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CHEMICAL AND PHYSICAL CHANGES IN GAMMA IRRADIATED PLASTICS

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CHEMICAL AND PHYSICAL CHANGES IN GAMMA IRRADIATED PLASTICS

To best utilize the unique properties of plastics materials of construction for applications where radiation exists, it is of prime importance to ascertain beforehand their capabilities and limitations in radiation fields. This can be accomplished in basically two ways: (1) by a study of the physical property changes induced by radiation, and (2) by a study of the chemical changes induced which are ultimately responsible for the physical changes(1). The former method appears to be most widely used for the more immediate needs of practical application of plastics where radiation exists. In general, this procedure consists of exposing the materials to the desired radiation dose in a relatively short time by using substantially higher radiation dose rates than will be encountered in service. Thus, the evaluation procedure can be done in a matter of a few hours or days rather than weeks or years. After the exposures, the materials are examined physically (often with particular emphasis on those properties which are of most importance for the application) to obtain the desired information. The latter method listed above consists in studying the chemical changes induced by radiation. For the work reported here, infrared techniques were used to determine changes occurring in the molecular structure of the materials after having been subjected to radiation bombardment. This technique was supplemented by mass spectograph analyses of any gaseous products given off during the irradiation of the materials in vacuo. The study of chemical changes has been used more for studies basic to radiation chemistry and mechanisms of change rather than for determining materials' suitability for use in radiation fields.

The work reported here was undertaken to determine the suitability of combining the above two methods of study by correlating physical property changes with the infrared analyses of molecular or chemical changes, and to obtain information on the actual chemical changes which were taking place to eventually cause the physical property changes. This report covers irradiations in air and in vacuo out to a gamma dose of 1×10^8 r (one irradiation was carried out to 3×10^8 r). Future reports are planned which will include more materials and irradiations out to 1×10^9 r.

EXPERIMENTAL PROCEDURE AND RESULTS

In general, the experimental procedure consisted in obtaining original infrared spectra and physical properties and comparing these values with those obtained after the various materials had been exposed to several doses of gamma radiation. Gaseous products given off during the irradiation of the materials in a vacuum were analyzed using a mass spectrometer.

Chemical Changes

The chemical or molecular changes induced in the plastics from exposure to gamma radiation were determined by infrared and mass spectrometer techniques.

Infrared. The infrared technique gives information on the molecular structure of organic polymers. Infrared light is passed through the specimens and split into varying wave lengths by a prism. Absorption bands are the result of the absorption at a particular frequency of the energy passed through the specimens. The frequency at the absorption band is characteristic of the chemical bonds whose change in dipole moment have the respective vibrational frequencies. A more complete description of the infrared equipment and its operation are available in the literature(2,3).

The infrared measurements were made using a Perkin-Elmer Model 12-C infrared spectrometer which had been modified for double-pass operation. Atmospheric absorption was reduced by blowing dry air through the monochromator housing. Sodium chloride (NaCl) optics were used from 4000 to 650 cm^{-1}. Measurements were taken on the same specimens which were used for the physical property studies.

Mass Spectrometer analyses of gaseous products consisted of semi-quantitatively measuring the masses of chemical compounds given off from organic polymers after irradiation in vacuo. This technique gives information on the chemical nature of the gaseous products and is helpful in the interpretation of the infrared observations.

Physical Property Changes

Physical properties were studied by recording changes in the following properties:

Tensile Strength measurements were made in accordance with ASTM D 412-51T using Die C type dumbbell test specimens and a Scott tensile tester. Values are given in pounds per square inch (psi) necessary to break the specimen.

Ultimate Elongation measurements were obtained as a part of the tensile strength tests. Values are given as the per cent the specimen had elongated at the time of break.

Flexibility. A 180-degree bend test was made after the radiation exposures by folding the tensile specimen back on itself. Positive finger pressure was applied to insure that the specimen sides were in contact and to reduce the radius of bend to a minimum.

Hardness measurements were not made as all of the materials examined were in thin films.

Materials Evaluated

Table I in the Appendix lists the various plastics materials which were used in this work. Because of the demands imposed by the infrared studies, films in the nominal thickness range of three mils (.003") to twenty mils (.020") were used for the major part of this work. Thus, by selecting materials with varying thickness, chemical and physical changes as a function of specimen thickness could be determined.

Figure 1 shows the structural repeating units of the materials evaluated.

Irradiating the Materials

All materials were exposed to approximately 1.24 Mev gamma radiation from a Cobalt-60 isotope source of about 30,000 curies strength emitting gamma rays at a dose rate of about 1.3×10^6 r/hr. The irradiations were carried out in air at 25 C at normal atmospheric pressure except for those in vacuo at 25 C. Figure 2 shows a schematic diagram of the Hanford Cobalt-60 source used and the arrangement of the specimens being irradiated.

Units of radiation dose or exposure are given in terms of the Roentgen (r). This unit is equal to the gamma ray ionization producing one electrostatic unit of charge in one cubic centimeter of air and is equivalent to the absorption of 83.3 ergs of energy per gram of air. Dose rate, the amount of energy available for absorption in a material per unit time, is expressed as Roentgens per hour (r/hr). Millions of Roentgens or megaroentgens is expressed as Mr.

Measuring the Properties

The infrared measurements were taken on one end of each of two tensile specimens after a one-hour conditioning period at 25 C and 50% relative humidity. These measurements were made approximately four hours after the specimens had been removed from the radiation source. The reported optical density values are calculated from the average percent transmission readings of the two specimens. The average readings of the two specimens agreed to within plus or minus 2%.

Physical property measurements were made at 25 C and 50% relative humidity on each of five test specimens approximately one hour after the infrared analyses. Each reported percent change value was calculated from the arithmetic average of the five measured values. A statistical analysis of typical data showed that the 95% confidence limits were approximately plus or minus 8% for tensile strength and plus or minus 10% for elongation.

Mass spectrometer analyses of the contents of the evacuated containers were made on all materials irradiated in vacuo. In these instances there was a delay of about a day before the infrared and physical tests could be made. Data from the mass spectrometer included the percentages and total pressures of any gaseous products formed during the irradiations. Data reported are accurate to within plus or minus 1% for the major constituent.

Results

The infrared and physical property data obtained from exposing the plastics to various doses of gamma radiation in air and in vacuo at 25 C are presented in Table II. This table shows physical property changes induced by exposure to gamma radiation as percent change of the original property values which are given opposite zero irradiation dose. Results of the infrared studies on the same irradiated plastics are shown in the table under chemical properties. Units given are optical densities, Log (T_o/T), where T_o has been corrected to $T_o = 100\%$ by the "baseline" method(2). The optical densities are proportional to the concentrations assuming Beer's Law to hold true. The structural groups and frequencies at which the absorptions were measured are given in Figure 3. Original optical densities of the unirradiated materials are shown opposite zero irradiation dose. Also shown opposite zero irradiation dose and under the Remarks column is the original color of each material. Significant color changes and other observations needing comment are also noted in this column opposite the particular radiation dose causing the phenomenon.

Results of the mass spectrometer analyses are given in Table III. This table shows the various gaseous products formed from the irradiation of each plastic in vacuo. These products are identified from data on their respective masses. The mass spectrometer technique will not sharply define products whose masses vary by about two mass units. For example, C_2H_x could be either ethane or ethylene with masses of thirty and twenty-eight respectively.

DISCUSSION

The data presented in Table II show how gamma radiation affects the chemical structures and physical properties of plastics classified as carbonates, ethylene, fluorocarbon, polyester, styrene, and vinyl chlorides. Chemical changes induced by exposure to radiation can not always be determined by a combination of the infrared and mass spectrometer techniques. On the other hand, chemical changes which are taking place(1) but are not detectable, are in almost every case reflected in physical property changes. At short and intermediate doses, some of the materials are not significantly changed or damaged, but at the higher exposures all of the materials were more or less damaged depending upon their chemical composition or structure.

It is not the purpose here, with respect to chemical structure changes, to assign vibrational modes to all the infrared bands observed, but rather to take those in which changes are observed and assignments well established, and comment on them. The principal effects discussed are unsaturation, oxidation, and results from the mass spectrometer for each material studied.

Carbonates

Lexan and Macrofol have essentially identical spectra (see Figure 4) and they are considered identical for the chemical discussion. The variation in optical density values reported are attributed to thickness differences.

There is noted in these samples a number of bands in the unsaturation region 875-1000 cm^{-1} and also relative changes in these with irradiation. On the basis of available structural information(4) the assignment of these bands to unsaturation is difficult, and since the changes are minor, no such correlation will be assumed here.

The effect of oxidation is more readily determined. There is evidence of increasing carbonyl content at about 1750 cm^{-1}. The high frequency of this group is attributed to the -OCOO- group. The optical densities in Table II are not too accurate because of the large intensities involved - even in the unirradiated specimens. There are definite shoulders found on the high wavelength side which can be attributed to ketone and acid carbonyl(5). The hydroxyl (-OH) absorption increases with radiation exposure to a total dose of 3×10^8 r.

Samples of Macrofol were irradiated in vacuo to a total dose of 1×10^8 r. There was insufficient gas evolution to determine gaseous products by the mass spectrometer technique. There was no indication of carbonyl formation, but the hydroxyl increase was identical with that for the irradiation in air. On this evidence it is suggested that a chain cleavage or depolymerization reaction may be responsible:

(1)

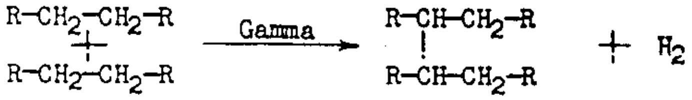
Figure 5 shows how the chemical and physical changes of Lexan are affected by exposure to gamma radiation. Both Lexan and Macrofol behaved almost identically with respect to physical property changes induced by exposure to ionizing radiation. At the initial dose of 5×10^6 r both materials exhibited a slight improvement in both tensile strength and elongation. Both of these properties were lowered at a slight rate with increased exposure to radiation out to about 5×10^7 r. Further exposure out to 1×10^8 r increased the rate of degradation of both properties but the materials were in good condition and possessed much of their original flexibility and toughness. Both materials became more yellow in color with increased exposure to radiation. Lexan, which was exposed to a dose of 3×10^8 r, became quite brittle and could not be tested for physical properties. As the properties of Macrofol were changed about equally for both the air and vacuum irradiations out to 1 x 10^8 r, it appears that oxidation does not play an important role in the degradation of the carbonate plastics.

Ethylenes

The three diferent types of polyethylene studied here included a "conventional" or low density type, Alathon 3, NC-10; a "linear" or high density type, Marlex 50; and a low density type which had been given a controlled electron radiation dose to improve some of its properties, Irrathene. The original spectra of these materials are reproduced in Figure 6. Basic differences are noted in the unsaturation region 1000-850 cm^{-1}, and in the 725 cm^{-1} doublet. Marlex 50 shows vinyl unsaturation ($RCH=CH_2$) at 909 cm^{-1}. Alathon 3, NC-10 and Irrathene have a peak at about 888 cm^{-1} which is assigned to vinylidene ($RR'C=CH_2$), and the Irrathene has an initial peak at 964 cm^{-1} for transvinylene ($RCH=CHR$)(6). A large amount of work has been done on the chemical charges in irradiated polyethylene. The work of Dole(7) and Miller(8) are cited as being typical. In general, radiation has been found to decrease vinyl and vinylidene unsaturation and increase transvinylene. For irradiations carried out in air an increase in carbonyl at about 1720 cm^{-1} is also observed. The 725 cm^{-1} doublet is further split into branches at 730 and 720 cm^{-1} which is only observable in thin films three mils or less in thickness. The 720 cm^{-1} band is the most intense in Alathon and Irrathene originally, and least intense in the case of Marlex 50. With increasing dose, the relative intensities of these bands shift in the Irrathene, but remain unchanged in the other two materials.

Alathon 3, NC-10. Table III shows that 97.5% of the evolved gas at a dose of 1 x 10^8 r is hydrogen. This is in excellent agreement with Dole(7) and Charleby(9) for pile irradiation of polyethylene. Each hydrogen molecule liberated would result in one carbon to carbon bond being formed since oxidation can not occur in vacuo. The formation of transvinylene unsaturation as well as crosslinking could result:

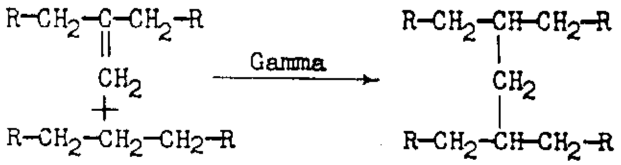
$$R{-}CH_2{-}CH_2{-}R \xrightarrow{\text{Gamma}} RCH{=}CHR + H_2 \qquad (2)$$



$$\begin{array}{c} R{-}CH_2{-}CH_2{-}R \\ + \\ R{-}CH_2{-}CH_2{-}R \end{array} \xrightarrow{\text{Gamma}} \begin{array}{c} R{-}CH{-}CH_2{-}R \\ | \\ R{-}CH{-}CH_2{-}R \end{array} + H_2 \qquad (3)$$

The mechanism suggested is free-radical with one or two ionizing events(10). The radiation yield (molecules/ 100 e.v.) for transunsaturation in Alathon at 1 x 10^8 r in vacuo is G (−C═C−) 2.7 based on Anderson and Seyfried's specific absorption coefficient(11) while the hydrogen yield was G (H_2) 5.3. Thus, about 50% of the hydrogen evolved resulted in intermolecular crosslinks.

It has been suggested that the vinylidene site is contributing to crosslinking(7). The vinylidene group does not decrease as rapidly when irradiated in vacuo as in air - indicating oxidation as a factor in removing this group, The tertiary carbon atom as well as the double bond would be vulnerable to oxidative attack. The formation of ketone groups well within the polymer chains as well as acid and aldehyde carbonyl are indicated in the infrared spectrum(5). From a mechanism suggested by Dole(7) , the following crosslinking reaction results:



$$\begin{array}{c} R{-}CH_2{-}\underset{\|}{C}{-}CH_2{-}R \\ CH_2 \\ + \\ R{-}CH_2{-}CH_2{-}CH_2{-}R \end{array} \xrightarrow{\text{Gamma}} \begin{array}{c} R{-}CH_2{-}CH{-}CH_2{-}R \\ | \\ CH_2 \\ | \\ R{-}CH_2{-}CH{-}CH_2{-}R \end{array} \qquad (4)$$

In Alathon the terminal groups or chain ends are almost exclusively methyl groups, the only exception being the vinylidene (see above). Reactions of oxidation, chain cleavage, and crosslinking could all take place at these sites. In low density polyethylenes there are found short chain branches which are generally 3 to 5 carbon atoms long(12). Chain cleavage at these short chain branches could lead to additional crosslinking as well as hydrocarbon evolution in the C_3 to C_5 range.

The various crosslinking reactions suggested would tend to increase the tensile strength (at least to the degree obtained for the total doses investigated). Figure 7 shows both chemical and physical changes induced by gamma radiation at various doses out to 1×10^8 r in 15 mil Alathon. It can be concluded then, that the degrading (loss of properties or usefulness) of this plastics material by radiation in air is caused in part by oxidation reactions where these reactions are prohibiting the crosslinking mechanism.

Four thicknesses of Alathon were examined - nominal 3, 5, 10, and 15 mils. The original elongation of each thickness appears to be a function of the film thickness - the thicker the material, the greater the elongation. On the other hand, the tensile strength appeared to be essentially independent of the thickness with the exception of the 10 mil sample which had substantially higher original tensile strength. This was attributed to some variation in processing during manufacture.

The elongation of all the Alathons was reduced as the radiation exposure was increased with the greatest rate of decrease occurring between 1 and 5×10^7 r. The tensile strength, with the exception of the 15 mil sample, was moderately reduced until an exposure of about 5×10^7 r after which it leveled off and then assumed a trend of increasing. The greater decrease shown by the 10 mil material was probably a reflection of its original value which differed considerably from the others. The 15 mil sample exhibited a different trend. Its tensile strength was improved considerably with increased radiation exposure out to a point somewhat beyond 1×10^7 r after which it assumed the general trend of the other materials. This is in agreement with work on thicker polyethylenes(13). The instances where the tensile strength and elongation were increased slightly at the low exposures in some of the polyethylenes is attributed to slight variations in the uniformity of the specimens. All materials exhibited a a slight yellow tint after an exposure of 5×10^7 r which became somewhat darker with increased exposure.

The 15 mil sample which was irradiated in vacuo out to a dose of 1×10^8 r did not suffer as much damaging change as compared to the air irradiation to the same dose. The elongation was reduced considerably but not to the extent as in air. The tensile strength, on the other hand, was affected quite differently. The exclusion of oxygen apparently is beneficial with respect to the tensile strength as at the dose in question it had increased slightly. Whether or not the absence of oxygen changes the tensile strength trend or simply lessens the damaging effects will be investigated and reported at a future date.

Marlex 50. This material is affected quite differently from exposure to radiation than the other ethylenes studied. This is attributed to the high crystallinity, about 95%, of this material which precludes the vinylidene structure and short chain branches. Thus, the crosslinking ability of this resin is greatly reduced. The vinyl unsaturation is found to decrease (even in vacuo) to a negligible amount at 1×10^8 r. Crosslinking reactions as well as oxidation could be effective in removing this group.

The formation of transvinylene would proceed as in equation (2) above. The mass spectrometer analyses indicated large hydrogen evolution again. The lack of higher mass units (C_5 and C_6) being evolved here is attributed to the lack of short chain branches in this linear polymer. The oxidation attack is faster in the Marlex than in the Alathon which would explain the rapid degradation of this polymer in thin films when irradiated in air.

Marlex 50 which is representative of the so-called linear or high density types of polyethylene is characterized by its physical toughness and rigidity as compared with the lower density materials. In addition, as stated previously, they are much more crystalline, about 95% as compared to about 50%. This crystallinity apparently is the chief reason which renders this material very susceptible to damage from exposure to ionizing radiation. The material rapidly deteriorated at low exposures and was extremely brittle and crumbly after a dose of 5×10^7 r where it has lost all of its tensile strength and elongation. Exclusion of air helped considerably as the material was not brittle after being irradiated in vacuo to 1×10^8 r. Here it had lost most of its elongation, yellowed slightly, but retained a substantial amount of its tensile strength. In thicker films, this material is not nearly as drastically damaged and behaves more in the manner exhibited by the lower density polyethylenes(13).

Irrathenes. U-101 and U-201 are representative of the polyethylene materials which were electron irradiated to produce the Irrathene 101 and 201 materials respectively. The 201's differ only in that they contain small amounts of an antioxidant. The Irrathenes before gamma irradiation have more transvinylene and less vinylidene than the U-101 and U-201 after correcting for thickness differences. The chemical reactions taking place such as crosslinking, oxidation, etc. would be similar to those suggested for Alathon.

Table II shows that radiation induced oxidation in the 201's, as determined by carbonyl formation, is less than that for the 101's. This is attributed to the effectiveness of the antioxidant. This difference is not reflected in the physical property changes of these materials which, within the experimental error of the measurements, changed to about the same extent. The 0.010" films of Alathon and Irrathene 101 showed about the same decrease in elongation when irradiated in vacuum while the tensile strength of Irrathene increased slightly more under these conditions.

The degree that oxidation affects the physical properties depends also on the effects of other competing reactions. In general, the U-101 and U-201 oxidize more than the Irrathenes 101 and 201 respectively showing that the crosslinking which had taken place from the original electron irradiation (during process of manufacture) has made the material more stable to oxidation attack. The magnitude of these two effects, initial crosslinking and presence of an antioxidant, are approximately equal on oxidation resistance.

The vinylidene group decreases rapidly at first and then slowly to doses of 5×10^7 r and 1×10^8 r. It is probable here that surface oxidation, with some penetration, is active in removing this group to a greater extent than the crosslinking reactions. The oxidation attack was lessened at higher doses because of a "protective" layer of oxide being formed. It is noted that the rate of formation of carbonyl is tending toward saturation at the higher doses. This effect is contrary to that in Alathon. The crystallinity, molecular weight variations, and/or initial crosslinking may account for these differences.

The 725 cm^{-1} band in polyethylene has been assigned to $-CH_2-$ rocking mode(14). This band has been observed to split into two components (in solids) at 731 and 721 cm^{-1}(6,14,15). The 731 cm^{-1} band has generally been assigned to a vibration in the crystalline part of the material. Keller and Sandeman(15) have further stated that the 721 cm^{-1} band arises from both amorphous and crystalline phase vibrations. This interpretation is satisfactory for the original spectra of the four polyethylenes as indicated above. Upon irradiating the Irrathene 101 and U-101 a decrease in the 721 cm^{-1} band is observed in two mil films. According to the above assignments, a decrease in amorphous content, or more specifically of the $-CH_2-$ rocking mode in the amorphous areas, of the samples would be responsible. It does not seem reasonable to imply that gamma radiation would produce a more ordered polymer unless one could consider a three dimensional network chain, produced by crosslinking, as a more crystalline material. It appears that more complicated factors are occurring and further experimental work will be done on this problem.

The mass spectrometer results indicate further differences in the ethylene polymers. Figure 8 shows the mass spectral cleavage pattern in all of these materials studied. The C_6H_x mass is not found and the amount of C_5H_x is considerably smaller for the Irrathene 101 as compared to the Alathon. There is a larger amount of CH_4 and C_2H_x evolved from the Irrathene. The first effect is explained by the initial crosslinking of the short chain branches (4-6 carbon atoms long) during the manufacture or processing of polyethylene into Irrathene. The increased evolution of methane and ethane/ethylene is harder to account for but must again be tied in with the crosslinking of the material initially.

With respect to physical property changes induced in the Irrathene by exposure to gamma radiation, the elongation followed the same pattern as exhibited in the Alathons. The tensile strength also showed the same trend as shown by the Alathons except that at the first exposure of 5×10^6 r the tensile strength appeared to be increased to a slightly greater extent. This could be attributed to both the fact that the initial electron irradiation processing caused this, and the fact that the nominal 10 mil Irrathene films were approximately 11 mils whereas the Alathon was about 9 mils. This latter fact might contribute more as the thickness is approaching that of the Alathon 15 mil material whose tensile strength was increased considerably at the first exposure.

All of the Irrathenes became slightly yellow at a dose of 5×10^7 r and became darker on continued exposure. No detailed discussion is given to the U-101 and U-201 materials which were representative of the polymers from which the Irrathenes were made. They were the same general type as the Alathons and behaved in essentially the same manner.

Fluorocarbon

Teflon 1 polytetrafluoroethylene was used here as being representative of a fluorocarbon plastic. Ryan(16) has given an empirical formula for the evolution of fluorine from Teflon:

$$X = 3.78 \times 10^{-7} Y^{1.151} \qquad (5)$$

where X equals micrograms of fluorine liberated gas per gram of Teflon irradiated to a gamma dose of Y Roentgens. The vacuum irradiation of Teflon did not evolve sufficient gas to be measured by the mass spectrometer (this could possibly have been due to absorption or reaction of fluorine with the glass container). The total moles evolved (assuming all fluorine gas) was considerably smaller than the above equation indicates. This is probably because equation (5) was based on irradiations carried out under sodium hydroxide solution and in the present case no effort was made to keep fluorine from reacting with the glass vessel. The possibility of fluorocarbon evolution can not be ruled out.

Ryan(16) assigned bands at 1754 and 1538 cm^{-1} to $-CF{=}CF-$ and $-CF{=}CF_2$ respectively, observing these after irradiations to 1×10^8 r. In the present work no changes were found in ten mil films for these bands to an exposure of 5×10^6 r. At this dose Teflon had become severely damaged having lost all of its elongation and about 60% of its original tensile strength. Figure 9 graphically illustrates how the physical properties of Teflon are affected by exposure to gamma radiation. After being exposed to 5×10^6 r Teflon was quite brittle and failed the 180-degree bend test.

It can be seen that low doses of radiation greatly affect the physical properties of Teflon. Whether or not these large physical property changes were caused by either small or large structural changes in Teflon has not been established here. However, the work reported here seems to agree with the conclusions of Ryan(16) that the breaking of one in one thousand C-F bonds results in major physical property changes.

Polyester

Tobin(17) has recently published assignments for the bands found in Mylar A polyester (polyethylene terephthalate). There were no changes in the infrared spectrum after irradiating this material to a dose of 1 x 10^8 r in the present work, and there was insufficient gas evolution for mass spectrometer analysis. The benzene ring along the main chain, because of its resonance stability, contributes significantly to the radiation resistance of this material. At some higher exposure a degradation of the polymer would undoubtedly occur.

Figure 10 shows how the physical properties of Mylar are affected by exposure to ionizing radiation. Both the tensile strength and elongation were reduced with increased radiation dose at about equal rates. At the highest exposure studied, 1 x 10^8 r, the material retained a substantial amount of both physical toughness and flexibility. The irradiation in vacuo to 1 x 10^8 r did not change this material much more than the irradiation in air to a dose of 5 x 10^7 r. This indicates that oxidation plays at least some part in the damage induced in this material.

Styrene

The thermal degradation of polystyrene has been studied using infrared techniques by Achhammer et al.(18). They give reactions for crosslinking, hyperoxide formation, etc. At a total dose of 1 x 10^8 r no changes were observed in the infrared spectrum of Polyflex polystyrene and there was no indication of gas evolution from the specimens irradiated in vacuo to 1 x 10^8 r.

As this material had zero initial elongation, only tensile strength was evaluated. It behaved almost precisely in the same fashion as did Mylar polyester - a gradual lowering with increased radiation exposure. This tensile strength behavior is graphically illustrated in Figure 10 along with Mylar. At a dose of 1 x 10^8 r the material appeared to be substantially unchanged from its original condition with the exception of a slight yellowing and loss of tensile strength. In vacuo to 1 x 10^8 r, the material appeared to be slightly more damaged with respect to tensile strength reduction than it was in air at the same dose. This indicates that oxidation plays little or no part in the radiation induced damage to polystyrene. The benzene ring structure is again given credit for the radiation stability of this material.

Vinyl Chlorides

The two Geon polyvinyl chloride materials used in these studies contained plasticizer which gave rise to an intense carbonyl absorption band at about 1720 cm^{-1}. The presence of this band in the specimens masked any oxidation effects which might have occurred. The mass spectrometer results given in Table III show a large amount of carbon dioxide evolved which must have come from the plasticizers. There was also hydrocarbon evolution in the C_2-C_6 range, typical of vinyl type polymers. There was found larger amounts of methane (6.6%) which was probably evolved from the plasticizers also. Significantly, no chlorine or chlorohydrocarbon gases were found - showing little or no reactions taking place in the main polymer chain.

In contrast to the chemical changes in the Geon which were not readily identifiable, physical property changes were quite pronounced. Figure 11 graphically shows physical property changes in Geon 8640 4 mil material as a function of radiation exposure. All of the Geon samples exhibited a gradual decrease in tensile strength to a dose of 5 x 10^7 r after which it began to increase. Geon 8630 in the 20 mil thickness exhibited less decrease than did the others. The decrease followed by an increase suggests that chain cleavage occurs initially after which crosslinking predominates. With the exception of the Geon 8630 20 mil sample which showed a slight increase in elongation before assuming a downward trend, these materials decreased in elongation with increased radiation exposure. The Geon 8640 4 mil material which was irradiated in vacuo to 1 x 10^8 r was less damaged than its counterpart irradiated to the same dose in air. This establishes the fact that oxidation plays an important role in the radiation induced damage to polyvinyl chloride. As noted in Table II the materials were very much discolored with increased radiation dose.

Effect of Sample Thickness in Polyethylene

As was stated previously and as noted in Table II, radiation induced changes in polyethylene are also a function of sample thickness. This effect of specimen thickness was studied using Alathon 3, NC-10 as being representative of a typical polyethylene. Primary changes that were noted were in carbonyl and in transvinylene.

Oxidation. The plot of Log (T_0/T) (optical density) vs. L, thickness which is shown in Figure 12 for the carbonyl absorption in Alathon indicates that oxygen is penetrating into the specimens in amounts that may be quite significant in thinner films. Ballentine et al.$^{(19)}$ have stated that oxidation would be a surface effect, and unsaturation by ionizing radiation would be independent of the bulk. This would be expected to hold true for oxidation of films where the surface to [illegible] was small. The actual distribution of oxygen (in this case carbonyl) in the sample depends upon at least two factors: (1) the availability of reaction sites with which oxygen may combine, and (2) the kinetics of oxygen diffusion and carbonyl formation rate.

Consider, for example, two samples of homogeneous composition varying only in thickness (L) receiving the same gamma radiation. We have then

where "0" represents reaction sites (free radicals, excited atoms, ions, etc.) created by the ionizing radiation. The function of thickness is just to increase the number of these sites, but the number per unit volume remains the same. The effect of increasing the gamma dose is only to increase the number of sites produced per unit volume. The sites "O" react in a number of ways: oxidation, crosslinking, recombination, etc. It is reasonable to assume that of the total number of sites available, the number that could produce carbonyl formation would be homogeneously distributed in the samples prior to any reactions taking place. The total oxidation absorbance would seen then to more strongly depend on the kinetics of oxygen diffusion.

To show how chemical effects vary with sample thickness and radiation dose, a function Q (called here the "chemical effects function") is derived here (see Figure 13). It is defined as follows:

$$Q = \frac{\text{Log}\ (T_o/T)}{L\ (Mr)} \qquad (6)$$

Figure 14 shows a plot of Q vs. L. This curve shows that carbonyl absorption should change linearly with the radiation dose. The curve is useful in determining absorbance values at a particular thickness and has been used here to plot the curves in Figure 12 on which the experimental points are plotted, and on Figure 15, Log (T_o/T) vs. Mr (millions of Roentgens or Megaroentgens). From equation (6) the relationship between thickness and oxidation has been derived (see Figure 16) and is as follows:

$$L/A = BL + C \qquad (7)$$

Figure 18 is a plot of A vs. L compared with two curves from Figure 12. Equation (7) is valuable for extrapolation of data. It adequately predicts zero carbonyl absorbance at zero thickness and also a limiting value for the absorbance as the oxidation is increased. This limiting value is equal to 1/B.

Unsaturation. The unsaturation increase in polyethylene as illustrated by equation (2) is transvinylene[7,8]. This type of bond formation ultimately requires hydrogen abstraction from adjacent carbon atoms. The reaction mechanisms necessary should be possible in any part of the sample, especially assuming a homogeneous composition. The reaction would further depend on the sample thickness, if it was sufficiently large to reduce the probability of hydrogen molecules escaping.

Figure 19 shows the increase in transvinylene formation as a function of thickness. The changes in this property with radiation exposure are shown in Figure 20. The tendency to saturate at higher exposures is evident. These curves are analogous in shape to the oxidation of polyethylene as a function of thickness, and in fact, an equation of the form of (7) can be derived by replacing L with Mr. The result is not quite as accurate as in the case of oxidation.

The vinylidene unsaturation decreases and Figure 21 shows the effect of thickness on this property. An approximate linear variation is indicated. However, because of the competing reactions effecting this group (oxidation and crosslinking) and their dependence (especially oxidation) on the thickness of the material, no simple relationship can be assumed here.

SUMMARY AND CONCLUSIONS

Several plastics materials were irradiated in a gamma radiation source at various doses out to 1×10^8 r. Of these materials classified as polycarbonates, polyethylenes, polyfluorocarbons, polyesters, polystyrenes, and polyvinyl chlorides, the aromatic containing carbonate, polyester, and styrene materials were found to be the most resistant to the damaging effects of radiation as reflected in both chemical and physical property changes. The low density type polyethylenes were next with the plasticized polyvinyl chlorides following. The high density polyethylene was considerably poorer than the low density types because of more severe oxidation occurring in the thin specimens evaluated. The fluorocarbon was the poorest of the materials studied. To completely classify all of the above materials more irradiations are needed at higher exposures.

For those materials which are susceptible to radiation induced oxidation, it has been found that the specimen thickness plays an important role in the extent of both chemical and physical property changes caused by exposure to ionizing radiation. This is because the chemical effects and resulting physical property changes caused by oxidation are a function of the total amount of oxidation to the materials and its distribution within them. The increase in carbonyl with sample thickness does not follow a surface to volume ratio until the samples exceed about 30 mils in thickness.

A function Q, called the chemical effects function, has been derived as a consequence of the above thickness dependency of oxidation. This function is useful for both the extrapolation of data and correcting for thickness differences.

Irradiating the plastics materials in vacuo, although eliminating the effects caused by oxidation, does not necessarily prevent changes from occurring. This is because other effects such as crosslinking which are often obscured by oxidation now manifest themselves. For example, it has been found that oxidation inhibits crosslinking. in polyethylene.

In the polyethylenes studied, oxidation is much more pronounced in the linear or high density materials than in the lower density types as evidenced by a drastic reduction of both tensile strength and elongation. On the other hand, the low density materials which were processed by electron irradiation oxidize at a slower rate when subjected to gamma radiation because they were somewhat crosslinked during processing. The differences in effects between the high and low density polyethylenes can in large measure be attributed to differences in crystallinity.

At exposures up to 1 x 10^8 r a good correlation between chemical and physical property changes is not always possible. This is because incipient and small chemical changes which are not detectable by infrared and/or mass spectrometer analyses can lead to either small or large physical property changes which are observable. In the instances when both chemical and physical property changes can be observed, a good correlation or relationship can be obtained. Here both methods of evaluation serve to supplement each other to explain the ultimate changes which are induced in plastics by ionizing gamma radiation.

ACKNOWLEDGEMENT

Acknowledgement is made to the following individuals of the Hanford Atomic Products Operation, General Electric Company, Richland, Washington: S. W. Smith and F. M. Newby for their assistance in carrying out the irradiations, H. J. Anderson for the mass spectometer analyses, and R. E. Nightingale for helpful discussions concerning the interpretation of the infrared results.

Robert Harrington   Richard C. Giberson
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Nonmetallic Materials Development Operation
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APPENDIX

TABLE I

PLASTICS USED FOR GAMMA IRRADIATION STUDIES

Material, Supplier, and Designation	Type or Description and Specific Gravity
Carbonates	
General Electric Company	
Lexan	Polycarbonate resin - 1.20
Naftone, Inc.	
Macrofol	Polycarbonate resin - 1.20
Ethylenes	
DuPont Polychemicals Department	
Alathon 3, NC-10*	Polyethylene, low density type, no additives - 0.921
Phillips Chemical Company	
Marlex 50	Polyethylene, high density type, no additives - 0.960
General Electric Company	
U-101	Polyethylene, low density type, no additives; material used to make Irrathene 101 - 0.920
U-201	Polyethylene, low desity type, contains antioxidant; material used to make Irrathene 201 - 0.920
Irrathene 101	Irradiated polyethylene, low density type, no additives - 0.920
Irrathene 201	Irradiated polyethylene, low density type, contains antioxidant - 0.920

TABLE I - Continued

Material, Supplier, and Designation	Type or Description and Specific Gravity
Fluorocarbon	
DuPont Polychemicals Department	
Teflon 1	Polytetrafluoroethylene, no additives - 2.160
Polyester	
DuPont Film Department	
Mylar A	Polyethylene terephthalate, no additives - 1.390
Styrene	
Plax Corporation	
Polyflex	Polystyrene, no additives - 1.050
Vinyl Chlorides	
B. F. Goodrich Chemical Company	
Geon 8630*	Polyvinyl chloride, plasticized - 1.340
Geon 8640*	Ditto

* Materials evaluated in more than one thickness (See Table II).

TABLE II

CHEMICAL AND PHYSICAL PROPERTIES OF IRRADIATED PLASTICS

Material and Thickness	Dose	Physical Properties		Chemical Properties					Remarks
		Original & Percent Change		Measured Optical Densities					
		Elongation	Tensile	Unsaturation			Oxidation		
	(r x 10^{-6})	%; Δ%	psi; Δ %	Trans	Vinylidene	Vinyl	Carbonyl	Hydroxyl	
Carbonates									
Lexan (.003")	0	95	6745	—	—	—	.903	.120	a
	5	3.1	14.6	—	—	—	.917	.125	
	10	- 7.4	- 2.1	—	—	—	.920	.128	b
	50	- 22.7	- 0.1	—	—	—	.915	.134	c
	100	- 33.0	- 12.9	—	—	—	.917	.142	d
	300	—	—	—	—	—	1.020	.426	e
Macrofol (.003")	0	75	6795	—	—	—	.936	.059	f
	5	6.5	14.6	—	—	—	.945	.064	
	10	0.0	- 0.1	—	—	—	.960	.070	g
	50	- 3.9	- 2.1	—	—	—	.979	.104	h
	100	- 28.6	- 12.9	—	—	—	1.000	.150	h
	100-Vacuum*	- 22.1	- 15.7	—	—	—	.930	.151	d
Ethylenes									
Alathon 3, NC-10 (.003")	0	380	1915	—	.024	—	—	—	i
	5	- 3.7	1.1	—	.019	—	.040	—	
	10	- 7.9	- 2.5	.016	—	—	.090	—	
	50	- 86.8	- 33.7	.027	—	—	.380	—	j
	100	- 95.8	- 32.8	.054	—	—	.830	—	k
	100-Vacuum	- 50.0	46.4	.057	.013	—	—	—	j

TABLE II - Continued

Material	Dose	Elongation	Tensile	Trans	Vinylidene	Vinyl	Carbonyl	Hydroxyl	Remarks
Ethylenes (Cont.)									
Alathon 3, NC-10 (.005")	0	510	2330	—	.047	—	—	—	i
	5	5.1	9.8	.015	.038	—	.060	—	
	10	- 3.0	- 4.2	.046	.030	—	.140	—	
	50	- 84.1	- 42.5	.072	—	—	.720	—	j
	100	- 84.9	- 42.7	.127	—	—	1.250	—	k
	100-Vacuum	- 67.5	8.2	.140	.018	—	—	—	j
Alathon 3, NC-10 (.010")	0	570	2825	—	.051	—	—	—	i
	5	3.0	6.5	.026	.042	—	.070	—	
	10	- 3.3	- 8.2	.051	.034	—	.130	—	
	50	- 81.8	- 57.2	.176	—	—	.740	—	j
	100	- 91.6	- 57.7	.173	—	—	1.350	—	k
	100-Vacuum	- 65.9	1.6	.240	.025	—	—	—	j
Alathon 3, NC-10 (.015")	0	650	2330	—	.071	—	—	—	i
	5	- 10.6	17.8	.052	.058	—	.070	—	
	10	- 10.9	22.2	.088	.052	—	.170	—	
	50	- 82.7	- 42.7	.285	.027	—	.820	—	j
	100	- 90.4	- 40.2	.380	—	—	1.500	—	k
	100-Vacuum	- 73.1	7.1	.384	.042	—	—	—	j
Marlex 50 (.002")	0	600	4280	.021	—	.095	.035	—	i
	5	- 91.7	- 12.7	—	—	.067	.060	—	
	10	- 97.8	- 35.3	—	—	.055	.110	—	
	50	-100.	-100.	.053	—	—	.438	—	l
	100	—	—	—	—	—	—	—	m
	100-Vacuum	- 95.3	- 7.5	.092	—	—	—	—	j
U-101 (.005")	0	535	2180	.006	.045	—	.029	—	i
	5	- 0.6	6.4	.011	.031	—	.047	—	
	10	- 10.8	- 13.4	.017	.021	—	.136	—	
	50	- 81.2	- 47.4	.070	.017	—	.788		j
	100	- 96.6	- 46.8	.076	—	—	1.130		k

TABLE II - Continued

Materials	Dose	Elongation	Tensile	Trans	Vinylidene	Vinyl	Carbonyl	Hydroxyl	Remarks
Ethylenes (Cont.)									
Polyethylene U-201 (.005")	0	575	1895	.011	.054	—	.039	—	i
	5	- 5.2	5.0	.017	.037	—	.066	—	
	10	- 10.8	- 4.2	.019	.030	—	.106	—	
	50	- 92.5	- 35.3	.059	.024	—	.750	—	j
	100	- 96.4	- 34.2	.107	.014	—	1.010	—	k
Irrathene 101 (.010")	0	525	2390	.067	.045	—	.052	—	i
	5	2.7	9.8	.083	.044	—	.135	—	
	10	- 5.2	5.1	.095	.043	—	.215	—	
	50	- 68.3	- 47.3	.197	.036	—	.755	—	j
	100	- 94.4	- 44.4	.212	.032	—	1.168	—	k
	100-Vacuum	- 64.8	11.4	.307	.028	—	—	—	j
Irrathene 201 (.010")	0	595	2405	.068	.045	—	.058	—	n
	5	- 6.2	13.4	.078	.039	—	.090	—	
	10	- 9.4	2.9	.097	.035	—	.171	—	
	50	- 69.8	- 46.7	.162	.036	—	.635	—	j
	100	- 94.5	- 46.3	.209	.027	—	.863	—	k
Fluorocarbon	0	165	2695	—	—	—	—	—	i
Teflon 1 (.010")	0	165	2695	—	—	—	—	—	i
	.1	- 9.1	- 44.6	—	—	—	—	—	
	.5	- 78.8	- 54.8	—	—	—	—	—	
	1	- 87.0	- 59.2	—	—	—	—	—	
	5	-100.0	- 61.1	—	—	—	—	—	e
	5-Vacuum	- 78.8	- 47.7	—	—	—	—	—	

TABLE II - Continued

Materials	Dose	Elongation	Tensile	Trans	Vinylidene	Vinyl	Carbonyl	Hydroxyl	Remarks
Polyester									
Mylar A (.003")	0	150	20,340	—	—	—	—	—	o
	5	0.0	0.0	—	—	—	—	—	
	10	- 13.3	- 6.4	—	—	—	—	—	
	50	- 20.0	- 15.6	—	—	—	—	—	
	100	- 30.3	- 34.1	—	—	—	—	—	
	100-Vacuum	- 23.3	- 22.8	—	—	—	—	—	
Styrene									
Polyflex (.002")	0	0	11,270	—	—	—	—	—	o
	5	—	- 6.4	—	—	—	—	—	
	22	—	- 15.9	—	—	—	—	—	
	55	—	- 13.4	—	—	—	—	—	
	100	—	- 23.2	—	—	—	—	—	j
	100-Vacuum	—	- 25.5	—	—	—	—	—	
Vinyl Chlorides									
Geon 8630 (.004")	0	245	2555	—	—	—	—	—	p
	5	- 10.7	- 25.6	—	—	—	—	—	q
	10	- 21.3	- 34.5	—	—	—	—	—	r
	50	- 26.5	- 36.2	—	—	—	—	—	s
	100	- 38.8	- 31.5	—	—	—	—	—	t
Geon 8630 (.020")	0	300	2735	—	—	—	—	—	p
	5	4.0	- 5.7	—	—	—	—		
	5	4.0	- 5.7	—	—	—	—	—	q
	10	4.6	- 6.2	—	—	—	—	—	r
	50	- 19.2	- 10.2	—	—	—	—	—	s
	100	- 28.3	- 6.0	—	—	—	—	—	t

TABLE II - Continued

Materials	Dose	Elongation	Tensile	Trans	Vinylidene	Vinyl	Carbonyl	Hydroxyl	Remarks
Vinyl Chlorides (Cont.)									
Geon 8640 (.004")	0	225	3150	—	—	—	—	—	o
	5	- 8.5	- 13.3	—	—	—	—	—	u
	10	- 11.8	- 28.1	—	—	—	—	—	v
	50	- 44.4	- 44.4	—	—	—	—	—	w
	100	- 46.7	- 42.3	—	—	—	—	—	x
	100-Vacuum	- 29.1	- 22.4	—	—	—	—	—	w
Geon 8640 (.020")	0	325	3580	—	—	—	—	—	o
	5	- 5.3	- 5.1	—	—	—	—	—	u
	10	- 2.2	- 4.1	—	—	—	—	—	v
	50	- 22.2	- 32.0	—	—	—	—	—	w
	100	- 32.3	- 31.2	—	—	—	—	—	x

* Irradiated in vacuo.
a- Light tan transparent.
b- Light yellow.
c- Light amber.
d- Slightly darker amber.
e- Very brittle, broke on bend test, could not test.
f- Light amber transparent.
g- Very slightly darker amber.
h- Darker amber.
i- Off-white translucent.
j- Light yellow tint.
k- Slightly darker yellow.
l- Quite brittle, broke on bend test.
m- Crumbled, could not test.
n- Off-white, slight yellow tint.
o- Clear transparent.
p- Transparent, slight cloudiness.
q- Light tan translucent.
r- Light orange translucent.
s- Dark brown opaque.
t- Darker brown opaque.
u- Very light orange transparent.
v- Light orange-tan transparent.
w- Dark brown-orange transparent.
x- Dark brown-amber, slightly transparent.

TABLE III

GAS EVOLUTION FROM PLASTICS IRRADIATED IN VACUO TO 1 x 10^8 r

Materials	Percent Gas Evolved									Remarks
	H_2	CH_4	C_2H_x	O_2	C_3H_x	CO_2	C_4H_x	C_5H_x	C_6H_x	
Macrofol	—	—	—	—	—	—	—	—	—	a
Alathon 3, NC-10	97.5	0.09	1.10	0.01	0.60	—	0.40	0.10	0.10	
Marlex 50	97.8	0.10	1.10	0.20	0.40	—	0.10	—	—	b
Irrathene 101	96.9	0.28	2.30	0.01	0.20	—	0.30	0.10	—	
Teflon 1	—	—	—	—	—	—	—	—	—	c,d
Mylar A	—	—	—	—	—	—	—	—	—	e
Polyflex	—	—	—	—	—	—	—	—	—	f
Geon 8640	40.0	6.60	4.00	0.25	2.60	34.00	3.00	1.00	2.00	

a - Less than 3.2 x 10^{-4} moles per gram evolved at standard temperature and pressure.
b - 0.3% N_2 found due to incomplete vacuum.
c - Total dose was 5 x 10^6 r.
d - Less than 3.9 x 10^{-5} moles per gram evolved at standard temperature and pressure.
e - Less than 2.1 x 10^{-4} moles per gram evolved at standard temperature and pressure.
f - Less than 4.2 x 10^{-4} moles per gram evolved at standard temperature and pressure.

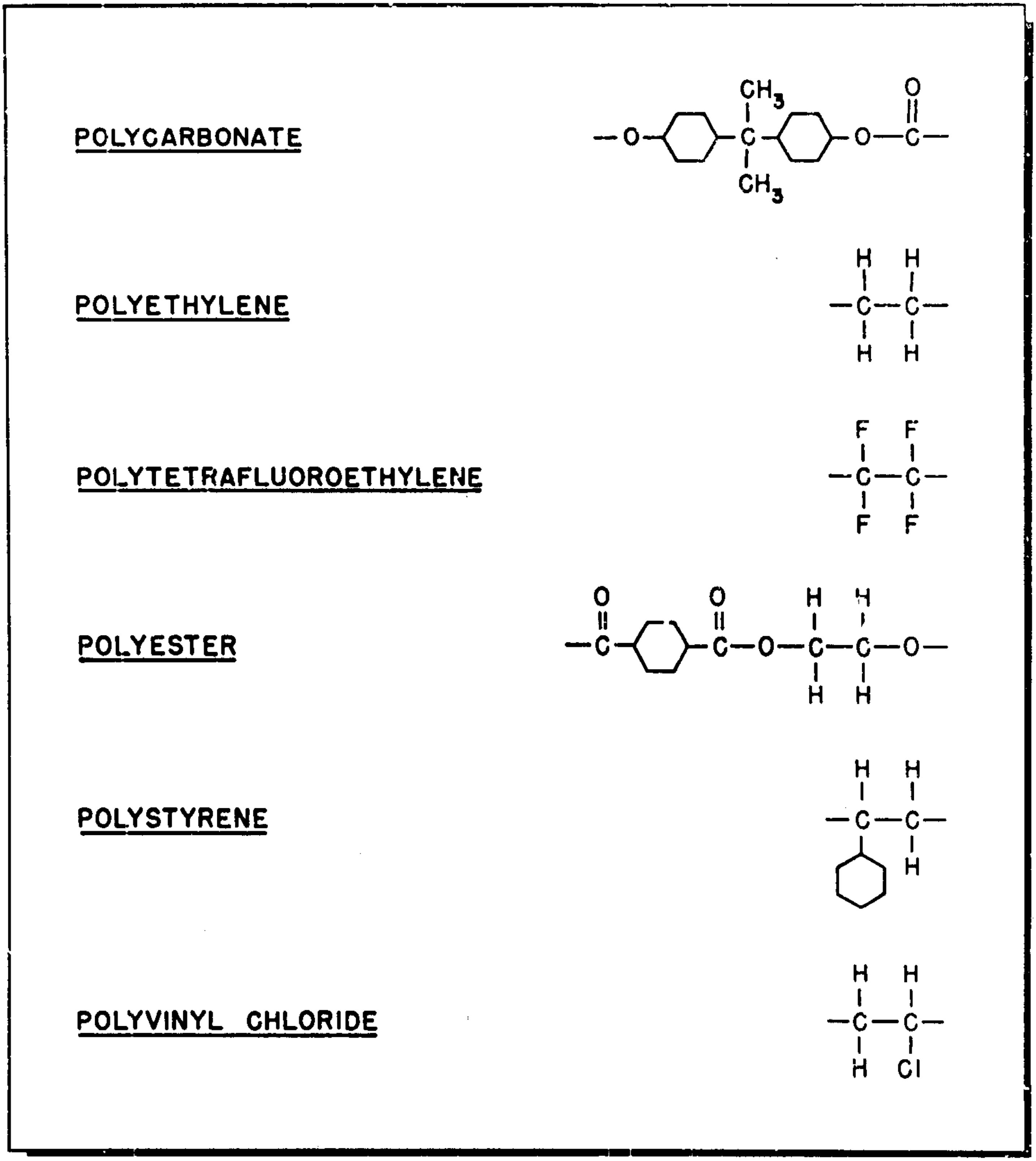


FIG. 1 — REPEATING STRUCTURAL UNITS OF PLASTICS

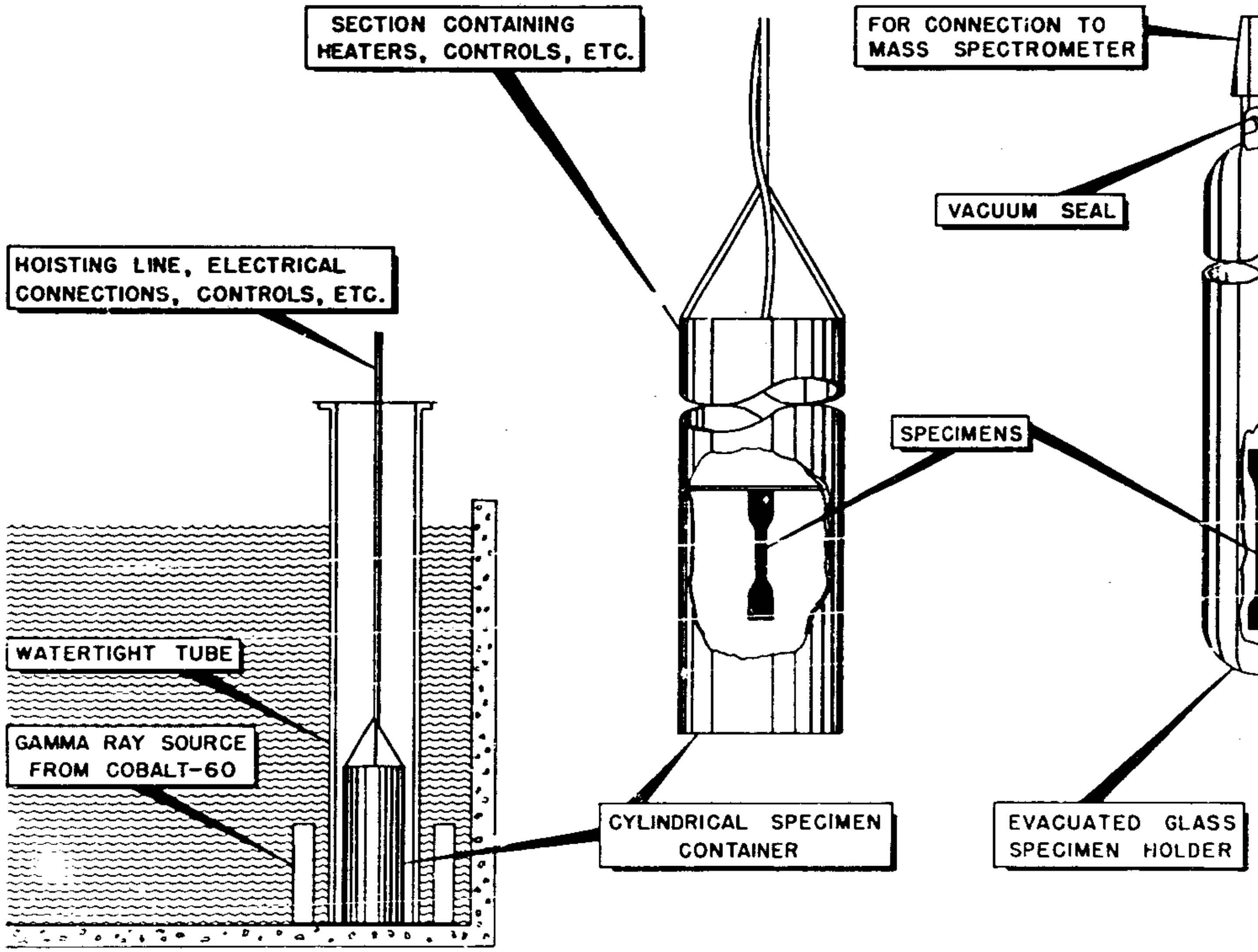


FIG. 2 – SCHEMATIC DIAGRAM OF COBALT-60 SOURCE AND ARRANGEMENT OF SPECIMENS BEING IRRADIATED

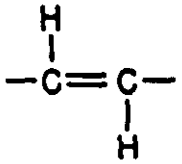
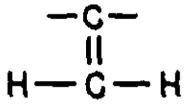
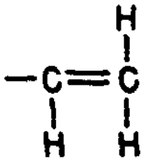
TYPE	ABSORBING GROUP	FREQUENCY
UNSATURATION		
TRANSVINYLENE	 $-\overset{H}{\overset{\vert}{C}}=\underset{H}{\underset{\vert}{C}}-$	965 cm^{-1}
VINYLIDENE	 $\begin{array}{c} -C- \\ \Vert \\ H-C-H \end{array}$	888
VINYL	 $-\underset{H}{\underset{\vert}{C}}=\overset{H}{\overset{\vert}{\underset{H}{\underset{\vert}{C}}}}$	909
OXIDATION		
CARBONYL	$C=O$	~1720
HYDROXYL	$O-H$	~3550

FIG. 3 – CHEMICAL EFFECTS AND ABSORPTION FREQUENCIES

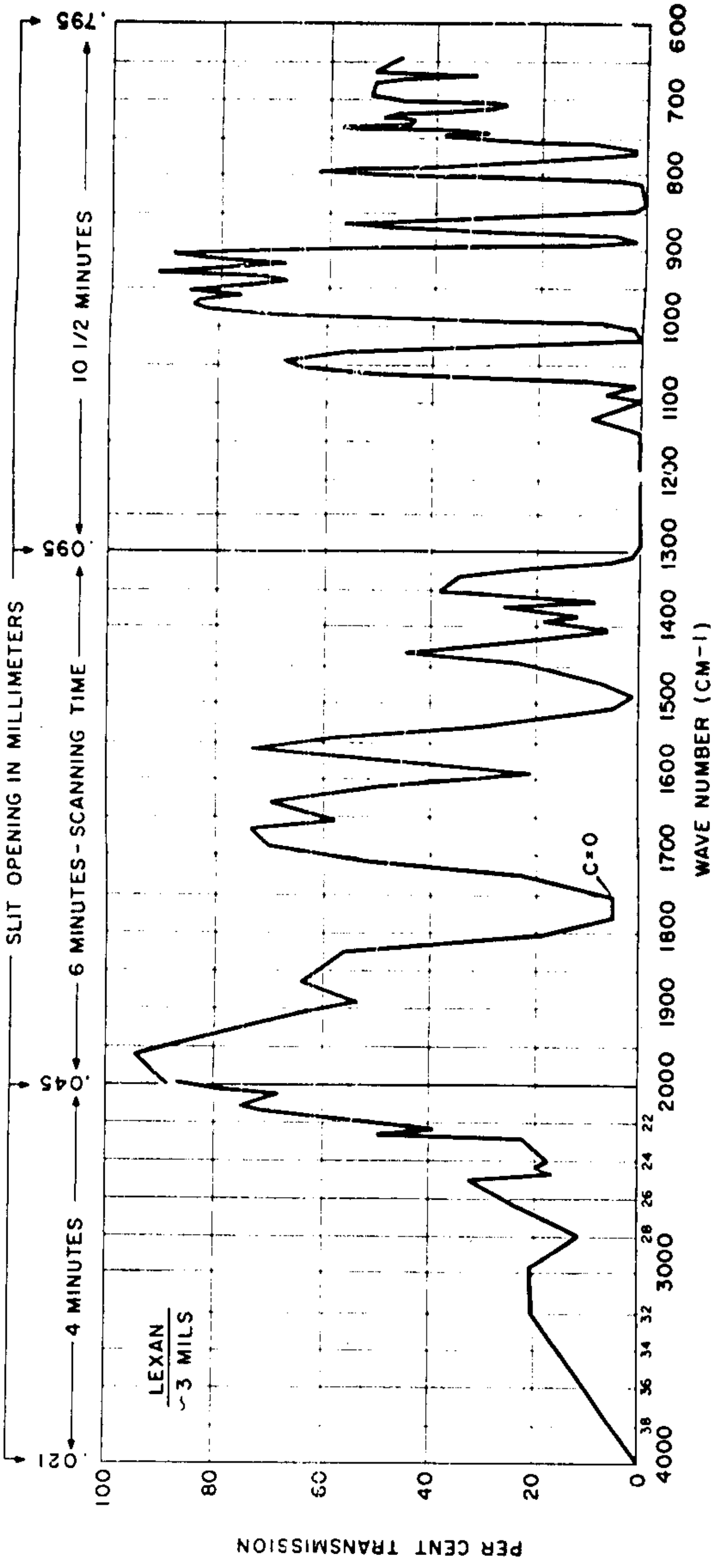


FIGURE 4

ORIGINAL SPECTRA OF POLYCARBONATE

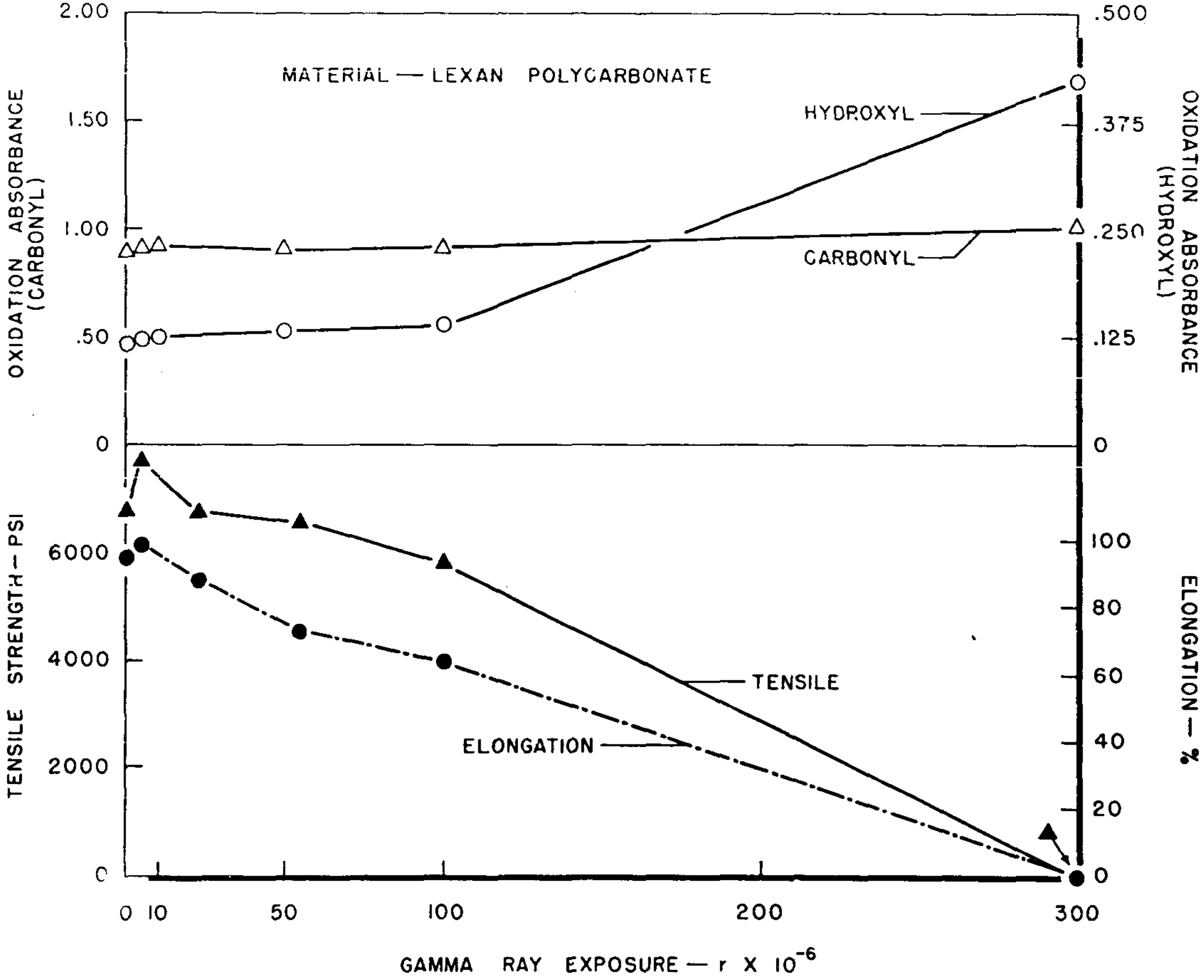


FIG. 5 — CHEMICAL AND PHYSICAL CHANGES IN A POLYCARBONATE PLASTIC INDUCED BY EXPOSURE TO GAMMA RADIATION IN AIR AT 25 C AND NORMAL ATMOSPHERIC PRESSURE

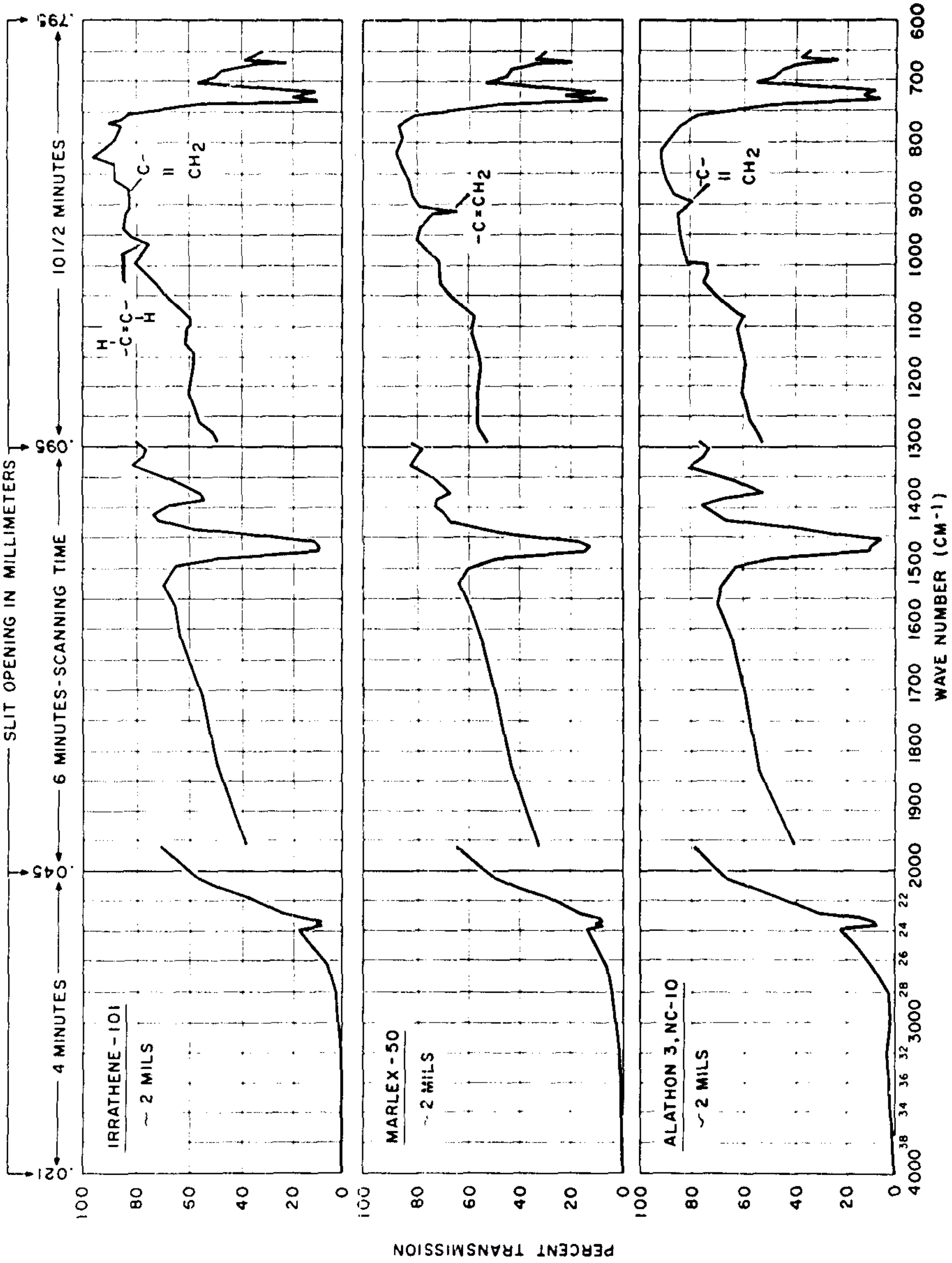


FIGURE 6

ORIGINAL SPECTRA OF POLYETHYLENES

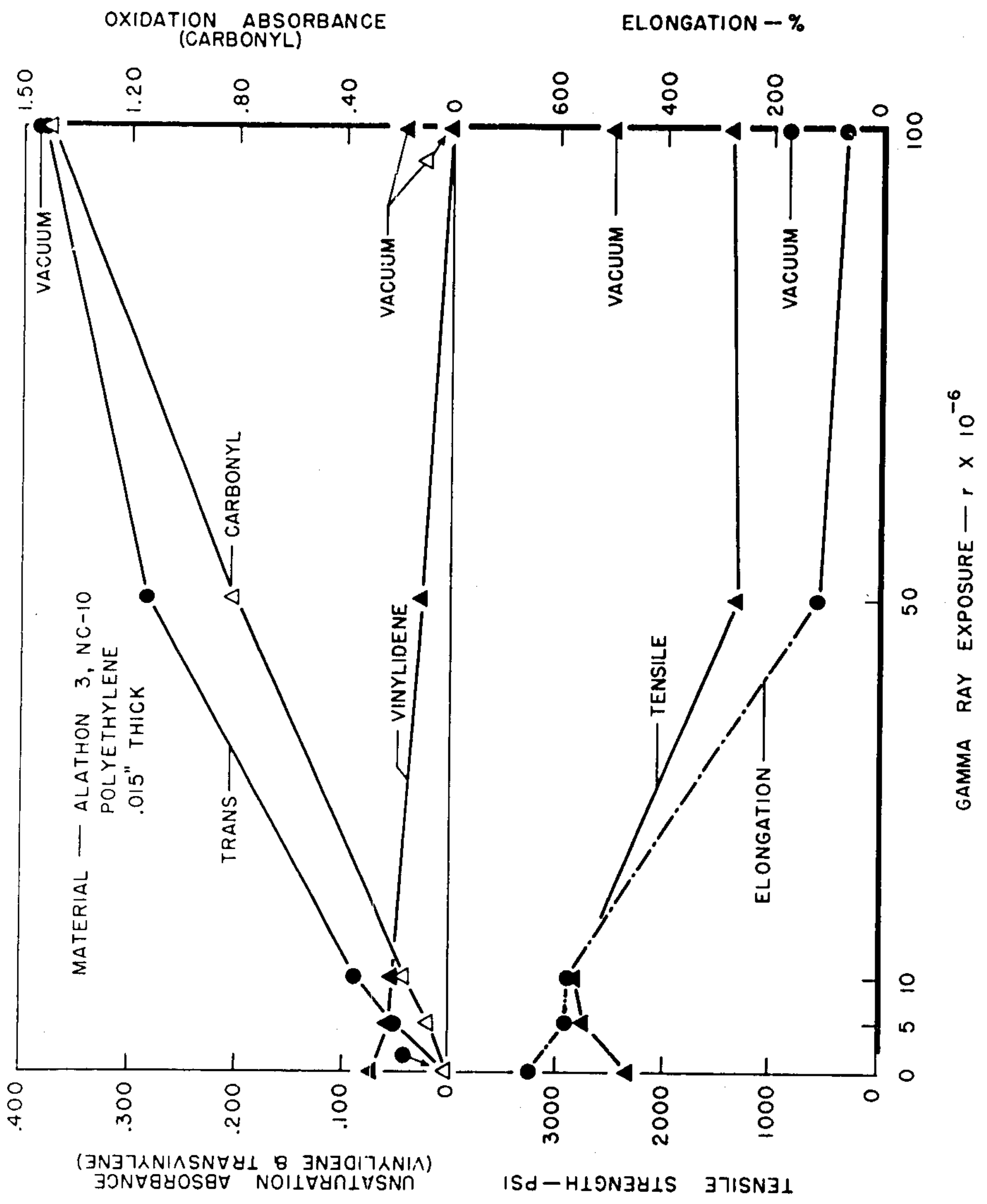


FIG. 7 – CHEMICAL AND PHYSICAL CHANGES IN POLYETHYLENE PLASTIC INDUCED BY EXPOSURE TO GAMMA RADIATION AT 25 C

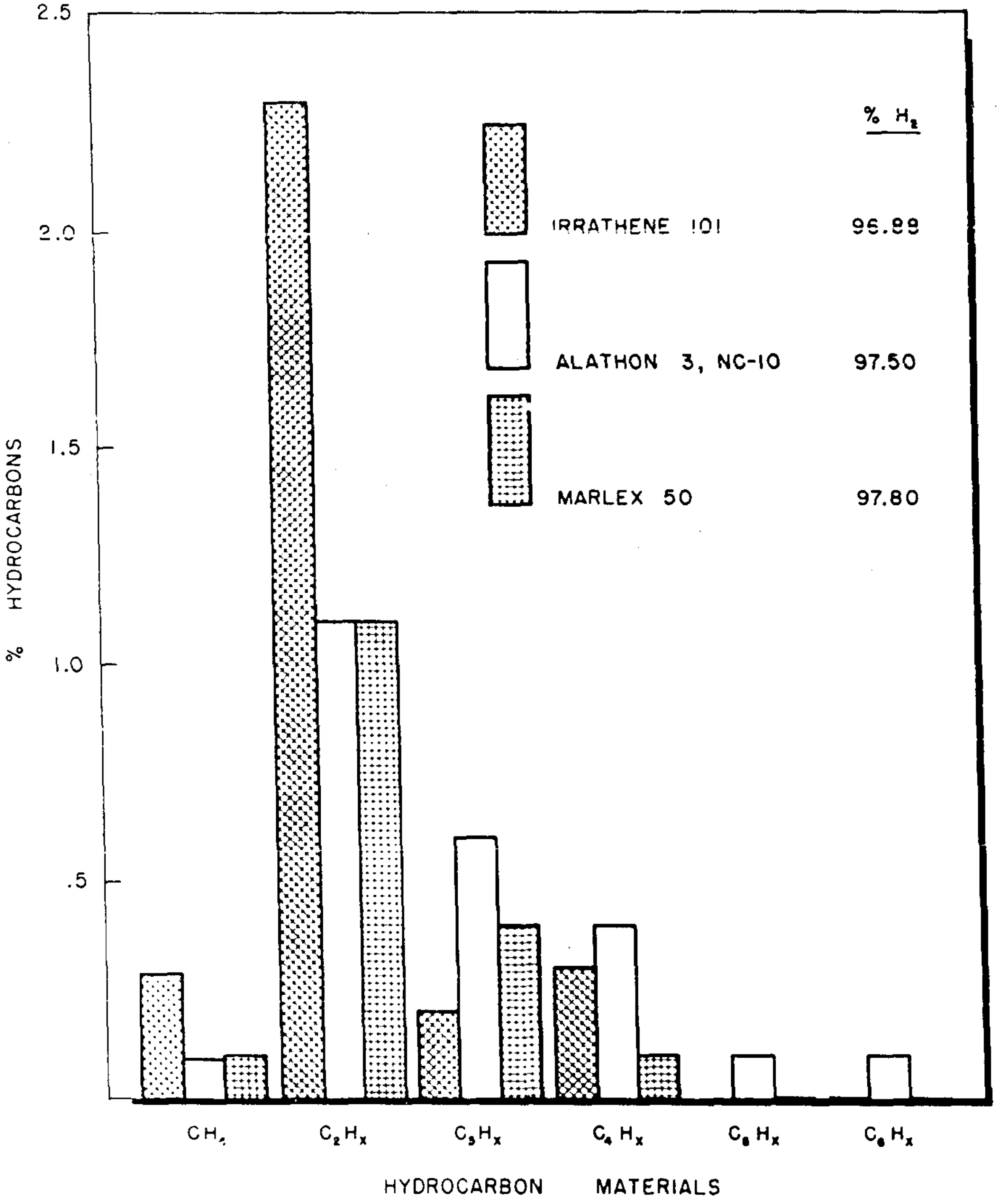


FIG. 8-MASS SPECTRAL CLEAVAGE PATTERN OF POLYETHYLENE PLASTICS

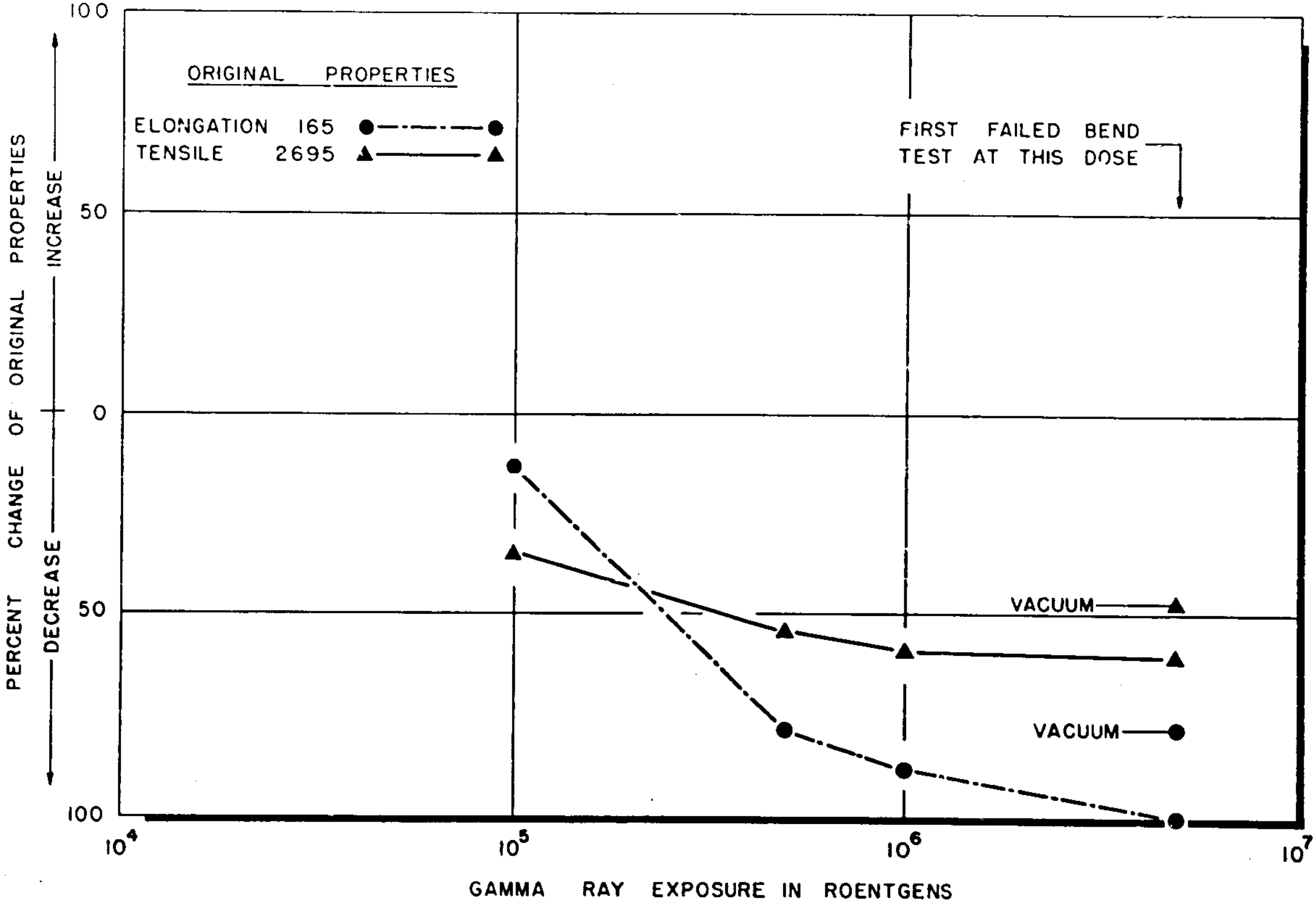


FIG. 9— CHANGE IN PROPERTIES OF TEFLON POLYTETRAFLUOROETHYLENE INDUCED BY EXPOSURE TO GAMMA RADIATION IN AIR AT NORMAL ATMOSPHERIC PRESSURE AND IN VACUO AT 25 C

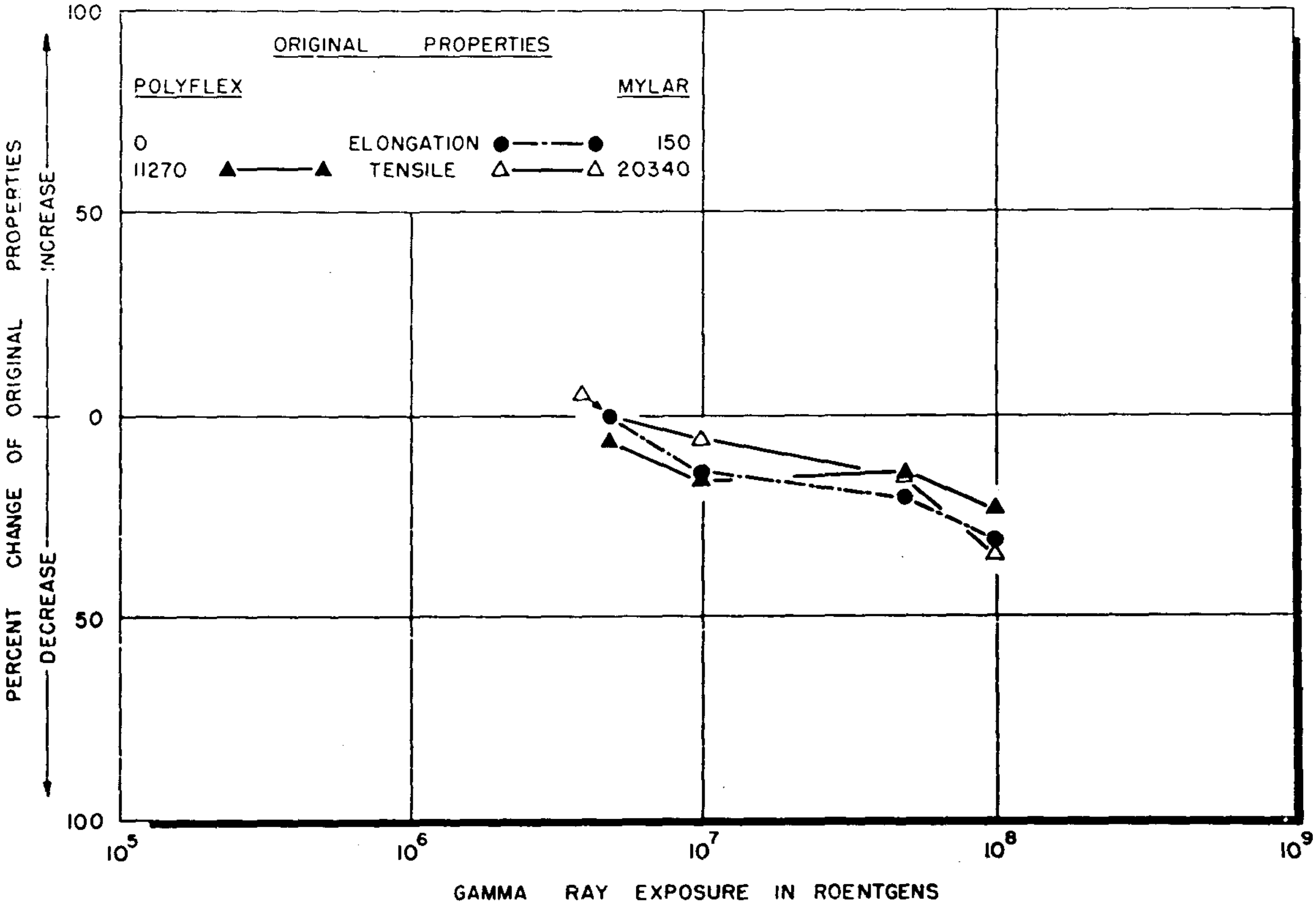


FIG. 10- CHANGE IN PROPERTIES OF POLYSTYRENE AND POLYESTER PLASTICS INDUCED BY EXPOSURE TO GAMMA RADIATION IN AIR AT 25 C AND NORMAL ATMOSPHERIC PRESSURE

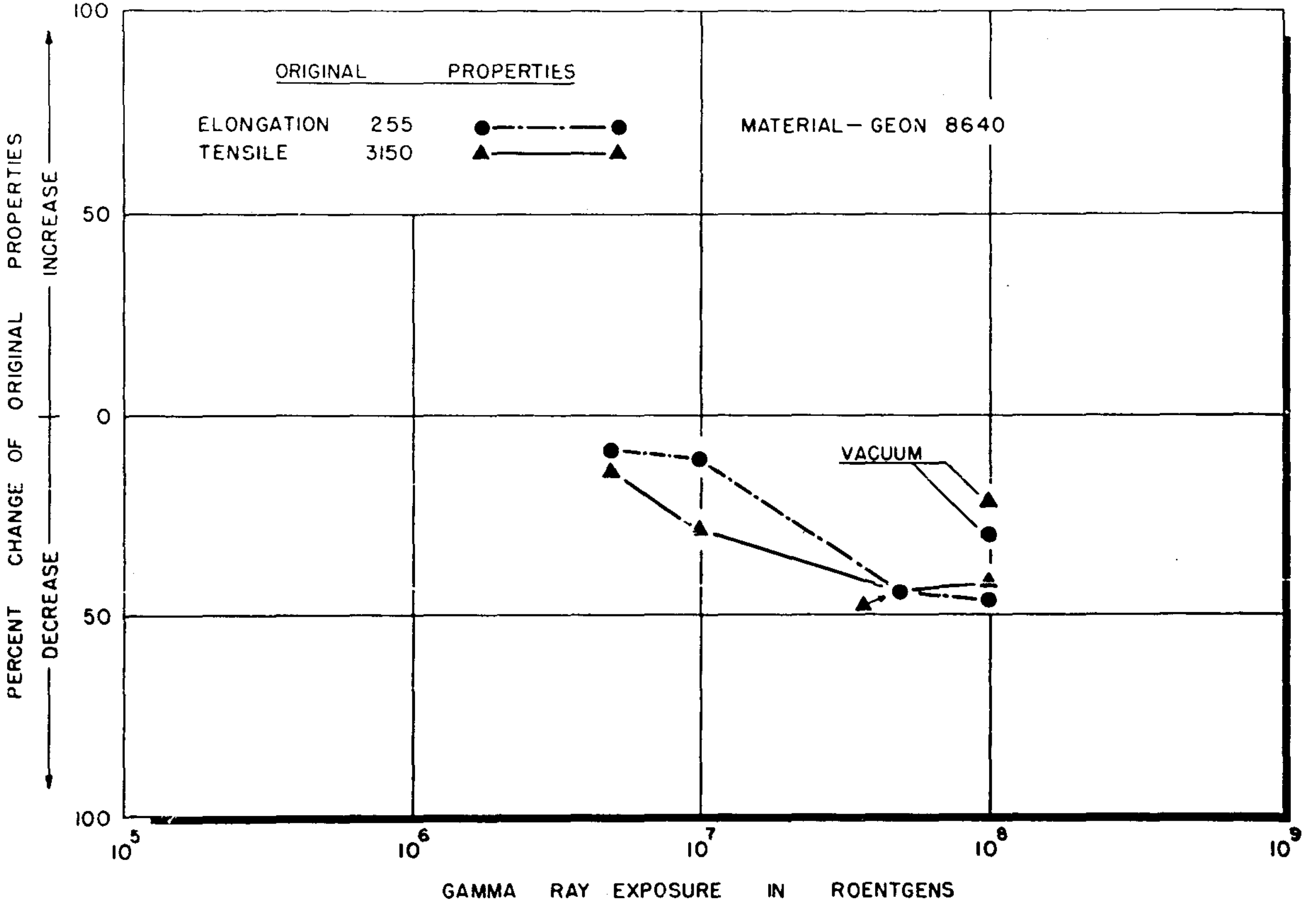


FIG. 11 — CHANGE IN PROPERTIES OF PLASTICIZED POLYVINYL CHLORIDE INDUCED BY EXPOSURE TO GAMMA RADIATION IN AIR AT NORMAL ATMOSPHERIC PRESSURE AND IN VACUO AT 25 C

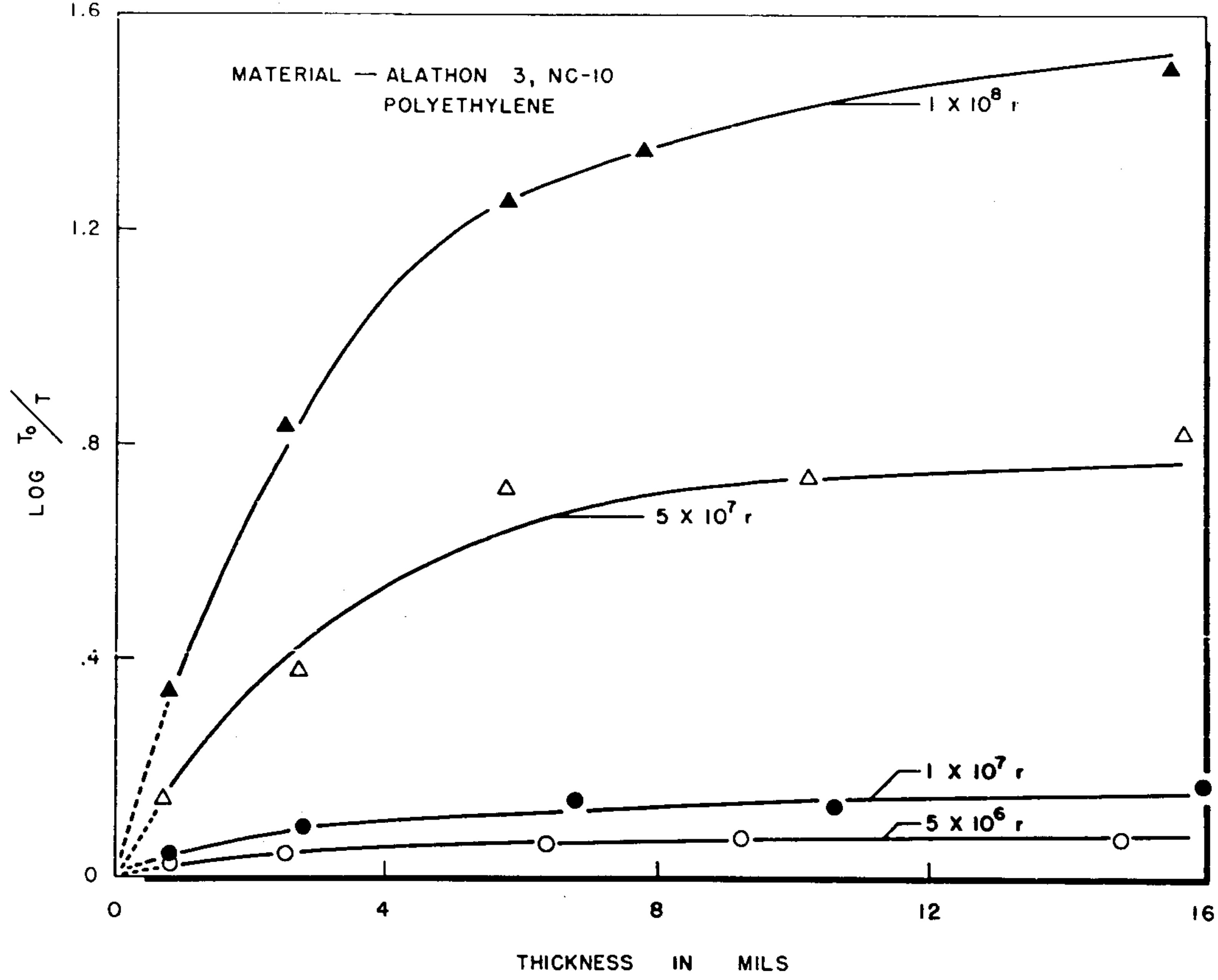


FIG. 12 - OXIDATION OF POLYETHYLENE AS A FUNCTION OF THICKNESS

The function Q, which is proportional to the radiation efficiency (as shown below) has been defined to eliminate the need of determining specific absorption coefficients for the carbonyl groups. These are difficult to determine because acid, ketone, and aldehyde groups are all contributing to the intensity of the absorbance and the resolution of the prism spectrometer is not sufficient to determine the individual contributions. The principle assumption is that each of these groups contributing to the band would be formed in the same ratio, independent of total exposure and thickness.

The weight fraction of a functional group is given by$^{(11)}$:

$$\text{Weight Fraction} = \frac{\text{Log } (T_0/T)}{(P)\ (K_{0.1}'')\ (L)\ (10)}$$

where T is the percent transmission of light (about 1720 cm^{-1}) through the sample; T_0 is the background transmission which has been corrected to 100%; P is the density in grams/cm^3; $K_{0.1}''$ is the specific absorption coefficient in cm^2/gram for a 0.1 mm sample cell; and L is the thickness in mm.

The above equation assumes Beer's Law to hold. Rugg et al.$^{(5)}$ have demonstrated this in 30 mil films of polyethylene with up to 0.1% by weight C=O. It is probable that the concentration of carbonyl in the irradiated films is higher than this but the assumption will still be made.

The radiation efficiency G (molecules of functional group per 100 e.v. absorbed by sample), is given by:

$$G = \frac{\text{Weight Fraction X N X 100}}{\text{M X D}}$$

Fig. 13 - Derivation of Chemical Effects Function Q

where N is Avagadro's number; M is the molecular weight of functional group in grams/mole; and D is the radiation dose in e.v./gram (it is assumed that the Roentgen equivalent is 83.3 ergs/gram). By combining these equations and rearranging we have:

$$\frac{(P)\ (K_{0.1''})\ (10)\ (M)}{(N)\ (100)}\,G = \frac{\mathrm{Log}\ (T_o/T)}{LD}$$

Multiplying by a constant k to change D to Mr (Megaroentgens; 5.24×10^{13} e.v./gram equals one Roentgen; see also assumption for D above) we have:

$$\frac{k}{10N}\ (P)\ (K_{0.1''})\ (M)\ G = \frac{\mathrm{Log}\ (T_o/T)}{LMr}$$

For a given material and functional group measured, (P) $(K_{0.1''})$ and (M) are constant. k/10N is a constant (see above), therefore let

$$K = \frac{k}{10N}\ (P)\ (K_{0.1''})\ (M)$$

and finally:

$$Q = KG = \frac{\mathrm{Log}\ (T_o/T)}{LMr} \qquad (6)$$

Fig. 13 - Continued

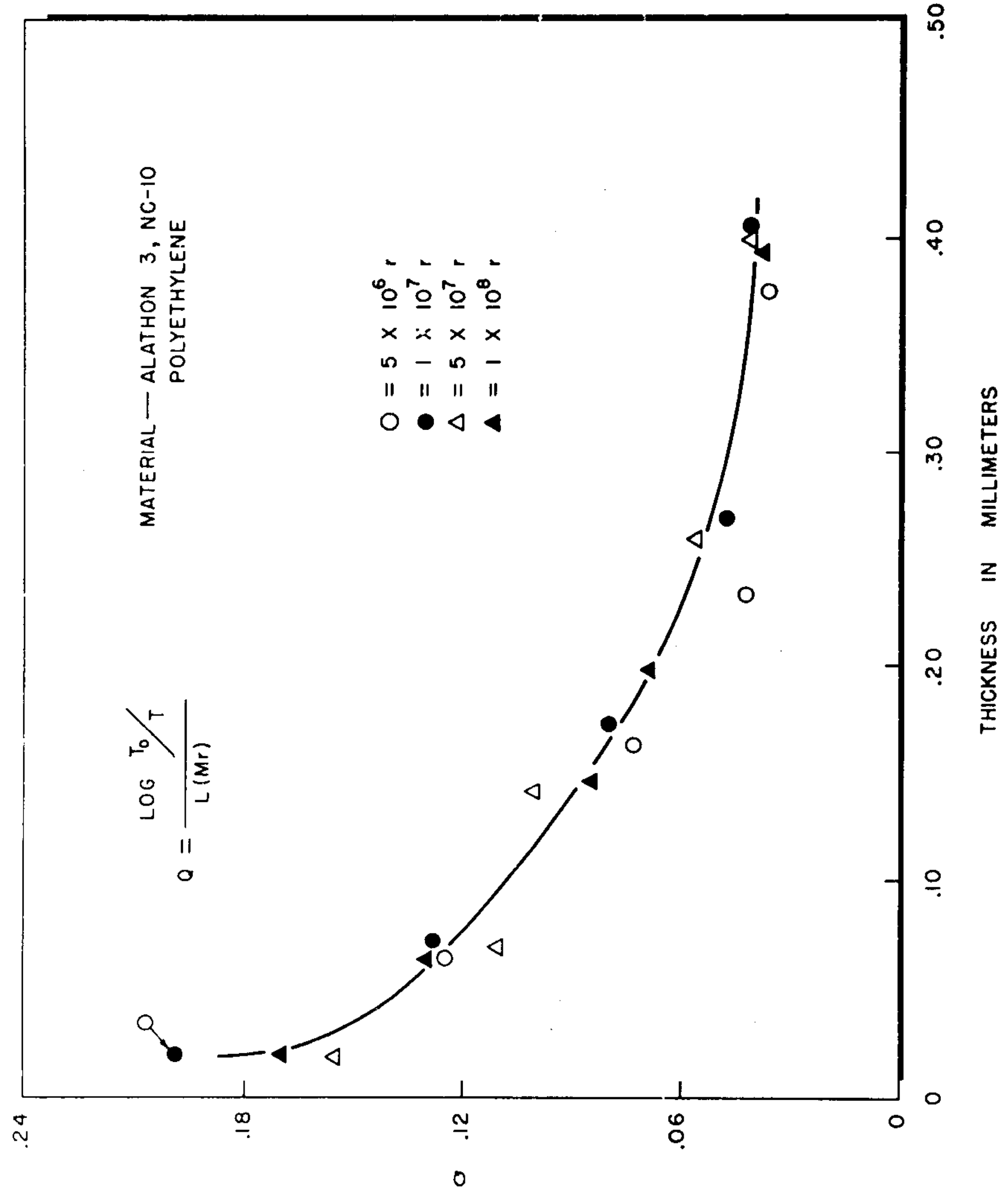


FIG. 14-CHEMICAL EFFECTS FUNCTION VS. THICKNESS FOR OXIDATION OF POLYETHYLENE PLASTIC

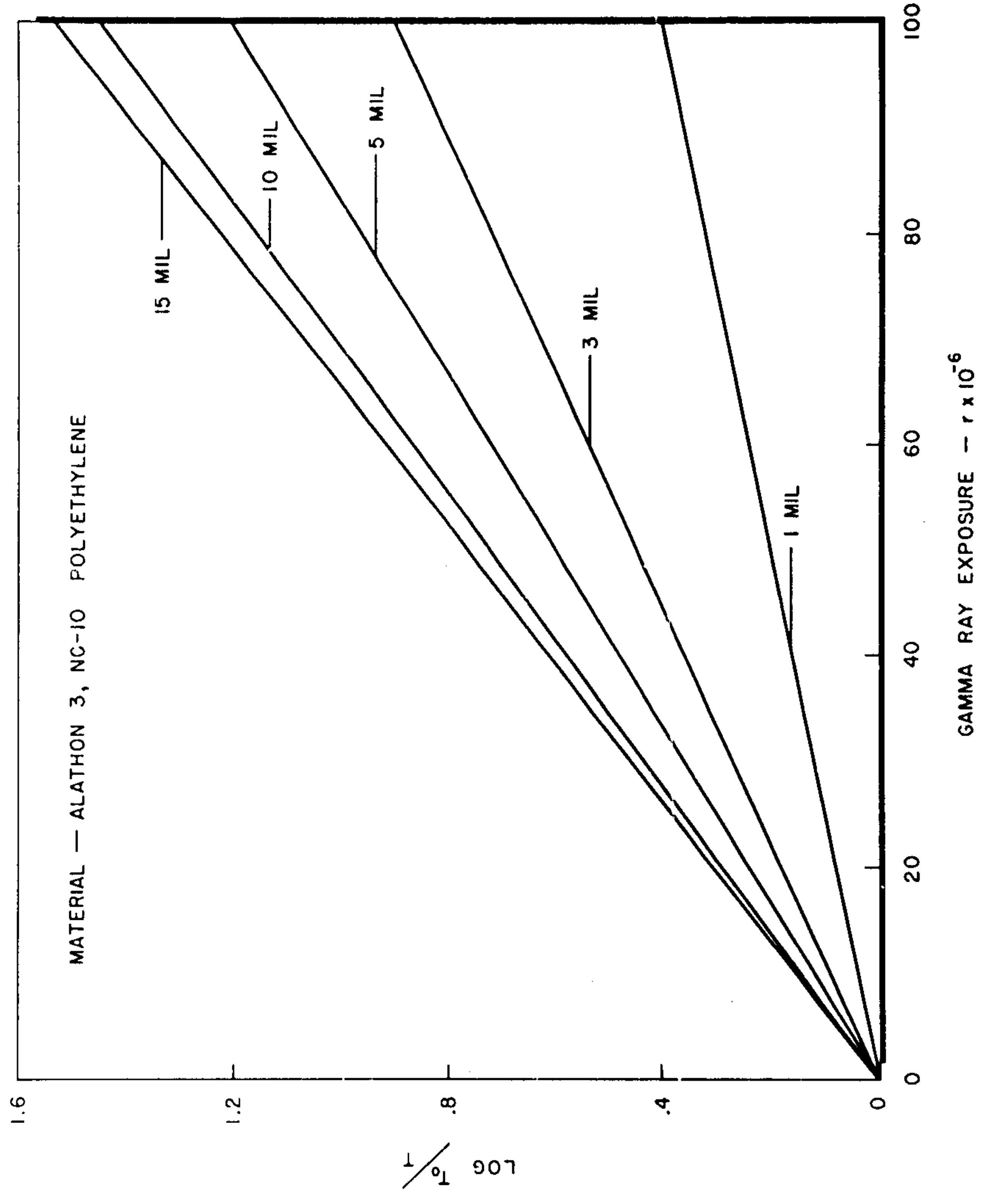


FIG. 15 – OXIDATION OF POLYETHYLENE AS A FUNCTION OF GAMMA RADIATION EXPOSURE

An interesting property of Q as defined previously can be shown as follows: the reciprocal of (6):

$$\frac{1}{Q} = \frac{LMr}{A}$$

where A equals Log (T_o/T). Figure 17 shows a plot of 1/Q vs. L which is seen to give a straight line. Thus,

$$\frac{1}{Q} = mL + b$$

$$\frac{LMr}{A} = mL + b$$

$$A = \frac{LMr}{mL + b}$$

where m and b are constants. Taking Mr as constant and defining B equal to b/Mr, and C equal to m/Mr, we have

$$A = \frac{L}{BL + C}$$

and rearranging:

$$\frac{L}{A} = BL + C \qquad (7)$$

Fig. 16 - Derivation Relating Carbonyl Absorption With Sample Thickness

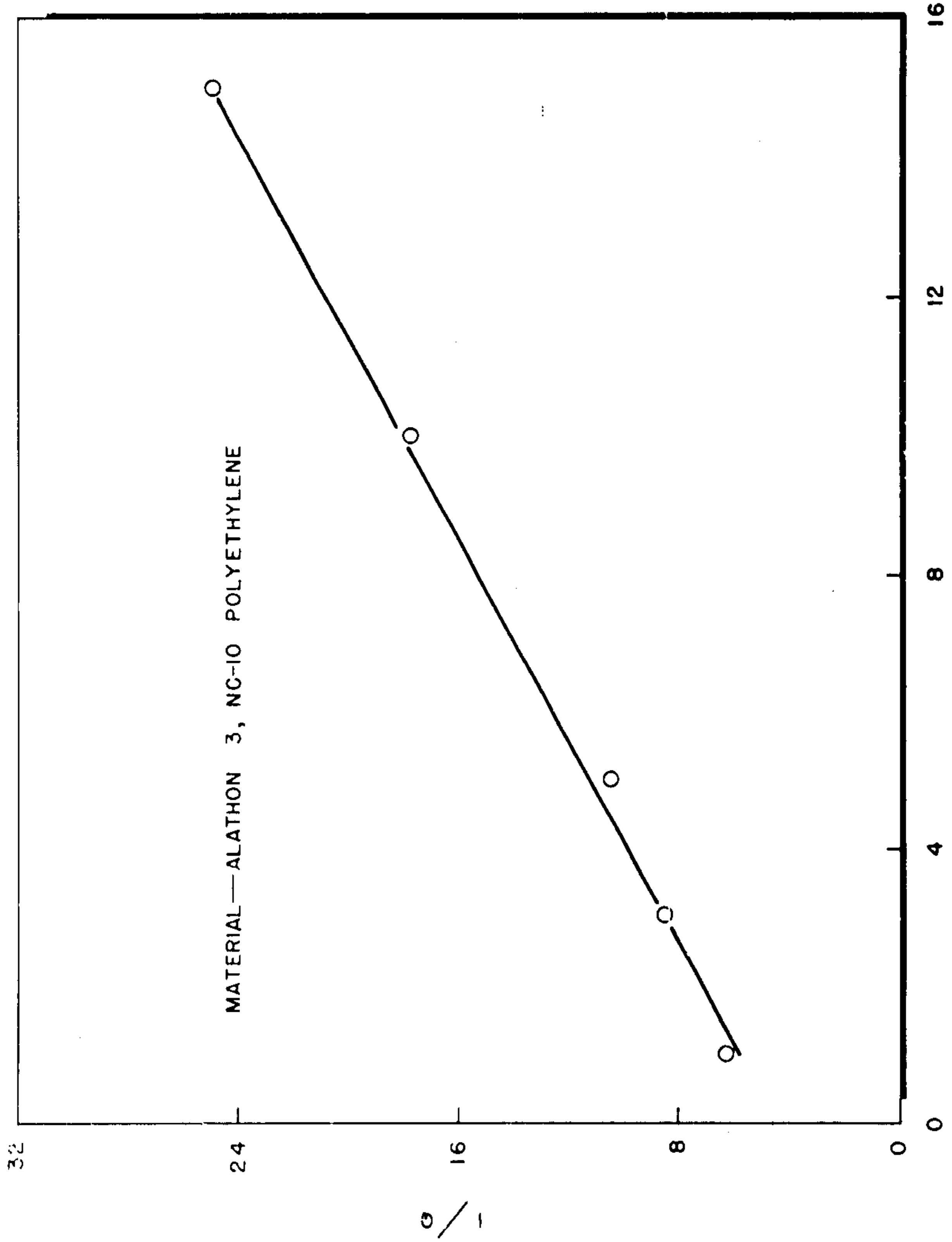


FIG. 17– LINEAR NATURE OF 1/Q AS A FUNCTION OF THICKNESS

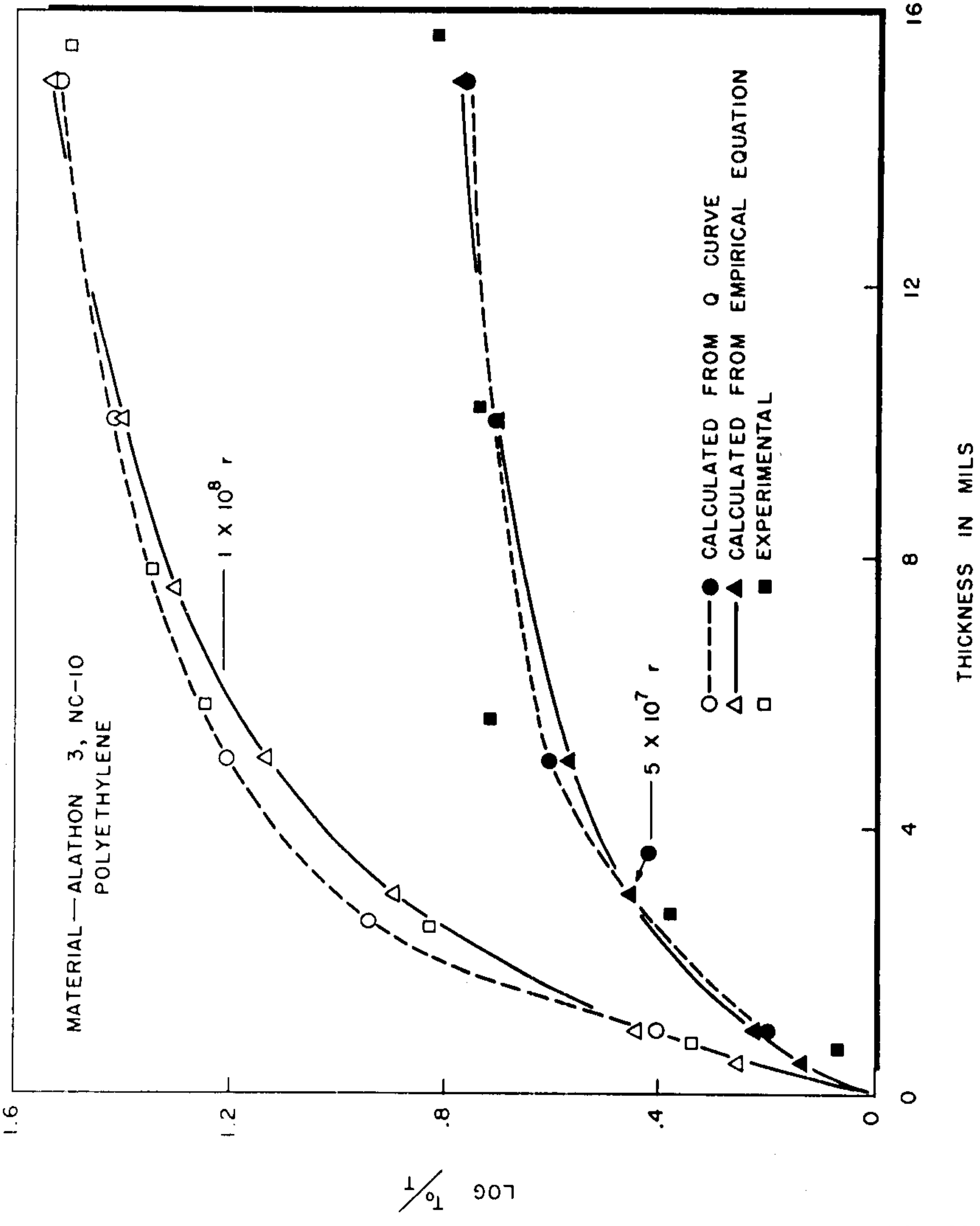


FIG. 18 - CALCULATED AND EXPERIMENTAL CARBONYL ABSORPTION IN POLYETHYLENE

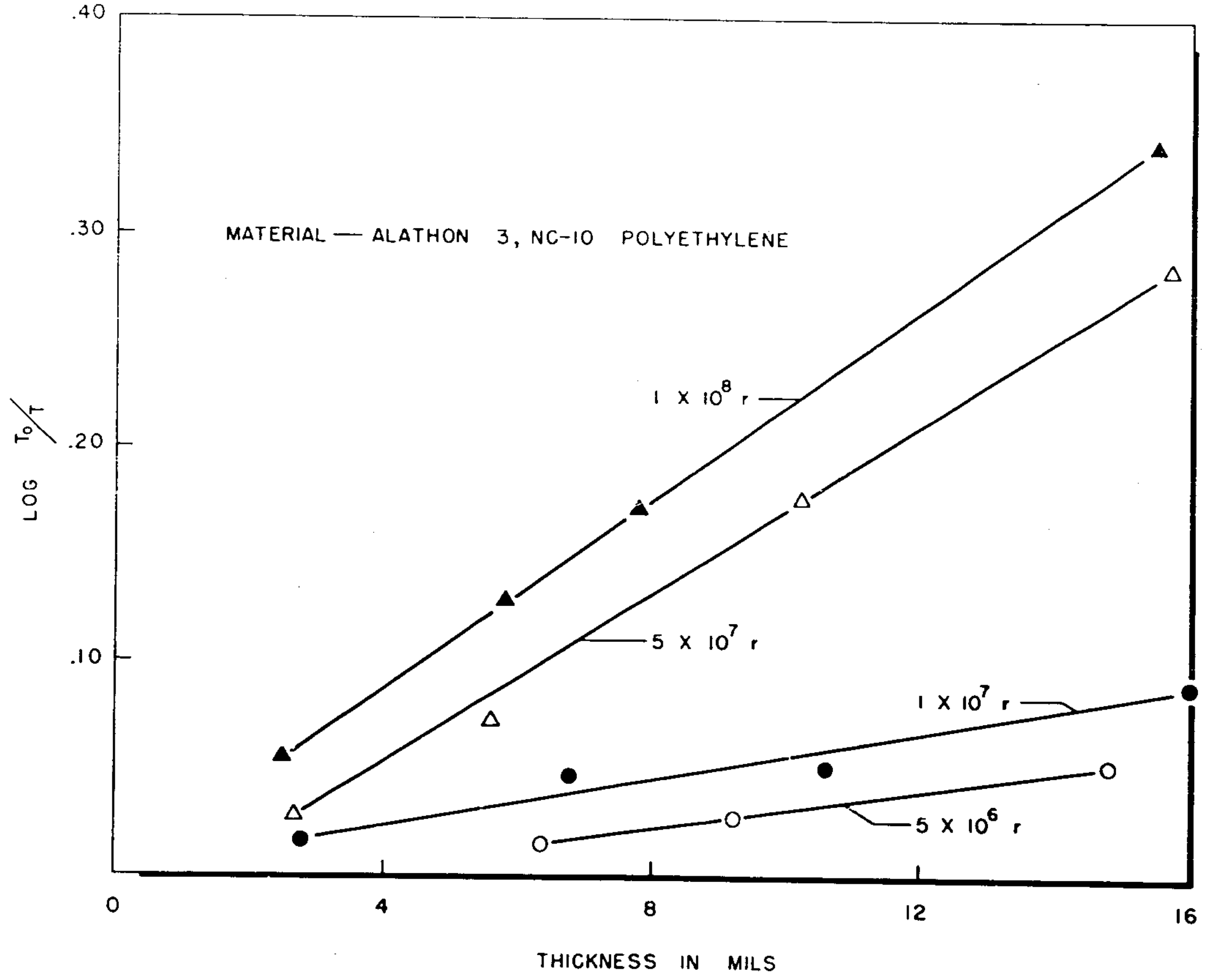


FIG. 19 - INCREASE IN TRANSVINYLENE IN POLYETHYLENE WITH INCREASING THICKNESS

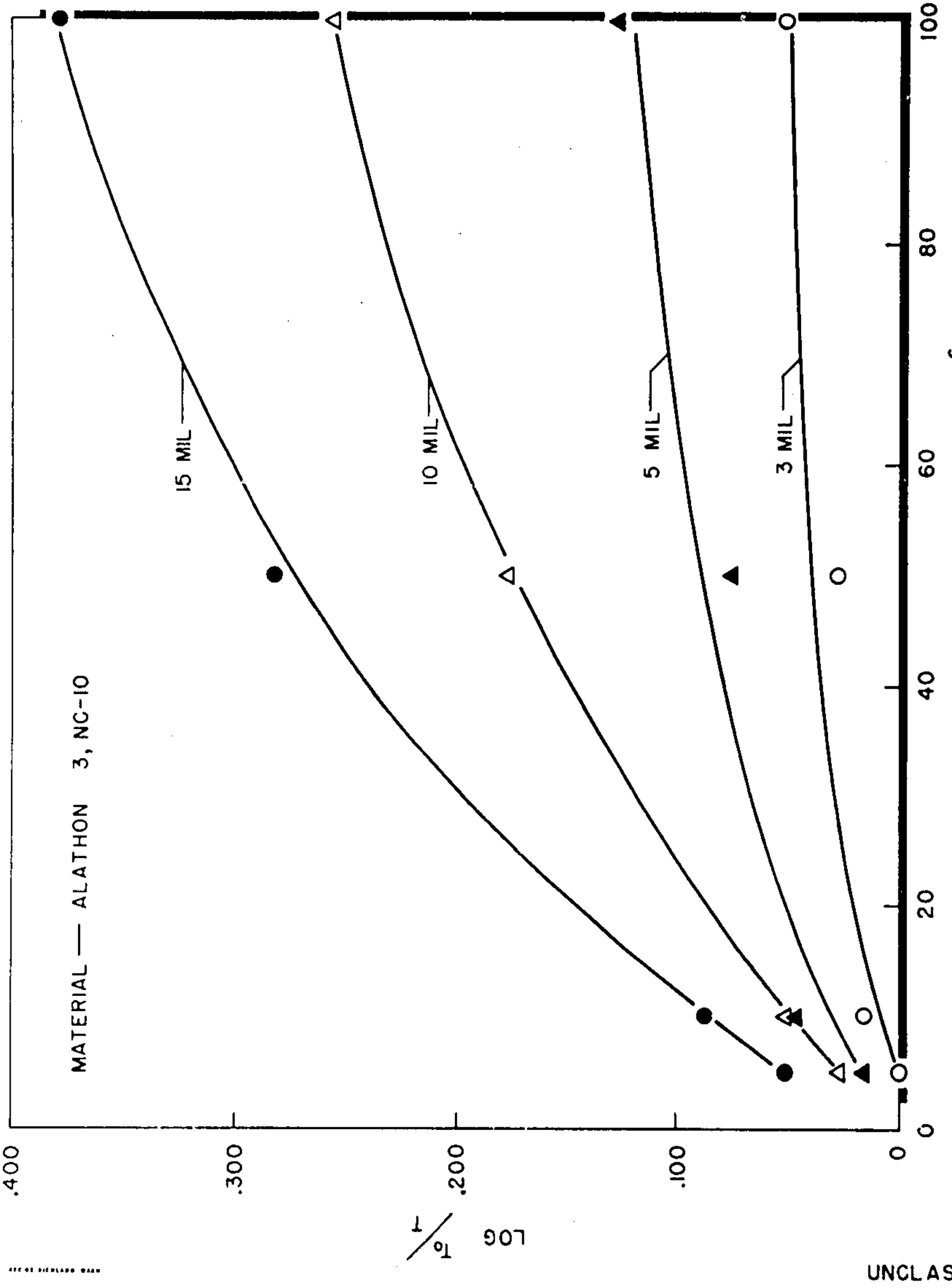


FIG. 20 – INCREASE IN TRANSVINYLENE IN POLYETHYLENE WITH INCREASING RADIATION DOSE

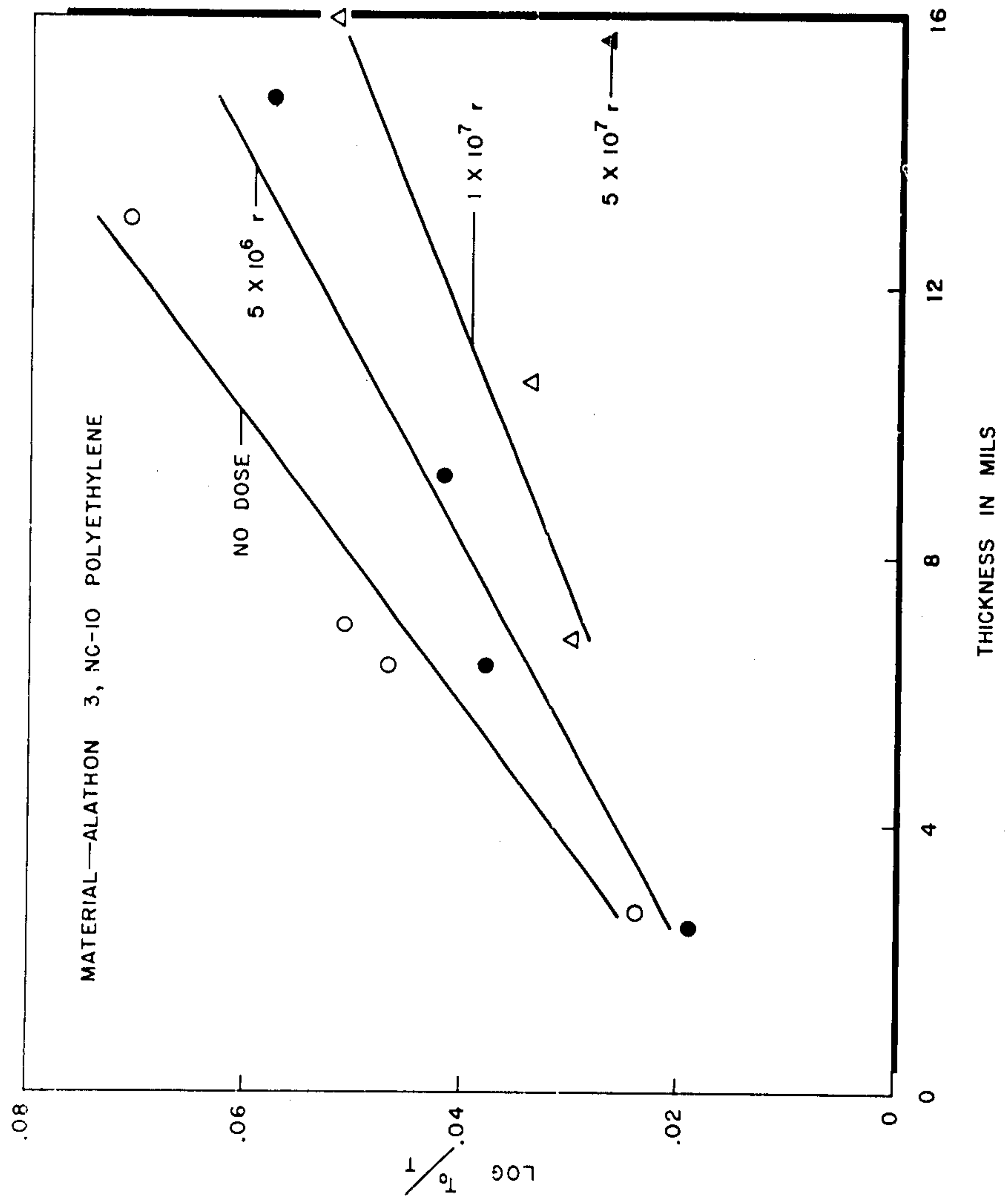


FIG. 21—INCREASE IN VINYLIDENE IN POLYETHYLENE WITH INCREASING THICKNESS