralin was even still less effective, with a rate constant only about a third as large as those for benzene and toluene. Not shown in Table I are the results of some experiments with decalin, 2, 4-dimethylnaphthalene, and cumene. The first of these latter solvents, the completely saturated analog of tetralin, caused immediate gelation of the polybutadiene solution so that the polymeric product could not be analyzed by infrared. The second of these solvents, as a fully aromatic counterpart to tetralin and decalin, showed definite evidence for cis-trans isomerization, but unfortunately the resulting polymer spectra could not be analyzed quantitatively owing to extensive interference in the cis region of the spectra. Cumene, on the other hand, produced a very small but finite effect such that the isomerization rate in a 1% solution of polymer in this solvent was about twice that of the pure polymer in the solid state. The common and essential feature of all the solvents promoting the isomerization of CB is, of course, the presence of the benzene ring in the molecule of the given solvent. Furthermore, the first four solvents in Table I along with cumene comprise a series of aromatic compounds for which the solution isomerization rate decreases more or less regularly with increasing amount of carbon atom substituents attached to the ring. This decrease in rates, it should be pointed out, is greater than would be calculated on the basis of just a decrease in the electron fraction of the benzene ring in the solvent molecules. The trend in isomerization rates noted here may have to do, therefore, with the relative extents to which excitational energy originally located in the benzene nucleus of these compounds is dissipated through intramolecular transfer out of the ring into the substituents, thereby affecting the relative amounts of energy available for transfer to the polymer molecules, and hence affecting the isomerization rates in solution.

Since the measured rate constants for any given polymer solution varied considerably from run to run (see the data of Runs 8, 10, 14 and 16), in order to minimize this variance in examining the possible effect of polymer concentration or the presence or absence of antioxidant on the isomerization rate, it was necessary to carry out the runs in pairs. The members of the pairs were treated identically. They were irradiated simultaneously at the same dose rate and to the same integrated dose, and the resulting polymer samples were then worked up at the same time. Runs 12 and 13, 14 and 15, and 26 and 27, carried out in this manner, clearly indicate a very small but real increase in the rates of isomerization with dilution. However, there is no simple relationship expressing this slight concentration dependence of the isomerization rate and, from a mechanistic standpoint, it may be virtually ignored. This minor effect apparently stems from the fact that over the concentration range of about 4-18 g./l., the average polymer molecule in each solution is surrounded by almost, but not quite, the same number of solvent molecules, and that this number diminished very gradually with increase in polymer concentration. Thus. the slight concentration effect may be regarded as reflecting the relative distribution of the polymer molecules in the various solutions rather

than indicating any important kinetic factor which needs to be considered particularly in discussing the mechanism of the solution isomerization.

The small but very definite retardation of the solution isomerization caused by the presence of antioxidant is shown in runs 8 and 9, 10 and 11, 16 and 17, 18 and 19, 20 and 21, and 24 and 25. (The difference in concentration between the members of any of these pairs of runs is too small to have any significant effect on the isomerization rate.) No simple relationship between the concentration of antioxidant in the solution and the magnitude of the retardation was observed in the preliminary experiments, and a study of such a possible relationship was postponed to a later date. For the present, however, it was sufficient to observe that the antioxidant did exert a small retarding effect on the solution isomerization, although it gave a much more pronounced effect in the case of the solid state isomerization, as mentioned earlier.

Since the intensities of the Co^{60} γ-ray sources used in this work naturally decreased with time, it was convenient to report the kinetic data in terms of dose rather than time. Accordingly, the first order rate constants, k and k', presented in Table I, have the units of $[\text{ergs/gram (C)}]^{-1}$ rather than, say, sec.^{-1}. The radioactive decay was taken into account in determining the average radiation intensity during any particular run, so that the term dR in the kinetic expressions above equals $I\,dt$, where I is the constant intensity assumed for the given run, and t is the time of irradiation. The data for the sets of solution runs 8, 10, 14 and 16, and 9, 11 and 17, and 18, 23 and 24, as well as for the solid state runs 1-7, show that k (and presumably also k' by analogy) is independent of the dose rate. It follows from this, noting that $I\,dt$ may be substituted for dR in the expressions 2 and 3, that the time rate of isomerization, $-d(\underline{\text{cis}})/dt$ (or $-d(\underline{\text{trans}})/dt$), in addition to being first order in cis (or trans) content, is directly proportional to the radiation intensity.

As may be seen in Table I, the k (or k') results for any particular polymer system show considerable variability. Although the polymer concentration or the presence or absence of antioxidant does have a real effect on the value of the first order rate constant in the solution isomerization, the effects are small enough that the values are found to lie within the range of variability observed for k (or k') in this work. Consequently, it was considered justifiable to average the values obtained for the rate constant for each of the systems studied in order to facilitate drawing comparisons between these systems. The energy yields corresponding to these averages were calculated as G_o (or G'_o) values, that is, the number of cis (or trans) double bonds initially isomerized per 100 e.v. of energy absorbed by both polymer and solvent, in the solution case, and by the polymer alone, in the solid state case.

2.1.4 Discussion

2.1.4.1 Efficiency of the Solution Isomerization

The G_o values for the isomerization of CB in a 1% solution by weight in benzene and in the solid state were found to be about 1.3 and 16, respectively. Inasmuch as the former value is based on the energy absorbed by the entire solution, if no

energy transfer occurred between solvent and polymer molecules, the effective energy yield for the isomerization in the particular solution under consideration would have to be around 130 when calculated in terms of the energy absorbed only by the polymer. But the pure polymer gave a yield of only one-eighth this value, so that energy must be transferred from the solvent to the polymer in order for the solution isomerization to have this very high effective yield. Since the fate of much of the ionizational and excitational energy produced on γ-irradiation is to end up in low lying excited states (9), a large part of the energy transfer from solvent to polymer could well proceed from the benzene triplet (3.6 e.v.) (10) to the low lying triplet state of the vinylene unit (3.2 e.v.) (11). On an energy basis, charge transfer as well as transfer between higher excited states could also be involved here since benzene and the olefinic groups in the polymer have similar ionization and excitation potentials. Thus, for example, benzene has an ionization potential of 9.25 e.v. (12) and an excitation potential of about 6.76 e.v. (very strong singlet) (13), while the vinylene group has an ionization potential of about 9.27 e.v. (as in trans-butene-2) (14) and an excitation potential of about 6.5 e.v. (15, 16). In this case, as a result of very rapid internal conversion processes ($\sim 10^{-13}$ sec.) (17) affecting highly excited states whether formed directly or through neutralization of ions, the result may again be a low lying excited state of the olefinic group as the precursor in the isomerization. At any rate, the net energy transfer to the polymer molecules in the benzene solution isomerization is thus seen to be of the order of some seven times the energy acquired by the polymer solute directly on γ-irradiation. This is not an unreasonably high value to find for the extent of energy transfer in view of the fluorescence studies by Kallmann and Furst (18-20) who showed, for example, that the presence of 4.5 g./l. of p-terphenyl or 1 g./l. of anthracene in benzene gave a radiation-induced fluorescence of the solution which was about 28 and 6 times, respectively, as great as in pure benzene. It should be noted in passing that the G_o value for the isomerization of CB in benzene obtained in the present work (ca. 1.3) is higher than that reported earlier (6): namely, 0.92. This new value is considered to be more accurate since it is based on more extensive and refined experiments.

The G'_o values obtained for the isomerization of TB in benzene-d_6 and in the solid state (0.30 and 3.90, respectively) are only about one-fourth the corresponding values for CB isomerization. This arises from the fact that, since $k/k' = 4$, a trans double bond, after excitation to a higher energy level in which free rotation can occur and subsequent return to the ground state with re-establishment of the double bond, has only one-fourth the chance of being converted to the cis configuration as remaining in the trans form.

2.1.4.2 Efficiency of the Solid State Isomerization

In addition to showing considerable energy transfer from solvent to solute in the solution isomerization of CB or TB, this work demonstrates that the solid state isomerization of polybutadiene involves a very highly efficient utilization of the energy introduced into the system on γ-irradiation. Thus, in the case of CB, some 16 double bonds are isomerized initially for every 100 e.v. absorbed in the pure solid polymer, or one double bond for every 6.2 e.v. absorbed anywhere in the system. If it is assumed that the absorption of energy from the γ-radiation is completely random in nature and that the amount absorbed in each portion of the

polymer chain is proportional to the electron density of that portion, it follows that the methylenic and olefinic groups in the polymer $[(-CH_2-CH=CH-CH_2-)_n]$ would each absorb directly approximately half of the total radiant energy. Thus, in the absence of intramolecular energy transfer, the effective energy yield would be one cis double bond isomerized for every 3.1 e.v. of energy directly absorbed by the double bonds. This apparent energy requirement is just the same as the excitation energy of the triplet state of the double bond ($\sim$ 3.2 e.v.) (11). To obtain such a result, however, would require that virtually all the energy absorbed directly by the vinylene units be completely used for the isomerization. This can scarcely be the case in view of the fact that the Compton and secondary electrons generated by the γ-rays do not deposit their energy in quanta of just 3-3.5 e.v., but rather produce an assortment of ionized and excited molecules with energies ranging from about 10-15 e.v. on down. Furthermore, a significant fraction of the total radiant energy is dissipated as heat as a result of internal conversion and collisional deactivation processes. Consequently, in order to achieve the high isomerization yields indicated above, it would appear that in addition to the energy absorbed directly by the double bonds most of the energy acquired by the methylenic groups must also be made available to the double bonds for isomerization purposes. This can presumably occur through nearly instantaneous transfer of ionizational and/or excitational energy from the methylenic groups to the neighboring vinylene groups, inasmuch as the energy levels of these groups are favorably disposed to such transfer processes: both the ionization and excitation potentials of the olefinic groups are lower than the corresponding ones of the methylenic groups. Thus, according to W. C. Price (21), the ultraviolet absorption of ethane commences at about 1350 Å while that of ethylene commences at about 1740 Å. The latter absorption corresponds roughly to the 6.5 e.v. state discussed by Carr and Stücklen (15, 16). On the other hand, the methylenic group has an ionization potential which is certainly not less than 10.2 e.v. (22) whereas the vinylene unit has an ionization potential of about 9.3 e.v. (14).

In determining the fate of all the energy absorbed by CB in the solid state case, apart from the very efficient isomerization, it is only necessary to take into account the relatively minor factors of crosslinking and concomitant hydrogen production. This is because no other important structural changes occur in this polymer on γ-irradiation. In particular, there is no perceptible decrease in either the vinyl or vinylene content in CB up to quite high doses (1.5×10^{10} ergs/gram (C)), although some vinylene disappearance was observed in TB. Vinyl decay in polyethylene is well-known (23), and vinylene decay in cis or trans polybutadiene in the presence of polyethylene has recently been reported (24). Further work on the subject of vinylene disappearance in polybutadiene is in progress here. For the present, this factor will be disregarded in the discussion of energy utilization in CB. Consider, now, the energy requirements for the processes ensuant on absorption of 100 e.v. by the solid polymer. The energy required to form a crosslink is just the energy required to break a C-H bond (4.2 e.v.) since the subsequent steps leading to the formation of a crosslink and a molecule of hydrogen are exothermic and so no additional energy is needed (24). For a G-value of crosslinking G(X) of about 3.6 (25), approximately 3.6 x 4.2 or 15.1 e.v. is consumed in this reaction. (Actually this G(X) $\sim$ 3.6 is the value obtained for an emulsion polybutadiene which has a low cis/trans ratio ($\sim$ 1/5) and considerable vinyl unsaturation, and therefore it may not be quite the same for CB. However, this value will have to serve for

the present, in the absence of a precise determination of G(X) for CB, but it is probably not very different from the true value for this polymer.) Also, if the isomerization proceeds through the 3.2 e.v. triplet state of the vinylene group, the energy consumed in isomerizing CB in the solid state (G_o = 16.1) would be 16.1 x 3.2 or 51.5 e.v. The isomerization and crosslinking reactions thus account for 66.6 e.v. out of the total 100 e.v. absorbed, the balance of the energy probably ending up as heat. If higher excited states of the vinylenes also take part to some extent in the isomerization, an even larger fraction of the total energy input would then be accounted for.

The energy utilization in CB can be considered also from a somewhat different point of view. For roughly every 30 e.v. deposited in a γ-irradiated system, one ionization and two or three excitations are produced (26). Since most ions are very rapidly neutralized to form highly excited molecules (9), about four excited species can thus be formed for an energy input of about 30 e.v., or an average of one such species for each 7.5 e.v. If the energy deposited throughout the pure solid polymer is available for isomerization, the mean energy required to isomerize a double bond (at least initially, and in the case of CB in particular) would then be of the order of just this same 7.5 e.v. This is so regardless of the energy path taken by the excited state of the double bond in reaching the isomerized configuration, whether the excited double bond isomerizes at the instant it is quenched to the ground state or isomerizes after first being converted to some lower excited state. The rather close agreement between the observed energy requirement of 6.2 e.v. and the rough estimate of 7.5 e.v. indicates that the above argument regarding extensive intramolecular energy transfer is sound. Of course, if the isomerization proceeds also through lower energy states excited directly by slow electrons, the average energy consumed per double bond isomerized would be expected to be less than 7.5 e.v. and possibly as low as about 5 e.v. It is thus evident that the solid state isomerization of CB is a highly efficient reaction when viewed from the standpoint of energy utilization.

2.1.5 Conclusion: Mechanisms of Radiation-Induced Isomerization

The results of the "unsensitized" cis-trans isomerization of polybutadiene have thus been interpreted in terms of an energy transfer mechanism. This involves, in the solid state case, the direct as well as indirect excitation of the π electrons of the double bonds through collisions between polymer molecules and the energetic electrons generated by the γ-rays. Energy acquired by the methylenic groups is, for the most part, transferred intramolecularly into the double bonds. In the solution case, such processes also occur but they are much less important there than collisions of the second kind between the polymer double bonds and excited solvent molecules. The essential feature of the energy transfer mechanism is that the double bond is excited to a higher energy level in which the electrons are no longer involved in bond formation (the so-called antibonding state) so that free rotation is then possible about the remaining single σ bond connecting the carbon atoms of the original double bond. On return of the antibonding state to the ground state with release of its excitational energy, the double bond is re-established, but with the trans form predominating, although not to quite the same extent as in the sensitized case (6, 7). Thus, the unsensitized isomerization in solution and in the solid state proceeds towards a radiostationary state in which the cis/trans ratio in

polybutadiene is 20/80, in contrast to the thermodynamic equilibrium ratio of 8/92 obtained with bromine atom and thiyl radical sensitization.

The mechanisms for the two types of isomerization are, therefore, fundamentally different in that the sensitized reaction involves the formation of a transitory radical adduct whereas the unsensitized isomerization takes place via an excited state of the polymer double bond. This difference in mechanism is probably responsible for the ultimate cis/trans ratio being lower in the sensitized case than in the unsensitized one. In the former case thermodynamics must determine the value of this ratio, but in the latter case the relative populations of the cis and trans forms in the higher energy levels determine the final value of the cis/trans ratio (27). Thus, while the more stable form predominates in the thermodynamic equilibrium, the less stable form is often favored in a system exposed to strong illumination (28). The classical example of a pronounced difference between the values of the cis/trans ratio for thermodynamic and photostationary equilibria is the maleic acid-fumaric acid interconversion. On ultraviolet irradiation (29) this system reaches a steady state having a cis/trans ratio of about 3/1, whereas on heating (30) the maleic acid (cis) is nearly all converted to fumaric acid (trans), the ratio being less than 1/10. On the other hand, with dibromoethylene (31) the cis/trans ratios for the thermal and photochemical equilibria are nearly the same (60/40 and 57/43, respectively, at 150°C.), with the trans form being at a somewhat higher concentration in the photo-excited case. Since the thermodynamic ratio for dibromoethylene isomerization at room temperature (catalyzed by hydrogen bromide) is about 63/37, the trans structure is clearly the less stable form of this compound. The situation with polybutadiene is thus more comparable to that of dibromoethylene than to that of the maleic acid-fumaric acid isomerization insofar as the spread in values of the cis/trans ratio for the thermodynamic and photochemical (or radiation chemical) equilibria are concerned. While no a priori prediction can be made about the exact cis/trans ratio which will obtain in a given radiation system, it is to be expected that the concentration of the less stable isomeric form will be higher in the radiation case than in the thermal (or catalyzed) one, and this is what has been found for polybutadiene. In view of the fact that Kailan (32) obtained essentially the same ratio in the isomerization of maleic or fumaric acid whether the system was exposed to the penetrating rays from radium or to mercury light, it would be interesting to find out if ultraviolet irradiation of polybutadiene (in the absence of a sensitizer) would give a ratio similar to that obtained here with γ-rays. Unfortunately, however, the photochemical analog of the radiation-induced unsensitized isomerization of polybutadiene has not been accomplished, so that this notion could not be tested.

The dependence of the rate of the unsensitized isomerization on the first power of the radiation intensity, as well as the reaction being first order in isomerizing species, is accounted for by the energy transfer mechanism postulated for this reaction. The rate-determining step is a composite of the first and/or the second and third processes

$$Vl + C_6H_6^* \longrightarrow Vl^* + C_6H_6 \qquad (4)$$

$$Vl + e \longrightarrow Vl^+ + e' \qquad (5)$$

$$Vl + Ml^{\ddagger} \longrightarrow Vl^{\ddagger} + Ml \qquad (6)$$

where Vl*, Vl^{+} and $Vl^{\ddagger}$ represent excited or ionized forms of the vinylene group (Vl) originally cis or trans, which may be in the same or in different excited states, e' is an electron with energy less than that of the electron e by an amount corresponding to the ionization or excitation energy imparted to the vinylene group. $Ml^{\ddagger}$ represents excited or ionized methylenic groups which transfer their energy to the vinylenes. Whether the vinylene group is ionized, then neutralized to form a highly excited state, or excited directly to some upper energy level, the π electrons of the double bond are uncoupled and the barrier to interconversion overcome. Regardless of the particular energy route followed by the energetic double bonds in undergoing isomerization, the kinetics of the reaction will be determined by an expression of the form

$$-d(cis)/dt = k_4 (cis)(C_6H_6^*) + k_5 (cis)(e) + k_6(cis)(Ml^{\ddagger}) - (\text{corresponding terms in } trans)$$

in the case of CB, for example. Since the populations of C_6H_6*, energetic electrons and $Ml^{\ddagger}$ are each proportional to the rate of energy input, this equation reduces to the simpler form

$$-d(cis)/dt = k(cis)I - k'(trans)I \qquad (7)$$

An alternative form of equation 7, viz.,

$$-d(cis)/dR = k(cis) - k'(trans)$$

and an analogous one for the decrease in trans were used to derive the kinetic expressions 2 and 3, representing a reversible reaction which is first order in isomerizing species and dependent on the first power of the intensity.

The possible participation of "sub-excitation" electrons in the unsensitized isomerization needs to be considered. Reaction 5, although intended to represent mainly the contribution of highly energetic electrons, can also serve for the sub-excitation electrons. Platzman (33) has estimated that the latter are responsible for about 20% of the total energy absorbed on irradiation. Since the energy required to excite the vinylene group to its lowest triplet state is about 3.2 e.v., if all the sub-excitation electrons were somehow employed in the isomerization and these were the sole means for promoting this reaction, the maximum G value in the solid state case would be about 6, whereas the value obtained for CB is 16.1. Thus, sub-excitation electrons cannot play an important role in the solid state isomerization. On the other hand, such electrons may be quite important in the solution isomerization case. Since the lowest excitation potential of benzene is 3.6 e.v., there will be many electrons with energy ϵ in the range $3.2 < \epsilon < 3.6$ and thus capable of exciting the vinylene groups in the polymer. If only one out of every five sub-excitation electrons produced in the benzene solution of CB manages to reach a vinylene group and still have energy in the indicated range, the observed yield of 1.3 in the solution isomerization could be entirely accounted for. It appears, therefore, that sub-excitation electrons may well play an important role in the

solution isomerization case, if not a major one.

It might be thought that part of the observed cis-trans isomerization in CB could have resulted from a double bond migration such as

$$-CH_2-CH=CH-CH_2- \rightsquigarrow -\dot{C}H-CH=CH-CH_2- \rightleftharpoons -CH=CH-\dot{C}H-CH_2-$$

$$-CH=CH-\dot{C}H-CH_2- + H \longrightarrow -CH=CH-CH_2-CH_2-$$

Any double bonds formed in this way would be assumed to be predominantly in the trans configuration and so give rise to an apparent isomerization in contradistinction to a genuine cis-trans isomerization of a particular double bond. Infrared analysis could not, of course, differentiate between these two processes in the case of CB. However, some very preliminary work with a high cis polybutadiene-2, 3-d_2 (DCB) showed quite definitely that migration does not occur to any significant extent. On γ-irradiation of this polymer $[(-CH_2-CD=CD-CH_2-)_n]$ in the solid state, only a trace of trans -CD=CH- units were formed, ($G<0.8$) which could arise from double bond migration, whereas there was considerable formation of trans -CD=CD- units through isomerization of the corresponding cis -CD=CD- units originally present in this polymer. Moreover, the rate of isomerization in DCB was roughly of the same order of magnitude as in ordinary CB. The nearly complete absence of migration fits in well with the views on intramolecular energy transfer advanced above, and indicates that such transfer for the most part occurs before the energy is consumed in breaking C-H bonds. As a result, very few free radical sites are formed alpha to the double bonds, and what crosslinking does occur in the solid CB polymer probably takes place mainly through very fast ion-molecule (and perhaps also Stern-Volmer) processes

$$\begin{matrix} -CH_2-CH=CH-CH_2- \\ -CH_2-CH=CH-CH_2- \end{matrix} \longrightarrow \begin{matrix} -CH-CH=CH-CH_2- \\ | \\ -CH-CH=CH-CH_2- \end{matrix} + H_2^+ \qquad (8)$$

rather than through free radical combination processes

$$\begin{matrix} -\dot{C}H-CH=CH-CH_2- \\ -\dot{C}H-CH=CH-CH_2- \end{matrix} \longrightarrow \begin{matrix} -CH-CH=CH-CH_2- \\ | \\ -CH-CH=CH-CH_2- \end{matrix} \qquad (9)$$

which can be expected to be infrequent, Weiss (34) has recently stressed the importance of a reaction such as (8) while tending to reject a reaction such as (9).

Apart from the observation that free radicals probably do not play an important role in the radiation chemistry of polybutadiene, it is worth pointing out that no free radical has ever been found to promote the isomerization of this polymer other than the bromine or thiyl radical considered previously (6, 7), and these, of course, were not present in the systems examined here. Thus, free radicals are not involved in the unsensitized isomerization of polybutadiene, which is instead an interesting example of a radiation-induced reaction involving energy transfer processes exclusively.

The function of the antioxidant in decreasing somewhat the rate of isomerization in solution and markedly inhibiting the reaction in the solid state can best be accounted for in terms of quenching of excited states in the manner discussed over thirty years ago by Privault (35) and Perrin (36).

To conclude, reference should be made to the very recent work of Williams and Dole (18) who found that in the γ -irradiation of polyethylene-polybutadiene blends the polybutadiene component underwent cis-trans isomerization. Although the G-value for this isomerization was not determined by these workers, a rough calculation by the present author suggests a value of around 3 cis double bonds isomerized per 100 e.v. absorbed by the polymer blend. Since the blend contained 5% CB, the yield based on the energy absorbed only by the latter polymer is about 60, or some 3-1/2 times the yield of the pure CB polymer (16.1). It follows, therefore, that some 2-3 times as much energy was transfered intermolecularly from the polyethylene to the polybutadiene in the blend as was absorbed directly by the latter polymer. This transfer of energy which apparently "sensitizes" the CB isomerization was also responsible for "protecting" polyethylene to some extent against vinyl decay and evolution of hydrogen. Further research on the energy yields in the isomerization of CB in various blends with polyethylene would be of considerable theoretical interest.

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2.2 Selection and Synthesis of Monomers for Polymerization

(This research was conducted and reported by W. L. Beears, R. J. Fawcett, and J. D. Wenrick)

2.2.1 Introduction

It is well known that aromaticity in a polymer imparts radiation resistance. Although a very limited investigation (37) correlating polymer structure with radiation-induced changes is available in the literature, no comprehensive study has been made relating the nature and position of the aromatic substituents on the polymer chains to the resistance of these polymers to radiation damage. Therefore, a monomer synthesis program was designed to show how the aromatic group's position on and distance from the polymer main chain affect the degree of radiation protection.

Acrylate monomers were selected for study in the present program because (1) they produce fairly heat-resistant polymers, (2) they can generally be polymerized by using familiar polymerization techniques, and (3) success in the synthesis of these monomers was reasonably certain. It is reasoned that the criteria regarding radiation-resistant structures which result from such a study will be generally applicable to other polymer systems. Therefore, four groups of twelve acrylate

monomers in all were selected for synthesis (of which two were purchased), as shown on page 18.

The radiation-induced polymerization of 2-naphthyl dodecane (38) indicated that the protective effect of an aromatic ring diminishes gradually over a distance approximating twelve carbon atoms along the polymer "backbone" in either direction from the site of attachment. In order to determine the magnitude and extent along the polymer chain of such protection in elastomeric high polymers, the distance from benzene ring to site of possible attack in our series of monomers was restricted variously to one, three, five, and seven atoms. The series was also designed to include monomers with different combinations of two aromatic substituents. In the event that the separation lengths of three atoms or less all indicate the same degree of protection of reactive sites, a logical extension of this series would involve increasing the distance of separation in certain of the more promising monomers.

The proposed series of monomers permits the study of the influence of numerous variations in structure of the aryl-substituted monomers on the radiation stability of their homopolymers. The experimental results should indicate (1) the influence of the distance of the aromatic group (the number of atoms away) from the nearest reactive site on radiation-induced crosslinking (monomers I A, I B, and I C) and chain scission (monomers III A, III B, and III C), (2) the decrease in rate of chain scission when a methyl group attached to a tertiary main chain carbon atom [such as in poly (ethyl methacrylate)] is replaced by a phenyl group [such as in poly (ethyl 2-phenyl acrylate)] , (3) the diminution in the latter protective effect as the distance of the phenyl group from the main chain increases (monomers IV A, II A, IV B, II B, IV C, and II C), (4) in general, the influence of both the position and the intramolecular distance of the aromatic ring with respect to possible crosslinking or chain scission sites upon radiation resistance (monomer II A versus monomers I C and IV A, monomer II B versus monomers IV C and II B, in terms of position and distance, respectively, in each case), and (5) the result of multiple substitution with aromatic rings near a probable reactive site.

The purity of the monomers and their homopolymers is very important in a study such as this. Consequently, great care has been taken to purify and identify the monomers.

2.2.2 Experimentation

Initial work was devoted to synthesizing the monomers in Groups I and III in an attempt to get results more quickly in order to correlate molecular structure and radiation resistance. Two intermediates, 4-phenyl butanol-1 and 4-phenyl-1-bromobutane required for synthesis of the proposed series of monomers could not be obtained commercially and had to be prepared in the laboratory. The synthesis of these intermediates and the proposed acrylates are described below.

2.2.2.1 4-Phenyl Butanol-1 ( $(CH_2)_3\ CH_2OH$)

A forty-gram (1.05-mole) quantity of lithium aluminum hydride was suspended in one pound of dry ether in a three-liter three-neck flask which was predried and fitted with a stirrer, thermometer, reflux condenser, dropping funnel, and nitrogen

Group I

(A) $CH_2=CH-COOC_2H_5$

Ethyl acrylate

(B) $CH_2=CH-COO(CH_2)_4$ 

4-Phenylbutyl acrylate

(C) $CH_2=CH-COO$ 

Phenyl acrylate

Group II

(A)  $C(=CH_2)-COOC_2H_5$

Ethyl 2-phenyl acrylate

(B)  $C(=CH_2)-COO(CH_2)_4$ 

4-Phenylbutyl 2-phenyl acrylate

(C)  $C(=CH_2)-COO$ 

Phenyl 2-phenyl acrylate

Group III

(A) $CH_2=C(CH_3)-COOC_2H_5$

Ethyl methacrylate

(B) $CH_2=C(CH_3)-COO(CH_2)_4$ 

4-Phenylbutyl methacrylate

(C) $CH_2=C(CH_3)-COO$ 

Phenyl methacrylate

Group IV

(A)  $(CH_2)_4-C(=CH_2)-COOC_2H_5$

Ethyl 2-(4-phenylbutyl) acrylate

(B)  $(CH_2)_4-C(=CH_2)-COO(CH_2)_4$ 

4-Phenylbutyl 2-(4-phenylbutyl) acrylate

(C)  $(CH_2)_4-C(=CH_2)-COO$ 

Phenyl 2-(4-phenylbutyl) acrylate

inlet tube. The system was maintained under a nitrogen atmosphere prior to and during the reduction. Three hundred and forty grams (1.77 moles) of ethyl 4-phenylbutyrate in two pounds of dry ether were added dropwise to the lithium aluminum hydride in ether suspension while stirring the mixture rapidly. This effected a steady gentle reflux of ether at the pot temperature of 34-35°C. The addition time required about 2.5 hours, and the mixture was stirred for ten minutes longer. Thirty-two grams (0.364 moles) of ethyl acetate were added during twenty minutes, and the resulting mixture was stirred for an additional hour to assure complete destruction of the lithium aluminum hydride. The mixture was poured into 200 grams of ice water, and 1,000 milliliters of ten per cent sulfuric acid solution was added. The layers were separated and the aqueous phase was extracted twice with ether. The organic phases were combined and dried over anhydrous magnesium sulfate. This run was repeated twice. The ether product layers were combined and filtered free of magnesium sulfate. The ether was stripped from the filtrate up to a pot temperature of 98°C at atmospheric pressure. The crude product remaining was distilled through a 1"x20" vacuum-jacketed column packed with 1/4" stainless steel protruded packing and fitted with a total-reflux variable take-off head. Six hundred and five grams of 4-phenylbutanol-1, boiling at 101-103°C/1.8 mm, was obtained as a colorless liquid for a 78 per cent yield. This product had $\eta^{20}/_{D}$ = 1.5198, $d^{23.6}/_{4}$ = 0.9810, and analyzed for 10.71% hydroxyl. Theory for 4-phenylbutanol-1 requires 11.5% hydroxyl. The literature constants for this compound are $\eta^{20}/_{D}$ = 1.5220 and $d^{14}/_{4}$ = 0.988. (39). A repeat run on this reduction gave 98 per cent yields of 4-phenylbutanol-1 of similar purity.

2.2.2.2 1-Bromo-4-Phenyl Butane ( $-(CH_2)_3CH_2Br$)

Three hundred grams (2.0 moles) of 4-phenylbutanol-1 were placed in a 500-milliliter three-neck flask fitted with a stirrer, thermometer, condenser, and sintered glass inlet tube. The alcohol in the flask was heated to 96°C with an oil bath, and the addition of HBr was started. This gave an exothermic reaction, but the temperature was maintained at 100-120°C by regulating the rate of HBr addition. A total of 136 grams of HBr were added to the reaction solution during 1.5 hours. After this addition, the mixture was cooled to room temperature and the layers were separated. The upper organic phase was washed once with 200 milliliters of hot water, once with 100 milliliters of 10 per cent sodium carbonate solution, and four times with 50 milliliter portions of distilled water. The organic layer was dried over $CaCl_2$. The dried product was filtered free of calcium chloride and distilled through a 1"x10" vacuum-jacketed silvered column packed with 1/4" Berl saddles and fitted with a total reflux variable take-off head. A 380-gram quantity of 1-bromo-4-phenyl butane, boiling at 73-74°C/0.3 mm, was obtained in 89.5 per cent yield. This product had $\eta^{25}/_{D}$ = 1.5361 compared to a literature value (40) of $\eta^{20}/_{D}$ = 1.5382. It analyzed 37.4 per cent bromine as against 37.5 per cent theoretical. A repeat run gave an 87.3 per cent yield of product of the same purity.

2.2.2.3 Phenyl Acrylate (CH_2=CH-COO )

2.2.2.3.1 Method A (41)

Fifty-one grams (0.58 moles) redistilled phenol and 215 milliliters distilled water were placed in a 500-milliliter three-neck round-bottom flask fitted with a

stirrer, thermometer, and dropping funnel. While this mixture was stirred, 23.2 grams (0.58 moles) of solid sodium hydroxide were added. The resulting clear solution was cooled to 25°C, and 50 grams (0.54 moles) acrylyl chloride in 50 milliliters of benzene were added dropwise during one hour while the reaction solution was stirred rapidly. The temperature of the reaction solution was maintained at 25°C during this time. At the end of the addition, the stirring was stopped and the upper product-benzene layer was separated. This layer was washed once with 50 milliliters of 1 per cent sodium hydroxide followed by three washes with distilled water. The organic layer was dried over magnesium sulfate. The magnesium sulfate was removed by filtration, and one gram of phenyl β-naphthyl amine was added to the filtrate to inhibit polymerization. The benzene was removed by distillation up to a pot temperature of 60°C at 20 mm pressure, and the residue was distilled through a 1"x12" vacuum-jacketed silvered column fitted with a total reflux variable take-off head. A 32.3-gram (50%) yield of phenyl acrylate, boiling at 39.5°C/0.28 mm, was obtained. This product had $d^{20}/_4$ = 1.0766 and $\eta^{20}/_D$ = 1.5206. The reported literature constants for phenyl acrylate (42) are $d^{20}/_4$ = 1.0762 and $\eta^{20}/_D$ = 1.5210.

2.2.2.3.2 Method B (43)

Forty-nine grams (0.54 moles) of redistilled phenol and 50 grams (0.54 moles) of acrylyl chloride were placed in a 500-milliliter flask fitted with a stirrer, condenser, and thermometer. This solution was stirred and heated at 100°C for six hours to remove HCl. The reaction product was diluted with two volumes of ether and washed once with 50 milliliters of 1 per cent sodium hydroxide solution and three times with 50-milliliter portions of distilled water. The organic layer was separated and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether removed from the filtrate under reduced pressure. The residue, after the addition of one gram of phenyl β-naphthyl amine to inhibit polymerization, was distilled through a 1"x12" vacuum-jacketed silvered column packed with glass helices and fitted with a total reflux variable take-off head. A 19.9-gram (25%) yield of phenyl acrylate boiling at 44.5°C/0.45 mm was obtained. This product had a $d^{20}/_4$ = 1.0756 and $\eta^{20}/_D$ = 1.5205.

2.2.2.4 4-Phenylbutyl Acrylate (CH_2=CH-COO$(CH_2)_4$ )

Ninety grams (0.6 moles) of 4-phenylbutanol-1, 45 grams (0.625 moles) of glacial acrylic acid, 200 milliliters of benzene, 2 grams of p-tertiarybutylcatechol, and 2 grams of concentrated sulfuric acid were charged into a 500-milliliter three-neck flask fitted with a thermometer and a 1"x10" vacuum-jacketed silvered column packed with stainless steel protruded packing. The column was fitted with an azeotrope esterification-type head. Eleven milliliters of water were removed in three hours at 87-90°C pot temperature. The reaction solution was cooled to room temperature and two grams of phenyl β-naphthylamine were added. This solution was washed with 100 milliliters of a solution containing 10 per cent sodium carbonate and 1 per cent sodium hydroxide. This was followed by the addition of 2 grams of phenyl β-naphthylamine to prevent polymerization and then by washing with 100 milliliters of distilled water. The oily benzene-product layer was separated and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration, and the solvent was removed from the filtrate under reduced pressure.

The residue was distilled through a 1"x10" vacuum-jacketed silvered column packed with 1/4" copper protruded packing and fitted with a total reflux variable take-off head. A 73.5% yield of product (based on 4-phenylbutanol-1) boiling at 99°/0.6 mm. was realized. It had $\eta^{20/D}$ = 1.5056 and $d^{20/4}$ = 1.0062; saponification number 273.5 (theory 274). Quantitative analysis gave C 76.60% and H 7.92% for the $C_{13}H_{16}O_2$ as compared with the calculated values of C 76.40% and H 7.89%. Gas chromatography indicates 100 per cent purity, and dodecyl mercaptan titration of the double bond (44) indicates 97.5 per cent purity.

2.2.2.5 Phenyl Methacrylate ($CH_2=C(CH_3)-COO-C_6H_5$)

This monomer was prepared from 47 grams (0.534 moles) of redistilled phenol and 56 grams (0.534 moles) of methacrylyl chloride using Method B described under phenyl acrylate. Forty-one grams (67%) of phenyl methacrylate boiling at 57-8°C/0.8 mm. was obtained as a colorless liquid. It had a $d^{20/4}$= 1.0544 and $\eta^{20/D}$= 1.5157. The literature (43) reports $d^{20/4}$ = 1.056 and $\eta^{20/D}$= 1.5172 for this compound.

2.2.2.6 4-Phenylbutyl Methacrylate ($CH_2=C(CH_3)-COO(CH_2)_4-C_6H_5$)

This monomer was prepared using the same procedure described under 4-phenylbutyl acrylate. From 90 grams (0.6 moles) of 4-phenylbutanol-1, 54 grams (0.625 moles) of glacial methacrylic acid, 200 milliliters of benzene, 2 grams p-t-butyl catechol, and 2 grams of concentrated sulfuric acid, there were obtained 80 grams (61%) of 4-phenylbutyl methacrylate. This product boiled at 114°C/0.9 mm. and had $d^{20/4}$ = 0.9948; $\eta^{20/D}$ = 1.5032; saponification number 254.5 (theory 257). (Calc'd. for $C_{14}H_{18}O_2$: C, 77.01%; H, 8.3%; found: C, 78.21%, H 8.65%). Gas chromatography indicates 99.6 per cent purity and dodecyl mercaptan titration of the double bond, 102 per cent purity.

2.2.2.7 Ethyl 2-Phenyl Acrylate ($C_6H_5-C(=CH_2)-COOC_2H_5$)

2.2.2.7.1 Method A

2.2.2.7.1.1 Ethyl Ethoxalyl Phenyl Acetate ($C_6H_5-CH(COOC_2H_5)-COCOOC_2H_5$)

An 87.6-gram (0.5-mole) quantity of absolute ethanol was placed in a 500-milliliter flask fitted with a condenser, Hershberg stirrer, thermometer, and dropping funnel. Eleven and one-half grams (0.5 moles) of thinly-cut sodium was added to the alcohol while the mixture was stirred. The temperature rose to 80°C, and the reaction of the sodium was soon completed to give a clear solution. The excess ethanol was removed under water vacuum to give a fluffy white powder of

sodium ethoxide. The sodium ethoxide was suspended in 150 milliliters of dry ether, and 75 grams (0.513 moles) of diethyl oxalate were added dropwise while stirring the reaction mixture and maintaining the temperature at 25°C. An 82-gram (0.5-mole) quantity of ethyl phenyl acetate was then added from a dropping funnel during five minutes while maintaining the reaction temperature at 25° and stirring the reaction solution. When the addition was complete, heat was applied slowly. When the temperature reached 32-33°C, a solid product formed very rapidly. The reaction mixture was heated at reflux, 35-36°C, for one hour, and the solid product was removed by filtration. This product was washed twice by suspending it in ether and filtering off the white solid product after each washing. After the second washing, the solid product was air dried. The air-dried solid was dissolved in 200 milliliters of distilled water, and this solution was acidified with 1:1 hydrochloric acid. The upper oily product layer was separated, and the lower water layer was extracted twice with small quantities of ether. These extracts were combined with the product layer, and this solution was dried over magnesium sulfate. The magnesium sulfate was removed by filtration, and the ether was distilled from the filtrate up to a pot temperature of 50°C at 20 mm. pressure. A 202-gram (81%) yield of crude ethyl ethoxalyl phenyl acetate was obtained.

2.2.2.7.1.2 Ethyl 2-Phenyl Acrylate

Into a 500-milliliter three-neck flask fitted with a stirrer and thermometer were placed 50 grams (0.179 moles) of ethyl ethoxalyl phenyl acetate, 75 milliliters of distilled water, and 25 milliliters of 38 per cent formalin. Twenty-two and one-half grams (0.163 moles) of potassium carbonate dissolved in 50 milliliters of distilled water were added while stirring the reaction mixture rapidly. The temperature rose to 40°C and gas evolution was observed. The stirring was continued for 2.5 hours after the addition of the potassium carbonate, and the temperature was allowed to drop to room temperature. The upper product layer was diluted with two volumes of ether and washed twice with 25-milliliter portions of water. The ether product layer was dried over magnesium sulfate. The magnesium sulfate was removed by filtration, and the ether was distilled from the filtrate under reduced pressure. The residue obtained was distilled through a 1"x10" vacuum-jacketed silvered column packed with 1/8" glass helices and fitted with a total reflux variable take-off head. A 17.3-gram (61%) yield of product boiling at 65-66°C/0.3 mm. was obtained. This product analyzed for 86.3 per cent ethyl 2-phenyl acrylate by gas chromatography. It had $d^{16/4} = 1.0480$ versus a reported literature value (45) of $d^{16/4} = 1.0508$. The impurity was identified as ethyl phenyl acetate by comparing its peak to that of an authentic sample of ethyl phenyl acetate in a gas chromatogram.

2.2.2.7.2 Method B

2.2.2.7.2.1 Ethylhydrogenphenyl Malonate (46) ( $COOC_2H_5$ C-COOH H)

A 274.5-gram (1.16-mole) quantity of redistilled commercial diethyl phenylmalonate was placed in a three-liter three-neck flask fitted with a stirrer, thermometer, and dropping funnel. The diethyl phenyl malonate was cooled to 4 to 5°C. Sixty-five and one-half grams (1.16 moles) of potassium hydroxide dissolved in a

mixture of 900 milliliters of distilled water and 900 milliliters of ethyl alcohol were added to the diethyl phenyl malonate, while stirring rapidly, at a rate such that the temperature of the reaction mixture did not exceed 10°C. After the addition of all the potassium hydroxide solution, the temperature of the reaction solution was raised to 25°C. The stirring was continued at this temperature for 1.5 hours. The solution was then cooled to 5-10°C, and 118 grams (1.2 moles) of concentrated hydrochloric acid was added. The temperature was controlled at 10-15°C during this addition. The ethyl alcohol was removed under vacuum, and the lower oily product layer which precipitated was separated. The upper water layer was extracted twice with methylene chloride, and these extracts were combined with the product layer. The solvent was removed from the product methylene chloride solution under reduced pressure (20 mm) up to a pot temperature of 45°C. The solid residue which remained represents a 97.5 per cent yield of crude product. This product was purified by one recrystallization from 200 milliliters of 1:1 methylene chloride-ligroin solution.

2.2.2.7.2.2 Ethyl 2-Phenyl Acrylate

Ninety-seven and one-half grams (0.47 moles) of ethyl hydrogen phenyl malonate were added portionwise to 39.6 grams (0.543 moles) of diethylamine in a one-liter three-neck flask fitted with a stirrer and thermometer at a rate such that the temperature did not rise above 20°C. Cooling was supplied by a wet ice bath. A pasty solid mass resulted. A 21.3-gram (0.71-mole) quantity of 37 per cent formalin was added to this mixture, cooled to 15°C, in five-milliliter portions. After a few minutes the pasty solid dissolved and the clear solution started to evolve a gas. The reaction mixture was stirred at 20-25°C for three hours, and then it was heated at 70°C for forty-five minutes. Two immiscible layers formed. The upper product layer was separated and diluted with an equal volume of hexane. This solution was washed with dilute (1:1) hydrochloric acid until the washings remained acid. Six washings with distilled water were required to remove the excess HCl from the organic layer. The hexane was removed from the washed organic phase under reduced pressure (20 mm) up to a pot temperature of 40°C. A sixty-eight gram (69.5%) yield of crude ethyl 2-phenyl acrylate was obtained. This product was not distilled, but analysis by gas chromatography showed that it contained 75.9 per cent ethyl 2-phenyl acrylate and 22.8 per cent ethyl phenyl acetate.

2.2.2.7.3 Method C

WARNING! BECAUSE OF THE EXTREME TOXICITY OF NICKEL CARBONYL, THIS SYNTHESIS MUST BE CARRIED OUT IN AN EXCEPTIONALLY WELL-VENTILATED HOOD.

2.2.2.7.3.1 Ethyl 2-Phenyl Acrylate

Five hundred grams (4.85 moles) of phenyl acetylene, 1460 milliliters of ethyl alcohol, and 194 milliliters of concentrated hydrochloric acid were placed in a three-liter, three-neck flask fitted with a stirrer, nitrogen inlet, thermometer, condenser, and dropping funnel. The contents of the flask and dropping funnel were flushed with nitrogen, and the dropping funnel was filled with 485 milliliters of ethyl alcohol and 160 milliliters of nickel carbonyl. The contents of the reaction flask were heated to 55°C under a stream of nitrogen, and then 25 milliliters of the nickel

carbonyl-ethyl alcohol solution were added. This caused formation of a transient deep brown color. The remainder of the nickel carbonyl-ethyl alcohol solution was added, after this initial exothermic reaction, at a rate such that the temperature of the reaction solution was maintained at 55°C. The intermittent use of a cold water bath was required. This addition took approximately forty-five minutes. After the addition of the nickel carbonyl-ethyl alcohol solution, the reaction solution was stirred for thirty minutes at a temperature ranging from 50° to 30°C. The condenser was set for downward distillation, and 1150 milliliters of peroxide-free ether were added to the reaction solution in three approximately equal quantities as room in the flask became available. The flask contents were warmed to 98°C until everything volatile under these conditions had distilled. The distillate containing the excess nickel carbonyl was discarded. From this point on, the reaction solution can be handled in the open laboratory.

The reaction solution was poured into a mixture of 1750 milliliters of distilled water and 250 milliliters of concentrated sulfuric acid. This operation was carried out with vigorous stirring while cooling the reaction solution in a wet ice bath. The upper product layer separation was aided by the addition of an equal volume of peroxide-free ether. The ether-product layer was washed twice with saturated sodium bicarbonate solution and three times with distilled water. This layer was separated and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration, and the volatiles were removed from the filtrate under reduced pressure (20 mm) up to a pot temperature of 80°C. After the addition of two grams of phenyl β -naphthylamine to inhibit polymerization, the residue was distilled through a 1"x18" jacketed column packed with 1/4" stainless steel protruded packing and fitted with a total reflux variable take-off head. A 40 per cent yield of ethyl 2-phenyl acrylate boiling at 62-63°C/0.33 mm was obtained as a colorless liquid. It had a $d^{16}_{4} = 1.0508$, $\eta^{20}_{D} = 1.5252$, and a saponification number of 311.6 (theory 318). The literature reports (45) $d^{16}_{4} = 1.0508$ and $\eta^{16}_{D} = 1.5261$. Unsaturation determination by dodecyl mercaptan addition to the double bond indicates 98.7 per cent purity and gas chromatographic analysis, 99.9 per cent purity.

2.2.2.7.3.2 <u>4-Phenylbutyl 2-Phenyl Acrylate</u> (C-COO$(CH_2)_4$)

CH_2

Into a 250-milliliter round bottom flask fitted with a nitrogen ebullator, thermometer, and total reflux variable take-off head were placed 35.2 grams (0.2 moles) ethyl 2-phenyl acrylate, 30 grams (0.2 moles) 4-phenylbutanol-1, and 1.3 grams tetraisopropyl titanate. The reactants were heated under a slow stream of nitrogen to effect removal of the ethyl alcohol formed during the reaction. Ten milliliters of distillate were collected during heating at 112°-239°C for 1.5 hours. The volatiles from this crude reaction product were separated by distillation through a 1"x10" vacuum-jacketed silvered column packed with 1/4" stainless steel protruded packing and fitted with a total-reflux variable take-off head. The residue was distilled with the head attached directly to the pot, since the product was so high boiling it could not be distilled through the 1"x10" column. A 35.5-gram (63.5%) yield of 4-phenylbutyl 2-phenyl acrylate boiling at 148-50°C/0.23 mm was obtained as a colorless liquid. It had a $d^{20}_{4} = 1.0600$, $\eta^{20}_{D} = 1.5565$, and a

saponification number of 196 (theory 200). Dodecyl mercaptan addition to the double bond indicated 97 per cent purity. Gas chromatography indicates only 92 per cent. Further work is underway to track down the cause of these discrepencies in the analytical results.

2.2.2.7.3.3 Ethyl 2-(4-Phenylbutyl) Acrylate ( $(CH_2)_4$-C($=CH_2$)-$COOC_2H_5$)

2.2.2.7.3.3.1 Diethyl 2-(4-Phenylbutyl) Malonate ($(CH_2)_4$-CH($COOC_2H_5$)-$COOC_2H_5$)

Twenty-five hundred milliliters of absolute ethanol were distilled from 100 grams of sodium into a 5000-milliliter three-neck round bottom flask fitted with a reflux condenser, thermometer, stirrer, and dropping funnel. A 97.5-gram (4.23-mole) quantity of finely cut sodium was added to the distilled ethanol which was kept under a slow stream of nitrogen. Seven hundred grams (4.38 moles) of redistilled diethyl malonate were added in a slow stream during one-half an hour. The reaction solution was stirred vigorously and maintained at 79-80°C during the addition. After the addition was complete, the reaction solution was heated at ethanol reflux for 15 minutes. A 492-gram (4.2-mole) quantity of 4-phenylbutylbromide-1 was added dropwise over a 1.5-hour period while stirring the solution vigorously and maintaining the temperature at 80°C. The reaction was held at reflux (80°C) for an additional twenty-four hours. Ethanol was stripped off up to a pot temperature of 102°C, and the remaining residue was poured into 500 milliliters of distilled water in a two-liter separatory funnel. The water layer was separated from the organic layer. The organic layer was washed with 200 milliliters of distilled water and then placed under vacuum to remove solvents and residual water. The oily residue was distilled through a 1"x12" vacuum-jacketed silvered column fitted with a total reflux variable take-off head. Nine hundred and forty-two grams of product boiling at 135°C/0.35 mm, were collected for a 76% yield. This product had an $\eta^{20}/_{D} = 1.4840$.

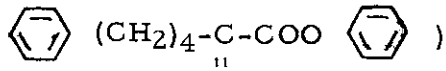
2.2.2.7.3.3.2 Ethylhydrogen 2-(4-Phenylbutyl) Malonate ($(CH_2)_4$-CH($COOC_2H_5$)-$COOH$)

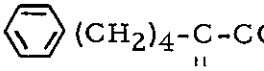
Into a five-liter three-neck round bottom flask were charged 1109 grams (3.79 moles) of diethyl 2-(4-phenylbutyl) malonate and 213 grams (3.79 moles) of potassium hydroxide in 2100 milliliters of ethanol. This solution was allowed to stand at room temperature for five days. Ethanol was removed under reduced pressure, and the residue was dissolved in 1700 milliliters of distilled water in a separatory funnel. This solution was extracted twice with 400 milliliter portions of ether to remove any unreacted diethyl 2-(4-phenylbutyl) malonate. Three hundred and twenty milliliters (3.8 moles) of concentrated hydrochloric acid were added to the aqueous phase, and

the resulting insoluble organic layer was separated. The volatiles were removed from this organic layer under high vacuum to yield 91.5 grams of the half ester for a 91.3 per cent yield.

2.2.2.7.3.3.3 Ethyl 2-(4-Phenylbutyl) Acrylate ($(CH_2)_4$-C(=CH_2)-$COOC_2H_5$)

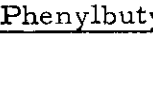
Nine hundred and fifteen grams (3.46 moles) of the ethyl hydrogen 2-(4-phenyl--butyl) malonate from above were charged into a three-liter three-neck round bottom flask fitted with a stirrer, thermometer, and dropping funnel. The contents of the flask were cooled to 7°C, and 253 grams (3.46 moles) of diethylamine were added dropwise with vigorous stirring over a 50-minute period at a temperature ranging from 13 to 20°C. Due to the exothermic nature of the reaction, an ice bath was required to maintain these temperatures. The slightly viscous liquid was stirred for 15 minutes while it was cooled to 10°C. Three hundred and seventy-five grams (3.63 moles) of 37 per cent formalin were added dropwise over a half-hour period while stirring the reaction solution vigorously and maintaining the temperature at 8-15°C. At the end of the addition, the ice bath was removed and the reactants in the flask were stirred vigorously and warmed to room temperature. The contents were heated at 50°C for 1.5 hours with evolution of gas and formation of a two phase organic-inorganic liquid system. The lower aqueous layer was removed, and the remaining organic layer was washed with 500 milliliters of distilled water and then with 300 milliliters of 6 N hydrochloric acid. These were followed by two washings with 500 milliliters of water, one washing with 100 milliliters of 1 per cent sodium hydroxide, and ten washings with 500-milliliter portions of water. The organic layer was separated and dried over magnesium sulfate. The magnesium sulfate was removed by filtration, and the volatiles were removed from the filtrate under high vacuum. Seven hundred and twenty-five grams of a colorless but slightly turbid liquid were obtained. This product was filtered through Celite to give a 724-gram (90%) yield of ethyl 2-(4-phenylbutyl) acrylate. It had a $d_{20/4}$ = 0.9840, $\eta_{20/D}$ = 1.5008, and a saponification number of 240.5 (theoretical 241.5). (Calc'd for $C_{15}H_{20}O_2$: C, 77.54% H, 8.68%; found: C, 77.50%, H, 8.7%.) Gas chromatographic analysis indicated this monomer was 99.4 per cent pure, and dodecyl mercaptan titration of the double bond indicated 99.5% purity.

2.2.2.7.3.4 Phenyl 2-(4-Phenylbutyl) Acrylate ()

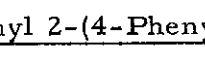
2.2.2.7.3.4.1 2-(4-Phenylbutyl) Acrylic Acid ()

Forty grams (1.0 mole) of sodium hydroxide, dissolved in a mixture of 200 milliliters of distilled water and 100 milliliters of ethanol, and 232 grams (1.0 moles) of ethyl 2-(4-phenybutyl) acrylate were charged into a one-liter three-neck round bottom flask fitted with a stirrer, thermometer, and reflux condenser. The reaction mixture was stirred vigorously and heated to 80°C. The reflux condenser was removed, and the solution was heated to distill off ethanol. When the pot

temperature reached 92°C, foaming occurred and the solution became very viscous. An additional 100 milliliters of water was added and the heating continued until the temperature reached 99°C. The total time of heating was three hours. The solution was cooled to room temperature and 160 milliliters of 6 N hydrochloric acid were added. This gave a two-layer system. The lower aqueous layer was removed and the upper product layer was washed three times with 100-milliliter portions of distilled water. The organic layer was separated and the volatiles removed under reduced pressure to give a 204-gram (100%) yield of the crude acid.

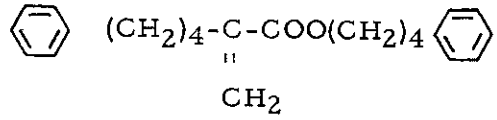
2.2.2.7.3.4.2 2-(4-Phenylbutyl) Acrylyl Chloride ()

Into a 500-milliliter single-neck flask fitted with a reflux condenser were placed 204 grams (1.0 moles) of 2-(4-phenylbutyl) acrylic acid and 218 milliliters (3.0 moles) of thionyl chloride. The reaction solution stood at room temperature for two hours, and during this time gas was evolved. At the end of this time, the solution was heated at 80°C for one hour. The excess thionyl chloride was removed under reduced pressure while heating on a steam bath. The remaining residue was distilled through a 3/4"x12" vacuum-jacketed silvered column packed with 1/4" glass helices and fitted with a total reflux variable take-off head. A 161-gram (67%) yield of 2-(4-phenylbutyl) acrylyl chloride boiling at 132-3°C/3.0 mm was obtained. This product had an $\eta^{20/D} = 1.5278$.

2.2.2.7.3.4.3 Phenyl 2-(4-Phenylbutyl) Acrylate ()

Sixty-seven grams (0.71 moles) of phenol and 28.4 grams (0.71 moles) of sodium hydroxide were charged into a 500-milliliter flask fitted with a stirrer, thermometer and dropping funnel. Two hundred milliliters of water were added, and the reaction mixture was stirred. The resulting clear solution was cooled to 10°C, and 161 grams (0.67 moles) of 2-(4-phenylbutyl) acrylyl chloride dissolved in 150 milliliters of benzene were added dropwise over a twenty-minute period. Very little exothermic reaction was noted, but the reaction solution graudally warmed to 30.5°C during 1.5 hours. At the end of 2.5 hours the reaction mixture was heated to 63°C. The heat was removed at this temperature, and the mixture was stirred vigorously for one hour longer as the temperature decreased. The upper, organic layer was separated and washed three times with 100-milliliter portions of distilled water. These were followed by one wash with 100 milliliters of 1 per cent sodium hydroxide solution and three washings with 100 milliliters of water. The organic layer was separated and the volatiles were removed under high vacuum (1 mm). The forerun was removed through a 3/4"x12" vacuum-jacketed silvered column packed with 1/4" glass helices. The pot temperature reached 235°C and the pot temperature 120°C at 0.4 mm pressure. The column was removed and distillation continued with the distillation head attached directly onto the distillation pot. Forty grams of product boiling at 151-173°C/ 0.2 mm were obtained, and 115 grams of polymer residue remained in the pot. The product had a saponification number of 215 (theory 200). Gas chromatographic analyses indicated 98 per cent purity. When the phenyl group is attached directly to the carboxyl group, as it is in this monomer,

the dodecyl mercaptan method cannot be used to determine unsaturation. Since the dodecyl mercaptan also reacts with the phenyl group to give erroneous results, unsaturation was determined by the morpholine method (47). Said analysis indicated that this monomer was only 85 per cent pure. These analytical methods are being checked further to determine the reasons for the differences in results.

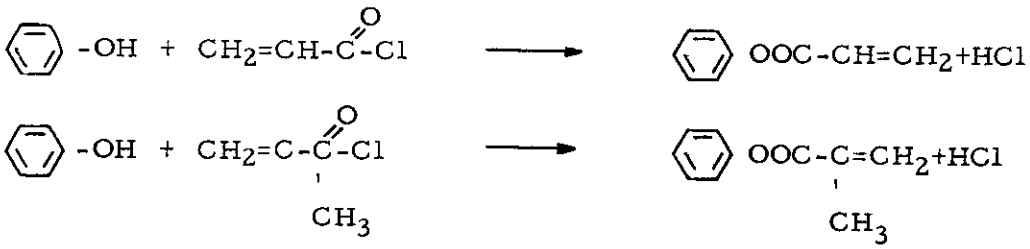
2.2.2.7.3.5 4-Phenylbutyl 2-(4-Phenylbutyl) Acrylate ()

One hundred twenty-four grams (0.533 moles) of ethyl 2-(4-phenylbutyl) acrylate, 80 grams (0.533 moles) of 4-phenylbutanol, and four grams of p-toluene sulfonic acid were charged into a 250-milliliter round-bottom flask fitted with a thermometer, nitrogen ebullator, and take-off head which was connected to a dry ice trap. The reactants were heated to 170°C under a slow stream of nitrogen to drive off ethanol from the interchange reaction. Water vacuum was applied, and heating continued up to 238°C pot temperature to effect completion of the interchange reaction. The forerun from the reaction product was distilled through a 1"x10" vacuum-jacketed silvered column fitted with a total reflux variable take-off head up to a head temperature of 165°C/0.3 mm and a pot temperature of 246°C. At this point the column was removed and the head was attached directly to the pot, since decomposition of the product was observed. Seventy-five grams (42%) of 4-phenyl-butyl 2-(4-phenylbutyl) acrylate, b.p. 181-185°C/0.25 mm, was obtained as a slightly yellow-colored liquid. It had an $\eta^{20/D}$ = 1.5353 and a saponification number of 165.6 (theory 166.8). Dodecyl mercaptan titration of the double bond indicates 97.11% purity. This monomer was not submitted for gas chromatographic analysis because of its high boiling point, which would make it difficult for the product to get through the chromatographic column without decomposition.

2.2.3 Results and Discussion

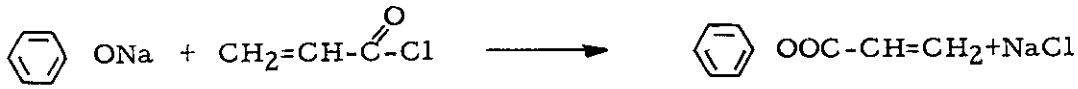
To aid the progress of the monomer synthesis program, monomers of the proposed series which were available commercially were purchased and purified. Ethyl acrylate, ethyl methacrylate, and phenyl acrylate were purchasable, but the phenyl acrylate which was bought proved to be unsatisfactory even after attempts to purify it. It was necessary therefore to synthesize this monomer along with the other nine monomers in the proposed series, which could not be purchased.

Phenyl acrylate and phenyl methacrylate were prepared from phenol and acrylyl chloride or methacrylyl chloride according to the following reactions (43):



Yields of phenyl methacrylate were generally good (67%), but those of phenyl acrylate

were poor (25%), due primarily to loss of monomer by polymerization in the pot. Phenyl acrylate was prepared in 50% yield from sodium phenoxide and acrylyl chloride by the method of Teyssié and Smets (41).

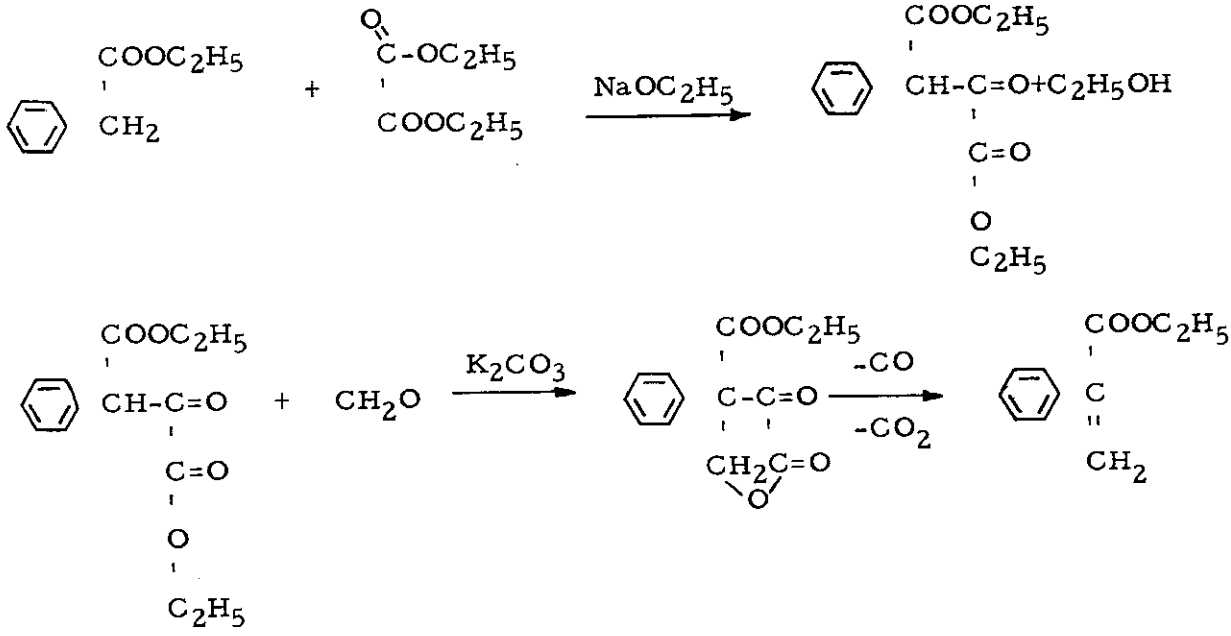


The yield was somewhat low due to polymerization of some of the product during purification, but this method appears to give generally higher yields of acrylates than those employed earlier. The physical constants of these phenyl acrylate and phenyl methacrylate esters agree well with those given in the literature. On this basis, they were considered sufficiently pure for polymerization

4-Phenylbutyl acrylate and methacrylate monomers were obtained in 60-75% yield by the acid-catalyzed esterification of 4-phenyl butanol-1 and acrylic or methacrylic acid. These monomers were 97.5 to 100% pure by analysis.

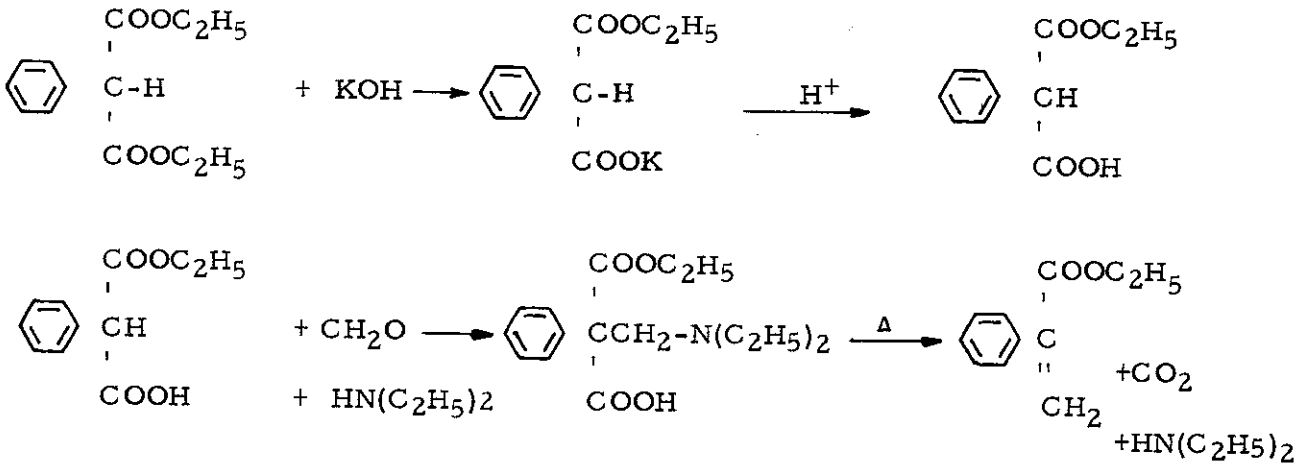
The most difficulty in monomer synthesis in the program to date was encountered with ethyl 2-phenyl acrylate. While this monomer does not polymerize readily, it was hard to obtain pure ethyl 2-phenyl acrylate because of side reactions which produce impurities that are difficult to remove. Three syntheses of ethyl 2-phenyl acrylate were investigated. Two of these gave product containing the same impurity, ethyl phenyl acetate. This impurity differs from ethyl 2-phenyl acrylate by only one carbon atom and because of its similar physical properties cannot be completely separated from the desired product.

The condensation of ethyl phenyl acetate with ethyl oxalate, followed by reaction of the resulting product with formaldehyde to give ethyl 2-phenyl acrylate, appeared attractive (48).



The ethyl phenyl acetate impurity does not result from the first step of the reaction as unreacted starting material, since that is quite completely washed out of the sodium salt of the ethyl ethoxalyl phenyl acetate product with ether before acidification. Under these conditions not nearly the amount of ethyl phenyl acetate present would be found as an impurity in the ethyl 2-phenyl acrylate. Ethyl phenyl acetate is most likely formed in the second step of the synthesis, since the reaction between formaldehyde and ethyl ethoxalyl phenyl acetate is run in the presence of strong aqueous potassium carbonate solution. This basic solution could cause hydrolysis of the ethyl ethoxalyl phenyl acetate to ethyl phenyl acetate as well as effect the desired condensation with formaldehyde. This appears to be what happens, since temperatures higher than 25°C favor formation of larger amounts of ethyl phenyl acetate and lower yields of ethyl 2-phenyl acrylate. At reaction temperatures of 25°C, a crude product containing 75% ethyl 2-phenyl acrylate and 25% ethyl phenyl acetate is obtained. At temperatures below 20 to 25°C, the ethyl ethoxalyl phenyl acetate formaldehyde reaction does not proceed to any appreciable extent. Reducing the potassium carbonate concentration by one-tenth to one-half in order to minimize the ethyl phenyl acetate formation did not effect the desired reaction to any measurable extent. A larger excess (240%) of formaldehyde appeared to favor formation of greater quantities of ethyl phenyl acetate. No explanation for this is evident. No conditions were found for this reaction which favored formation of ethyl 2-phenyl acrylate to the virtual exclusion of ethyl phenyl acetate. The German worker who reported this work identified his product from carbon-hydrogen analysis alone. Since the structure of the impurity and ethyl 2-phenyl acrylate differ by only one carbon atom, their carbon-hydrogen analyses will be very similar. If the author reporting the original work obtained a mixture of 25% ethyl phenyl acetate and 75% ethyl 2-phenyl acrylate similar to our mixture such would not be evident from a carbon-hydrogen analysis. Other routes to ethyl 2-phenyl acrylate were investigated due to the difficulties encountered here.

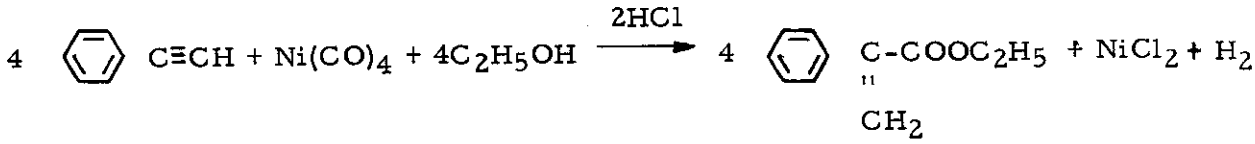
The Mannich reaction reported to give ethyl 2-benzyl acrylate (49) was modified for use involving ethyl hydrogen phenyl malonate, diethylamine, and formaldehyde to give ethyl 2-phenyl acrylate:



A 70% yield of crude ethyl 2-phenyl acrylate was obtained in this reaction, but it contained 29% ethyl phenyl acetate and only 71% ethyl 2-phenyl acrylate. The ethyl phenyl acetate is probably formed through decarboxylation of unreacted ethyl

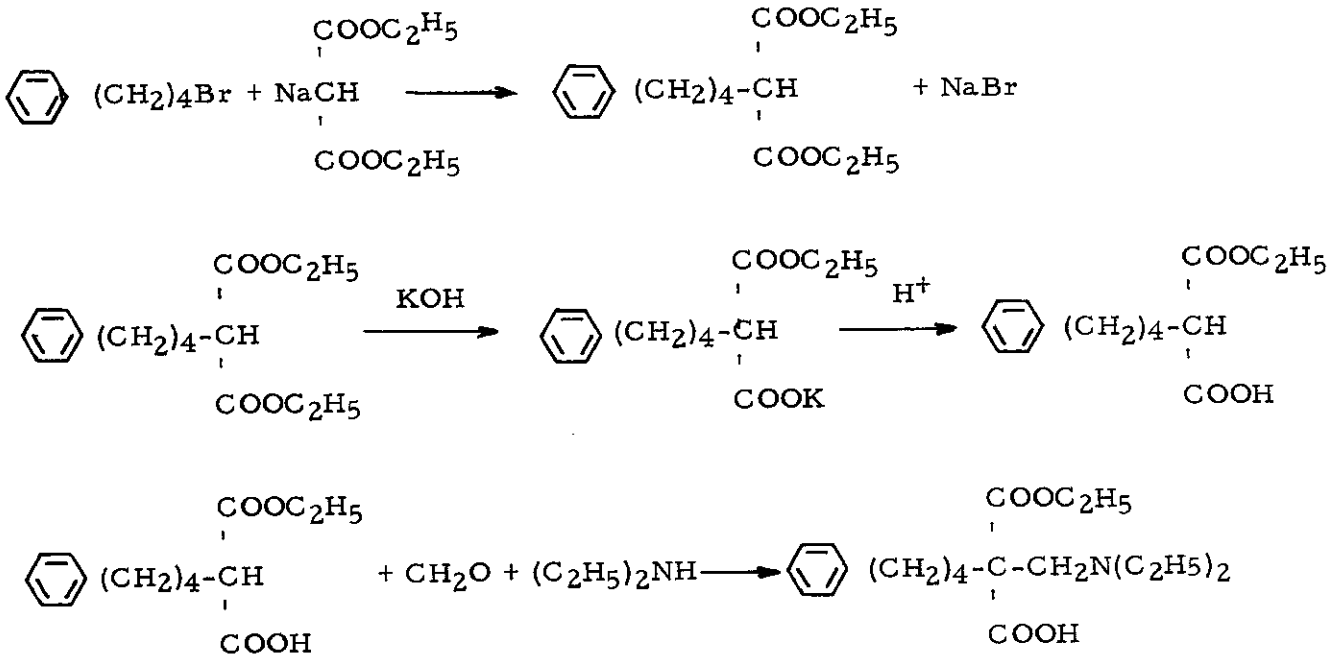
hydrogen phenyl malonate. In view of our previous experience with similar mixtures of these compounds, no attempt was made to separate them here.

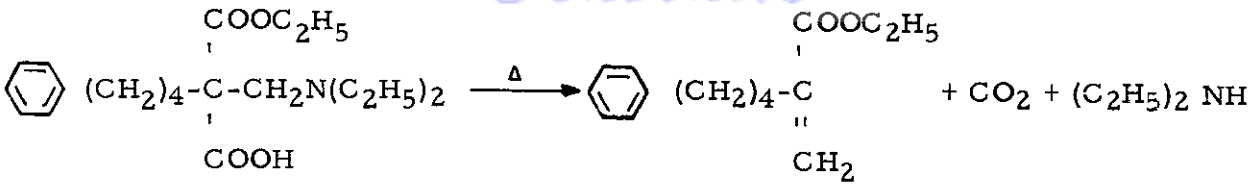
The reaction of nickel carbonyl and phenyl acetylene in ethyl alcohol is reported to give ethyl 2-phenyl acrylate (50).



The product from this reaction contained no ethyl phenyl acetate as would be expected. The resulting ethyl 2-phenyl acrylate analyzed 99.8% pure by gas chromatography. In the initial run, yields were low (28%), but in a subsequent run they were increased to 40 per cent. According to the literature (50), yields up to 47% are about the best which can be expected. Since ethyl 2-phenyl acrylate is used as the starting material for the other two esters of the 2-phenyl acrylic acid series, it was important that a sufficient quantity of pure monomer be available. This synthetic route made that possible.

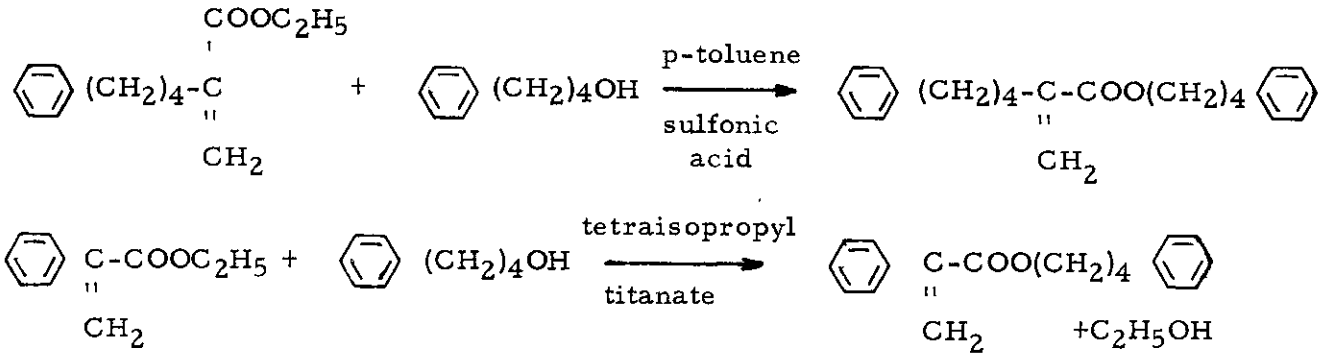
One of the monomers which was expected to be most difficult to synthesize turned out to be one of the easier ones to prepare. Ethyl 2-(4-phenylbutyl) acrylate was obtained in 90% yield and 99.6% purity in the Mannich reaction (49) involving ethyl hydrogen 2-(4-phenylbutyl) malonate, diethylamine, and formaldehyde. However, the overall yield for the three-reaction sequence necessary to make this monomer was 61%:





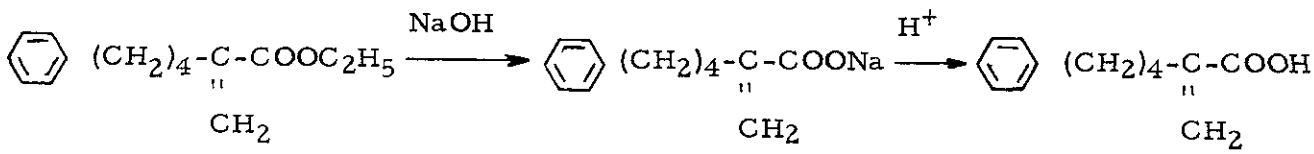
The latter series of reactions is analogous to one of those tried for the synthesis of ethyl 2-phenyl acrylate (49), but no troublesome side reaction products formed through decarboxylation of the substituted ethyl hydrogen malonate such as were encountered previously.

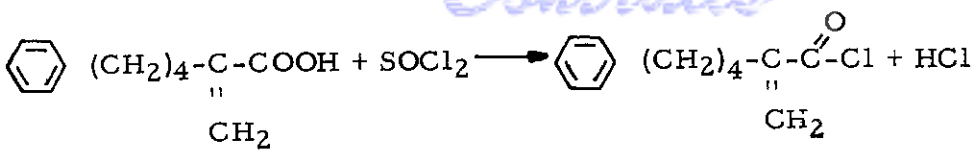
The esters, 4-phenylbutyl 2-phenyl acrylate and 4-phenylbutyl 2-(4-phenylbutyl) acrylate were prepared by interchange of 4-phenyl butanol-1 with the corresponding ethyl esters:

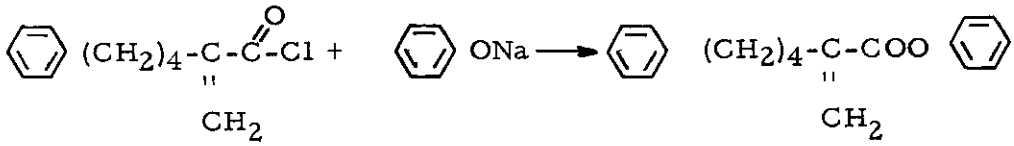


The monomer products from these interchanges were high boiling, 150-180°C/0.2 mm but appeared to distill without decomposition or polymerization. The products were 97-99% pure by chemical analysis, but gas chromatography (run on 4-phenylbutyl 2-phenyl acrylate only) indicated only 92% purity. It is known that at the 300°C column temperature required to get the sample through the chromatographic column, olefin could be split from the acrylate ester. At lower column temperatures (270°C), the amount of impurity was somewhat less, but this is about as low as one can reduce this temperature and still get the sample through the column. These experiments indicate that the impurity shown in the chromatogram may come from decomposition of the acrylate during chromatographic analysis and not from impurity in the original sample. Further chromatographic analyses must be run on this and similar model compounds before any firm conclusions can be drawn about the source of the impurity.

Synthesis of the third monomer of the 2-(4-phenylbutyl) acrylate series could not be effected by interchange, since phenyl esters cannot be prepared in this way. Phenyl 2-(4-phenylbutyl) acrylate was prepared from ethyl 2-(4-phenylbutyl) acrylate by a three-step reaction going through the acid chloride.







The acid chloride prepared above was extremely resistant to water hydrolysis. This might be due to insolubility or inherent chemical stability. The reaction between this acid chloride and sodium phenoxide is sluggish, and unreacted acid chloride is recovered from the reaction mixture. Only a small amount of product could be isolated from this run due to polymerization of the monomer in the pot during distillation. Three different analyses (saponification number, unsaturation, and gas chromatography) were run on this sample, and three different purities were indicated (107%, 85%, and 98%). Since no method of analysis was clearcut, it will be necessary to do further work on these methods before any definite conclusions as to purity of this monomer can be drawn. This monomer as well as the phenyl 2-phenyl acrylate, which still remain to be synthesized, might best be prepared from phenol and the free acid by a recently reported technique employing trifluoroacetic anhydride (51). This procedure would eliminate one complete and rather poor step in the conversion of the acid to the acid chloride in the present series of reactions. These high boiling phenyl esters are difficult to purify because they are liquids and cannot be distilled with suitable fractionation. They are more stable than the corresponding phenylbutyl esters, however, since it is not possible for olefin to split from the ester group. Since polymerization of the phenyl 2-(4-phenyl--butyl) acrylate occurred on heating, a suitable non-volatile inhibitor must be used to prevent this in the future.

The gas chromatographic analysis of the prepared monomers often indicated purities higher than those from chemical analysis. Chemical analysis may be more indicative of the true purity, however. The impurity peak may be masked by the peak of the major component in the gas chromatogram, or the impurity may be higher boiling and may not go through the gas chromatographic apparatus.

2.3 Synthesis and Development of Radiation-Resistant Polymers

(This research was conducted and reported by E. Witt)

2.3.1 Introduction

The study of the correlations between polymer molecular structure and composition and radiation-induced deterioration continued this year. The investigation of the butadiene-styrene series of homopolymers and copolymers in 1958 (5, 25) suggested that for maximum protection against radiation damage the protective agent (or structural group) should be an integral part of the polymer molecule and aromatic in nature. Whether the aromatic constituent should be in side branches of the main

chain, a part of the main chain, or both for maximum protection remains to be determined. In fact, this subject program of polymer synthesis and development proposes to investigate precisely these three approaches over a three to four year period. For this purpose special, tailor-made monomers are being polymerized to give high polymers representing each of the three categories. The ultimate goal is to combine the evaluation data of structural variations versus radiation stability and so specify polymer molecular structures which will produce elastomers having outstanding inherent radiation resistance.

The first of the above three categories, described from the standpoint of monomer synthesis on pages 16-33, is well underway. At this three-quarter point in the first year the radiation evaluation results are already quite encouraging and support our basic reasoning. The evaluations which have been completed thus far have involved the styrene-containing polymers. In order to expand the knowledge of the influence of side-branch aromaticity on radiation-induced changes within a polymer, several polymers which vary in the nature and amount of such aromatic branches have been made and studied. This investigation includes polymers of N-vinyl carbazole, the present group of 10 aromatic acrylates, and a series of ethyl acrylate-maleic anhydride copolymers in which the anhydride unit was reacted with several different aromatic amines.

2.3.2 Experimentation

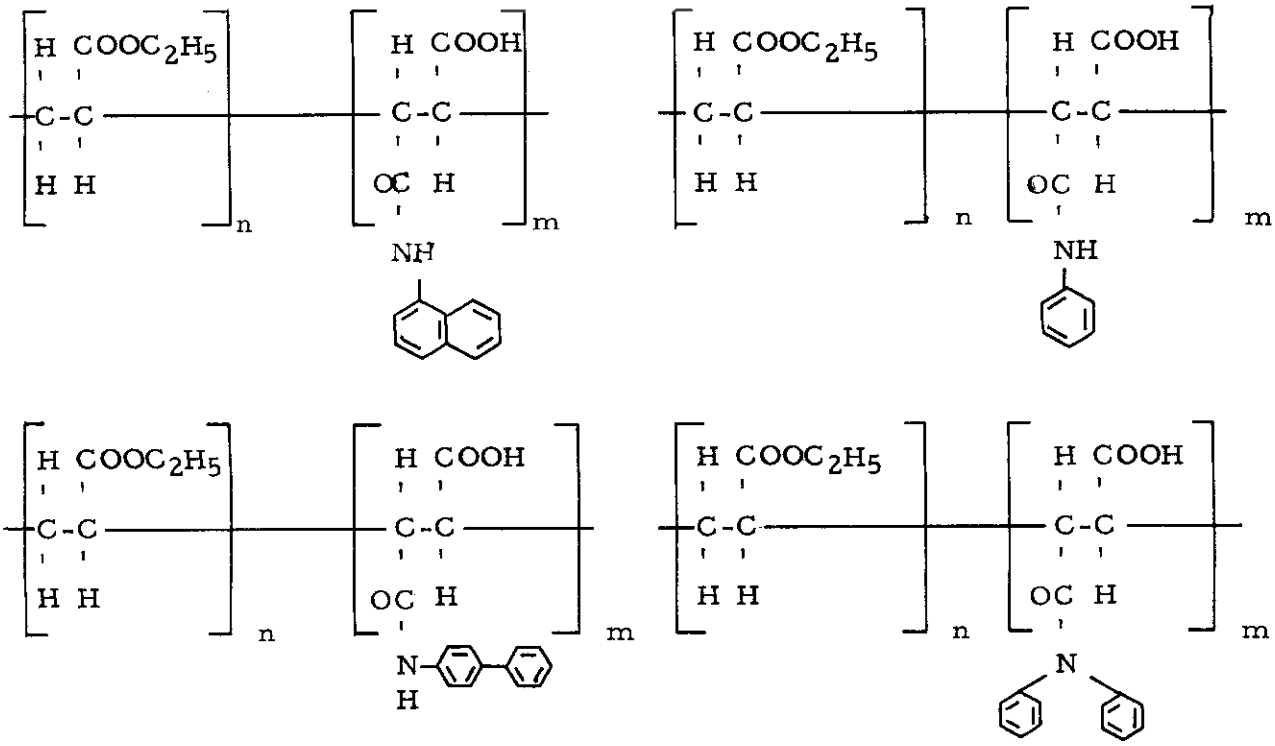
The polymers in this study were prepared by a free radical mechanism in solution. The basic polymerization recipe is as follows:

Ingredient	Parts by Weight
Monomer	100
Solvent	100
Sulfole B-8	0.2
Azoisobutyronitrile	2.0

Polymerization Temperature: 50°C.

All polymerizations were allowed to proceed to 100% conversion of monomer to polymer. The polymer was then precipitated out of solution by the addition of hexane, redissolved in solvent, and reprecipitated. This process of purification was repeated several times. The samples were then dried in a 50°C. vacuum oven.

In order to examine the effects of several variations in branch aromaticity, a series of copolymers of ethyl acrylate and maleic anhydride were prepared based on a 90/10 ratio of ethyl acrylate to maleic anhydride by weight. Subsequent to polymerization the anhydride unit was reacted with an equivalent ("equimolar") amount of each of various aromatic amines: namely, α-naphthylamine, aniline, 4-aminodiphenyl, and diphenylamine. The resulting substituted copolymers possessed branch aromaticity via amide linkages, represented as follows, respectively:



In the preparation of poly (2-ethylhexyl acrylate) the solvent polymerization yielded a polymer which was unworkable because of its low second order transition temperature. Therefore, an emulsion polymerization system was employed, producing a polymer of higher molecular weight which could be handled satisfactorily. Its basic recipe was:

Ingredient	Parts by Weight
Dupanol ME	3.0
2-Ethylhexyl Acrylate	100
Water	200
Potassium Pyrosulfite	0.2
Potassium Persulfate	0.4

Polymerization Temperature: 30°C.

Molecular weights of the polymers were determined by the analytical section, using the turbidity method of light scattering measurement. The measurements were made prior to exposing the polymers to a series of doses of ionizing radiation. The polymers were irradiated in evacuated, melt-sealed glass vials to eliminate oxidation of the samples. The extent of change in polymer structure (crosslinking and chain scission, principally) induced by Cobalt 60 gamma irradiation was determined by measuring sol and gel contents in the manner previously reported (5). The results of such evaluations of radiation stability are reported as G (x), the net number of crosslinks induced by the absorption of 100 electron volts of ionizing

radiation energy, and as β/α , the ratio of the number of scissions of the main chain which occur for each crosslink formed (52). It must be remembered that polymers may undergo chain scission as well as crosslinking reactions. G (x) is therefore the actual number of effective crosslinks formed minus the number of chain scissions produced by 100 electron volts. Conversely, for a polymer which predominantly undergoes main-chain scission the results are reported as G (s), the net number of main-chain scissions induced by the absorption of 100 electron volts of ionizing radiation.

2.3.3 Results and Discussion

The study of the degree of protection which aromatic substituents afford against radiation-induced deterioration is summarized in Table 2 for poly (ethyl acrylate-co-maleic anhydride), abbreviated EA/MA, via its series of reaction products with various aromatic amines. It has been shown previously (4, 5) that G (x) is proportional to the radiation dose R_G required to produce gelation and to the initial weight average molecular weight of the polymer, $\overline{M}_w$. The $\overline{M}_w$ value for the polymer with the α -naphthylamine substituent is seen to be lower by a factor of almost 10 than for the other three substituted polymers in this series. However, the close similarity in the intrinsic viscosities $[\eta]$ of the above series strongly suggests that the former $\overline{M}_w$ and the G (x) derived from it are in error. Using the average of the $\overline{M}_w$ values for the other three members of the series, namely samples B through D in Table 2, resulted in the second G (x) value for this polymer. Preliminary results from a rerun of this series indicate that the above assumption regarding the $\overline{M}_w$ of the α -naphthylamine-substituted polymer is correct and that the second value of G (x) can be taken as a close approximation of the true value.

Infrared analyses of polymers A to D in Table 2 disclosed that the amines had apparently reacted with the maleic anhydride unit in all cases except that of polymer D, involving diphenylamine. The infrared spectrum for the latter sample revealed the presence of unreacted anhydride units and free amine. To the extent that the aromatic amine did not react in this one case, it necessarily served as an antirad rather than as an integral protective part of the polymer molecule.

A comparison of polymers F and E shows that incorporation of the maleic anhydride units into the ethyl acrylate chain caused an increase in G (x) and an apparent disappearance of chain scission in the copolymer. Conversely, the substituents in polymers A, B, and C evidently brought about a decrease in G (x) and an increase in the rate of chain scission. If the second G (x) value is accepted for sample A, as appears probable, the observed trend is consistent with the relative resonance energies of the substituents. That is, G (x) decreases with increasing resonance energy.

Poly (N-vinyl carbazole), abbreviated poly NVC, was synthesized and evaluated for radiation stability by measuring the gel content as a function of the radiation exposure dose. A G (x) value of 0.022 was obtained for this polymer as compared with 0.045 for polystyrene. Thus, this polymer appears twice as radiation-resistant as polystyrene, which is recognized as one of the most radiation-resistant organic high polymers. Consequently, a series of copolymers involving N-vinyl carbazole was prepared using ethyl acrylate and 2-ethyl hexyl acrylate as comonomers in an

effort to derive elastomers with superior inherent radiation stability.

As shown in Figure 3, energy transfer occurs from both ethyl acrylate (EA) and 2-ethyl hexyl acrylate (2-EHA) units to the adjacent N-vinyl carbazole (NVC) units in their respective copolymers. Elastomers were obtained with up to 22.6 weight per cent NVC in the EA/NVC copolymer system and up to 46.4 weight per cent NVC in the 2-EHA/NVC system. However, the accuracy of the results for the 2-EHA/NVC series of copolymers is subject to rechecking, since difficulties arose in the measurement of the initial molecular weight because of instrument trouble. Said molecular weight values will be remeasured as soon as the light scattering equipment is back in service.

In order to gain further understanding of the relationships between molecular structure and radiation resistance of organic high polymers, four inter-related series of acrylate homopolymers were selected (see pages 16-18). In all cases the polymerization takes place through opening of the ethylenic double bond of the acrylic structure. Five such polymers have been prepared: poly (phenyl acrylate), poly (phenyl methacrylate), poly (4-phenylbutyl acrylate), poly-(4-phenylbutyl methacrylate), and poly (ethyl 2-phenyl acrylate). In addition, a polymer of related structure, poly (vinyl benzoate), has been synthesized for comparison with poly (phenyl acrylate). Of the previously mentioned polymers the poly (phenyl acrylate) and the poly (phenyl methacrylate) have been studied in regard to their radiation stability. As expected, the acrylate polymer undergoes a predominant crosslinking reaction when subjected to ionizing radiation, and the methacrylate polymer experiences principally chain scission. A G value for net crosslinking, G (x), of 0.054 and a β / α ratio of 0.48 were obtained for the acrylate polymer. These values are slightly greater than those for polystyrene (5), namely 0.045 and 0.35, respectively.

By determining the molecular weight of poly (phenyl methacrylate) as a function of radiation exposure dose from 0 to 1.8×10^9 ergs per gram (C), the net energy dissipated per main chain scission, E_s, was calculated from the slope of Figure 4 to be 270 e.v., giving a G (s) of 0.37. By comparing the various $\overline{M}_w$ values with their respective intrinsic viscosities $[\eta]$, a Staudinger relationship was obtained (in methyl ethyl ketone at 25°C.): namely, $[\eta] = 3.47 \times 10^{-4} M^{0.596}$, permitting extension of the study to 5.4×10^9 ergs per gram (C). By using the $\overline{M}_w$ values determined by viscosity measurements, the following values were obtained: E_s = 169 e.v. and G (s) = 0.59. It is to be noted that the discrepancies between $\overline{M}_w$ values determined by light scattering versus by viscosity measurements increase with increasing radiation dose. The discrepancies occurred principally in the region where no light scattering values were available. The averages of the values obtained by the two methods of measurement are $E_s = 220 \pm 50$ e.v. and G (s) = 0.48 ± 0.11.

2.3.4 Summary and Conclusions

This first year's program is at the three quarter mark. The rate of progress has been impeded by an unavoidable interruption in light scattering analytical services. The several causes of the delay are expected to be corrected by the end of February, 1960. The evaluations of polymer radiation stability which have

already been completed support the basic hypotheses of this monomer-polymer program. Polymers with exceptionally good radiation resistance have been prepared. For example, a plastic, poly (N-vinyl carbazole), has been produced having twice as good resistance to radiation-induced crosslinking as polystyrene. Furthermore, an elastomer, poly (N-vinyl carbazole-co-2-ethylhexyl acrylate) with 31.7 weight per cent NVC, has been synthesized which has a G (x) value of 0.15 as compared with 0.045 for polystyrene and 0.21 for Estane VC, a highly aromatic polyurethane (53).

The polymers discussed in the previous sections (2.3.1-2.3.3) together with the remaining phenyl-substituted polyacrylates (see pages 16-18), whose monomers are being prepared by the monomer synthesis group, should provide a clearer understanding of the protective effect of branch-type aromaticity. Such knowledge, complemented by that to come from the proposed second and third phases of the program (main-chain aromaticity and select copolymerization), should provide increasingly better criteria for selecting monomers and designing new polymers with outstanding radiation resistance. It is anticipated further that superior heat resistance will accompany the radiation stability.

APPLIED RESEARCH

3.1 Radiation-Resistant Practical Rubber Compounds

(This research was conducted and reported by E. E. Mooney)

3.1.1 Introduction

The program concerning the radiation resistance of elastomeric compounds has two main objectives: (1) establish "control behavior" of these compounds in a radiation field and (2) find means for protection of these compounds against radiation damage. This program necessarily involves the treatment of different elastomers, compounding ingredients, environments, and test methods. During the past year, work was directed toward gaining a measure of the effect of gamma radiation on the rheological properties of elastomeric compounds at room temperature in air. A compression set measurement based on ASTM Method B was developed for this purpose. The investigations which were undertaken followed from the survey work done during 1957 and 1958, when static elastomer dumbbells were exposed to heat and radiation and compression set studies were begun (4, 5, 54, and 55).

The types of practical compounds included in this program are hose, seals and packing, fuel cells, and wire insulation. In many additional cases simple ASTM or manufacturer-recommended formulations are used for purposes of keeping radiation effects reasonably isolated. The conventional polymers being evaluated so far are NR, SBR, CR, and NBR. The specialty polymers are Hycar 4021, Thiokol ST, Viton A, and Hypalon 20.

The compression set program broadly involves environmental testing in air, heat and organic fluids and evaluation of potential antirads. Many results for these items have already been reported (5, 55). Some of these and other variables affecting the radiation resistance of elastomeric vulcanizates during compression have been investigated this year. They included, for example, state of cure, type of cure, degree of compression, length of pre-irradiation set period, compound hardness (i.e., plasticizer content), polymer chemical composition, and preparation. Due to an unexpected delay in radiation service at the MTR Gamma Facility a major portion of this year's program must be reported at a later date. A paper entitled Radiation and Other Environmental Effects on Elastomeric Compounds was prepared by E. E. Mooney and S. T. Semegen. It was given orally at the Fourth Radiation Effects Symposium in Cincinnati, Ohio on September 16, 1959 and will appear in the printed proceedings. This preparation necessitated the elimination of continuation of stress-strain studies on elevated temperature-radiation effects (at 212°F and 280°F) which were tentatively planned for this year.

The survey of radiation effects on the extension and compression properties of elastomeric vulcanizates has produced improved test methods for analyzing these

effects. Future work should be directed in part toward the measurement of experimental variability in these test methods.

3.1.2 Experimentation

3.1.2.1 Recipes

The following compounds were tested for radiation resistance during compression:

Compound Numbers	Elastomer
(1) 81GJ421A to 431B	Hycar 1001
(2) 81GJ338B2, 1375, 1376	Natural Rubber
(3) 81GJ452 to 455	Neoprene GN
(4) 81GJ448 to 451	Hycar 1001
(5) 81GJ1371 to 1374	SBR 1500/1501
(6) 81GJ444 to 447	Hypalon 20
(7) 81GJ310 to 325	Hycar 1011 (Fuel Cell Liner)

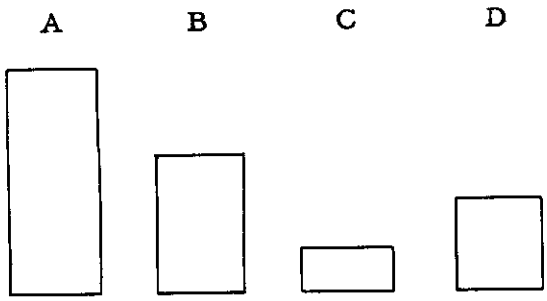
The recipes of these rubber compounds are given in Table 3. The potential antirads used were hydroquinone, Antiox 4010, and α -naphthylamine. All antirads have been used at a 5 phr level of concentration.

In a series of elastomeric vulcanizates in which experimental stocks are being compared to control stocks it is important that the states of cure for all compounds be reasonably equivalent. Recent data to be discussed presently testify to the necessity of equivalent cure also in stocks to be compared for radiation resistance. Stress-strain and Mooney Cure (ASTM D 1077-557) data were used in all cases for establishing equivalent cures. The procedure that was used is described in earlier work (4, 5). A tabulation of curing conditions for compression set samples, stress-strain properties, and hardness values for all stocks which were tested for compression set (given above) are listed in Table 4.

Compression set testing in this study involves a modification of ASTM Test D 395-55 Method B (5, 55). The major modification in the ASTM compression set test comes in the calculation of per cent compression set. For specimens exposed at room temperature to gamma radiation the ASTM method would require that there be no pre-exposure set. Under the present circumstances of operation, rubber specimens are compressed at the B. F. Goodrich Company Research Center, Brecksville, Ohio, and irradiated at the MTR Gamma Facility at Idaho Falls, Idaho. The period of time between initial compression and the start of irradiation results in pre-irradiation set. This pre-set is generally different for each rubber compound depending on the polymer, state of cure, type of compounding, etc. The phenomenon of pre-irradiation set is not unrealistic. Many compounds in service applications will be compressed for some period of time before exposure to radiation. The calculation used most satisfactorily thus far, to determine the net compression set induced by irradiation is the following:

COMPRESSION SET CALCULATION

Radiation Compression Set Pellet
(MTR Gamma Radiation Exposure)



A = Initial Thickness

B = Thickness after Pre-irradiation Set (or Thickness Just Prior to Irradiation at MTR Gamma Facility)

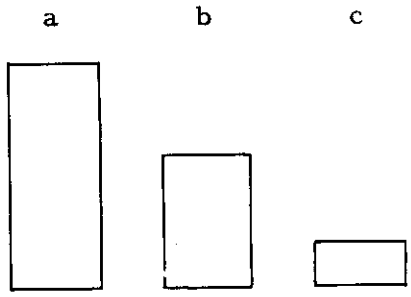
C = Spacer Thickness

D = Thickness after Irradiation

Radiation-Induced Compression Set:

$$S = (B-D)/(B-C)$$

Control (Unirradiated) Compression Set Pellet
(Brecksville Control Test)



a = Initial Thickness

b = Thickness after Room Temperature Set at Brecksville without Irradiation

c = Spacer Thickness

Control Compression Set, $\mathbf{x} = (a-b)/(a-c)$

Let x' = Control Compression Time (t')

$$= (a-b)/(a-c)_{t'} = (A-B)/(A-C)_{t'}$$

Then, after said time t',

$$B_{t'} = A - x'(A-C)$$

Given on the left are four views of a single rubber pellet for radiation testing and, on the right, three views of a control (unirradiated) pellet. The radiation test pellet has an initial thickness A. It is compressed to the thickness C in an aluminum compression jig at the B.F.Goodrich Company Research Center at Brecksville, Ohio, and shipped to the MTR Gamma Facility in Idaho. After irradiation the compressed pellet returns to Brecksville, the aluminum compression jig is opened, and the thickness D is measured. Hence, thicknesses A, C, and D are measured directly at Brecksville. While the radiation test pellet travels from Brecksville to Idaho and awaits irradiation the compression time prior to irradiation varies from 12 to 140 days depending on the experimental purpose, shipping time, and promptness of irradiation service. Hence, a sample having an initial thickness A which is compressed to thickness C will effectively relax to some lower initial thickness B before irradiation. Similar to ASTM procedure, the thickness B just prior to exposure is used in the calculation of the radiation-induced compression set (B-D)/(B-C).

However, experimentally the thickness B can be determined only indirectly.

The indirect determination of thickness B is accomplished using a separate group of control pellets whose various thicknesses are given by a, b, and c and are measured directly at Brecksville. A plot of control compression set $x = (a-b)/(a-c)$ versus compression time t (up to the 20-140 day range) is made. Knowing the time the irradiation of the test pellet begins, one can figure the total compression time t' prior to irradiation. Using this t' value, one can obtain the corresponding pre-irradiation control compression set, x', from the control compression set curve. Since x values are the same for both the radiation test and control test pellets, one can equate x' not only to $(a-b)/(a-c)_{t'}$ but also to $(A-B)/(A-C)_{t'}$. Hence, the thickness B at the time irradiation begins is calculated as $B_{t'} = A-x\,(A-C)$. The graphs given in Figures 5-18 are linear plots of radiation-induced compression set versus radiation exposure (the upper curve using the upper abscissa) and control compression set versus control compression time (the lower curve using the lower abscissa). Pre-irradiation control compression set, x', and the corresponding pre-irradiation compression time, t', are indicated by arrow on each control compression set curve. For purposes of simplicity and greater accuracy this entire radiation compression set calculation is now being done on the B. F. Goodrich Bendix G-15D electronic computor. The computor calculates control compression set values at the arbitrarily selected experimental times and then interpolates between control compression set values for quantity (x'). The computor then calculates thickness B and proceeds to compute radiation-induced compression set at the experimental radiation exposure doses.

For purposes of a fundamental investigation of the mechanism of radiation damage to vulcanizates during compression, the following empirically-derived equation has been applied satisfactorily to some of the data:

$S = -Ae^{-BR} + S_e$, where

S = the radiation-induced compression set at any gamma radiation exposure dose R,

S_e = the radiation-induced compression set at $R = \infty$,

$A = (S_e)e^{-C}$,

C = the intercept constant in the plot of Log $(1-S/S_e)$ versus R, and

B = the rate constant in (ergs per gram $(C)x10^{10})^{-1}$.

Using the radiation-induced compression set results which the Bendix G-15D computor calculates for each chosen radiation dose, the computor then can make a least squares fit of the above equation to the experimental points. In the cases of satisfactory fit of the equation to the experimental points, quantities A, B, and S_e amply describe the exponential stress decay of vulcanizates during compression in a radiation field. Such quantities provide a fundamental approach to the subject of the measurement of vulcanizate radiation resistance, antirad effectiveness, and test method reproducibility. Figure 19 shows plots of log $(1-S/S_e)$ versus radiation exposure dose for cases where the above equation makes a satisfactory fit to the

experimental points. For the cases where unsatisfactory fits to the data are observed it appears that the equation possibly needs to be expanded to include other exponential terms.

In order to establish the order of magnitude of radiation damage conveniently, two quantities are determined: radiation-induced compression set at 5.23×10^9 ergs/gram (C), S_R, and the exposure dose required to effect 50% compression set, R_S, in ergs/gram (C)$\times 10^{-9}$. These two quantities provide a tentatively satisfactory two-point means of comparison of all present and past compression set data. They are either taken directly from linear plots of radiation-induced compression set versus radiation dose or are calculated directly by the Bendix G-15D computor, using the above equation for compression set.

Radiation-induced compression set has been studied over the critical exposure dose range of 8.71×10^7 to 1.04×10^{10} ergs/gram (C), using four or five convenient gamma radiation doses in the range. Table 5 lists the data used and produced by the Bendix G-15D computor for the graphs in Figures 5-19. Since the MTR Gamma Facility uses air-equivalent ionization chambers for dosimetry and reports doses in roentgens, two exposure dose scales are shown for each plot. The conversion is 1 roentgen (air) = 87.1 ergs/gram (carbon) for the present work.

3.1.3 Results and Discussion

The plots of radiation-induced compression set data given in Figures 5-18 for various rubber compounds summarize several studies. Values of S_R (the radiation-induced per cent compression set at 5.23×10^9 ergs/gram (C)) and R_S (the gamma radiation exposure dose in ergs/gram (C)$\times 10^{-9}$ required to effect 50% compression set) provide a convenient means for comparison of compound resistance to radiation damage. The original stress-strain properties, especially the 200% modulus (M_2) and the 300% modulus (M_3) having the units psi, are the primary basis for establishing equivalent states of cure. Reference should be made to those properties given in Table 4. Pre-irradiation control compression set, x', gives a rough measure of the relaxation tendency inherent in the rubber compound. This value is also included to supplement stress-strain data in the evaluation of state of cure.

3.1.3.1 State of Cure

An Altax-sulfur cured Hycar 1001 stock containing 50 phr of SRF black was cured for six different periods of time. The resulting S_R, R_S, and x' values taken from Figures 5 and 6 are as follows, along with M_2 values from Table 4:

COMPOUND 81GJ421A

Chemical Cure (Minutes at 293°F)	Experimental Radiation Data S_R[1]	R_S[2]	X'[3]	M_2[4]
15	84	0.50	14	1100
20	78	0.63	12	1420
35	75	1.18	9	1790
45	73	1.44	9	2050
105	67	2.26	7	2290
210	68	2.65	6	2400

[1]Radiation-induced compression set (%) at 5.23×10^9 ergs/g (C).
[2]Radiation exposure dose (ergs/g (C)$\times 10^{-9}$) required for 50% set.
[3]Control compression set (%) immediately prior to irradiation.
[4]Two hundred per cent modulus (psi) before irradiation.

These results indicate that the more tightly cured the Hycar compound, the more resistant it is to radiation-induced compression set.

3.1.3.2 Type of Cure

Eleven different curing systems were used to cure Hycar 1001 stock containing 50 phr of SRF black. Comparisons of radiation resistance are made via the following data taken from Figures 7-10. There is considerable variation in x' values.

Compound 81GJ-	Type of Curing System	Experimental Data S_R[6]	R_S[7]	X'[8]	M_2[9]
430B	Polyac	90	0.31	52	710
424E	Lead-GMF[1]	84	0.64	39	890
423A	Altax-Tuads[2]	84	1.31	21	700
426A	Amberol ST-$SnCl_2$	85	1.73	27	980
429A	Tuads[2]	77	1.70	12	1130
427A	Sulfur Donor[3]-Altax	72	1.71	15	1450
425B	BMD[3]	73	1.93	10	1320
422A	Lime-DCP[4]	75	1.67	12	2020
421A	Altax-Sulfur	69	2.46	8	2290
428B	Altax-Sulfasan R[3]	68	2.65	10	1770
431B	MDB[5]-Litharge	57	3.71	34	2090

[1]Para-Quinonedioxime
[2]Tetramethylthiuram Disulfide
[3]Active Sulfur Source
[4]Dicumyl Peroxide
[5]Meta-Dinitrobenzene
[6]Radiation-induced compression set (%) at 5.23×10^9 ergs/g (C)
[7]Radiation exposure dose (ergs/g (C)$\times 10^{-9}$) required for 50% set
[8]Control compression set (%) immediately prior to irradiation
[9]200% Modulus (psi) of rubber compound before compression

indicating measurable differences in state of cure. This is further confirmed by the M_2 values from Table 4. Comparisons are justified primarily on the basis of comparable M_2 values. For example, with respect to radiation resistance of the various rubber compounds in the above testing the curing systems rate as follows:

(a) MDB > Altax-Sulfasan R ≅ Altax-sulfur > lime-DCP,
(b) Amberol ST-$SnCl_2$ > Altax-Tuads > lead-GMF > Polyac,
(c) Active sulfur donor-Altax ≅ BMD ≅ Tuads ≅ lime-DCP, and
(d) Altax-Sulfasan R ≥ Altax-sulfur > BMD,

where > indicates having greater radiation resistance. There are thus indications here that the type of curing system (and hence the kind of vulcanization crosslink) may have a substantial effect on the radiation resistance of a compound to compression set or, perhaps, stress relaxation also. This point should be further checked on a series of compounds whose state of cure has been more carefully adjusted.

3.1.3.3 Natural Rubber Compound

An ASTM-type natural rubber compound was tested for radiation resistance during compression. This stock was compounded both with and without 5 phr of hydroquinone in one case and a hydroquinone/Antiox 4010 (50/50) mixture with the following results taken from Figures 10 and 11 and Table 4:

Compound 81GJ	Potential Antirads	Radiation Test Data[1] S_R	R_S	x'	M_3
338B	None (Control)	80	1.64	22	1600
1375	Hydroquinone (HQ)	80	1.59	30	2000
1376	HQ/Antiox 4010	79	1.38	28	1870

[1] See Section 3.1.3 above.

No improvement is imparted to this natural rubber compound in terms of compression set by these additives.

3.1.3.4 Neoprene GN Compound

An ASTM-type Neoprene GN rubber compound was tested for radiation resistance during compression. The control stock was studied with and without 5 phr of hydroquinone in one case, Antiox 4010 in a second case, and a 50/50 mixture of the two in a third case as potential antirads. The results are as follows, taken from Figures 11 and 12 and Table 4:

Compound 81GJ-	Potential Antirads	Radiation Test Data[1] S_R	R_S	x'	M_3
452	None (Control)	81	1.49	31	1580
453	Hydroquinone (HQ)	72	1.59	39	2420
454	Antiox 4010	75	2.15	34	1980
455	HQ/Antiox 4010	69	1.96	37	2030

[1]See Section 3.1.3 above.

Antiox 4010 appears to improve the radiation resistance of this compound slightly.

3.1.3.5 Hycar 1001 Compound

An ASTM-type Hycar 1001 rubber compound was exposed to gamma radiation while in the compressed state. A series of four compounds included the control plus three experimental stocks containing separately 5 phr each of hydroquinone, Antiox 4010, and a 50/50 mixture of these two chemicals. The radiation test results are as follows (see Figures 13 and 14 and Table 4):

Compound 81GJ-	Potential Antirads	Radiation Test Data[1] S_R	R_S	x'	M_2
448	None (Control)	67	2.52	8	2290
449	Hydroquinone (HQ)	54	4.35	13	1740
450	Antiox 4010	57	3.92	10	1980
451	HQ/Antiox 4010	56	4.09	13	1880

[1]See Section 3.1.3 above.

Thus, the Hycar 1001 rubber compound appears receptive to antirad protection against radiation-induced compression set. This result was also shown in earlier work (4, 5).

3.1.3.6 SBR 1500/1501 Compound

An ASTM-type SBR 1500/1501 compound (styrene-butadiene rubber) was tested for radiation resistance during compression. The control stock was used with and without 5 phr separately of hydroquinone, Antiox 4010, and a hydroquinone/Antiox 4010 (50/50) mixture. The radiation test results (taken from Figures 14 and 15 and Table 4) are:

Compound 81GJ-	Potential Antirads	Radiation Test Data[1] S_R	R_S	x'	M_2
1371	None (Control)	66	2.74	13	1570
1372	Hydroquinone (HQ)	66	2.64	21	1430
1373	Antiox 4010	59	3.57	15	1430
1374	HQ/Antiox 4010	62	3.25	19	1290

[1]See Section 3.1.3 above.

Antiox 4010 appears to enhance the radiation resistance of this SBR stock.

3.1.3.7 Hypalon 20 Compound

A manufacturer-recommended Hypalon 20 rubber compound was also tested for radiation resistance. Hydroquinone, Antiox 4010, and a 50/50 blend of the two were again used separately in 5 phr quantities as antirads. The radiation test results as taken from Figures 15 and 16 and Table 4 are:

Compound 81GJ-	Potential Antirads	Radiation Test Data[1] S_R	R_S	x'	M_2
444	None (Control)	75	1.05	50	2840
445	Hydroquinone (HQ)	73	1.18	56	2460
446	Antiox 4010	83	1.48	54	2140
447	HQ/Antiox 4010	72	1.32	52	2480

[1]See Section 3.1.3 above.

Hydroquinone and Antiox 4010 do not enhance the radiation resistance of this Hypalon 20 compound significantly.

3.1.3.8 Hycar 1011 Fuel Cell Liner Stock

The application of the empirical equation for radiation-induced compression set, $S = -Ae^{-BR} + S_e$ where $A = S_e e^{-C}$, has been satisfactory for the Hycar 1011 Fuel Cell Liner Stock. The following tabulation illustrates the comparison between the Bendix G-15D computed equation values and experimental values taken from linear plots of radiation-induced compression set as a function of radiation exposure dose (Figures 17 and 18). The antirads were used at the 5 phr concentration level.

IDENTIFICATION OF COMPOUNDS

Compound 81GJ-	Potential Antirads
310	None (Control)
311	α -Naphthylamine
323	Hydroquinone
325	Antiox 4010

Rubber Compound 81GJ-	Modulus M_3 (psi)	Bendix G-15D Computations Equation Values[1] A	B	S_e	S_R	R_S	Exptl. Values[1] S_R	R_S
310	1640	0.640	3.33	0.914	80.1	1.31	81	1.31
311	1270	0.790	2.67	0.871	67.6	2.83	67	2.80
323	1280	0.792	2.67	0.824	62.8	3.35	63	3.34
325	1470	0.817	2.22	0.875	61.9	3.51	61	3.52

[1]See Section 3.1.3 above.

The M_3 values indicate approximately equivalent cures for all four compounds. Compound 81GJ310 has a lower A value than the others, indicating a larger intercept constant C. Large C values signify a rapid initial stress decay reaction during irradiation and perhaps rapidly destroyed crosslinks. The rate constant B shows the order of the radiation resistance of these rubber compounds to be the Antiox 4010 stock > the hydroquinone stock = the α-naphthylamine stock > the control stock. The equation values and the experimental values of S_R and R_S are in good agreement. Figure 19 shows the individual experimental and equation values for radiation-induced compression set, $S = (B-D)/(B-C)$, plotted in the form of log $(1-S/S_e)$ against the respective radiation exposure doses. The equation values of radiation-induced set make a satisfactory overall fit to the experimental points.

The application of such an equation to radiation-induced compression set data is needed if insight into the mechanism of radiation damage to vulcanizates under compression is to be gained. Other attempts have been made to use this equation in its present form. In many cases the deviation of equation values from experimental values is unsatisfactory. These cases seem to involve a combination of a fast initial exponential stress decay followed by a slower reaction of the same type. It is conceivable that a more generally satisfactory form for this equation expressing radiation-induced compression set would be of the type

$$S = S_e - Ae^{-BR} - Ce^{-DR} \quad .$$

A statistical approach to the application of an equation of this form will be considered.

3.1.4 Summary and Conclusions

Variables that can possibly affect the radiation resistance of vulcanizates during compression are being considered. A test method which measures compression set as a function of radiation exposure dose is being used in this connection. Only a portion of the studies underway at this three-quarter point in the year is given in this report.

Increasing (or "tightening") the initial state of cure of a Hycar nitrile rubber compound before compression and subsequent gamma irradiation during compression increases its radiation resistance. The type of curing system used for this Hycar compound seems to make considerable difference in its radiation resistance during compression. Hydroquinone and Antiox 4010 were evaluated as antirads. Natural rubber compounds showed no response to these additives; Hycar 1001 and Hycar 1011 were most improved by the antirads; and Neoprene GN, SBR 1500/1501, and Hypalon 20 stocks were intermediate in their response to the additives. The Hycar 1001 stock containing hydroquinone had only 54% net radiation-induced compression set at 5.23×10^9 ergs/gram (C) (as compared with 67% for the control compound) and required a radiation dose of 4.35×10^9 ergs/gram (C) to effect 50% compression set (as compared with 2.52×10^9 ergs/gram (C) for the control compound).

Some effort has been made to express mathematically the relationship between radiation-induced compression set and radiation exposure dose. The expression worked with thus far is apparently not general enough in its present form to lend itself to widespread application. Consideration of improvement of the equation to

produce a more generally satisfactory expression is planned.

Acknowledgment

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3.2 Radiation Testing of "O" Ring Seals

(This research was conducted and reported by J. W. Born)

3.2.1 Introduction

Rubber seals are critical end-items in the design, construction, and operation of aircraft. In addition to conventional performance requirements, such seals in nuclear-propelled aircraft will have to resist radiation damage. Until elastomers are synthesized with markedly superior radiation stability and are successfully built into serviceable end-items, current conventional rubbers will require additives which inhibit radiation damage. Such need will increase as performance requirements for nuclear aircraft increase.

Therefore, consideration has turned to the possibility of protecting rubber "O" ring seals with compound additives (antirads). The first experiment in such a program has been designed and is underway: namely, determination of the extent to which antirads can protect present "O" rings for aircraft from radiation damage. This work involves a cooperative study between the B. F. Goodrich Company and the Precision Rubber Products Corporation. The latter organization, using its proprietary rubber compounds which meet aircraft military specifications for non-radiation service, is responsible for compounding the potential antirads into said rubber stocks and adjusting cure thereafter to insure stress-strain properties which are comparable with those of the original compound in each case. It then has charge of molding and curing "O" ring and compression set samples, measuring the initial physical properties, and measuring the physical properties after irradiation.

The B. F. Goodrich role includes designing the experiment, irradiating the samples, evaluating the post-irradiation test results, and reporting the results to Wright Air Development Center. In addition, the B. F. Goodrich Company will measure radiation damage to molded cured samples of these same rubber "O" ring compounds. The testing techniques described by E. E. Mooney in Section 3.1 will be used for the latter semi-dynamic studies of compression set during irradiation.

3.2.2 Experimentation

3.2.2.1 Design of the Experiment

On November 13, 1959 this worker conferred at the Precision Rubber Products Corporation in Dayton, Ohio with Howard G. Gillette, Chief Chemist, and

John G. Sommer, Assistant Chief Chemist. The conference clarified the operational details of the "O" ring radiation testing program. The details were incorporated into the following revised subcontract with PRPC for the manufacture and testing of "O" ring compounds and samples.

The test program involving BFG and PRPC is designed to evaluate the effect of gamma radiation on "O" rings by both static and semi-dynamic testing. The B. F. Goodrich Company is to supply the four antirad additives for incorporation into the following four PRPC proprietary compounds:

Compound	Elastomer	Test Fluid	Immersion
7377	NBR	MIL-O-5606 (Hi)	70 hrs. at 275°F
8187	NBR/SBR	ASTM No. 3	70 hrs. at 300°F
2277	Neoprene	MIL-O-8515	70 hrs. at 350°F
17107	Viton A	MIL-O-8200	70 hrs. at 400°F

In addition to the conventional recipe each compound will have three antirad variations as follows:

Antirad Additives	Per cent of Total Antirad in Compound[1]			
	7377	8187	2277	17107
Hydroquinone	100%	100%	100%	
Antiox 4010	100%	100%	100%	
UOP-88				100%
Stabilite-FLX	100%			100%
Antiox 4010/HQ[2]		50%/50%	50%/50%	
Antiox 4010/UOP-88				50%/50%

[1]These weight per cents together with the numbers of parts of antirad per hundred parts of rubber (3.0 or 5.0 phr) indicate the quantities of the antirad or antirads to be added.

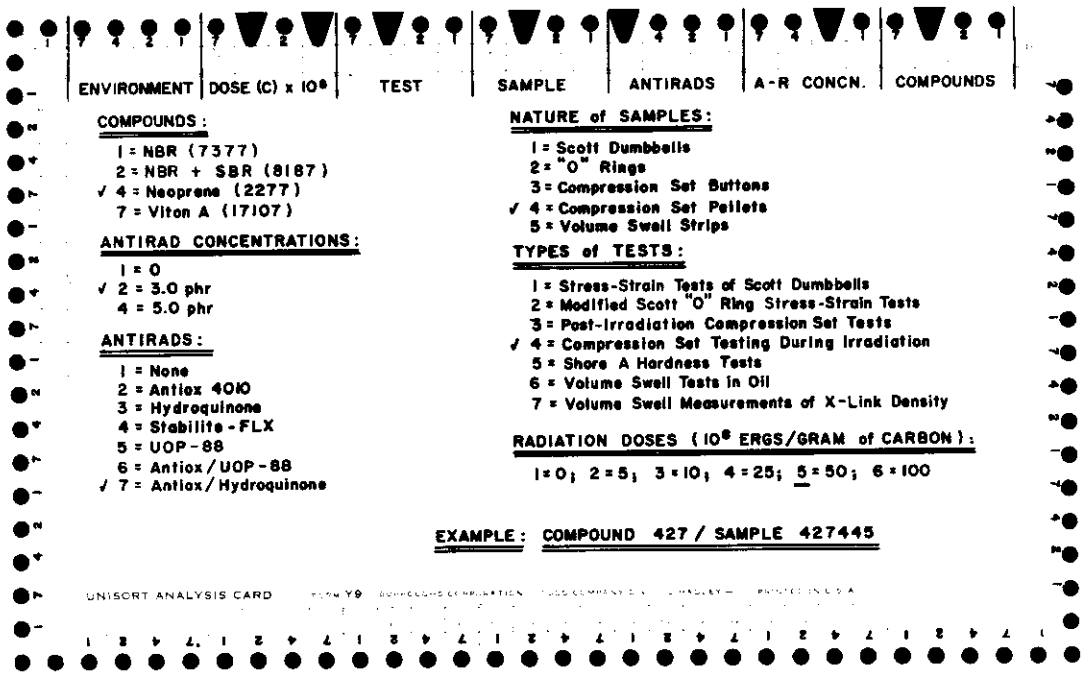
[2]HQ represents hydroquinone.

No "O" rings will be prepared until any necessary compounding changes are effected to offset the addition of the antirads with respect to initial stress-strain properties, particularly modulus and hardness. Precision Rubber Products Corporation is to furnish the following: 42 sets of "O" rings and 42 sets of compression set buttons for each of the four basic groups of compounds. A set of "O" rings consists of 8 samples; 5 rings for autographic tensile measurements plus 3 rings for volume swell determinations. There are two compression set buttons to a set. In addition, PRPC will supply uncured batches of all 28 rubber compounds to BFG for preparation of special compression set pellets. The latter samples are earmarked for measurements of compression set during irradiation.

Initial samples will be tensile tested by PRPC, and the results will be forwarded to BFG. After gamma radiation exposure doses of 5×10^8, 1×10^9, 2.5×10^9, 5×10^9, and 1×10^{10} ergs per gram of carbon in air at room temperature, the irradiated

samples will be returned to PRPC along with the unirradiated control samples for testing. Test results will be forwarded to BFG for evaluation and reporting. Tentative plans call for eventual measurements of compression set during irradiation in oil. It is hoped that a third phase in a later contract period will involve testing at elevated temperatures and under simulated service conditions.

Because of the size of the experimental program and its intercompany nature, it was necessary to devise a compound numbering index prior to the actual start of the work. The index is needed to make the keeping of records and cross-communication unambiguous, simple, and efficient. A sample identification system has been adapted to Unisort Analysis Card cataloging to accomplish the latter. It will provide additional advantages such as improved storage and quick retrieval of test data and easy comparison of experimental results as a function of one or more test variables.



The identification code system which will be used is defined and illustrated in the above sample Unisort card. The results of the static and semi-dynamic testing will be coded across the top of the cards. The bottom and sides of the card are available for anticipated eventual dynamic testing of "O" rings during irradiation. There are seven group blocks across the top with four numbers (1, 2, 4, and 7) in each block. These four numbers can be added in different combinations to give numbers from 1 through 14, which thus can represent 14 different items within the group. By convention the numbers and blocks are read (and coded) from right to left. Slots are punched to correspond to the desired numbers in each block. The seven blocks in order represent the four compounds, the three antirad concentrations, the six antirads and antirad combinations, the five types of samples, the seven types of tests, the five radiation doses, and the environment. The identificatinn code is detailed on the sample card.

As an example consider the sample number 427445. This represents a compression set pellet of Neoprene Compound 2277 with 3.0 phr of a 50/50 mixture of Antiox 4010 and hydroquinone, which has received a gamma radiation exposure dose of 50×10^8 ergs per gram of carbon and has undergone compression set testing during irradiation in air at room temperature. For the present no code number will be assigned to the environment of air at room temperature, since all tests during this first phase will take place under these conditions.

3.2.2.2 Sample Preparation

The Precision Rubber Products Corporation has completed the preparation of 18 size 214 "O" rings for volume swell measurements and 30 size 214 "O" rings for tensile strength and ultimate elongation measurements for each of the seven rubber compounds in the first of the four groups: namely, compounds 111, 122, 123, 124, 142, 143, and 144. That organization has also supplied the seven batches of uncured rubber stock representing the seven compounds for use by the B.F.Goodrich Company in molding and curing the special compression test pellets for use in measuring compression set during irradiation. The former organization is in the process of preparing the ASTM compression set buttons for use in the scheduled post-irradiation testing at PRPC. The delivery of the latter samples will complete the sample preparation for the first of the four groups of "O" ring compounds. The subsequent three groups are expected to be delivered to BFG at the rate of approximately one group a month. Delivery of all samples should thus be completed by April 30, 1960.

3.2.2.3 Sample Irradiation

All 336 "O" rings for this first group (7 compounds x 8 "O" rings per compound per dose x 6 radiation exposure doses) are presently being mounted on sample racks in preparation for gamma irradiation in the B.F.Goodrich Company Cobalt 60 Source-Shield Assembly (56). Figure 20 shows the design of the racks and the manner in which the samples are mounted on the racks. Two racks and hence two radiation chambers of the "pig" will be used. Since there are five radiation exposure groups, two and one half groups will be irradiated in each chamber in ambient air at room temperature. The gamma radiation fluxes will vary approximately from 0.8×10^7 to 1.3×10^7 ergs per gram (C) per hour. Irradiation will begin by the end of February, 1960, and will proceed at nearly the same rate as the sample production, completing one group approximately each month.

3.2.2.4 Sample Testing

As indicated in the sample identification system above on page 51, the number of tests to be reported will total seven. These will comprise pre-irradiation Scott stress-strain tests to select and insure optimum and comparable states of cure of all the rubber samples in a group, post-irradiation Scott stress-strain tests to measure the extent of "O" ring radiation damage, pre- and post- irradiation measurements of compression set buttons to determine the effect of irradiation on compression set properties of an unstressed sample, compression set testing during irradiation to determine net radiation-induced compression set in a stressed sample, Shore A hardness measurements, volume swell tests in the oils cited above on page 51, and volume swell measurements of crosslink density in suitable swelling

liquids. Like the others, the latter three measurements will be made both before and after irradiation.

GLOSSARY

acrylonitrile : vinyl cyanide (VCN), CH_2=CHCN.

age resister : an additive for rubber or plastic compounds which inhibits deterioration in physical properties caused by environmental factors such as heat, oxygen, and ozone, for example.

Altax : benzothiazyl disulfide.

Amberol ST : alkylated phenol formaldehyde resin.

antibonding state : that state of a carbon - carbon linkage in which one of the two electrons in the π - bond of a double bond is excited to an energy level such that these two electrons no longer comprise a bond and free rotation about the remaining σ bond can occur.

Antiox 4010 : N-cyclohexyl - N' - phenyl - p - phenylenediamine.

antirad : a chemical substance which inhibits radiation damage, particularly when incorporated into organic high polymers.

ASTM : the American Society for Testing Materials.

β/α : the ratio of the number of scissions of the main chain which occur for each crosslink formed.

benzene - d_6 : completely deuterated benzene, C_6D_6.

BMD : active sulfur source (proprietary).

Buna - N : an elastomeric copolymer of butadiene and acrylonitrile.

butadiene : 1, 3 - butadiene (vinyl ethylene), CH_2=CH-CH=CH_2.

CB : cis - polybutadiene.

cis - trans isomerization : the transformation of a cis configuration about an ethylenic double bond in a molecule to a trans configuration about the same ethylenic double bond.

coagulation : the process of converting a finely divided or colloidally dispersed suspension of a solid into particles of such larger size that reasonably rapid settling occurs.

collisions of the second kind : molecular interactions in which the excitational energy is transferred from an excited molecule or atom to an unexcited molecule or atom.

compression set : the relative residual deformation of a compressible sample when the compressive forces have been removed, usually expressed in percent.

copolymer : a very large molecule which is formed when two or more different monomers (small molecules) are combined by polymerization.

CR : the American Chemical Society designation for an elastomeric polymer of chloroprene.

curative = curing agent : a chemical substance which participates in the curing (vulcanization) of a polymer compound.

DCP : dicumyl peroxide.

degradation : reduction in molecular weight by scission of chemical bonds.

deuterio - phenyl group : C_6D_5 .

dumbbell : a stress - strain test sample which is cut from a relatively thin sheet of rubber or plastic with a metal die.

$[\eta]$ intrinsic viscosity : the limiting viscosity number obtained by measuring the specific viscosity at a series of concentrations, plotting specific viscosity/concentration against concentration, and extrapolating the zero concentration.

E (s) : the net energy dissipated per main chain scission in a polymer.

elastomer : a polymer of high molecular weight having elastic properties.

end - item : a manufactured product, or a distinct integral part thereof, which has a specific service funtion.

excitation : activation by absorption of radiation, usually effected by the transfer of an oscillator (commonly an electron) to a higher energy level.

gas chromatograph : an analytical instrument used to determine the structure and composition of gases and vaporizable liquids and solids, particularly useful in determining chemical purity.

gas chromatogram : the record of the spectrum obtained during analysis of a gas or vapor with the gas chromatography unit.

gel : that portion of a polymer usually produced by crosslinking, which is insoluble (as opposed to the soluble sol portion).

GMF : p-quinonedioxime.

G_o : a measure of the reaction yield of isomerization equal to the number of cis double bonds initially isomerized to trans per 100 electron volts of energy absorbed by the system.

G'_o : a measure of the reaction yield of isomerization equal to the number of trans double bonds initially isomerized to cis per 100 electron volts absorbed by the irradiated system.

G(s) : the number of main chain scissions induced in a polymer by the absorption of 100 electron volts of ionizing radiation energy.

G(x) : the number of crosslinks induced in a polymer by the absorption of 100 electron volts of ionizing radiation energy.

Hycar 1001 : butadiene / acrylonitrile copolymer (60/40).

Hycar 1011 : butadiene / acrylonitrile copolymer, 36 1/2 - 39 1/2% bound acrylonitrile, easy processing type.

Hycar 4021 : acrylic acid ester - halogen containing derivative copolymer.

Hypalon 20 : chlorosulfonated polyethylene.

intrinsic viscosity, $[\eta]$: the limiting viscosity number obtained by measuring the specific viscosity at a series of concentrations, plotting specific viscosity / concentration against concentration, and extrapolating to zero concentration.

ion - molecule process : the radiation chemical reaction between an ion and a neutral molecule.

k : the reaction rate constant for the cis-trans isomerization.

k' : the reaction rate constant for the trans-cis isomerization.

MDB : meta - dinitrobenzene.

monomer : the simple, unpolymerized form of a compound, having a relatively low molecular weight, which may be used either alone or with a different monomer or monomers to form various types and lengths of molecular chains called polymers or copolymers.

MTR Gamma Facility : the Materials Testing Reactor Gamma Facility of the National Reactor Testing Station at Idaho Falls, Idaho.

$\bar{M}_w$: weight average molecular weight.

natural rubber : cis - polyisoprene.

NBR : the American Chemical Society designation for an elastomeric copolymer of acrylonitrile and butadiene.

Neoprene GN : polychloroprene, crystallizable, sulfur - containing.

NR : the American Chemical Society designation for natural rubber, cis - 1, 4 polyisoprene (Hevea).

N - vinyl carbazole : $CH = CH_2$ - N 

"O" ring : a gasket seal, usually of rubber, having the shape of a torus.

π electrons : those two of the four electrons constituting a double bond which are associated with the particular reactivity of the double bond.

percent gel : the percent of a polymer mass which is insoluble.

Polyac : 30%p-dinitrosobenzene polymer, 70% inert mineral filler.

polymer : a high molecular weight material containing a large number of repeating structural units.

polymerization : the process by which two or more different monomers (small molecules) are combined to form a very large molecule (polymer).

pre-irradiation compression set : the total compression set which occurs between the initial compression of the sample and the start of its irradiation.

PRPC : Precision Rubber Products Corporation.

radiation = nuclear radiation : the electromagnetic (gamma) radiation and / or particulate (neutron, alpha, beta, and fission fragment) radiation, particularly gamma and neutron radiation from nuclear reactions or radioactive decay.

radiation damage : detrimental radiation - induced changes in the chemical and physical properties of a material.

radiation dose : the actual amount of radiation energy absorbed by the material in question when it is placed in a radiation field.

radiation exposure = radiation exposure dose : the amount of radiation energy absorbed by a material in a radiation field as computed by multiplying the irradiation time by the incident flux determined via dosimetry.

radiation stability : the ability of a material to resist radiation-induced changes in its chemical and physical properties.

radiolysis : the dissociation of a molecule induced by ionizing radiation (analogous to photolysis).

radiostationary equilibrium : a radiation analog of "photostationary equilibrium" which denotes the metastable equilibrium obtained during irradiation which is due solely to the absorption of the radiant energy.

relative viscosity, η_r : the ratio of solution flow time/solvent flow time.

R_G : the radiation dose required to produce gelation.

rubber compound : the polymer system which results from an intimate blending of one or more elastomers with pigments such as reinforcing agents, curing agent, age resisters, and inert fillers.

σ bond : a normal covalent bond between two atoms involving the sharing of two electrons by these atoms.

SBR : the American Chemical Society designation for an elastomeric copolymer of styrene and butadiene.

SBR 1500/1501 : butadiene - styrene copolymer, 76.5/23.5, rosin acid, cold-polymerized.

second order transition temperature : the temperature at which the transition from the rubber - like to the glassy state occurs in a high polymer.

sensitized isomerization : the reaction which results from the participation of some specific substance which is deliberately added to the system.

sol : that portion of a polymer which is soluble.

specific viscosity, η_{sp}: relative viscosity η_r minus 1.

state of cure : the degree of crosslinking in a vulcanized rubber or plastic compound, often detailed by modulus or other stress - strain measurements.

stereospecific : having a specific, preferred structural configuration as, for example, the arrangement of monomer units in all cis - 1, 4 or all trans -1, 4 polybutadiene in contrast to the random mixture of cis and trans units in an ordinary or non-stereospecific polybutadiene.

Stern - Volmer process : a process involving the reaction between an excited molecule and a molecule in the ground state.

styrene : the monomer from which polystyrene is prepared; one of the comonomers in SBR; vinylbenzene.

sub-excitation electron : an electron whose energy is less than the lowest excitation potential of any of the materials being irradiated.

Sulfasan R : dimorpholine disulfide.

Sulfur donor : an active source of sulfur for the vulcanization of rubber (proprietary).

TB : transpolybutadiene.

Thiokol ST : polymeric reaction product of propylene - dichloroformal and sodium tetrasulfide.

TMTM : tetramethyl thiuram monosulfide.

Tuads : tetramethyl thiuram disulfide.

unsensitized isomerization : the reaction which occurs even in the absence of any deliberately added "sensitizer".

vinyl group : $-CH=CH_2$

vinylene group : $-CH=CH-$

Viton A : vinylidene fluoride - hexafluoropropylene copolymer.

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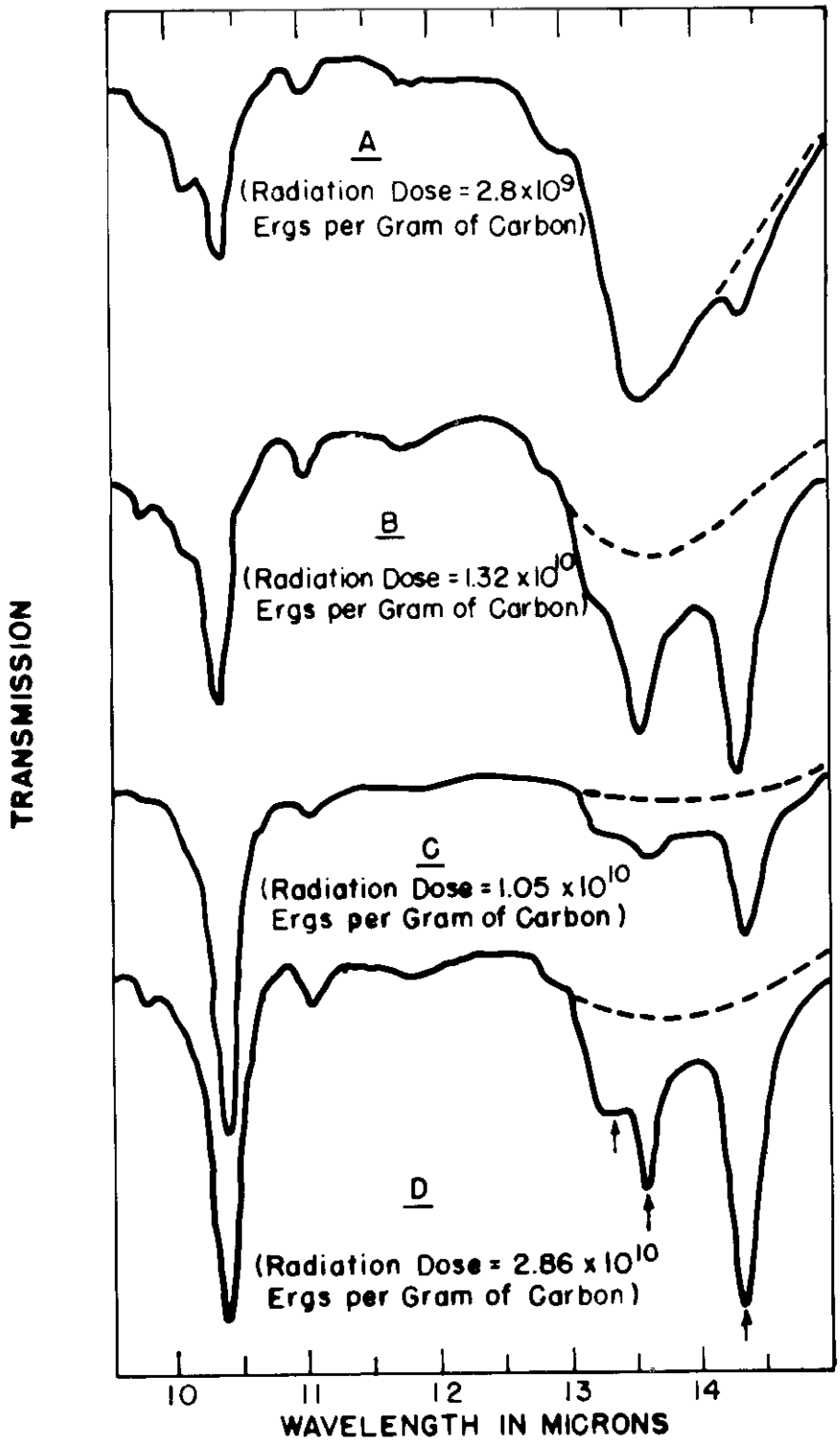

FIGURE 1. TYPICAL INFRARED SPECTRA OF PHENYLATED CIS- AND TRANS-POLYBUTADIENE. (The portion of the absorption band in the 13-15μ region above the dotted line in each of the spectra indicates roughly the contribution of the cis structure alone.)

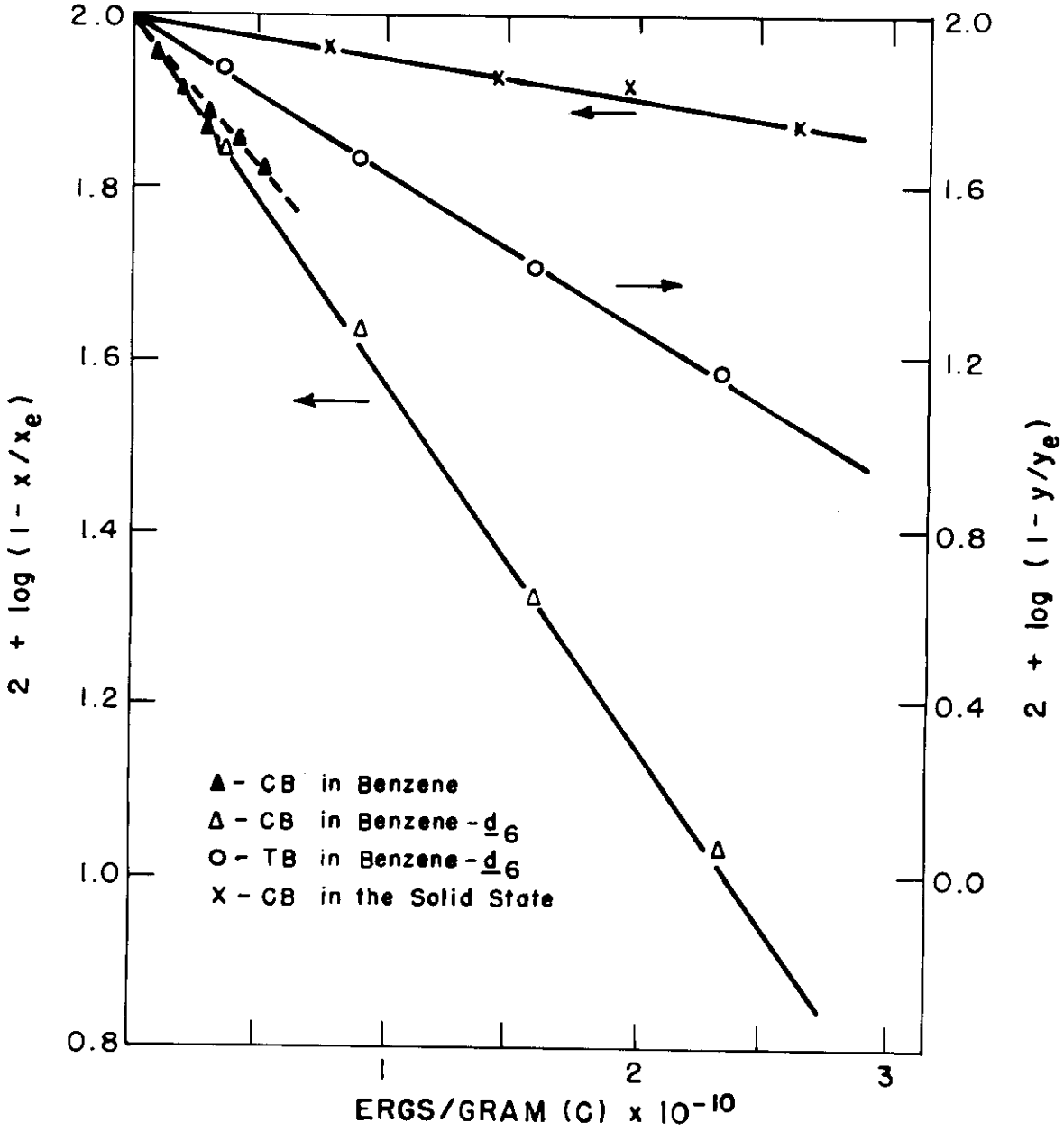

FIGURE 2. KINETIC PLOTS OF THE RADIATION-INDUCED ISOMERIZATION OF CIS- AND TRANS- POLYBUTADIENE.

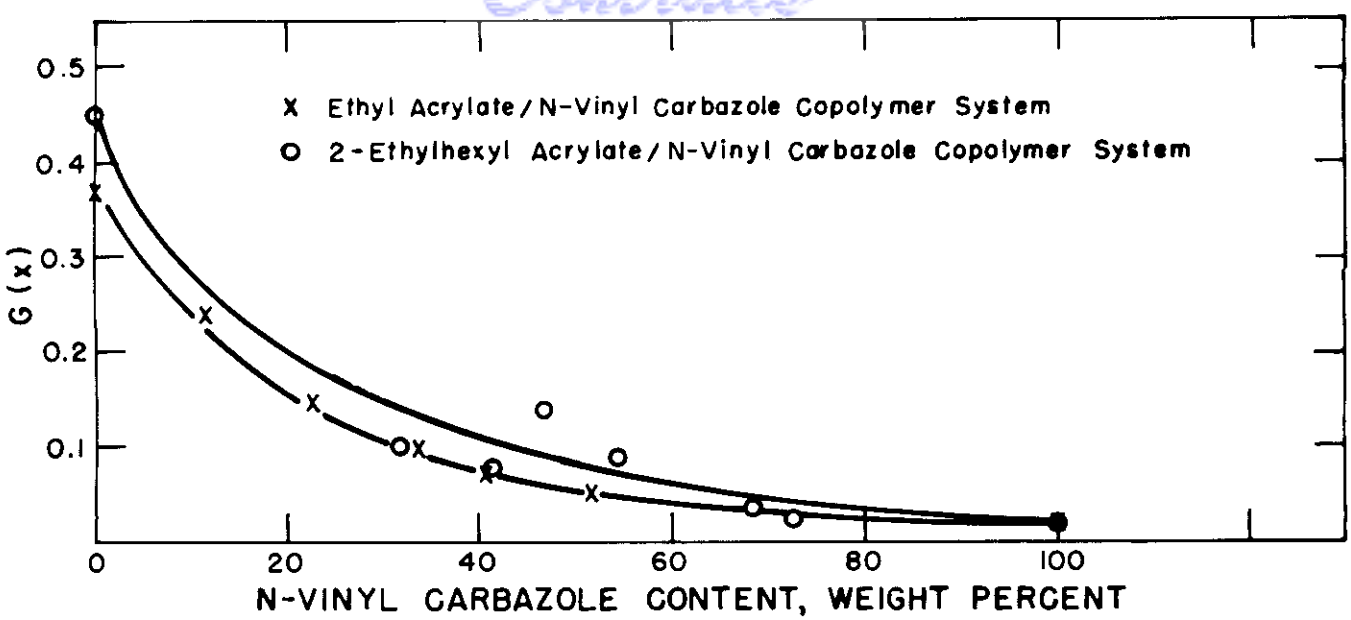

FIGURE 3. VARIATION IN RATE OF RADIATION-INDUCED CROSSLINKING, G(x), AS A FUNCTION OF N-VINYL CARBAZOLE CONTENT.

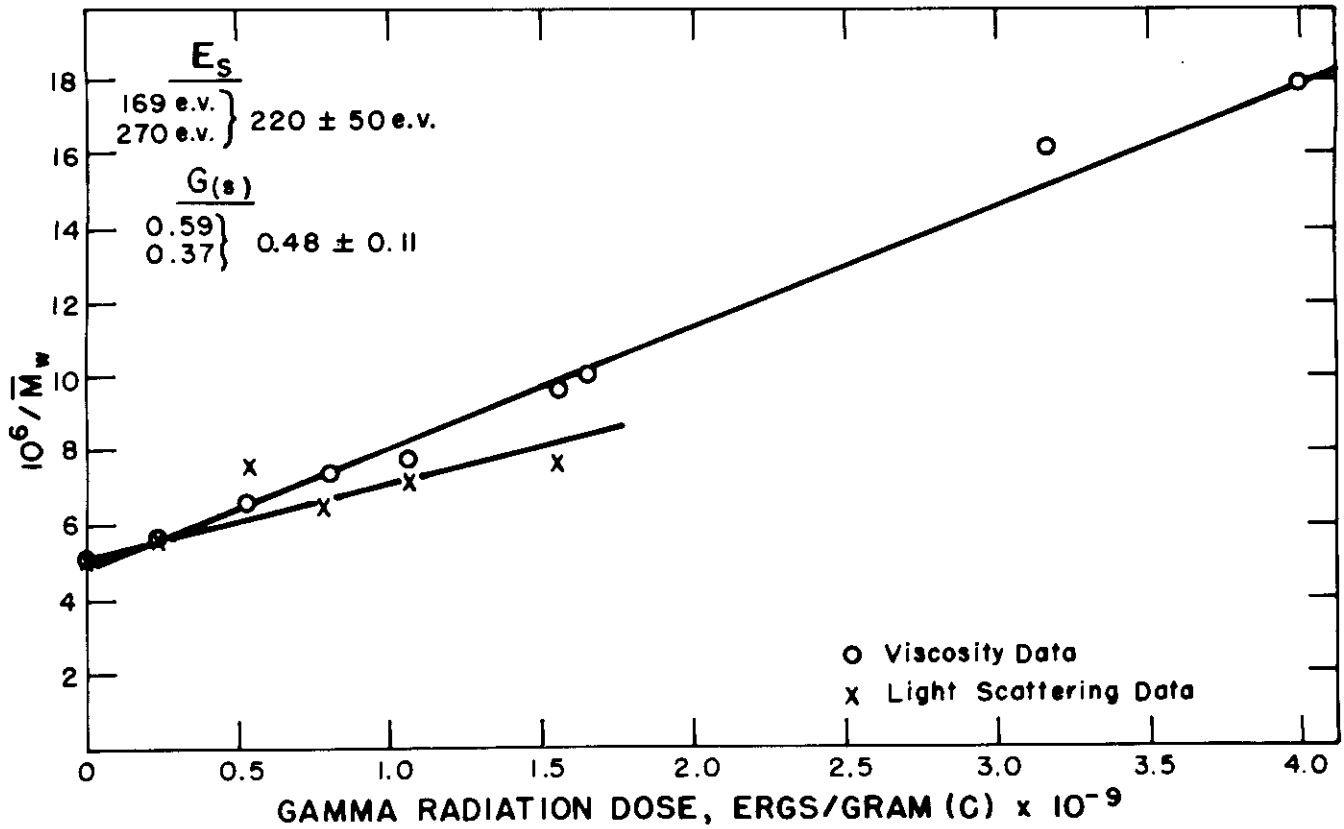

FIGURE 4. VARIATION IN MOLECULAR WEIGHT WITH RADIATION DOSE FOR POLY(PHENYL ACRYLATE).

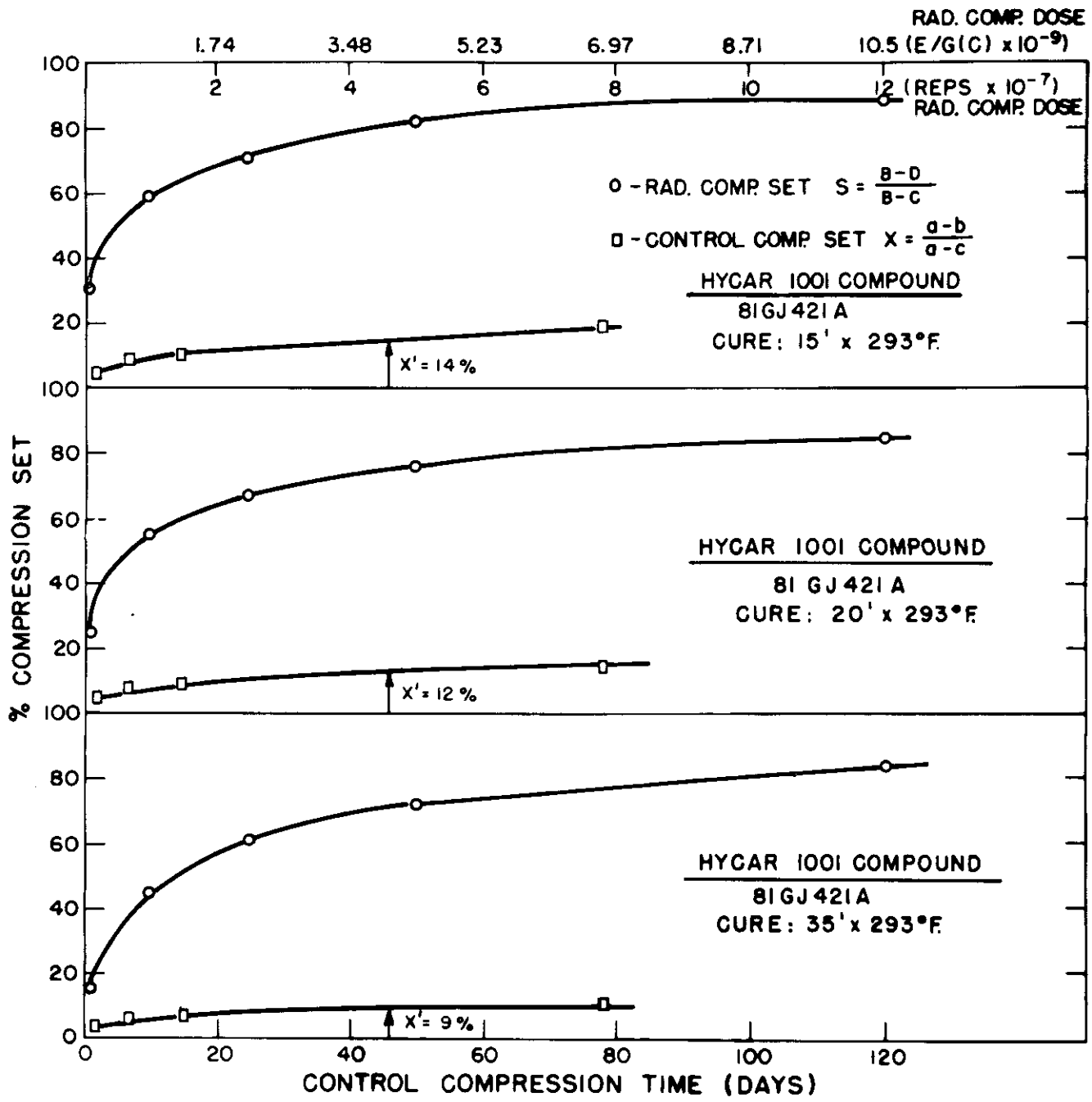

Figure 5. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

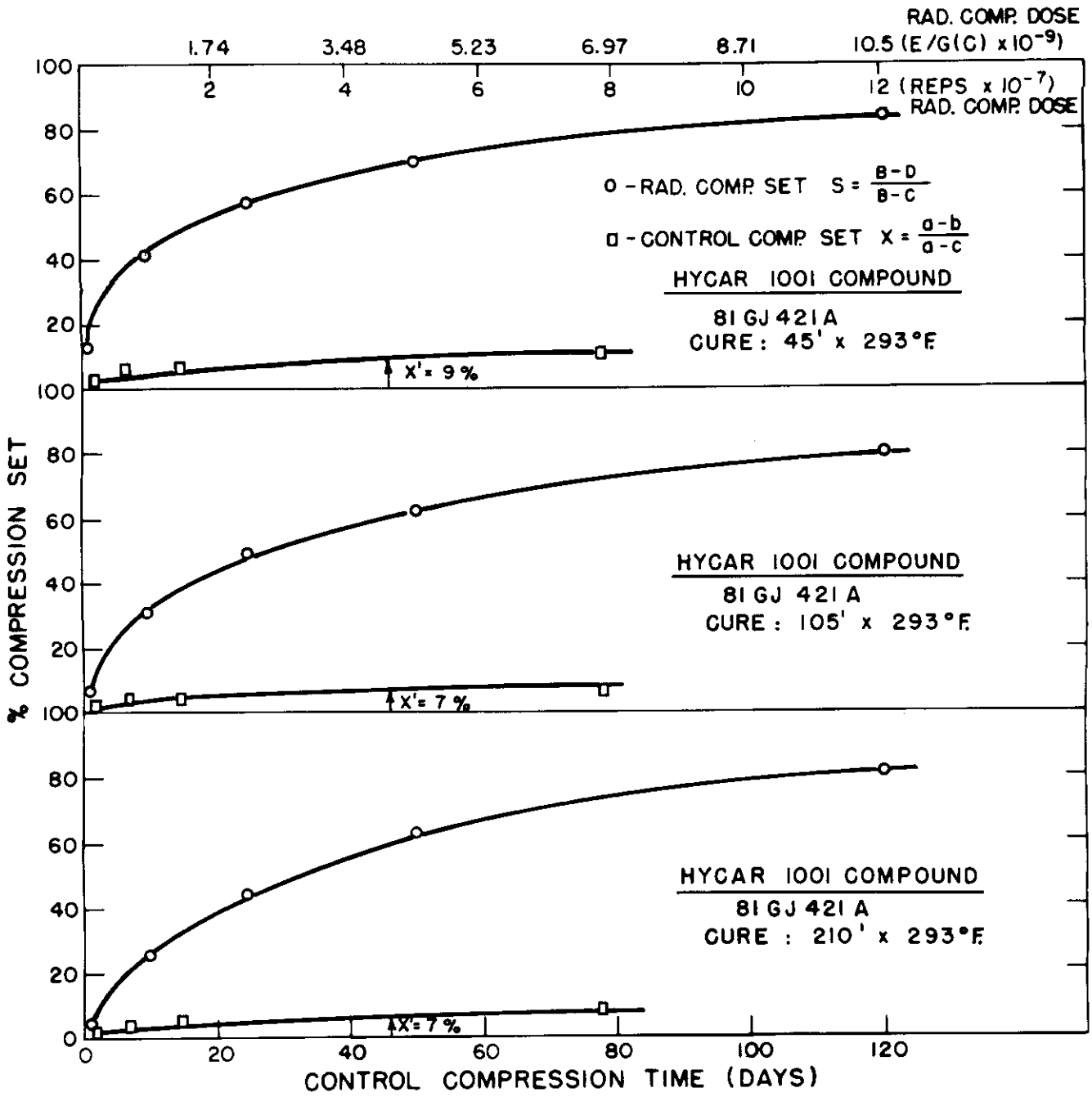

Figure 6. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

% COMPRESSION SET vs. EXPOSURE

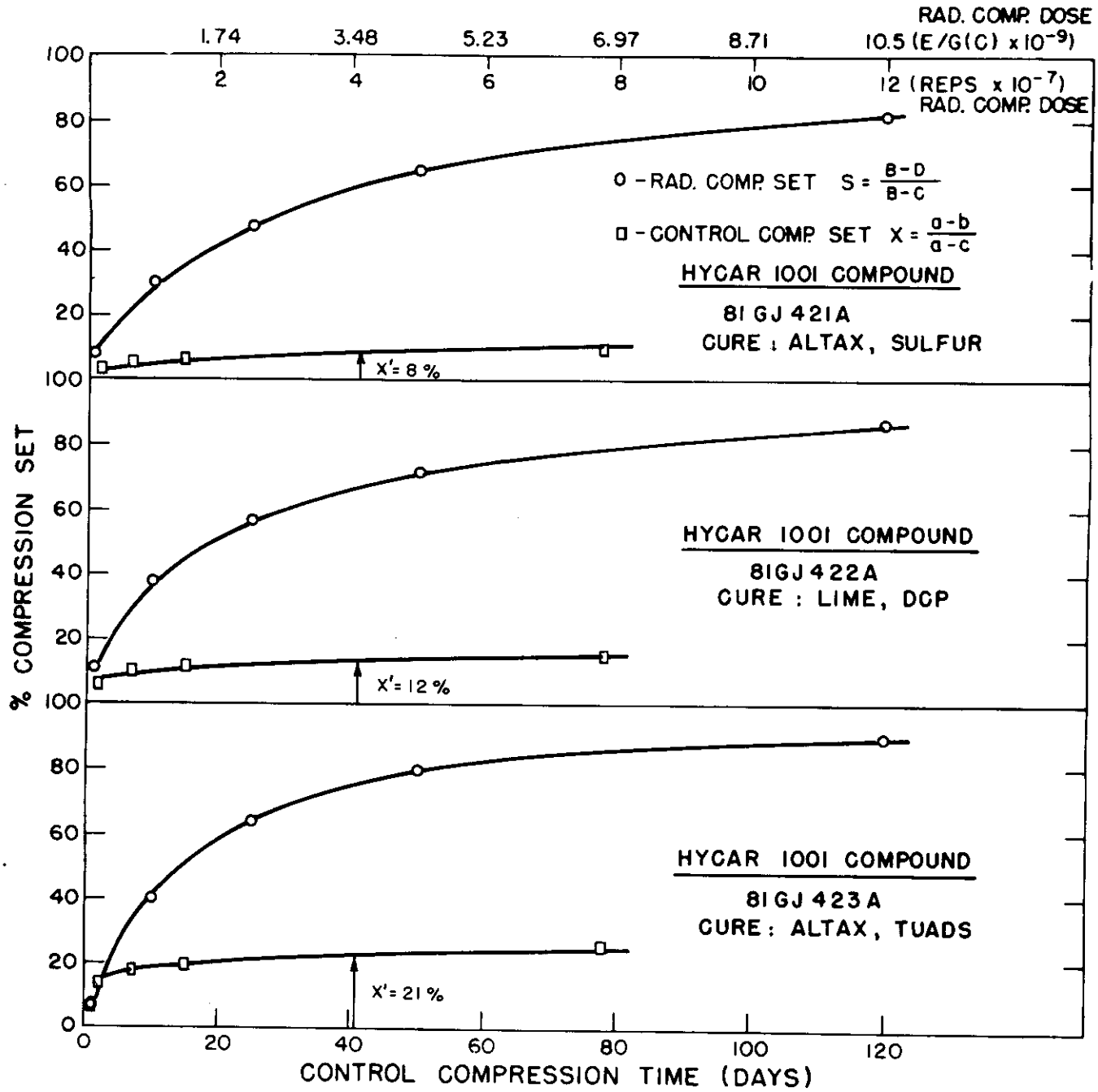

Figure 7. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

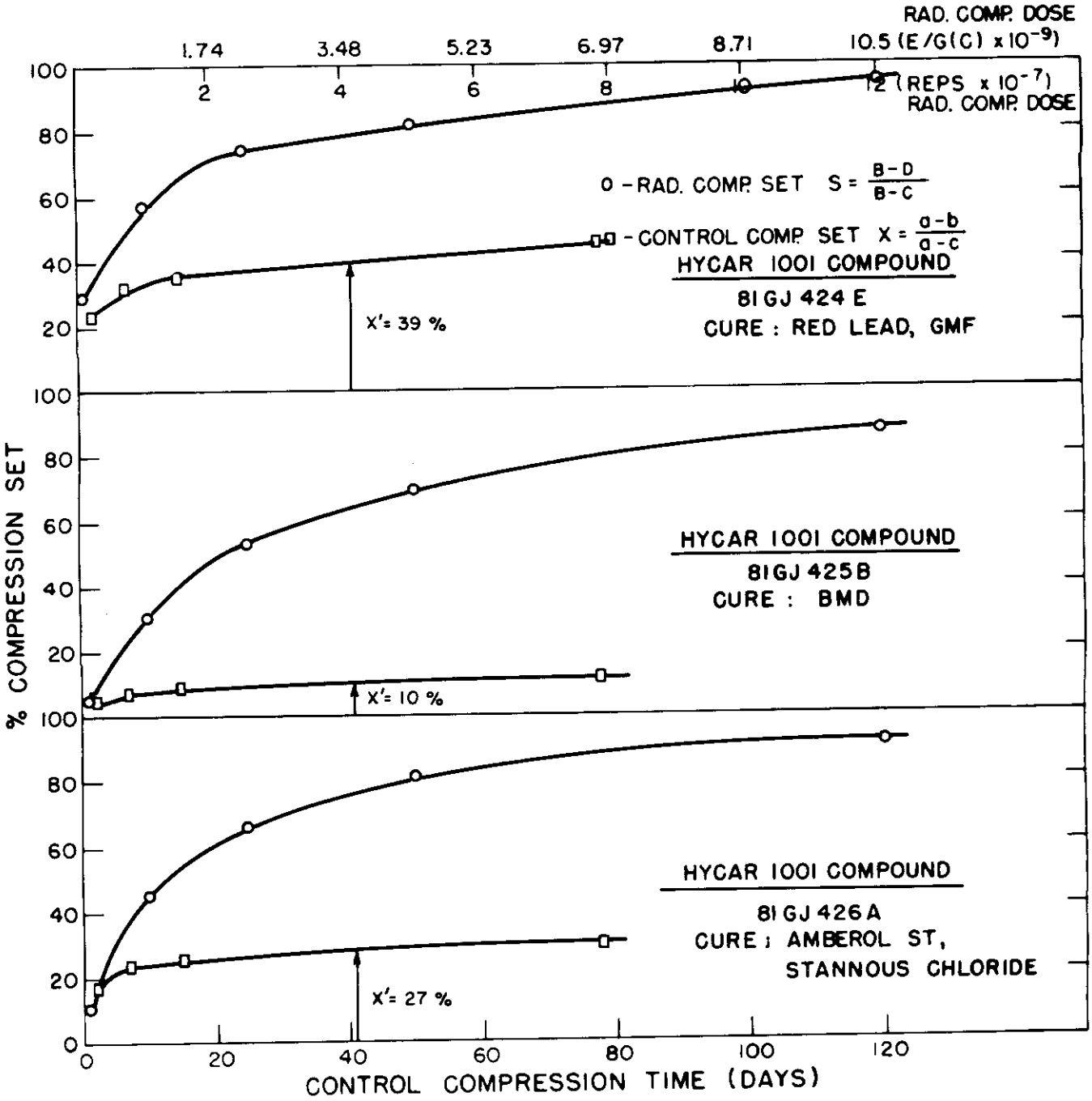

Figure 8. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

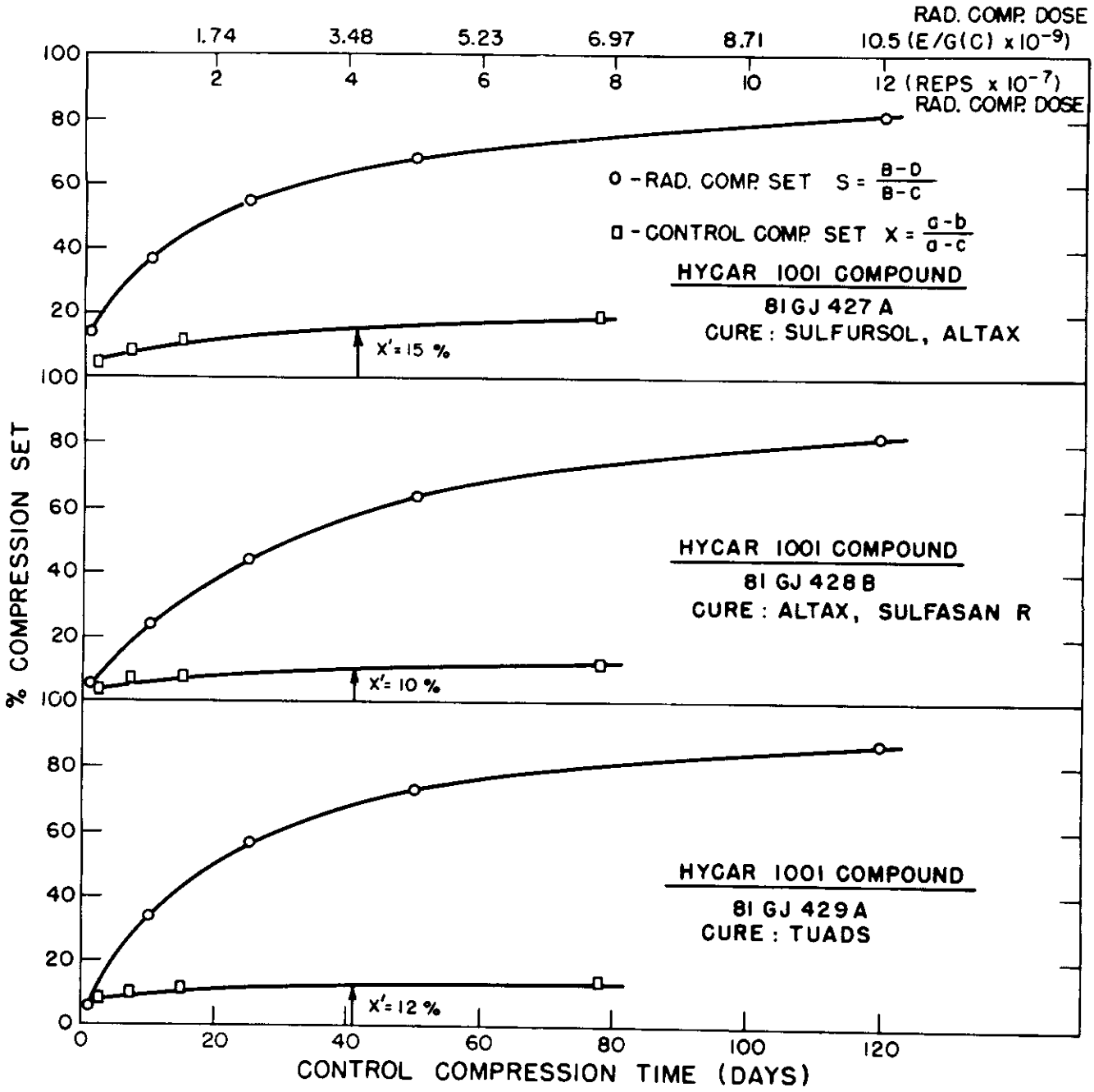

Figure 9. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

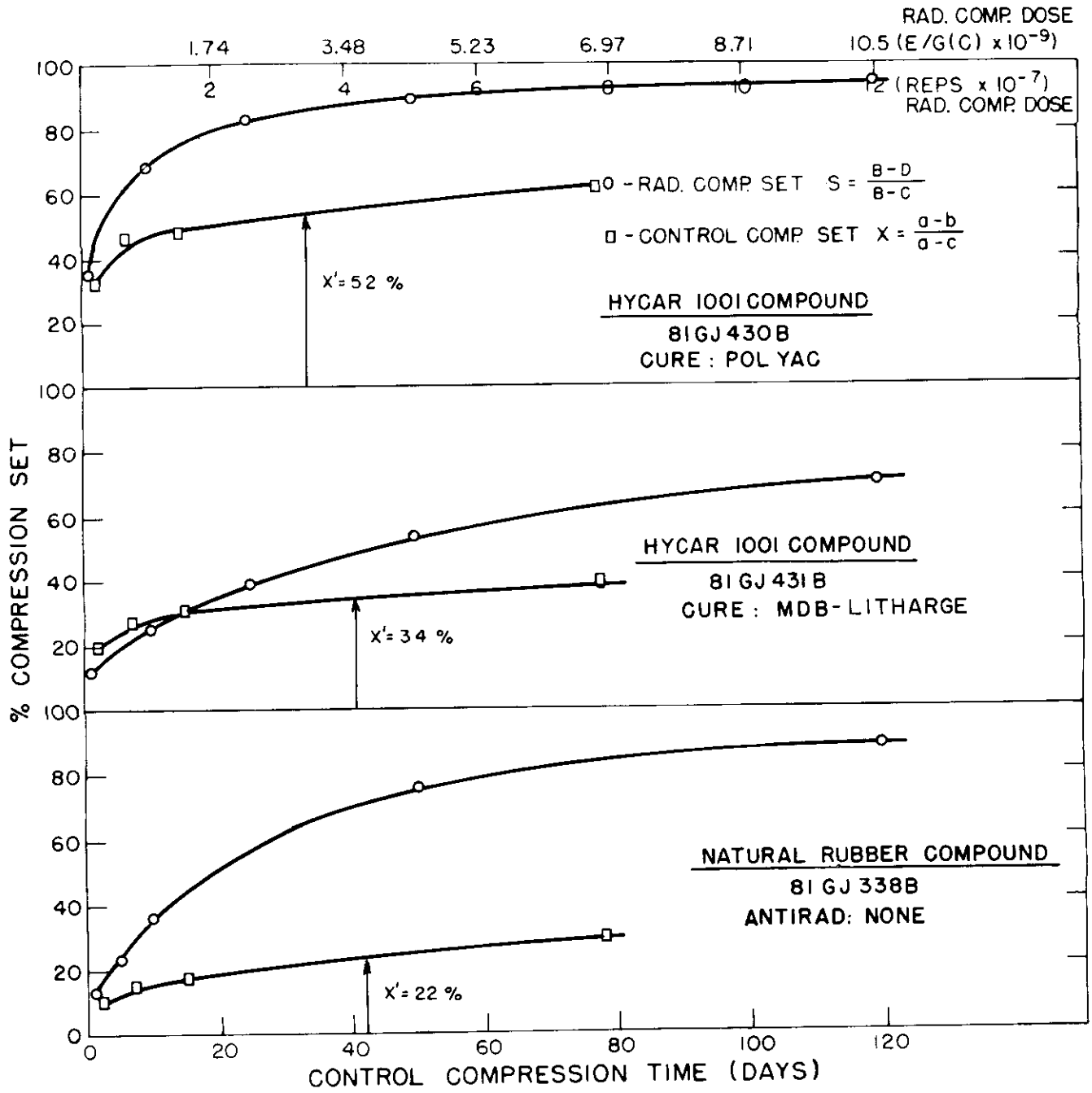

Figure 10 THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

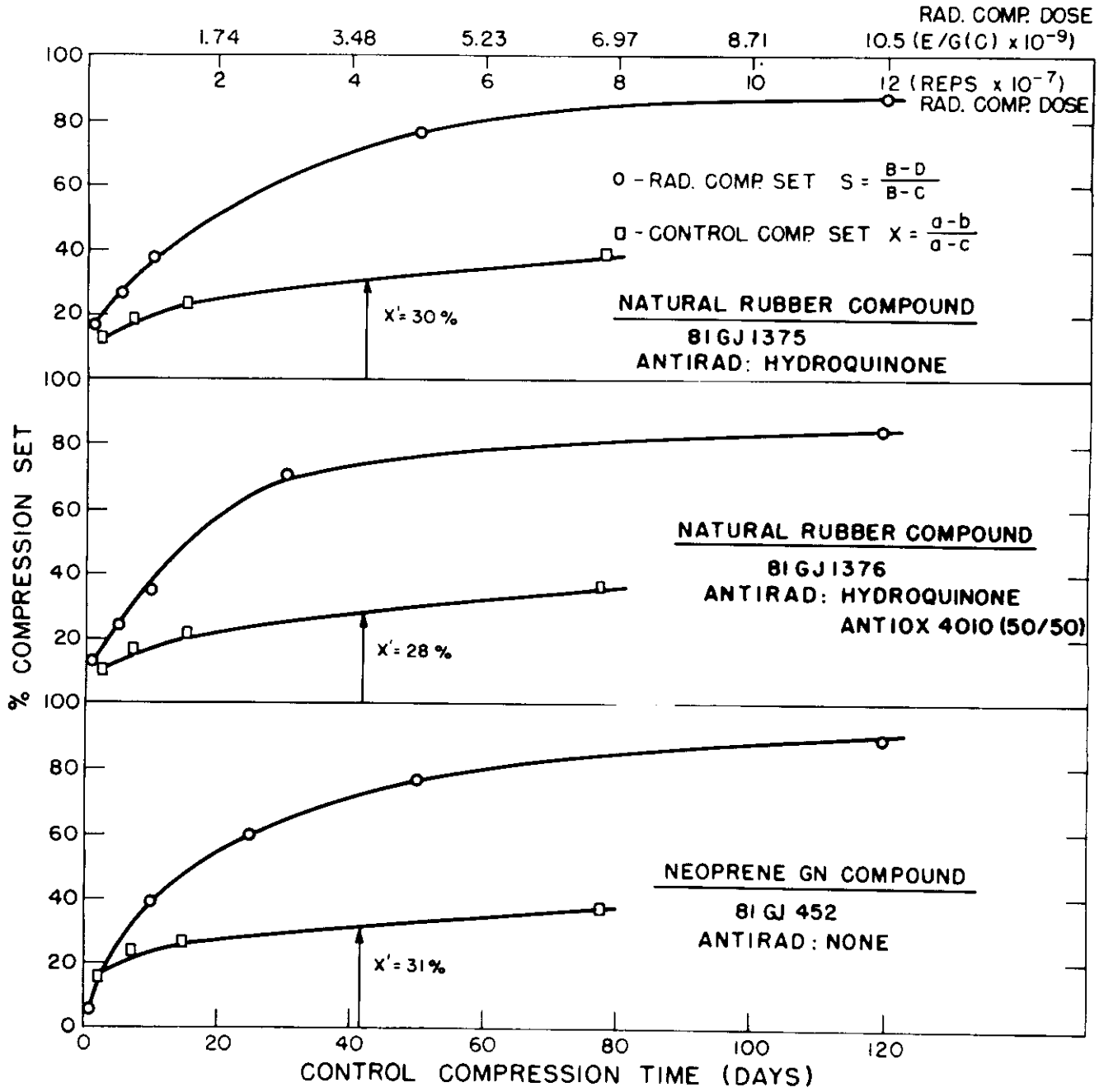

Figure 11. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

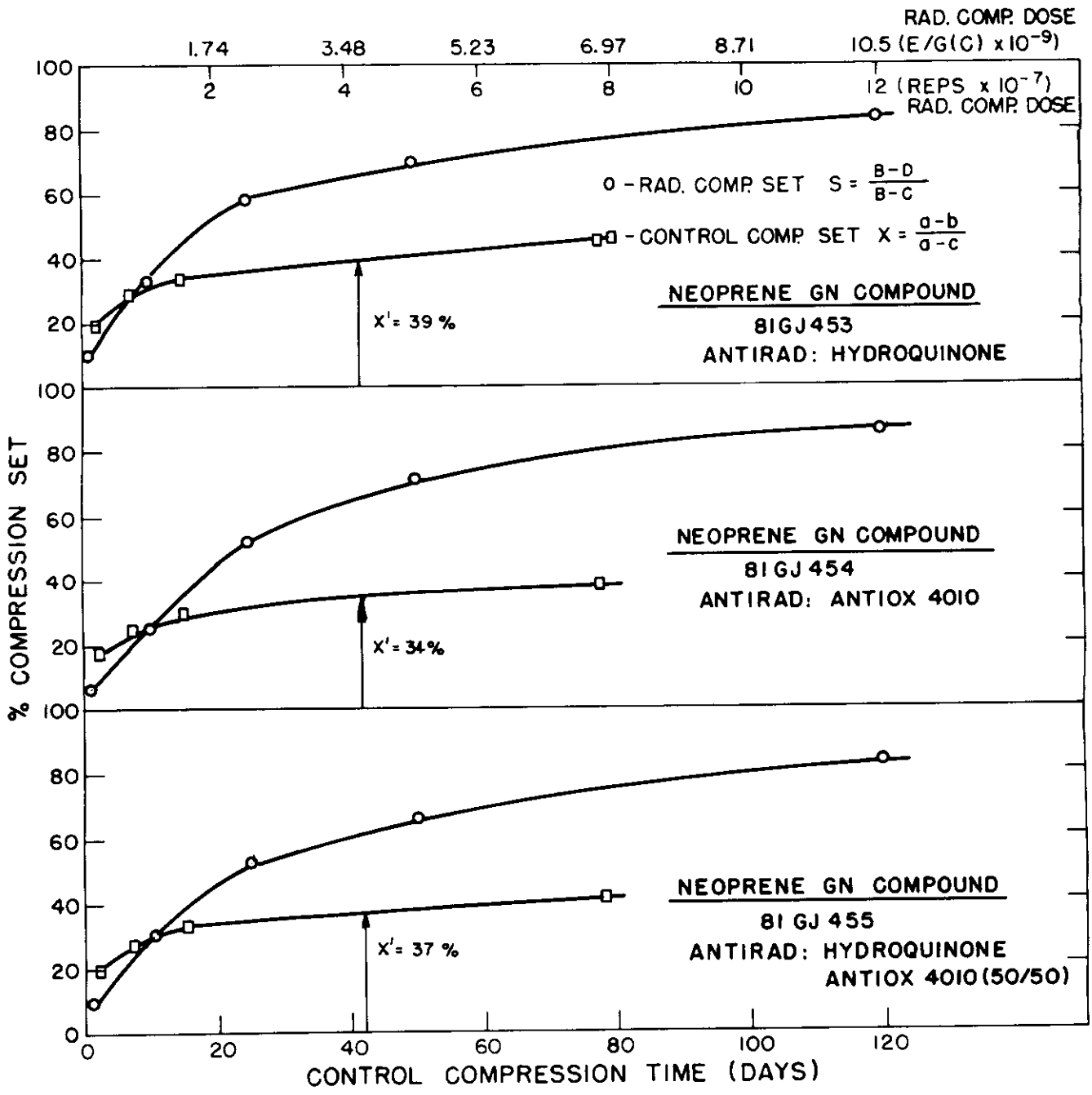

Figure 12. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

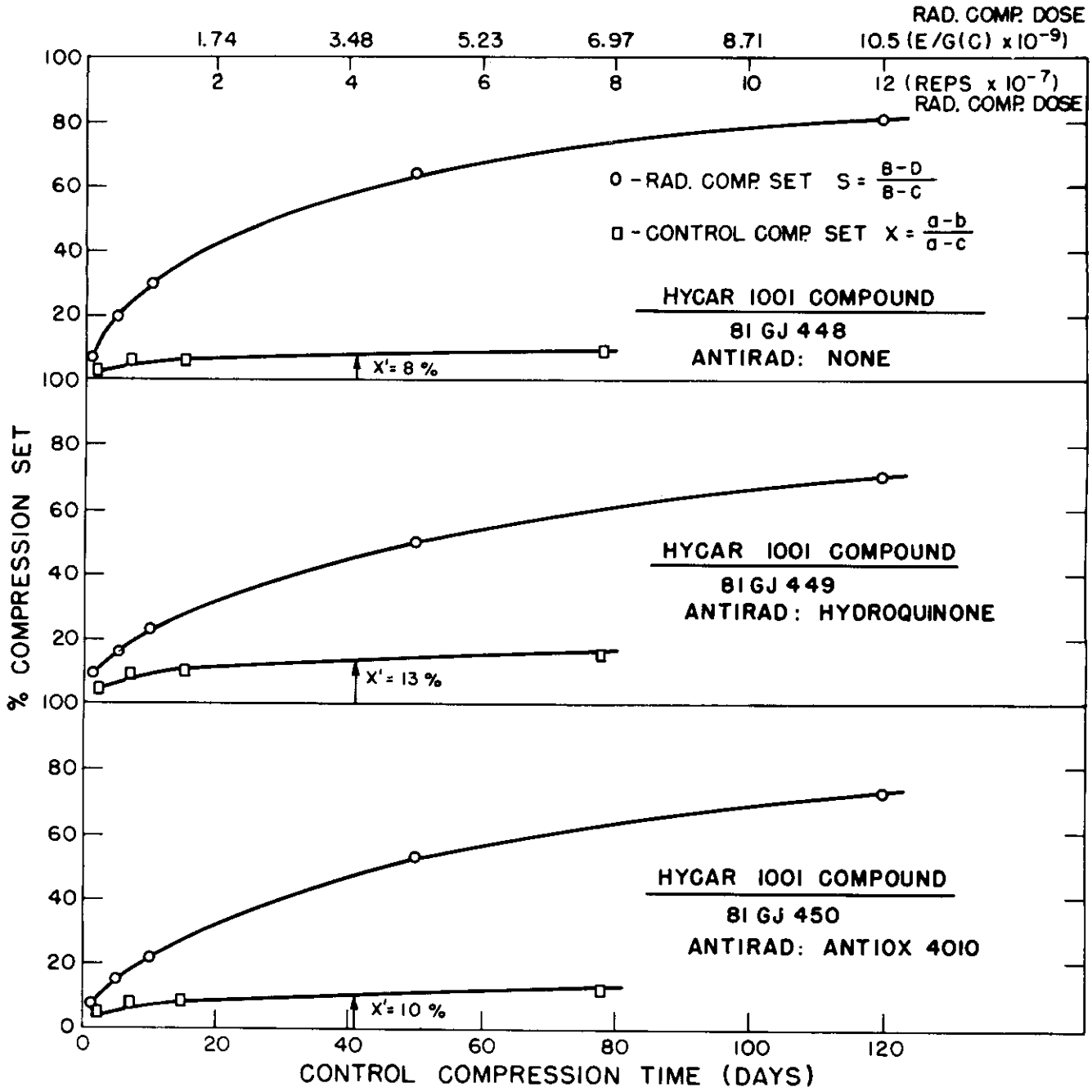

Figure 13. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

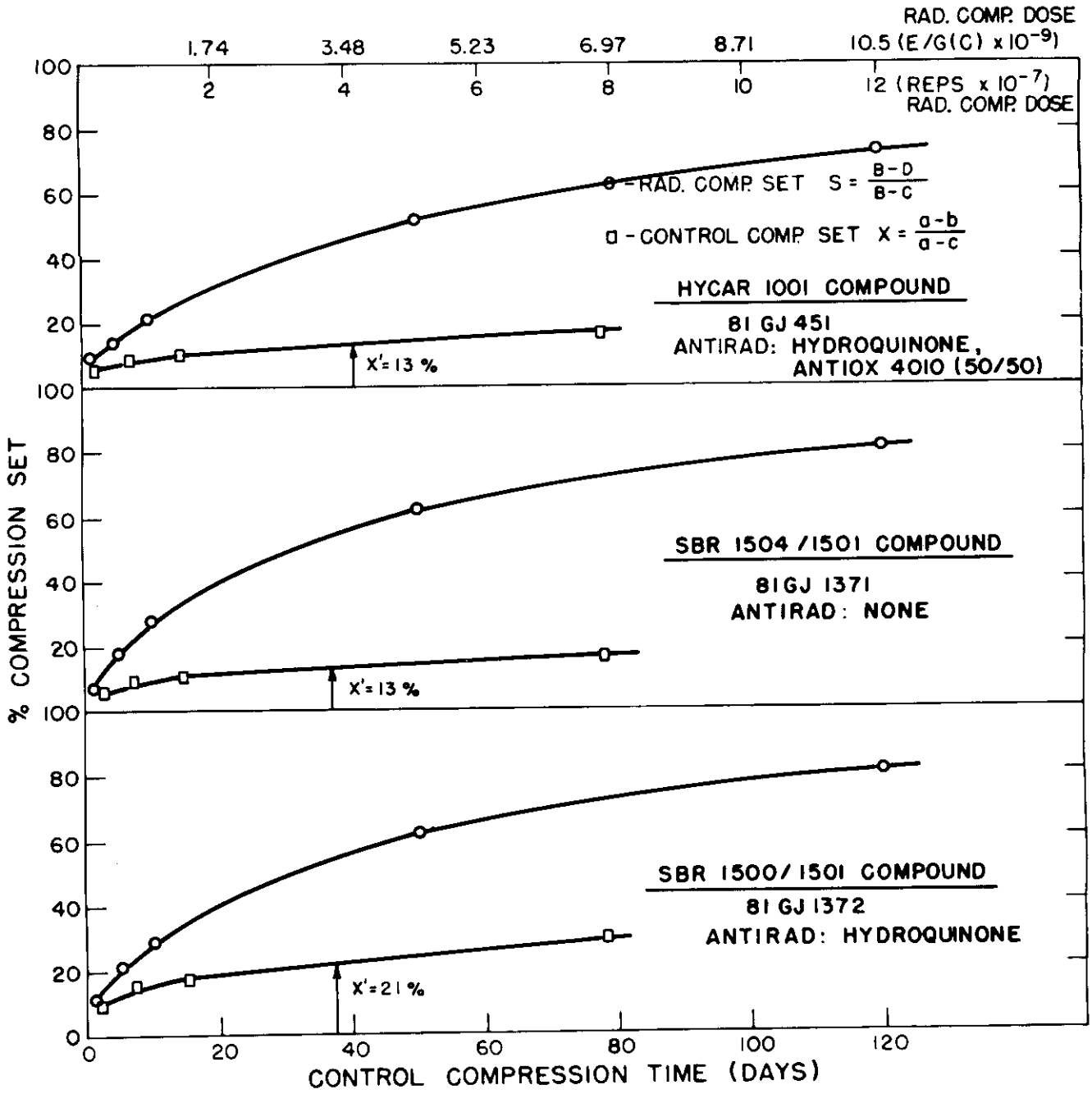

Figure 14. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

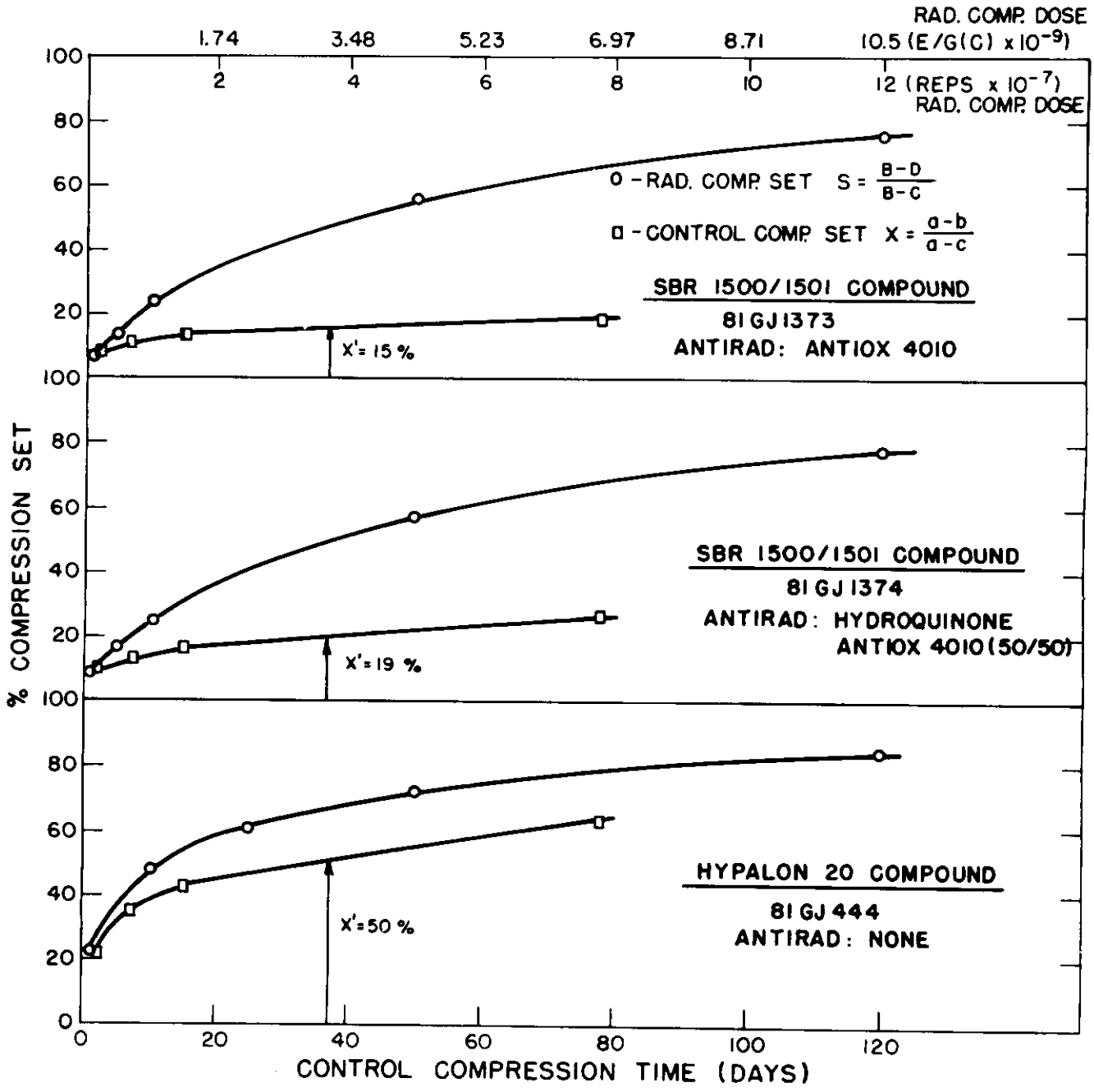

Figure 15. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

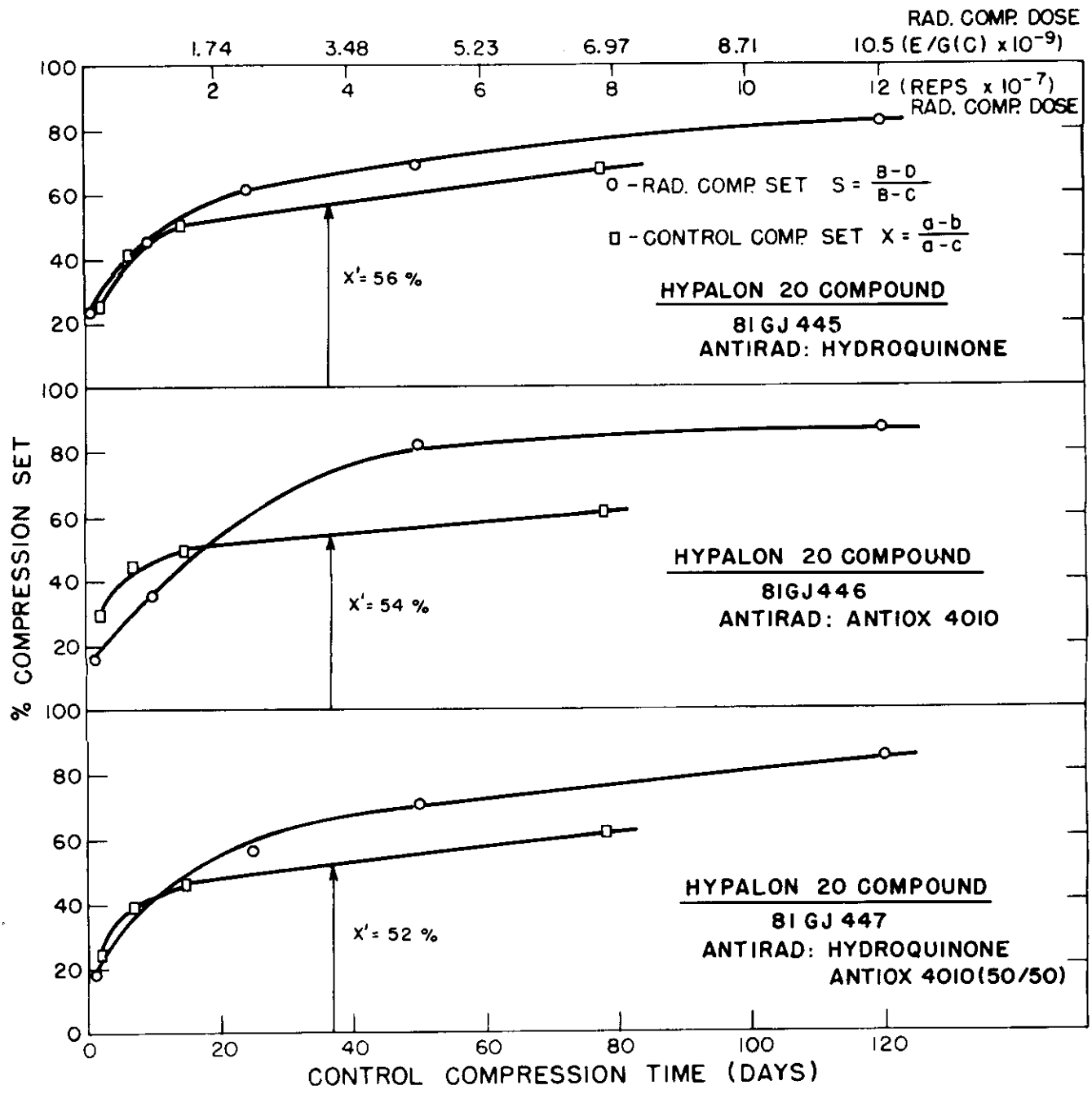

Figure 16. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

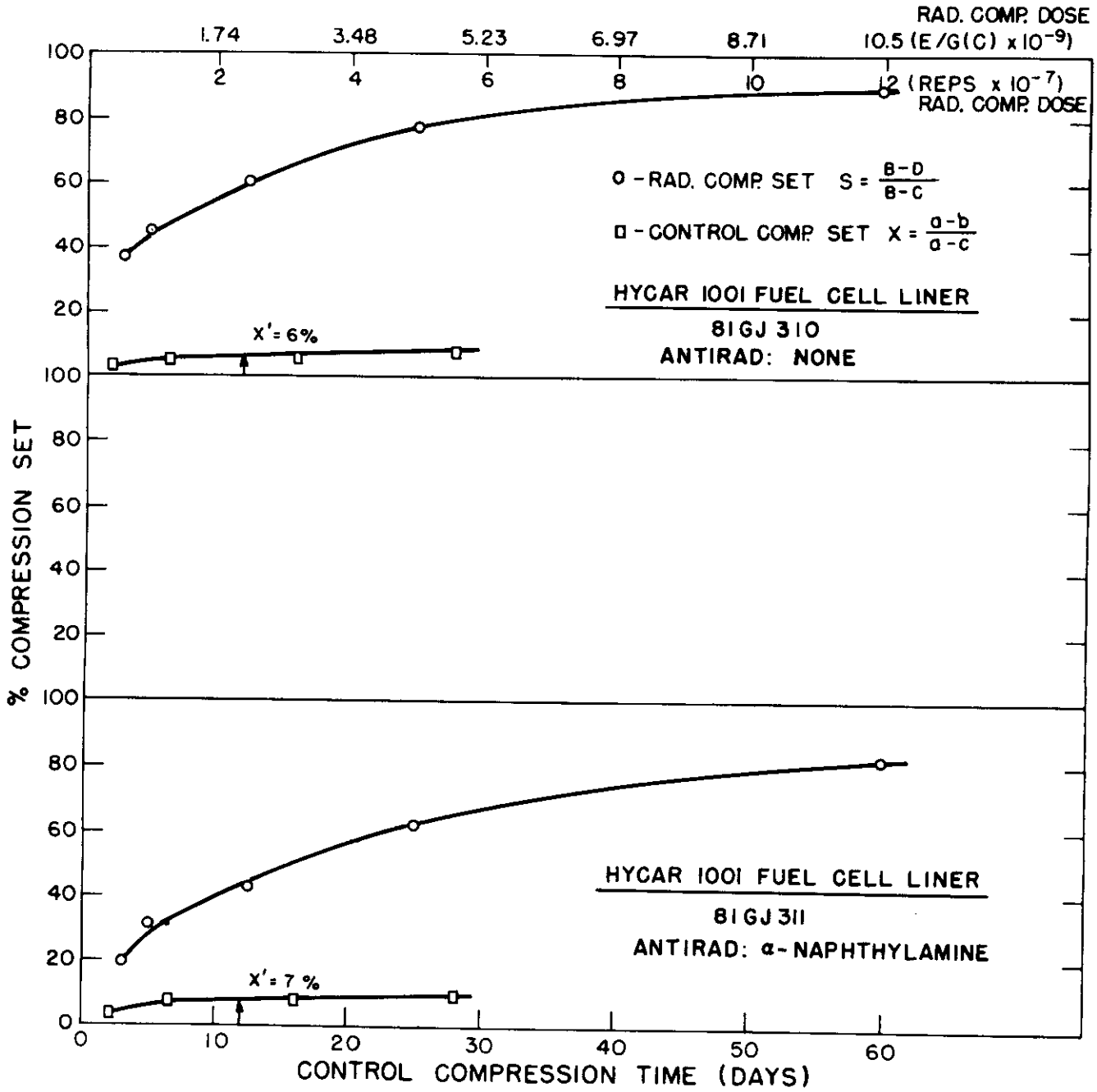

Figure 17. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

% COMPRESSION SET vs. EXPOSURE

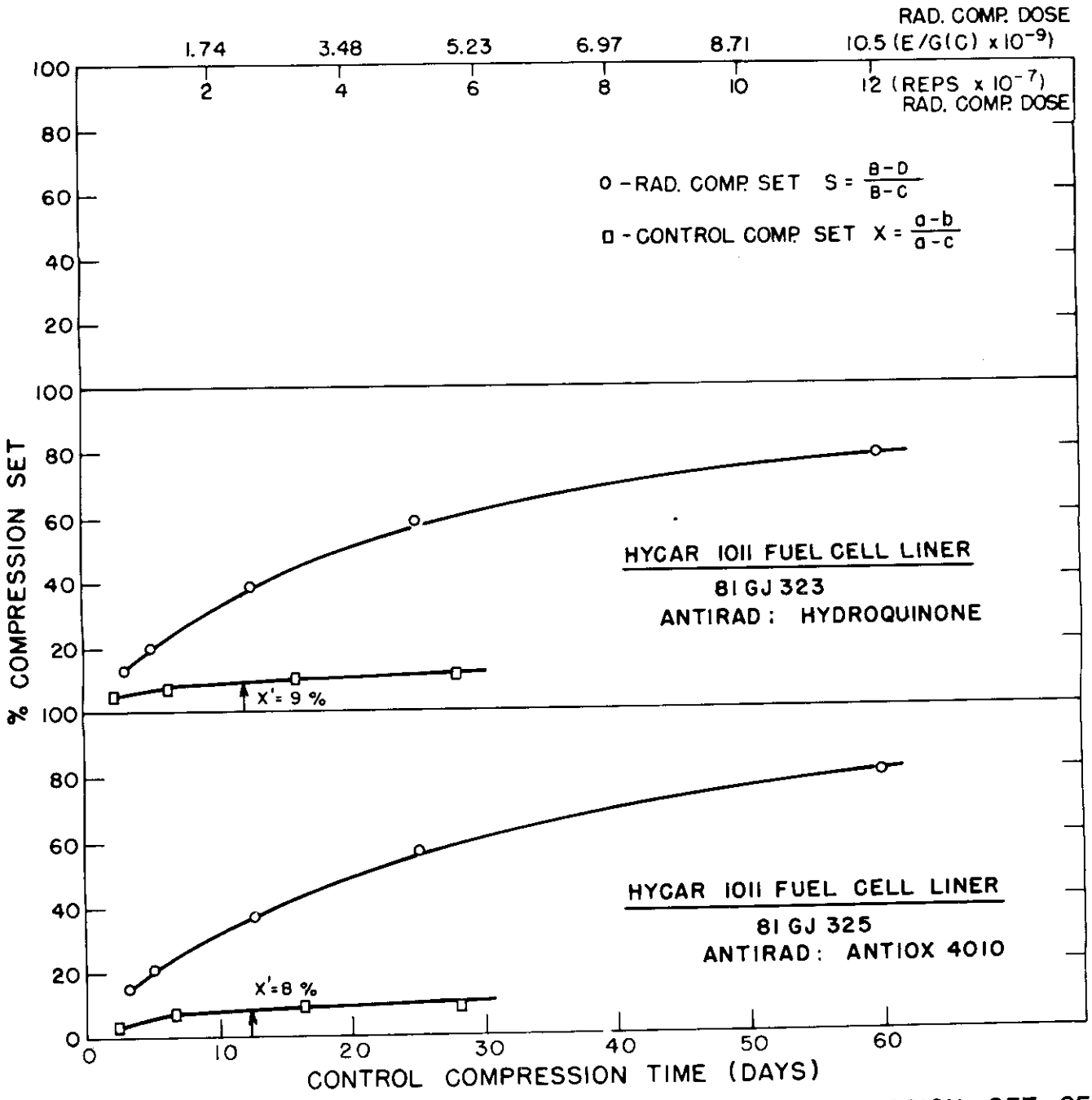

Figure 18. THE EFFECT OF GAMMA RADIATION ON THE COMPRESSION SET OF VARIOUS COMPOUNDS AT R.T. IN AIR.

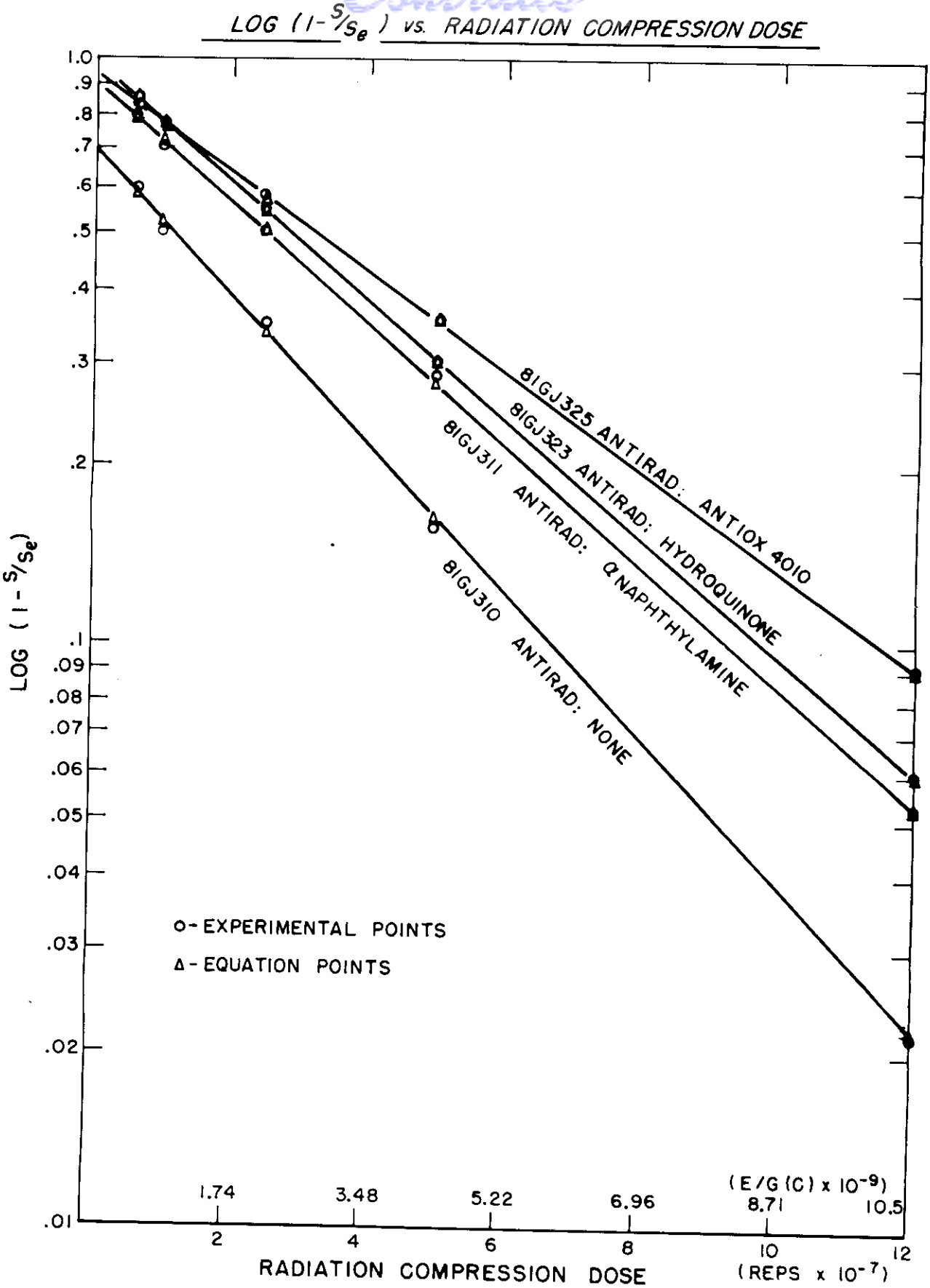

Figure 19. THE EFFECT OF GAMMA RADIATION ON HYCAR (NBR) FUEL CELL LINER STOCK AT R.T. IN AIR.

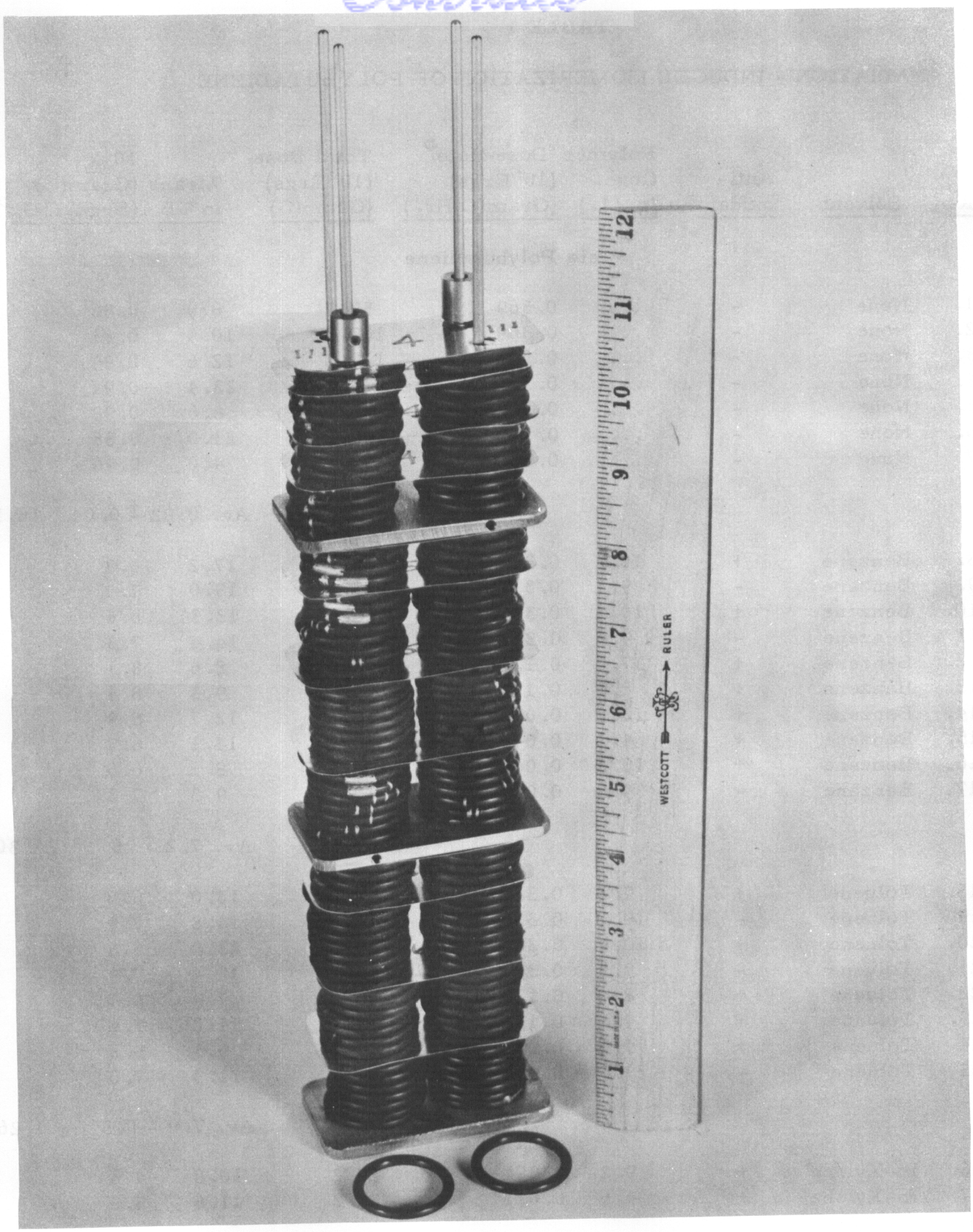

Figure 20. "O" RING SAMPLE ASSEMBLY FOR γ-IRRADIATION.

TABLE 1

RADIATION - INDUCED ISOMERIZATION OF POLYBUTADIENE

Run	Solvent	Anti-oxidant[a]	Polymer Conc. (g./l.)	Dose Rate[b] (10^8Ergs) (Gram(C)Hr.)	Total Dose (10^8Ergs) (Gram(C)	%trans in CB	$10^7 \frac{k}{}$ (Gram(C) (Ergs)	G_o[b]
				cis Polybutadiene				
1.	None	-	...	0.369	59.2	6.9	0.86	
2.	None	-	...	0.369	105.3	10.9	0.91	
3.	None	-	...	0.369	118.2	12.6	0.99	
4.	None	-	...	0.345	274.1	22.4	0.91	
5.	None	-	...	0.122	71.3	8.6	0.98	
6.	None	-	...	0.122	256.1	21.0	0.88	
7.	None	-	...	0.076	19.9	4.0	0.90	
						Av.	0.92 ± 0.04	16.1
8.	Benzene	+	10.2	0.379	25.1	17.2	6.8	
9.	Benzene	-	9.5	0.379	25.1	19.0	7.9	
10.	Benzene	+	10.2	0.379	18.8	13.3	6.6	
11.	Benzene	-	9.5	0.379	18.8	14.4	7.3	
12.	Benzene	+	17.6	0.127	9.0	8.6	8.1	
13.	Benzene	+	8.8	0.127	9.0	9.1	8.4	
14.	Benzene	+	10.2	0.070	20.2	12.7	5.9	
15.	Benzene	+	4.1	0.070	20.2	14.1	6.7	
16.	Benzene	+	10.2	0.069	10.1	8.1	6.6	
17.	Benzene	-	9.5	0.069	10.1	9.3	7.6	
						Av.	7.2 ± .6	1.30
18.	Toluene	+	9.1	0.380	18.0	13.0	6.8	
19.	Toluene	-	10.7	0.380	18.0	14.8	7.9	
20.	Toluene	+	10.9	0.380	18.8	13.8	6.8	
21.	Toluene	-	9.5	0.380	18.8	15.4	7.9	
22.	Toluene	+	8.4	0.127	9.0	7.9	6.7	
23.	Toluene	+	9.1	0.127	13.5	11.0	7.0	
24.	Toluene	+	9.1	0.074	14.1	9.5	5.8	
25.	Toluene	-	11.0	0.074	14.1	11.3	7.0	
						Av.	7.0 ± 0.5	1.26
26.	m-Xylene	+	9.2	0.071	20.2	10.8	4.8	
27.	m-Xylene	+	4.6	0.071	20.2	11.6	5.2	
						Av.	5.0 ± 0.2	0.89

TABLE 1 (cont'd)

RADIATION - INDUCED ISOMERIZATION OF POLYBUTADIENE

Run	Solvent	Anti-oxidant[a]	Polymer Conc. (g./l.)	Dose Rate[b] (10^8Ergs) (Gram(C)Hr.)	Total Dose (10^8Ergs) (Gram(C))	%trans in CB	10^7k (Gram(C) (Ergs)	G_o[b]
			cis Polybutadiene					
28.	Ethyl benzene	+	12.4	0.375	34.1	16.3	4.8	
29.	Ethyl benzene	+	12.4	0.365	16.7	9.0	4.6	
						Av. 4.7 ± 0.1		0.84
30.	Tetralin	+	10.6	0.353	41.0	11.6	2.6	0.46
31.	Benzene-d_6	+	10.8	0.344	89.5	46.4	7.6	
32.	Benzene-d_6	+	10.8	0.344	167.0	63.4	7.4	
33.	Benzene-d_6	+	10.8	0.343	238.5	71.7	7.6	
						Av. 6.2 ± 0.1		1.35
			trans Polybutadiene					
						%cis in TB	10^7 K' (Gram(C) (Ergs)	G'o
34.	None	-	...	0.351	254.4	6.5	0.20[c]	3.90
35.	Benzene-d_6	-	10.2	0.344	89.4	11.4	1.8	
36.	Benzene-d_6	-	10.2	0.344	167.0	15.1	1.6	
37.	Benzene-d_6	-	10.2	0.343	238.5	17.3	1.7	
						Av. 1.6 ± 0.1		0.30

[a] The plus and minus signs indicate the presence and absence of antioxidant, respectively. [b] One rad (water) is equivalent to 90.0 ergs per gram (carbon). [c] Calculated on the basis of a 1% polymer solution by weight in the solution isomerization case. [d] This value is somewhat uncertain due to the difficulty of detecting small changes in *cis* content in TB.

TABLE 2

IDENTITY AND RADIATION STABILITY OF RELATED POLYMERS

	Polymer	$\bar{M}_w$	G(x)	B/α	[η] @25°C.
A.	EA/MA (90/10) + α - Naphthylamine	8,995	0.88	0.34	0.366 (MEK)
	EA/MA (90/10) + α - Naphthylamine	64,600[a]	0.12[b]	—	—
B.	EA/MA (90/10) + Aniline	65,600	0.21	0.32	0.377 (MEK)
C.	EA/MA (90/10) + 4 - Aminodiphenyl	59,700	0.19	0.45	0.347 (MEK)
D.	EA/MA (90/10) + Diphenylamine	68,500	0.25	0.20	0.344 (MEK)
E.	EA/MA (90/10)	647,000	0.74	0.00	0.495 (MEK)
F.	Ethyl Acrylate (EA)	127,000	0.37	0.20	0.453 (MEK)
G.	2 - Ethylhexyl Acrylate (2-EHA)	7,930,000	0.45	0.24	3.75 (C_6H_6)
H.	N - Vinyl Carbazole (NVC)	111,000	0.022	—	0.192 (Tol.)
I.	Phenyl Acrylate	244,000	0.054	0.48	0.535 (MEK)

a, b These values result from using for A the average of the $\bar{M}_w$'s for B, C, and D.

TABLE 3

RECIPES FOR RADIATION - INDUCED COMPRESSION SET STUDIES

1. Hycar 1001 Compound (Base Recipe) :

Pigment	Parts by Weight
Hycar 1001	100
SRF Black	50
Zinc Oxide	5
Stearic Acid	0.5
	155.5

Specific Gravity = 1.19

With the Various Curatives:

Compound No.	Curative	Parts by Weight
81GJ 421A	Altax	3.0
	Sulfur	2.0
81 GJ 422A	Hydrated Lime	4.0
	DCP	1.5
81GJ 423A	Altax	2.0
	Tuads	3.0
81GJ 424E	GMF	0.33
81GJ 425B	BMD	4.0
	Litharge	3.0
81GJ 426A	Amberol ST	12.0
	Stannous Chloride	1.5
81GJ 427A	Altax	3.0
	Sulfur Donor	4.0
81GJ 428B	Altax	2.0
	Sulfasan R	3.0
81GJ 429A	Tuads	4.0
81GJ 430B	Polyac	2.0
81GJ 431B	MDB -Litharge	7.5

TABLE 3 (cont'd)

RECIPES FOR RADIATION - INDUCED COMPRESSION SET STUDIES

2. Natural Rubber Compound:

81GJ 338B (Base Recipe - No Additive):

Pigment	Parts by Weight
Natural Rubber	100.
Age - Rite Powder	1.0
EPC Black	50.
Zinc Oxide	5.0
Stearic Acid	3.0
Altax	1.0
Sulfur	3.0
	163.0

Specific Gravity = 1.14

With 3 phr of Potential Antirad:

81GJ 1375 : Hydroquinone

81GJ 1376 : Hydroquinone / Antiox 4010 (50/50)

3. Neoprene GN Rubber Compound:

81GJ 452 (Base Recipe - No Additive) :

Pigment	Parts by Weight
Neoprene GN	100
EPC Black	35
Zinc Oxide	5.0
Stearic Acid	1.0
Magnesium Oxide	4.0
	145.0

Specific Gravity = 1.40

With 5 phr of Potential Antirad:

81GJ 453 : Hydroquinone

81GJ 454 : Antiox 4010

81GJ 455 : Hydroquinone / Antiox 4010 (50/50)

TABLE 3 (cont'd)

RECIPES FOR RADIATION - INDUCED COMPRESSION SET STUDIES

4. Hycar 1001 Rubber Compound:

81GJ 448 (Base Recipe - No Additive):

Pigment	Parts by Weight
Hycar 1001	100
SRF Black	50
Zinc Oxide	5.0
Altax	3.0
Sulfur	2.0
	160.0

Specific Gravity = 1.19

With 5 phr of Potential Antirad:

81GJ 449 : Hydroquinone

81GJ 450 : Antiox 4010

81GJ 451 : Hydroquinone / Antiox 4010 (50/50)

5. SBR 1500/1501 Rubber Compound:

81GJ 1371 (Base Recipe - No Additive):

Pigment	Parts by Weight
SBR 1500/1501	100
EPC Black	40
Zinc Oxide	5.0
Stearic Acid	1.5
Altax	3.0
Sulfur	2.0
	153.5

Specific Gravity = 1.13

With 5 phr of Potential Antirad:

81GJ 1372 : Hydroquinone

81GJ 1373 : Antiox 4010

81GJ 1374 : Hydroquinone / Antiox 4010 (50/50)

TABLE 3 (cont'd)

RECIPES FOR RADIATION - INDUCED COMPRESSION SET STUDIES

6. Hypalon 20 Rubber Compound:

81GJ 444 (Base Recipe - No Additive):

Pigment	Parts by Weight
Hypalon 20	100
HAF Black	20
Rosin	2.5
Tetrone A	1.0
Magnesium Oxide	30.0
	153.5

Specific Gravity - 1.34

With 5 phr of Potential Antirad:

81GJ 445 : Hydroquinone

81GJ 446 : Antiox 4010

81GJ 447 : Hydroquinone / Antiox 4010 (50/50)

7. Hycar 1011 Fuel Cell Liner Rubber Compound:

81GJ 310 (Base Recipe - No Additive):

Pigment	Parts by Weight
Hycar 1011	100
SRF Black	80
Zinc Oxide	5.0
Stearic Acid	1.0
Dibutyl Phthalate	30
TMTM	0.3
Altax	1.0
Sulfur	1.0
	218.3

Specific Gravity = 1.24

With 5 phr of Potential Antirad:

81GJ 311 : Alpha - Naphthylamine

81GJ 323 : Hydroquinone

81GJ 325 : Antiox 4010

TABLE 4

STRESS - STRAIN, HARDNESS, AND CURE DATA FOR COMPOUNDS IN THE COMPRESSION SET STUDIES

Compound Number 81GJ-	Compression Set Cure * (Min. @293°F.)	Tensile Strength (psi)	Ultimate Elongation (%)	(Percent) Modulus (psi) [1]	Shore A Hardness
(1) Hycar 1001 Rubber Compound:					
421A	15	3410	540	1100 (M_2)	73
421A	20	3300	440	1420 (M_2)	—
421A	35	3250	370	1790 (M_2)	75
421A	45	3060	300	2050 (M_2)	73
421A	105	3300	240	2290 (M_2)	76
421A	210	—	200	2400 (M_2)	—
421A	100	2830	240	2290 (M_2)	72
422A	100	3540	300	2020 (M_2)	68
423A	100	3110	620	700 (M_2)	63
424E	240	3420	570	890 (M_2)	65
425B	80	2910	390	1320 (M_2)	68
426A	140	3130	520	980 (M_2)	69
427A	140	3190	440	1450 (M_2)	66
428B	100	3010	330	1770 (M_2)	68
429A	140	3320	470	1130 (M_2)	64
430B	240	2900	500	710 (M_2)	64
431B	140	3120	350	2090 (M_2)	70
(2) Natural Rubber Compound:					
338B	50	3060	540	1600 (M_3)	61
1375	50	3780	510	2000 (M_3)	77
1376	50	3880	510	1870 (M_3)	70

* block 4 x 2-1/2 x 1/2"

TABLE 4 (cont'd)

STRESS-STRAIN, HARDNESS, AND CURE DATA
FOR COMPOUNDS IN THE COMPRESSION SET STUDIES

Compound Number 81GJ-	Compression Set Cure (Min. @293°F.)	Tensile Strength (psi)	Ultimate Elongation (%)	(Percent) Modulus (psi)[1]	Shore A Hardness
(3) Neoprene GN Rubber Compound:					
452	105	3700	260	1580 (M_2)	69
453	85	3040	380	2420 (M_3)	71
454	105	3240	500	1980 (M_3)	66
455	85	3140	440	2030 (M_3)	68
(4) Hycar 1001 Rubber Compound:					
448	100	2880	250	2290 (M_2)	76
449	100	2640	260	1740 (M_2)	74
450	100	2840	280	1980 (M_2)	76
451	100	2810	290	1880 (M_2)	75
(5) SBR 1500 / 1501 Rubber Compound:					
1371	140	2920	430	1570 (M_3)	60
1372	120	2320	410	1430 (M_3)	63
1373	70	2320	410	1430 (M_3)	58
1374	100	2420	450	1290 (M_3)	62
(6) Hypalon 20 Rubber Compound:					
444	80	2840	200	2840 (M_2)	82
445	80	2500	240	2460 (M_2)	82
446	40	2630	250	2140 (M_2)	78
447	40	2840	250	2480 (M_2)	78
(7) Hycar 1011 Fuel Cell Liner Rubber Compound:					
310	30	1980	380	1640 (M_3)	54
311	120	1910	470	1270 (M_3)	53
323	140	1800	430	1280 (M_3)	47
325	110	1950	420	1470 (M_3)	54

[1] M_2 represents 200% Modulus and M_3, 300% Modulus.

TABLE 5

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

Legend:

t	=	Control Compression Time (Days)
x	=	Control Compression Set at Time (t)
t'	=	Pre-irradiation Compression Time (Days)
x'	=	Control Compression Set at time (t')
R'	=	Gamma Radiation Dose in ergs/g (c) x 10^{-9}*
S	=	Compression Set at Radiation Dose (R')
PC	=	Per Cent Compression

	CONTROL DATA		RADIATION TEST DATA			
Compound:	t	x	t'	x'	R'	S
(1) Hycar 1001 Compound:						
81GJ 421A : Cure = 15' X 293° F. ; PC=25						
	2.0	.055	45.8	.142	.089	.307
	7.0	.097	46.0	.142	.871	.582
	15.0	.101	46.0	.142	2.18	.706
	78.0	.186	46.0	.142	4.37	.815
			46.8	.144	10.5	.881
81GJ 421A : Cure = 20' X 293° F. ; PC=25						
	2.0	.055	45.8	.117	.089	.252
	7.0	.084	46.0	.117	.871	.545
	15.0	.092	46.0	.117	2.18	.673
	78.2	.143	46.0	.117	4.37	.761
			46.8	.117	10.5	.857
81GJ 421A : Cure = 35' X 293°F. ; PC=25						
	2.0	.042	45.8	.091	.089	.165
	7.0	.064	46.0	.091	.871	.455
	15.0	.072	46.0	.091	2.18	.616
	78.0	.110	46.0	.091	4.37	.730
			46.8	.091	10.5	.847

* 1 Roentgen (air) = 87.1 ergs/gram (carbon)

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 421A : Cure = 45' X 293°F. ; PC=25					
2.0	.038	45.8	.087	.089	.129
7.0	.063	46.0	.088	.871	.416
15.0	.067	46.0	.088	2.18	.575
78.2	.109	46.0	.088	4.37	.697
		46.8	.088	10.5	.836
81GJ 421A : Cure = 105' X 293°F. ; PC=25					
2.0	.034	45.8	.067	.089	.068
7.0	.055	46.0	.067	.871	.316
15.0	.050	46.0	.067	2.18	.481
78.2	.084	46.0	.067	4.37	.635
		46.8	.067	10.5	.805
81GJ 421A : Cure = 210' X 293°F. ; PC=25					
2.0	.033	45.8	.064	.089	.048
7.0	.042	45.9	.064	.871	.261
15.0	.050	45.9	.064	2.18	.452
78.0	.079	45.9	.064	4.37	.636
		46.8	.065	10.5	.820
81GJ 421A : Curatives = Altax - Sulfur ; PC=25					
2.0	.038	41.0	.075	.089	.063
7.0	.058	41.2	.075	.871	.295
15.0	.063	41.2	.075	2.18	.473
78.1	.092	41.2	.075	4.37	.640
		42.1	.075	10.5	.818
81GJ 422A : Curatives = Lime - DCP ; PC=25					
2.0	.066	41.1	.124	.089	.085
7.0	.098	41.2	.124	.871	.369
15.0	.109	41.2	.124	2.18	.561
78.1	.144	41.2	.124	4.37	.709
		42.1	.124	10.5	.859

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 423A : Curatives = Altax - Tuads ; PC=25					
2.0	.139	41.1	.213	.089	.056
7.0	.177	41.2	.213	.871	.394
15.0	.191	41.2	.213	2.18	.641
78.1	.245	41.2	.213	4.37	.792
		42.1	.214	10.5	.897
81GJ 424E : Curatives = GMF ; PC=25					
2.0	.230	41.0	.392	.089	.290
7.0	.322	41.2	.392	.871	.570
15.0	.351	41.2	.392	2.18	.739
78.1	.450	41.2	.392	4.37	.824
		42.1	.394	10.5	.953
81GJ 425B : Curatives = BMD - Litharge ; PC=25					
2.0	.051	41.1	.101	.089	.052
7.0	.072	41.2	.101	.871	.299
15.0	.089	41.2	.101	2.18	.528
78.1	.118	41.2	.101	4.37	.698
		42.1	.101	10.5	.873
81GJ 426A : Curatives = Amberol ST ; PC=25 Stannous Chloride					
2.0	.176	41.1	.270	.089	.099
7.0	.234	41.2	.270	.871	.445
15.0	.256	41.2	.270	2.18	.661
78.1	.289	41.2	.270	4.37	.810
		42.1	.270	10.5	.914
81GJ 427A : Curatives = Altax - Sulfur Donor; PC=25					
2.0	.050	41.0	.145	.089	.146
7.0	.091	41.2	.145	.871	.374
15.0	.116	41.2	.145	2.18	.558
78.1	.187	41.2	.145	4.37	.680
		42.1	.146	10.5	.825

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 428B : Curatives = Altax - Sulfasan R ; PC=25					
2.0	.042	41.0	.096	.089	.046
7.0	.067	41.2	.096	.871	.240
15.0	.079	41.2	.096	2.18	.442
78.1	.120	41.2	.096	4.37	.631
		42.1	.096	10.5	.829
81GJ 429A : Curatives = Tuads ; PC=25					
2.0	.074	41.0	.120	.089	.059
7.0	.095	41.2	.120	.871	.328
15.0	.107	41.2	.120	2.18	.561
78.1	.139	41.2	.120	4.37	.729
		42.1	.121	10.5	.873
81GJ 430B : Curatives = Polyac ; PC=25					
2.0	.321	33.8	.517	.089	.354
7.0	.463	34.0	.517	.871	.685
15.0	.478	34.0	.517	2.18	.825
78.1	.610	34.0	.517	4.37	.900
		33.8	.517	10.5	.934
81GJ 431B : Curatives = MDB-Litharge; PC=25					
2.0	.195	41.0	.338	.089	.114
7.0	.277	41.2	.338	.871	.248
15.0	.301	41.2	.338	2.18	.390
78.0	.390	41.2	.338	4.37	.533
		42.1	.339	10.5	.709

(2) Natural Rubber Compound;

81GJ 338B : Antirad = None ; PC=25					
2.0	.097	40.0	.218	.087	.137
7.0	.147	43.0	.223	.868	.362
15.0	.172	43.0	.223	.438	.229
78.1	.288	42.0	.221	4.36	.753
		41.0	.220	10.5	.885

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 1375 : Antirad = Hydroquinone ; PC=25					
2.0	.132	40.0	.295	.087	.160
7.0	.187	43.0	.302	.868	.376
15.0	.232	43.0	.302	.438	.260
78.2	.390	42.0	.300	4.36	.761
		41.0	.297	10.5	.870
81GJ 1376 : Antirad = Hydroquinone/ Antiox 4010 (50/50) ; PC=25					
2.0	.108	40.0	.271	.087	.131
7.0	.170	43.0	.278	.868	.344
15.0	.211	43.0	.278	.438	.246
78.2	.363	42.0	.276	4.36	.698
		41.0	.274	10.5	.854

(3) Neoprene GN Compound;

81GJ 452 : Antirad = None ; PC=25					
2.0	.155	39.8	.304	.088	.046
7.0	.217	42.8	.309	.871	.389
15.0	.259	42.0	.308	2.18	.599
78.1	.373	42.0	.308	4.36	.765
		40.8	.306	10.4	.904
81GJ 453 : Antirad = Hydroquinone ; PC=25					
2.0	.198	39.8	.385	.088	.103
7.0	.293	42.8	.390	.871	.332
15.0	.342	42.0	.388	2.18	.590
78.0	.450	41.9	.388	4.36	.691
		39.8	.385	10.4	.837
81GJ 454 : Antirad = Antiox 4010 ; PC=25					
2.0	.182	39.8	.336	.088	.073
7.0	.252	42.8	.340	.871	.254
15.0	.302	42.0	.339	2.18	.525
78.0	.388	41.9	.339	4.36	.712
		40.8	.336	10.4	.865

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

	t	x	t'	x'	R'	S
81GJ 455 : Antirad = Hydroquinone/ Antiox 4010 (50/50) ; PC=25						
	2.0	.198	39.8	.363	.088	.094
	7.0	.285	42.8	.368	.871	.292
	15.0	.331	42.0	.366	2.18	.531
	78.1	.414	41.9	.366	4.36	.656
			40.8	.365	10.4	.839

(4) Hycar 1001 Compound;

81GJ 448 : Antirad = None ; PC=25						
	2.0	.037	38.8	.077	.087	.066
	7.0	.065	41.8	.079	.868	.307
	15.0	.065	41.8	.079	.438	.191
	78.0	.097	40.8	.078	4.36	.638
			39.9	.078	10.5	.818
81GJ 449 : Antirad = Hydroquinone ; PC=25						
	2.0	.053	38.8	.127	.087	.083
	7.0	.097	41.8	.130	.868	.226
	15.0	.106	41.8	.130	.438	.152
	78.0	.161	40.8	.129	4.36	.500
			39.9	.128	10.5	.709
81GJ 450 : Antirad = Antiox 4010 ; PC=25						
	2.0	.047	38.8	.100	.087	.062
	7.0	.078	4.8	.102	.868	.216
	15.0	.086	41.8	.102	.438	.151
	78.0	.125	40.8	.102	4.36	.528
			39.8	.101	10.5	.732
81GJ 451 : Antirad = Hydroquinone/ Antiox 4010 (50/50) ; PC=25						
	2.0	.055	38.8	.129	.087	.086
	7.0	.097	41.8	.132	.868	.219
	15.0	.106	41.8	.132	.438	.134
	78.0	.167	40.8	.131	4.36	.513
			39.8	.130	10.5	.732

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
(5) SBR 1500/1501 Compound;					
81GJ 1371 : Antirad = None ; PC=30					
2.0	.061	35.0	.132	.087	.060
7.0	.096	38.0	.134	.868	.281
15.0	.113	38.0	.134	.438	.174
78.0	.171	37.0	.134	4.36	.621
		36.0	.133	10.5	.811
81GJ 1372 : Antirad = Hyroquinone ; PC=30					
2.0	.105	35.0	.214	.087	.108
7.0	.160	38.0	.220	.868	.296
15.0	.179	38.0	.220	.438	.206
78.0	.291	37.0	.218	4.36	.622
		36.0	.216	10.5	.812
81GJ 1373 : Antirad = Antiox 4010 ; PC=30					
2.0	.078	35.0	.146	.087	.040
7.0	.108	38.0	.149	.868	.232
15.0	.131	38.0	.149	.438	.133
78.0	.180	37.0	.148	4.36	.553
		36.0	.147	10.5	.769
81GJ 1374 : Antirad = Hydroquinone/ Antiox 4010 (50/50) ; PC=30					
2.0	.095	35.0	.192	.087	.085
7.0	.138	38.0	.197	.868	.243
15.0	.159	38.0	.197	.438	.169
78.0	.264	37.0	.196	4.36	.572
		37.0	.196	10.5	.776
(6) Hypalon 20 Compound;					
81GJ 444 : Antirad = None ; PC=25					
2.0	.198	34.8	.493	.088	.214
7.0	.351	37.8	.503	.871	.456
15.0	.430	37.0	.500	2.18	.606
78.0	.631	36.9	.500	4.36	.720
		35.8	.497	10.4	.843

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 445 : Antirad = Hydroquinone ; PC=25					
2.0	.251	34.8	.556	.088	.233
7.0	.415	37.8	.565	.871	.445
15.0	.500	37.0	.563	2.18	.613
78.0	.679	36.9	.562	4.36	.682
		35.9	.560	10.4	.827
81GJ 446 : Antirad = Antiox 4010 ; PC=25					
2.0	.293	34.8	.531	.088	.184
7.0	.448	37.8	.537	.871	.353
15.0	.496	37.0	.535	2.18	.619
78.0	.609	36.9	.535	4.36	
		35.8	.533	10.4	.873
81GJ 447 : Antirad = Hydroquinone/ Antiox 4010 (50/50) ; PC= 25					
2.0	.240	34.8	.510	.088	.181
7.0	.395	37.8	.401	.871	.454
15.0	.460	37.0	.515	2.18	.557
78.0	.619	36.8	.515	4.36	.705
		35.8	.512	10.4	.850
(7) Hycar 1011 Fuel Cell Liner;					
81GJ 310 : Antirad = None ; PC=30					
2.1	.037	12.8	.057	.523	.367
6.9	.054	12.3	.057	.878	.452
16.0	.058	12.1	.057	2.18	.593
28.0	.084	12.1	.057	4.36	.770
		12.1	.057	10.4	.893
81GJ 311 : Antirad = α-Naphthylamine ; PC=30					
2.1	.025	12.8	.071	.523	.178
6.9	.071	12.4	.071	.878	.253
16.0	.071	12.1	.071	2.18	.431
28.0	.099	12.1	.071	4.36	.622
		12.1	.071	10.4	.824

TABLE 5 (cont'd)

CONTROL AND RADIATION - INDUCED COMPRESSION SET DATA

t	x	t'	x'	R'	S
81GJ 323 : Antirad = Hydroquinone ; PC=30					
2.1	.049	12.8	.093	.523	.138
6.9	.077	12.3	.092	.878	.195
16.0	.102	12.1	.091	2.18	.378
28.0	.105	12.1	.091	4.36	.580
		12.1	.091	10.4	.774
81GJ 325 : Antirad = Antiox 4010 ; PC= 30					
2.1	.039	12.8	.082	.523	.146
6.9	.064	12.3	.080	.878	.206
16.0	.092	12.0	.079	2.18	.370
28.0	.085	12.0	.079	4.36	.565
		12.0	.079	10.4	.794