

# UNPUBLISHED PRELIMINARY DATA

*Final Report*

## VACUUM ULTRAVIOLET IRRADIATION OF POLYBUTADIENE

*Prepared for:*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D.C. 20546

TASK ORDER  
CONTRACT NO. NASr-49(20)

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA



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February 15, 1965

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*By:* MORTON A. GOLUB

*SRI Project PRU-5127*

*Approved:* A. G. BROWN, DIRECTOR  
INDUSTRIAL RESEARCH DIVISION

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ABSTRACT

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Polybutadiene in the solid state undergoes photochemical cis-trans isomerization, in the absence of deliberately added sensitizer, when irradiated in vacuo with krypton 1236 Å or mercury 2537 Å radiation. The isomerization is accompanied by loss of unsaturation which is more pronounced with krypton than with mercury radiation. The quantum yields for these two reactions in the case of krypton radiation were found to be 0.25 and 1.53, respectively, while the corresponding yields for the mercury irradiation were 0.09 and 0.07. The rather high G-values or 100-e.v. yields for the vacuum photochemical isomerization and the loss of double bonds (2.5 and 15.3) compare well with corresponding G-values for the radiation chemical analogs (7.2 and 13.6-7.9, respectively), thus calling attention to the likely similarity of mechanisms in these two systems. In particular, the high quantum yield or G-value for loss of double bonds with krypton irradiation strongly indicates a chain cyclization comparable to that postulated in the radiation chemistry of diene polymers. The photoisomerization with mercury light is considered to be sensitized by adventitious impurities present in the polymer which absorb in the ordinary ultraviolet range (where the polymer itself is transparent) and which transfer energy to the double bonds causing their excitation and isomerization. The significance of this work lies in the fact that it constitutes probably the first fundamental study of vacuum photochemical transformations in a high polymer; it has implications for further study in order to understand better the space environmental effects on polymeric materials.

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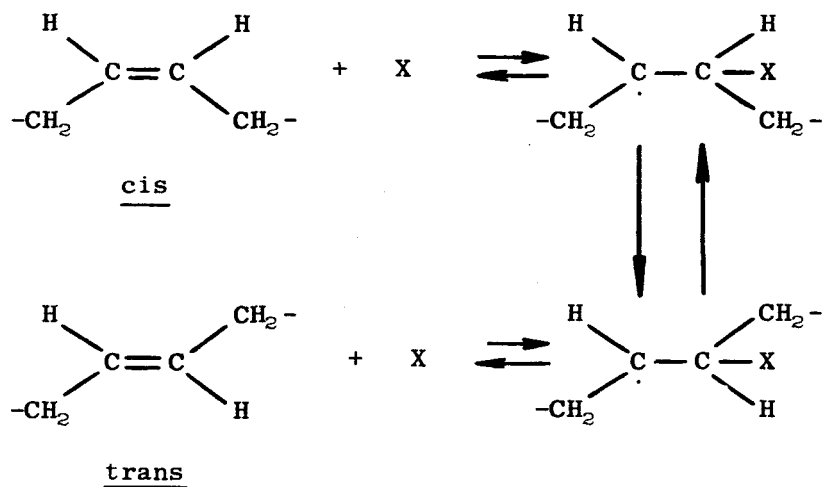
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## I INTRODUCTION

This Final Report on Contract No. NASr-49(20), "Vacuum Ultraviolet Irradiation of Polybutadiene," covers the period from July 15, 1964 to January 29, 1965. The aim of this research has been to explore the possibility of achieving the direct photochemical cis-trans isomerization of polybutadiene in the solid state (i.e., in the absence of any deliberately added sensitizer) analogous to the radiation-induced unsensitized isomerization of this polymer.<sup>1</sup> Inasmuch as the polymer double bonds begin to absorb effectively only below 1800-1900 Å, the direct photoisomerization could be expected to occur on theoretical grounds if the polymer is exposed to suitable radiation in the vacuum ultraviolet range. Attainment of this reaction not only should have considerable scientific interest from the standpoint of cis-trans isomerization of olefinic compounds generally,<sup>2</sup> but also would constitute one of the first vacuum photochemical reactions produced in a high polymer. Such a reaction should thus have a special significance in a broad study of space environmental effects on polymeric materials, in particular, those effects due to interaction with the extreme ultraviolet component of solar radiation.

Previous work by the author has shown that polybutadiene can be made to undergo cis-trans isomerization when irradiated in benzene solution with ultraviolet light<sup>3</sup> or  $\gamma$ -rays<sup>4,5</sup> in the presence of a suitable sensitizer such as an organic bromide, disulfide, or mercaptan. The mechanism of the sensitized isomerization was depicted as involving the formation of a composite radical structure from the polymer double bonds, either cis or trans, and the bromine atom or thiyl radical formed in the photolysis or radiolysis of the sensitizer. The transitory isomeric radicals which are thus formed can then interconvert. On release of the attached radical X, representing either Br· or RS·, the double bonds are reestablished with the thermodynamically more stable configuration, viz., trans, being formed predominantly. The mechanism is thus essentially the same as that indicated for the cis-trans isomerization of simple olefins

involving the same type of sensitizers.<sup>6</sup>



Isomerization of polybutadiene can also be induced thermally with sulfur,<sup>7,8</sup> sulfur dioxide,<sup>9</sup> or selenium.<sup>10</sup> Recently, the kinetics of the diphenyl disulfide photosensitized isomerization of polybutadiene was studied in detail.<sup>11</sup>

In addition to these various sensitized reactions, polybutadiene undergoes an "unsensitized" isomerization when  $\gamma$ -irradiated in benzene solution or in the solid state in the absence of any added sensitizer.<sup>1</sup> The mechanism in the solid state case is considered to involve direct excitation of the  $\pi$  electrons of the polymer double bonds to an antibonding state where free rotation and hence geometric interconversion can readily occur. In the solution case, the important agency for promoting the isomerization is assumed to be energy transfer from excited benzene molecules to the polymer double bonds, which are then able to interconvert. Whether in solution or in the solid state, the radiation-induced unsensitized isomerization of polybutadiene is an efficient process when viewed from the standpoint of energy utilization. The hypothesis of intramolecular energy transfer advanced<sup>1</sup> to explain the isomerization in the solid state has been supported by theoretical considerations<sup>12</sup> in which it was shown that each electronic excitation

in polybutadiene can isomerize 2.5 double bonds from the cis to trans configuration. Moreover, the hypothesis of efficient energy transfer from excited benzene molecules to the olefinic units<sup>1</sup> has likewise found support in other work on the radiation-induced isomerization of butene-2 in benzene.<sup>13</sup>

With polybutadiene clearly undergoing photosensitized, as well as radiation-induced sensitized and unsensitized cis-trans isomerization, it was of definite interest to see if it could also undergo a direct (unsensitized) photoisomerization. It was expected that such a reaction would entail a vacuum photochemical investigation of polybutadiene since the (unconjugated) -CH=CH- units in this polymer are transparent in the near ultraviolet, and only begin to exhibit absorption at around 1850 Å in the far ultraviolet. In principle, if the  $\pi$  electrons of the double bonds could be excited by absorption of quanta of this or shorter wavelength, analogous to the excitations produced by  $\gamma$ -rays, polybutadiene would indeed photoisomerize. Apart from the intrinsic scientific interest in a study of this kind, the indicated entry into the heretofore uncharted field of vacuum photochemistry of high polymers appeared very desirable in view of the Nation's space program, and the need to appreciate better the chemical effects of the short wavelength ultraviolet rays emitted from the sun (such as the Lyman alpha line at 1216 Å) on polymers exposed to outer space environment. At the same time, the possibility that adventitious trace impurities in polymer films could serve to photosensitize reactions in the near ultraviolet region, where the polymer per se is effectively transparent, made it desirable to examine also the conventional mercury irradiation of solid polybutadiene.

This report accordingly describes a fundamental, though preliminary, investigation of the cis-trans isomerization of thin films of polybutadiene irradiated in vacuo with either krypton 1236 Å radiation or with mercury 2537 Å radiation.



## II EXPERIMENTAL

Two polybutadiene samples were used in this work: a high-cis polymer (Ameripol CB), obtained from the B. F. Goodrich Research Center, Brecksville, Ohio, and a high-trans polymer, supplied by the Phillips Petroleum Company, Bartlesville, Oklahoma. The structures of these polymers, as determined by infrared analysis, consisted of approximately 96% cis-1,4, 2% trans-1,4, and 2% vinyl (or 1,2-polymerization) units in Ameripol CB, and about 93% trans-1,4, 5% cis-1,4, and 2% vinyl units in the high-trans polymer. The polymers were purified by several precipitations from benzene solutions using methanol as precipitant, and then redissolved in benzene to form dilute stock solutions, from which thin films were cast onto NaCl plates for krypton or mercury irradiations.

The krypton light source was a sealed microwave discharge lamp, constructed of quartz, similar to that described by Schlag and Comes<sup>14</sup> and having an initial intensity of about  $3-5 \times 10^{13}$  quanta/sec of 1236 Å radiation (along with about one-tenth this intensity of the other krypton resonance line at 1165 Å) passing through a lithium fluoride window 12 mm in diameter. The lamp, containing the rare gas at a pressure of 1.5-2.0 mm Hg, was excited by an 85-watt, 2450-Mc microwave generator, and the visible discharge was kept close to, but definitely above, the window. The experimental arrangement for the krypton irradiation of polybutadiene films in vacuo is depicted in Fig. 1a. Since the percent transmission of 1236 Å radiation by the window was found to diminish by a factor of ten roughly every 20 hours, the useful life of the lamp was limited to about 40 hours, and for the work described in this report it was necessary to employ four such lamps. The intensities of the lamps were determined by nitric oxide actinometry, and the progressive decrease in emission with time of operation was taken into account in calculating the total quanta deposited in the films.

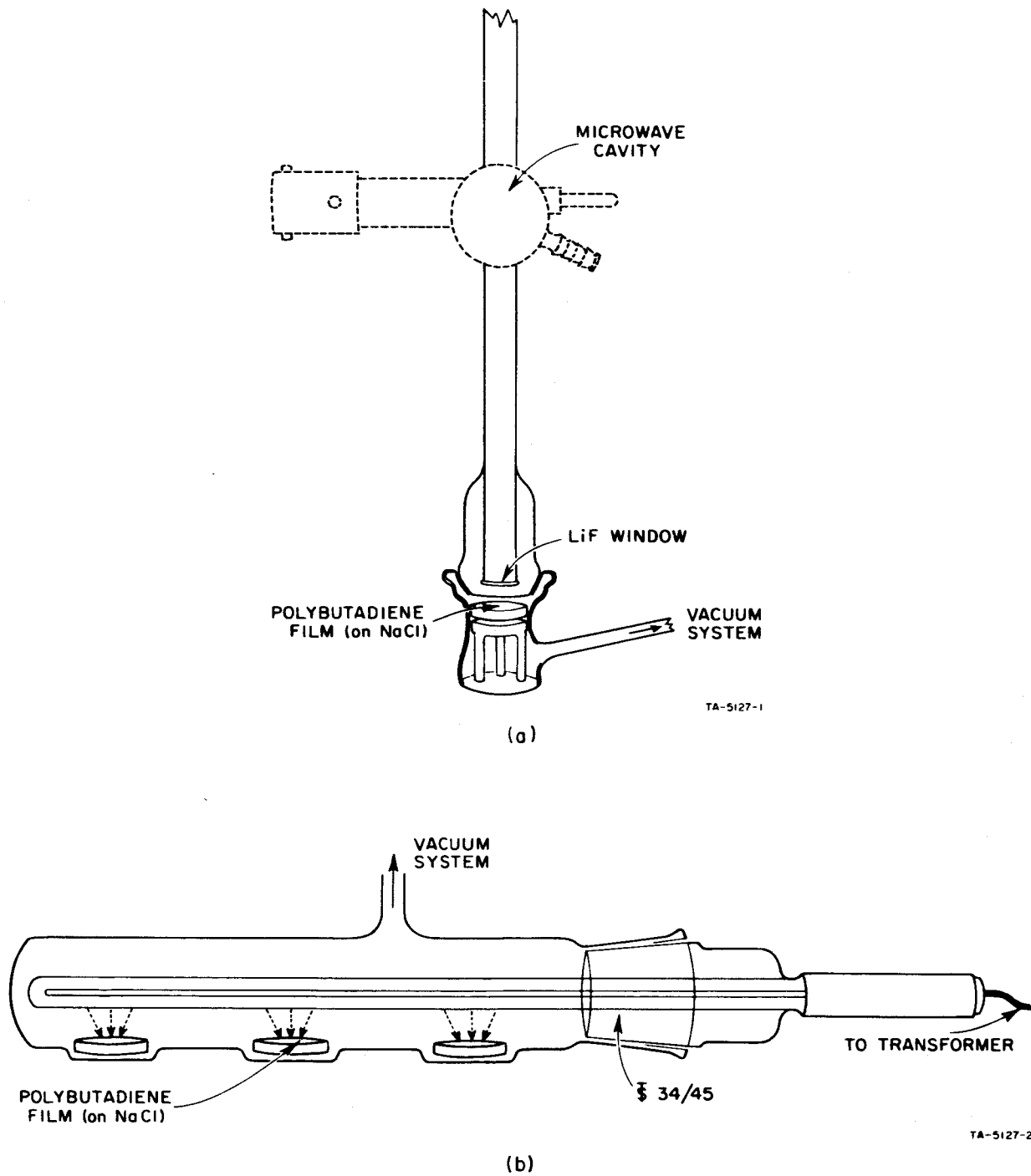


FIG. 1 EXPERIMENTAL ARRANGEMENTS FOR IRRADIATION OF POLYBUTADIENE FILMS IN VACUO WITH (A) KRYPTON 1236 Å AND (B) MERCURY 2537 Å RADIATIONS ....

Two mercury light sources were employed for conventional ultraviolet irradiations: a Pen-Ray ground-joint low pressure lamp (manufactured by Ultra-Violet Products, Inc., San Gabriel, Calif.) with a 10-inch quartz stem, activated by electrode discharge, and having an intensity of about  $2.5 \times 10^{15}$  quanta/cm<sup>2</sup>/sec of 2537 Å radiation (along with  $1.8 \times 10^{13}$  quanta/cm<sup>2</sup>/sec of the other mercury resonance line at 1849 Å) incident on the polymer films held at a distance of one-half inch from the stem and under vacuum conditions (see Fig. 1b); and a Hanovia 500-watt quartz medium pressure mercury lamp. The Pen-Ray lamp, which is effectively a monochromatic source ( $\approx 90\%$  of the output is at 2537 Å with only minor amounts of the higher wavelength mercury lines which are photochemically ineffective here) of steady and known intensity, was used to estimate the quantum yield for the mercury photoisomerization of polybutadiene. The intensity indicated above for this lamp was based on the manufacturer's specifications, no actinometry having been performed on it since the kinetic data for the mercury 2537 Å - induced reaction did not warrant any very precise determination of quantum yield. The Hanovia lamp, on the other hand, having a much higher intensity than the Pen-Ray lamp and emitting a broad ultraviolet spectrum, was used to determine in a very qualitative way the range of wavelengths capable of inducing the photoisomerization, as well as to reach the cis  $\rightleftharpoons$  trans equilibrium quite rapidly. For use of the Hanovia lamp, the supported films were sealed in evacuated tubes ( $<10^{-5}$  mm Hg) with quartz or Pyrex sides, and the tubes placed directly in front of this lamp. Since no isomerization occurred in the films irradiated in the Pyrex tubes, which cut out all radiations below 3000 Å, while considerable reaction occurred in the films irradiated in quartz tubes, which cut out the mercury 1849 Å line, it was concluded that the isomerization in the Pen-Ray case was due mainly, if not entirely, to the 2537 Å radiation. The contribution from the 1849 Å line could be ignored here since its intensity was less than 1% of that of the 2537 Å line and, moreover, it would penetrate no more than 1% of the thickness of the films used in the Pen-Ray work.

The films were analyzed before and after irradiation by infrared spectroscopy, the bands of interest being those at 13.6 and 10.4 $\mu$  (corresponding to the cis and trans -CH=CH- units, respectively), and at 11.0 $\mu$  (-CH=CH<sub>2</sub> units), with the 6.9 $\mu$  band (CH<sub>2</sub> bending vibration) or the 3.5 $\mu$  band (C-H stretching vibration of -CH<sub>2</sub>- and -CH= units) serving as (approximate) internal standards. For the very thin films ( $\approx$  2-3 x 10<sup>-5</sup> cm) used in the krypton irradiations, it was necessary to operate the infrared spectrophotometer (Perkin-Elmer 221) with the "10 X" scale expansion settings, at some loss in precision; with the mercury irradiations, on the other hand, the films were thick enough ( $\approx$  0.5-1.5 x 10<sup>-3</sup> cm) that the spectra could be run at normal (i.e., "1 X") settings. The thickness of the films was estimated from the measured absorbance of the 3.5 $\mu$  band in the "1 X" spectra, using the independent calibration that A<sub>3.5</sub> = 0.8 corresponds to a thickness of 1.48 x 10<sup>-3</sup> cm. The analysis for isomerization was essentially the same as that employed in previous work,<sup>1</sup> except that a new value of 3.65 was taken for the ratio of the trans to cis absorption coefficients. Thus, the isomerization was followed by noting changes in the percent cis content, which was calculated as 100[3.65A<sub>c</sub>/(3.65A<sub>c</sub> + A<sub>t</sub>)] where A<sub>c</sub> and A<sub>t</sub> are the absorbances of the cis and trans bands, respectively. The initial cis contents of the high-cis and high-trans polybutadienes used in this work were thus taken as 98 and 5%, respectively. In addition, changes in the quantity (3.65A<sub>c</sub> + A<sub>t</sub>) relative to A<sub>6.9</sub> (for mercury irradiations) or A<sub>3.5</sub> (for krypton irradiations) were considered as an indicator for photoinduced decrease in unsaturation; this analysis was quite uncertain in the case of the "10 X" spectra required for the krypton irradiations. The percent residual 1,4-unsaturation reported in the figures were thus calculated as

$$100[(3.65A_c + A_t)/A_{6.9} \text{ (or } 3.5)]_I / [(3.65A_c + A_t)/A_{6.9} \text{ (or } 3.5)]_0$$

where the subscripts I and o refer to the irradiated and unirradiated polymer films, respectively. Although some increases in vinyl absorption (11.0 $\mu$  band) were noted in the mercury irradiations, these new double

bonds generally amounted to no more than 5 to 8% of the original unsaturation, and so there was no need in this preliminary study to give them more than qualitative attention. In all of the infrared work, the measurements used were average values obtained by rotating the supported films to various positions with respect to the entrance slit of the spectrometer, thereby allowing for any non-uniformity in film thickness.

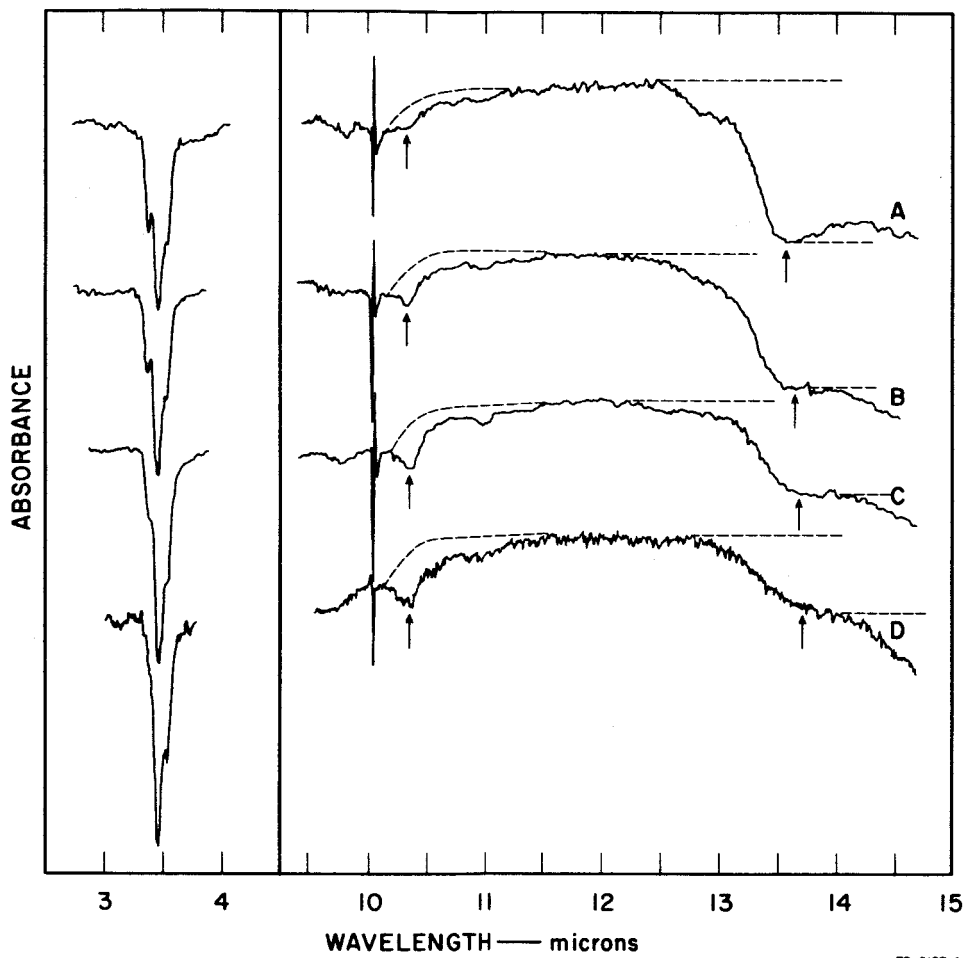
For the purpose of estimating the quantum yield in the Pen-Ray irradiations, ultraviolet spectra of the polybutadiene films were obtained before and after irradiation, using the Perkin-Elmer Model 4000 A Spectracord.

### III RESULTS

#### A. Krypton Irradiations

From the infrared spectra shown in Fig. 2, it is clear that polybutadiene undergoes a definite vacuum photochemical cis-trans isomerization, accompanied by a rather pronounced decrease in original unsaturation. Thus, the growth of the 10.4 $\mu$  band (trans -CH=CH- units) and the diminution of the 13.6 $\mu$  band (cis -CH=CH- units) signify the occurrence of isomerization, while the drop in unsaturation is indicated by the fact that the latter band has decreased relatively much more than the former band has grown, taking into account the different absorption coefficients for the cis and trans double bonds ( $\epsilon_{\text{trans}}/\epsilon_{\text{cis}} \approx 3.65$ ). Unfortunately, because the "10 X" spectra required for the very thin films trail off to infinite absorbance at around 14 $\mu$  and beyond, it was not feasible to examine the krypton irradiation of trans polybutadiene for a corresponding trans  $\rightarrow$  cis isomerization, or loss of double bonds in this polymer; any absorption at 13.6-14 $\mu$  due to new cis -CH=CH- units being formed would be obscured by the trailing off of the spectra in this region. Consequently, we are unable to indicate the photo-stationary cis/trans ratio for the krypton irradiation of polybutadiene as has been done<sup>1,15</sup> for the radiostationary equilibrium ( $\approx 33/67$ ).

The quantitative features of the two photoinduced reactions in cis polybutadiene are depicted in Figs. 3 and 4, from which it can be seen that the disappearance of double bonds is about six to eight times as fast as the isomerization. This situation is qualitatively similar to that obtained by Cundall<sup>16,17</sup> in the vacuum ultraviolet irradiation of trans-butene-2 with light from an aluminum arc (1800-2000 $\text{\AA}$ ) where, at low pressures, the rate of decomposition was much greater than the rate of isomerization. However, at higher pressures the butene isomerization yield was increased; unfortunately, no data are available on the relative amounts of isomerized butene and butene decomposition products with which to compare the relative rates of isomerization and loss of



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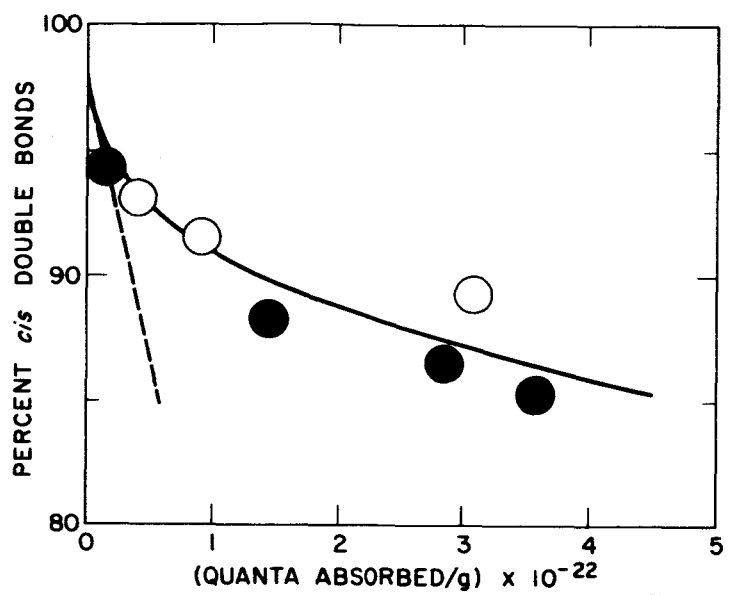
FIG. 2 INFRARED SPECTRA OF VERY THIN FILMS OF *cis* POLYBUTADIENE BEFORE AND AFTER IRRADIATION WITH KRYPTON 1236 Å RADIATION. A, B, C, and D represent 0, 0.15, 1.44, and  $3.58 \times 10^{22}$  quanta absorbed/g. polymer, respectively ....

double bonds in the krypton irradiation of polybutadiene. On the other hand, the vacuum photochemical results on polybutadiene stand in contrast to the corresponding radiation chemical results<sup>1,15</sup> where the rate of consumption of double bonds is approximately equal to the rate of isomerization for  $\gamma$ -irradiations in vacuo, and is about twice that rate for electron irradiations under nitrogen.

The calculation of the quanta of 1236 Å radiation absorbed by the polybutadiene films was based on the assumption that the films were just thick enough ( $\approx 2 \times 10^{-5}$  cm) to absorb virtually all of the incident photons, while being thin enough to permit maximum penetration of the films (and hence optimization of detectability of microstructural changes in the polymer). That assumption was justified by the fact that the film thickness required to absorb 99% of the 1236 Å radiation, calculated from Beer's law and the molar extinction coefficient for simple alkanes and alkenes at around this wavelength ( $\epsilon \approx 10^4$ ),<sup>18</sup> is approximately  $10^{-5}$  cm. Significantly, the percent double bonds isomerized in a film  $9.5 \times 10^{-5}$  cm thick was one-fifth the corresponding percentage in a film  $2 \times 10^{-5}$  cm thick for the same number of quanta incident on the two films; in other words, the actual number of double bonds isomerized, and hence the quantum yields, were the same in the two films, a result which is in line with the view that the 1236 Å light is indeed completely absorbed by a film of thickness  $2 \times 10^{-5}$  cm. The somewhat different results shown in Figs. 3 and 4 for two distinct films having essentially the latter thickness can presumably be attributed to small deviations in thickness uniformity.

From the slopes of the tangents of the curves in those figures, the (initial) quantum yields for the loss of double bonds and cis-trans isomerization are found to be 1.53 and 0.25, respectively. Since the 1236 Å quantum has an energy of 10.0 e.v., the G-values for these two vacuum photochemical processes can be taken as 15.3 and 2.5, respectively. These values are remarkably similar to corresponding G-values in the radiation chemical case, viz., 13.6 (or 7.9) for loss of double bonds in polybutadiene film irradiated with electrons under nitrogen (or  $\gamma$ -rays in vacuo) and 7.2 for cis-trans isomerization (with electrons or  $\gamma$ -rays).





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FIG. 3 *cis-trans* ISOMERIZATION OF POLYBUTADIENE INDUCED BY KRYPTON 1236 Å RADIATION. The open and closed circles represent two separate films of essentially the same thickness ....

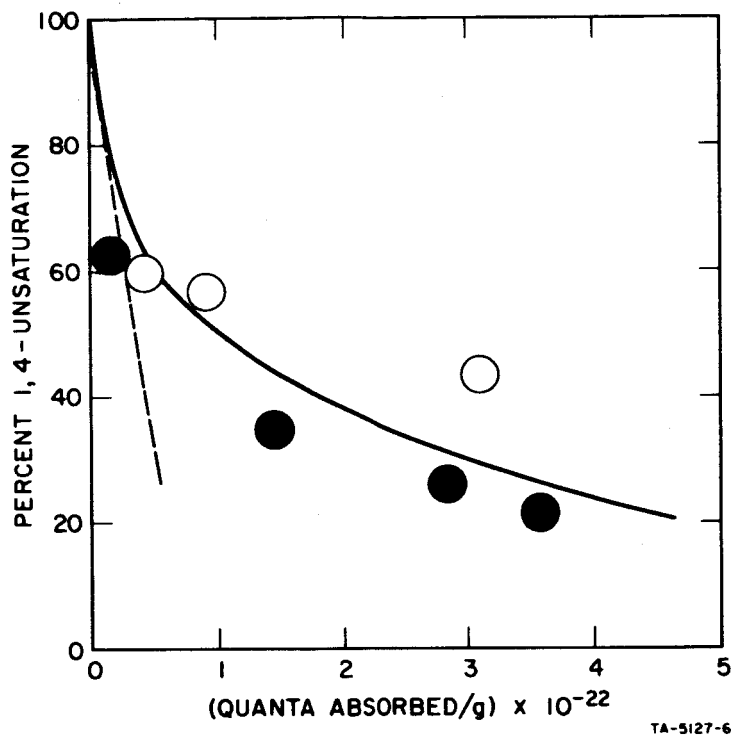
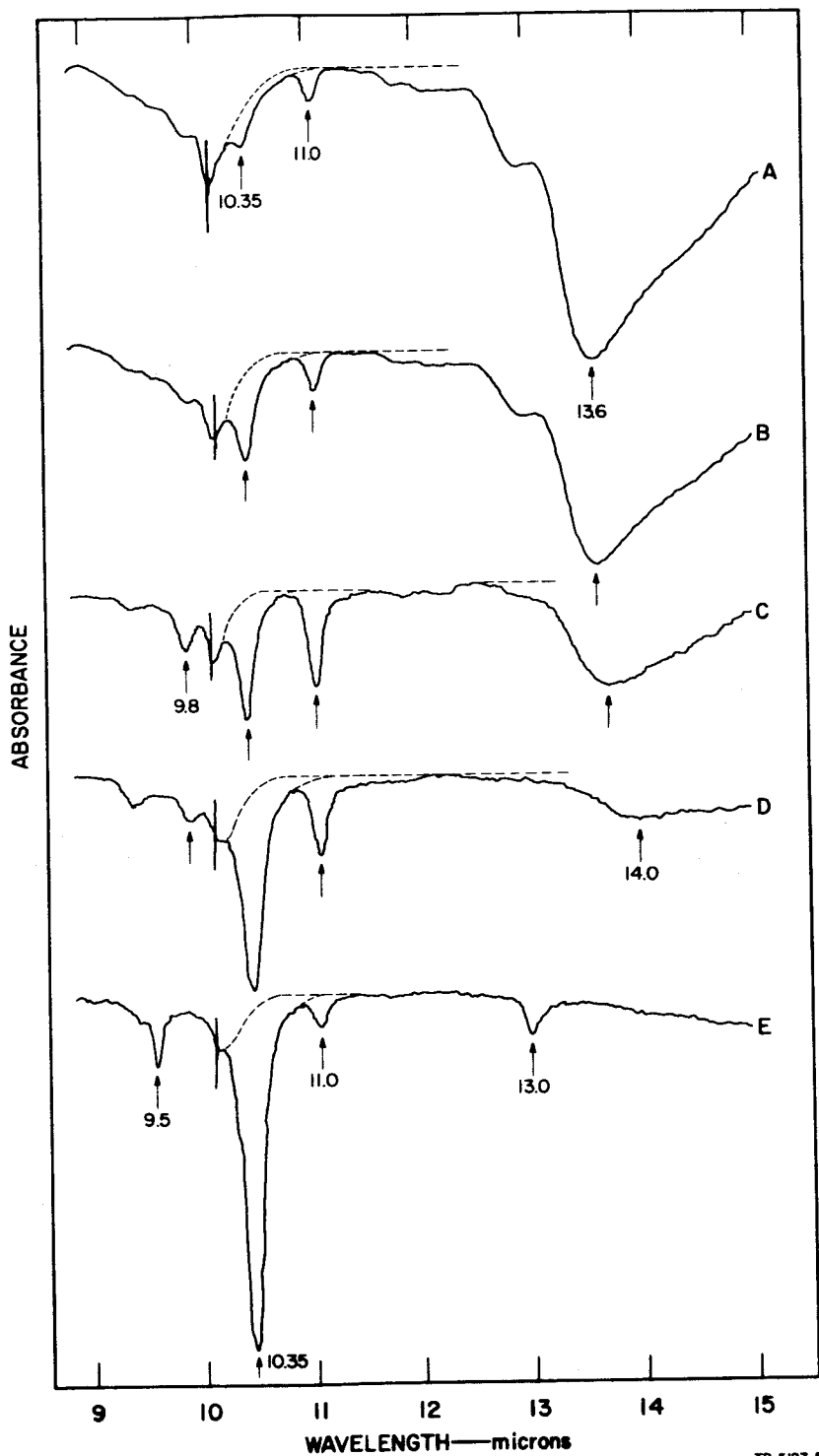


FIG. 4 LOSS OF ORIGINAL UNSATURATION IN KRYPTON-IRRADIATED *cis* POLYBUTADIENE FILMS. The symbols have the same significance as in the previous figure ....

Inasmuch as the energy of the 1236 Å photon exceeds the ionization potential of olefinic groups (e.g., 9.27 e.v. for trans-butene-2),<sup>19</sup> it is perhaps not too surprising that the vacuum photochemical and radiation chemical yields in polybutadiene are indeed similar. At the same time, it is interesting to note that Cundall has tentatively suggested<sup>17</sup> that the direct photoisomerization of butene-2 using 1800-2000 Å light has a quantum yield of 0.15 at high pressures, and about 0.05 at low pressures. The former value compares rather well with the quantum yield of 0.25 indicated above for the direct photoisomerization of polybutadiene film using 1236 Å light. Evidently, there is some parallelism between the vacuum photolysis of the macromolecule, polybutadiene, in the solid state, and that of the small molecule, butene-2, in the vapor state. Further work on the irradiation of these and similar systems at various wavelengths in the extreme ultraviolet range appears desirable in order to pursue analogies between vacuum photochemistry and radiation chemistry, on the one hand, and between small molecules and macromolecules, on the other.

#### B. Mercury Irradiations

As shown in Fig. 5, cis and trans polybutadienes isomerize towards a common, intermediate structure when irradiated with mercury light in vacuo and in the absence of any deliberately added sensitizer. Thus, the cis polymer displays a diminution of the 13.6μ band and a growth of the 10.4μ band, while the trans polymer shows a decrease in the latter band and a development of new absorption at 14.0μ. It is a characteristic of the infrared absorption bands of the -CH=CH- units that, whereas the trans band is invariably sharp with a nearly constant wavelength (≈ 10.4μ), the cis band is very broad and has a wavelength at maximum absorbance which shifts from 13.6μ (at high cis content in polybutadiene) to around 14.0μ as the cis content is progressively reduced. Consequently, incipient production of cis -CH=CH- units is difficult to detect in the spectrum of slightly isomerized trans polybutadiene, which fortuitously displays broad, nonspecific absorption in the 14-15μ range (see spectrum E), but the presence of the cis band



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FIG. 5 TYPICAL INFRARED SPECTRA OF *cis* AND *trans* POLYBUTADIENE FILMS BEFORE (A, E) AND AFTER ULTRAVIOLET IRRADIATION WITH MERCURY LIGHT. B, C: *cis* polymers exposed to Pen-Ray lamp for 20 hours, and to Hanovia lamp for 80 hours, respectively; D: *trans* polymer exposed to Hanovia lamp for 18 hours ....

in spectrum D is unmistakable; indeed, its peak is located at about the same wavelength as that of the corresponding band in the spectrum of highly isomerized cis polybutadiene (spectrum C). As the trans polymer isomerizes, its crystallinity bands at 9.5 and 13.0 $\mu$  disappear.

In contrast to irradiation of polybutadiene films with krypton light or with electrons or  $\gamma$ -rays, mercury irradiation results in the formation of a relatively large amount of vinyl groups (which absorb at 11.0 $\mu$ ) in the cis and trans polymers, reaching a more or less steady concentration of about 8% of the original unsaturation. Associated with the increased absorption at 11.0 $\mu$  is the development of a new band at 9.8 $\mu$ , the origin of which is not known at present but which might possibly be due to alkylcyclopropane groups being formed in the polymer as a side reaction to that leading to the vinyl groups. Although it is not very apparent in the spectra of Fig. 5, polybutadiene on mercury irradiation undergoes also a photoinduced loss of double bonds which, however, is much less severe than that encountered on krypton irradiation.

The effects produced by the nearly monochromatic 2537 $\text{\AA}$  source (Pen-Ray lamp) and by the broad ultraviolet spectrum (Hanovia lamp) are qualitatively the same, including production of vinyl groups, but the latter process is enhanced by the higher intensities employed with the Hanovia lamp. Contrariwise, it was found that at very low intensities of irradiation, but carried to suitably high doses of absorbed quanta, the formation of vinyl groups was suppressed. Evidently, the occurrence or non-occurrence of vinyl groups in the mercury irradiation of polybutadiene is critically dependent on the rate at which excitation energy is deposited in the solid polymer and on the rate at which the double bonds can dissipate this energy in isomerization; any excess energy beyond that required for the latter process is then available for inducing other chemical changes in polybutadiene. Consequently, the infrared spectra B and C of Fig. 5 are to be considered only as examples of polymer films at different stages of cis-trans isomerization and of development of vinyl unsaturation, and are not to be taken as reflecting fundamental differences in photochemistry produced by the two mercury lamps, or by different wavelengths in the near ultraviolet region.

Since the polybutadiene per se is theoretically transparent in the near ultraviolet, the source of the photochemistry with mercury light is undoubtedly the residual impurity which could not be fully removed from the polymer through several reprecipitations, viz., catalyst fragments and a very minor amount of carbonyl structure formed in the polymer backbone at the time of polymerization. As a result, the ultraviolet spectra of thin polybutadiene films show initially broad absorption commencing at around 300 m $\mu$ , with some 5 to 20% absorption at 254 m $\mu$ , depending upon the thickness of the films and the conditions of their preparation. Significantly, any quanta below 300 m $\mu$  absorbed by the polymer films have ample energy ( $> 4.1$  e.v.) to cause isomerization (olefinic triplet precursor requires 3.2 e.v.)<sup>20</sup> or chain scission (strength of C-C bond midway between the double bonds is about 60 kcal/mole or 2.6 e.v.). Thus, the ordinary ultraviolet photochemistry of polybutadiene should be independent of wavelength below a critical wavelength, and this is what is observed.

It should be pointed out that possible sensitization of the mercury photoisomerization by trace amounts of solvent (e.g., benzene) was ruled out by special irradiation experiments carried out on films cast from hexane solutions of reprecipitated polymer, as well as on films cast from benzene but dried in vacuo at around 100°C; in neither case was the isomerization significantly different from that in the films cast from benzene normally. It is worth noting, also, that several irradiations of cis polybutadiene-2,3-d<sub>2</sub> [(-CH<sub>2</sub>-CD=CD-CH<sub>2</sub>-)<sub>n</sub>] with mercury light confirmed the loss of double bonds (indicated by the development of the 4.65 $\mu$  band, due to CDH units, accompanying the diminution of the 4.5 $\mu$  band, due to -CD= units) and demonstrated unequivocally that the appearance of the trans -CH=CH- absorption on irradiation of ordinary polybutadiene was indeed due to cis-trans isomerization and not to double bond shifts.

Kinetic plots for the cis-trans isomerization and loss of double bonds in cis and trans polybutadienes irradiated in vacuo with mercury light are presented in Figs. 6 and 7. Coincidentally, the effects produced by 10 hours of Hanovia irradiation were equivalent to those produced by 40 hours of the Pen-Ray lamp, and so the data for the two

sources could be conveniently shown on the same plots. Since the trans polybutadiene films are initially crystalline and therefore quite opaque, it was necessary to heat them to around 70-80°C during irradiation so that they would be clear enough for the ultraviolet light to penetrate and produce important changes in them. Even so, the kinetic data for those films proved to be rather erratic. In addition, because the cis polymer films themselves became progressively more opaque in the course of irradiation (with the upper layers tending to screen out the radiation from reaching the lower layers), they likewise yielded data which showed considerable scatter. Consequently, Figs. 6 and 7 are to be regarded as providing only rough indications of the rates of the two major photochemical reactions in polybutadiene. The former figure shows that the mercury photoisomerization approaches a common equilibrium structure in which the cis/trans ratio lies in the range 65/35 to 55/45, which is definitely higher than that obtained in the radiation chemical case (33/67).<sup>1,15</sup>

From the initial slopes to the curves of Figs. 6 and 7, and taking the initial absorption at 254 m $\mu$  as  $\approx$  13% of the radiation (from the Pen-Ray lamp) incident on a typical film about  $1.0 \times 10^{-3}$  cm thick, we estimate the quantum yields for the Hg 2537-induced isomerization and loss of double bonds in cis polybutadiene as 0.09 and 0.07, respectively. Since these numbers are only rough approximations, no exact significance should be ascribed to them. Nevertheless, it is interesting to mention that they are much larger than the quantum yields for chain scission in the photodegradation of most polymers,<sup>21</sup> and, moreover, are much larger than the quantum yields for gas evolution in the photolysis of natural rubber ( $4 \times 10^{-4}$ )<sup>22</sup> or of sodium-butadiene rubber ( $2 \times 10^{-3}$ ).<sup>23</sup> On the other hand, the above quantum yield for loss of unsaturation in the cis-1,4-polybutadiene is considerably smaller than that reported for the sodium-butadiene rubber (0.73) which had a structure consisting of both internal (32% 1,4 polymerization units) and external (68% 1,2 units) double bonds. Clearly, further work on the photolyses of these and other diene polymers is highly desirable.

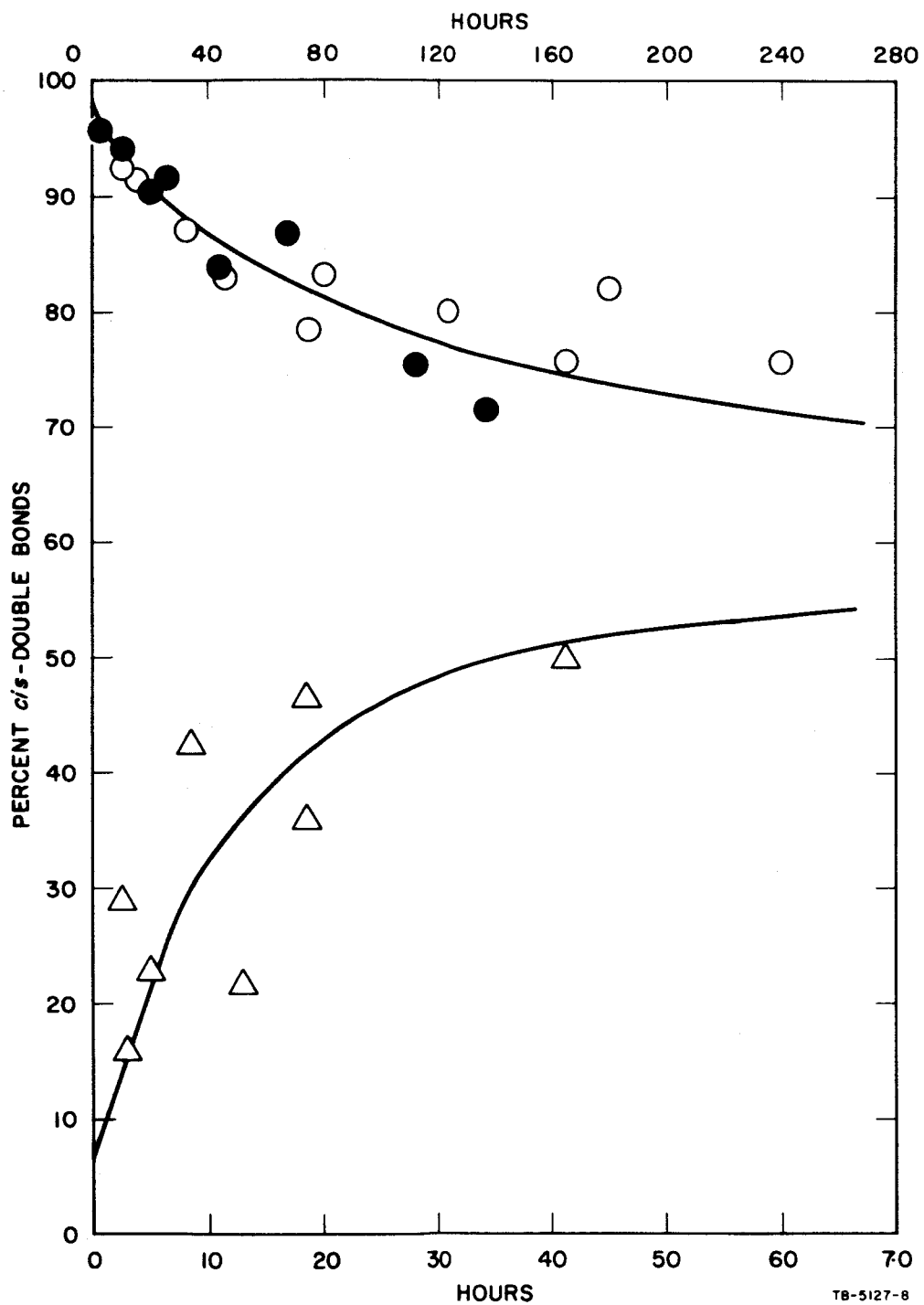


FIG. 6 *cis-trans* ISOMERIZATION OF POLYBUTADIENE INDUCED BY MERCURY ULTRAVIOLET RADIATION: *cis* (○) AND *trans* (△) POLYMERS EXPOSED TO HANOVIA LAMP (lower scale); *cis* POLYMER (●) EXPOSED TO PEN-RAY LAMP (upper scale).



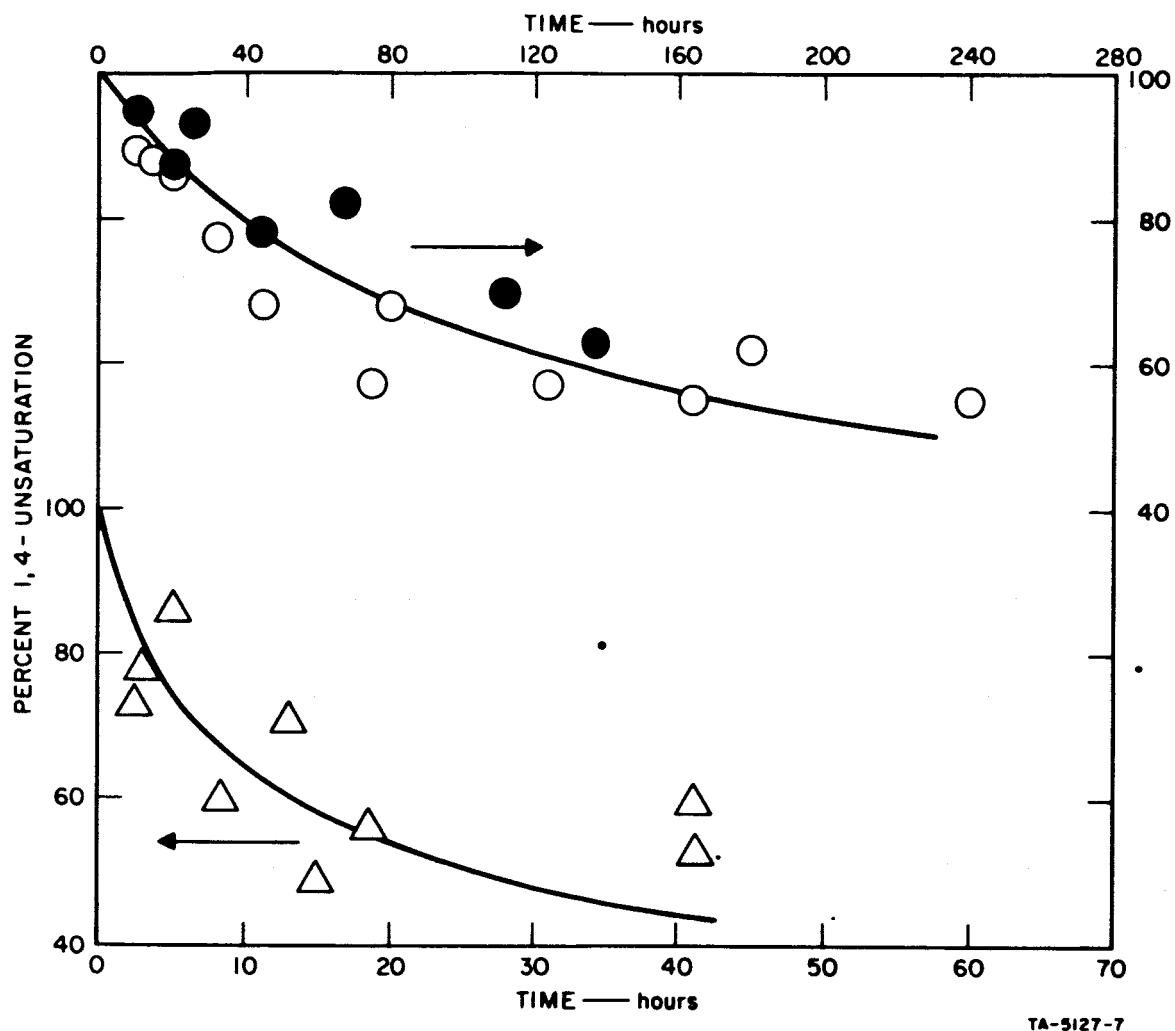
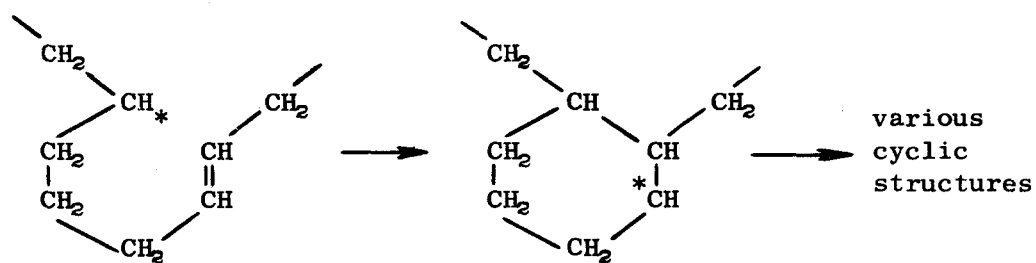


FIG. 7 LOSS OF ORIGINAL UNSATURATION IN MERCURY-IRRADIATED POLYBUTADIENE FILMS. Symbols have same significance as in previous figure.

#### IV DISCUSSION

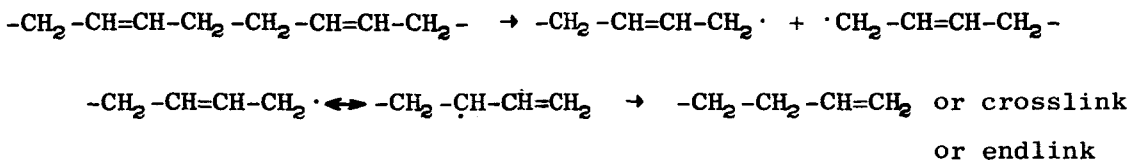
The present work has shown that polybutadiene, in addition to undergoing the photosensitized and radiation sensitized and unsensitized cis-trans isomerizations reported previously,<sup>1,3-5</sup> can also undergo direct photoisomerization on exposure in the solid state to either vacuum or near ultraviolet radiation. Although no sensitizer is added to the polybutadiene to promote the photoisomerization, this reaction in the case of near ultraviolet irradiation is, in fact, a sensitized reaction. The sensitizer, of course, is the adventitious impurities present in the polymer which absorb in the ordinary ultraviolet range (where the polymer itself is transparent) and which transfer the energy acquired thereby to the polymer double bonds, resulting in their excitation and eventual isomerization, presumably through the low-lying triplet (3.2 e.v.). On the other hand, the vacuum ultraviolet induced isomerization is truly an unsensitized reaction in that the quanta are absorbed directly by the polymer itself, the trace impurity making a negligible contribution to the over-all absorption in this case. The vacuum photoisomerization is then analogous to the radiation unsensitized isomerization, and can be considered, therefore, to have an essentially similar mechanism. Since that mechanism has been discussed at some length in the Introduction, there is no need to consider it further here. Suffice to say that, just as with electrons or  $\gamma$ -rays, absorption of krypton 1236 Å quanta (10.0 e.v.) by the  $-\text{CH}_2-$  or  $-\text{CH}=\text{CH}-$  units in polybutadiene can give rise to both ionized and excited states, the ultimate fates of which are to return to the ground states with a certain fraction of the available excitational energy being used to induce isomerization and other processes. Moreover, the photosensitized isomerization with mercury light observed in this work, to the extent that it involves energy transfer processes (in contrast to the radical adduct mechanism of other photosensitized isomerizations discussed earlier), can be considered to be similar mechanistically to that part of the radiation unsensitized (or vacuum photochemical) isomerization which involves lower excited states.

The present study has shown also that vacuum and ordinary ultraviolet irradiation of polybutadiene in the solid state leads to a loss of double bonds which is much more severe in the former than in the latter case. The quantum yields are such, in fact (1.53 and 0.07, respectively), as to suggest that the loss of double bonds with Kr 1236 irradiation is a chain reaction, similar to that depicted for the radiation-induced loss of unsaturation in polybutadiene<sup>15</sup> and in polyisoprene,<sup>24</sup> and is not a chain reaction with Hg 2537 irradiation. Since the krypton irradiation presumably involves both ions and (various) excited species, while the mercury irradiation involves only the lowest excited species, this result would seem to add weight to the arguments for an ionic rather than a free radical chain mechanism in the radiation chemical consumption of double bonds in diene polymers.<sup>15, 24, 25</sup> In any case, the sharp drop in unsaturation in the vacuum ultraviolet irradiation of polybutadiene can be visualized in terms of a cyclization process:

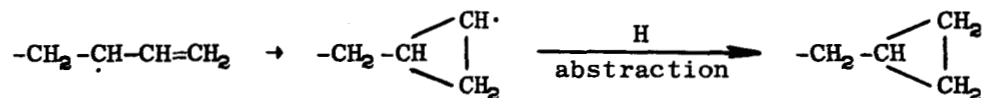


where \* denotes a free radical or carbonium ion.

That mercury irradiation brings about considerable chain scission in polybutadiene, whereas krypton irradiation (in common with the use of ionizing radiation) produces little or no such reaction, is shown by the presence and absence, respectively, of vinyl absorption in the infrared spectra of the irradiated polymers. The vinyl groups are believed to arise through the process:



and to reach a more or less equilibrium concentration as a result of competing saturation processes. It is noteworthy that with regard to chain scission and the development of vinyl absorption, the vacuum photochemical situation resembles the radiation chemical one rather than the ordinary photochemical case. As a further consequence of the scission, it is tempting to suggest that the 9.8 $\mu$  blip in the mercury photoisomerization arises from a process of the type:



inasmuch as the alkylcyclopropane group has characteristic absorption at that wavelength.

The significance of the present work--which constituted a preliminary, feasibility study seeking a possible isomerization of polybutadiene induced by radiation in the vacuum ultraviolet spectrum--obviously has broad implications for both photo- and radiation-chemistry alike. At the same time, it represents apparently the first fundamental examination of the vacuum photochemistry of any high polymer. So far as the author is aware, the only other study involving vacuum ultraviolet irradiation of a polymer is that of Cowling et al.<sup>26</sup> who exposed various polymers to a hydrogen discharge lamp, but that was only a very limited, qualitative examination.

## V RECOMMENDATIONS FOR FURTHER RESEARCH

We believe the results of this work to be sufficiently interesting scientifically that we wish to recommend further study of the polybutadiene system along the following lines. By means of extremely thin films, of the order of 200-500 Å thick, and using the "frustrated total reflectance" attachment for infrared spectroscopy, which should provide spectra comparable to those of the "1 X" type, we should be able to study more precisely than has been done heretofore the interaction of vacuum ultraviolet radiation with organic polymers. Thus, it should be possible with such films to obtain reliable measurements of absorption coefficients for various wavelengths of interest in the vacuum ultraviolet spectrum, and at the same time to be able to carry the reactions to high enough conversions for improved detectability and structural analysis. In view of the significant differences obtained between the vacuum and near ultraviolet photochemistry of polybutadiene with respect to chain scission and destruction of double bonds, for example, it would be of definite interest to compare the effects produced by krypton 1236 Å radiation (quanta of 10.0 e.v. and thus supra-ionizational from the standpoint of the polymer) with those produced by xenon 1470 Å radiation (quanta of 8.44 e.v. and thus sub-ionizational). Moreover, since the olefinic units have strong singlet-singlet absorption at around 1850 Å, it would be interesting to study also the irradiation of cis polybutadiene with light from an aluminum arc similar to what is being done by Cundall on butene-2. In this connection, it would be desirable also to undertake some vacuum ultraviolet irradiations of other simple olefins, such as cis-hexene-3, as model compounds for the diene polymers. The findings from such basic studies should contribute, among other things, to a better understanding of space environmental effects on polymeric materials.

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