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PHOTOCHEMISTRY OF UNSATURATED POLYMERS

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(With 1 illustration)

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### ABSTRACT

The mechanisms of the direct photochemical reactions which occur in unsaturated polymers when irradiated as thin films in vacuo are reviewed. Important reactions in 1,4-polyisoprene and 1,4-polybutadiene are cis-trans isomerization, loss of 1,4-unsaturation, formation of new external double bonds (vinylidene and/or vinyl units) and cyclopropyl formation. In 1,2-polybutadiene and 3,4-polyisoprene, on the other hand, the main reaction is consumption of the external double bonds through cyclization. Recent work on the photoinduced microstructural changes in cis and trans polypentenamers is also discussed.

### INTRODUCTION

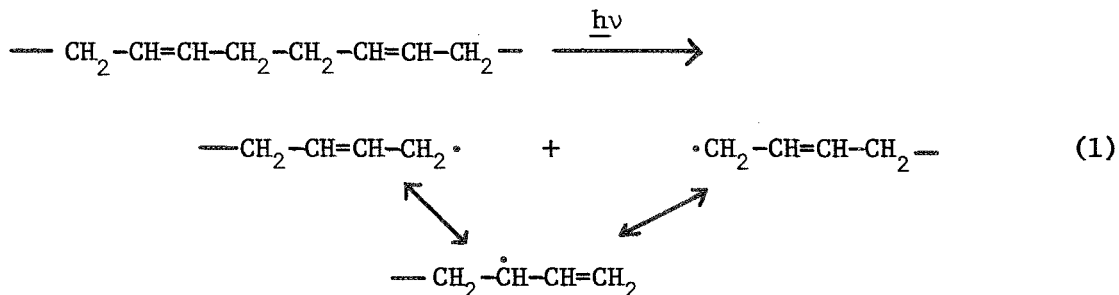
During the past decade extensive work has been carried out on the photochemistry of polymers, especially their photodegradation and photo-oxidation. As recent reviews<sup>1-7</sup> have given little attention to unsaturated polymers, and then mainly to photosensitized processes, this paper will comprise a review of the unsensitized photochemical transformations which occur in unsaturated polymers when irradiated as thin films in vacuo. The photo-induced microstructural changes to be discussed are those reported previously for polymers having principally internal C=C double bonds (cis- and trans-1,4-polybutadiene and 1,4-polyisoprene) or external double bonds (1,2-polybutadiene and 3,4-polyisoprene). In addition, some new related work on the photochemistry of cis and trans polypentenamers will also be examined.

### 1,4-POLYBUTADIENE

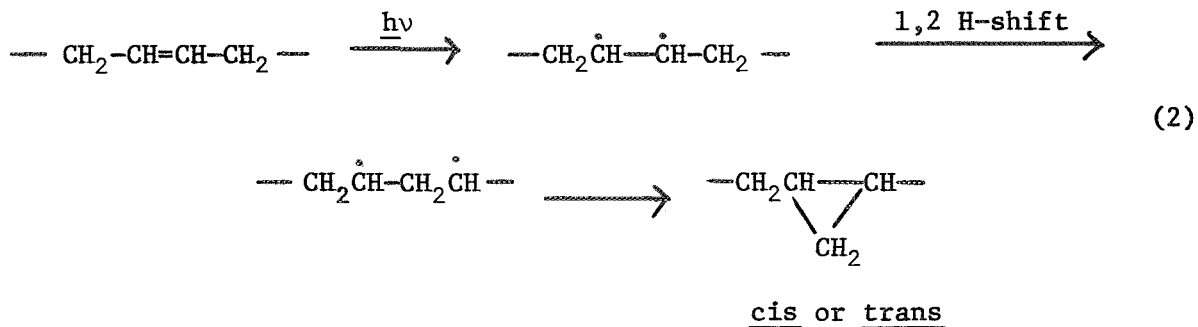
The first investigation of the direct photoinduced microstructural changes in an unsaturated polymer was reported at the IUPAC Symposium on Macromolecular Chemistry in Prague<sup>8</sup>. That study, consisting of both near (2537 Å) and far (1236 Å) ultraviolet irradiation of cis- and trans-1,4-polybutadiene films in vacuo, was an extension of earlier work in which these polymers were found to undergo an unsensitized radiation-induced isomerization in the solid state<sup>9</sup>. The latter process was attributed to excitation of the  $\pi$ -electrons of the double bonds to an antibonding state in which free rotation and hence geometric interconversion can occur. This interpretation implied that an analogous unsensitized photoisomerization could also take place if the polymers were exposed to suitable radiation in the far or vacuum ultraviolet where unconjugated C=C bonds show significant absorption. Irradiation of very thin cis-1,4-polybutadiene films in vacuo with 1236 Å radiation<sup>8</sup> did in fact lead to cis-trans isomerization, with a quantum yield of  $\sim 0.25$ . This was accompanied by a large decrease in unsaturation, with a quantum yield of  $\sim 1.53$ , suggesting a chain cyclization reaction. The vacuum photochemical results were rationalized on the basis that 1236 Å photons have sufficient energy ( $\sim 10$  eV) to cause ionization as well as excitation in polybutadiene and thus promote reactions similar to those obtained radiation chemically. The effective G-values (or 100-eV yields) for the isomerization and consumption of double bonds in the 1236 Å work (2.5 and 15.3) may be compared with the G-values obtained for the corresponding  $\gamma$ -ray-induced

reactions in 1,4-polybutadiene (7.2 and 13.6-7.9, respectively)<sup>10</sup>.

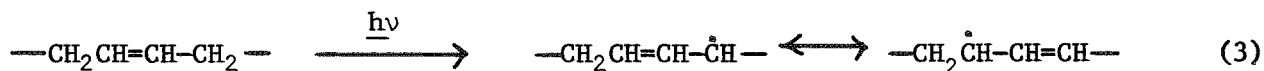
It was further found<sup>8</sup> that even near ultraviolet radiation at 2537 Å causes major microstructural changes in purified cis- and trans-1,4-polybutadiene films in vacuo at room temperature. One important reaction is isomerization which proceeds towards a photostationary cis-trans ratio of ~60:40. In addition, the 1,4-polybutadienes exhibit photoinduced loss of unsaturation, although not as extensively as with 1236 Å radiation. The quantum yields for 2537-Å-induced cis-trans isomerization and consumption of double bonds were ~0.036 and ~0.061, respectively; these values represent a revision<sup>11</sup> of earlier values<sup>8</sup>. In contrast to either 1236-Å- or γ-irradiation of 1,4-polybutadiene, 2537-Å-irradiation brings about the formation of vinyl double bonds and cyclopropyl groups distributed along the backbone. The vinyl groups have been depicted<sup>8</sup> as arising through chain scission (1) while the cyclopropyl



groups might form via process (2)<sup>11</sup>.



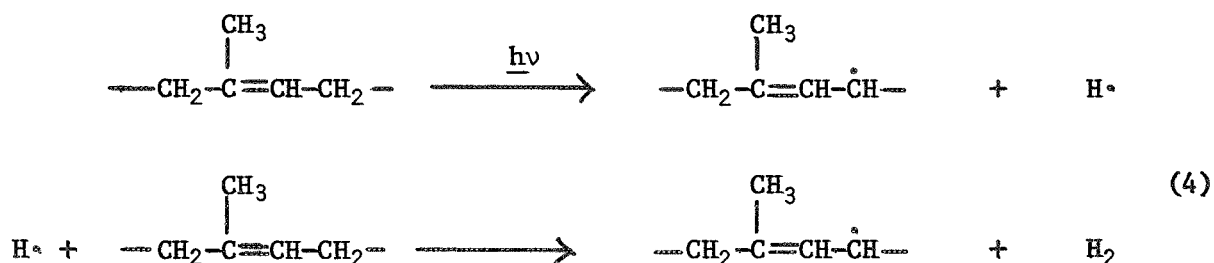
Ultraviolet irradiation of cis-1,4-polybutadiene-2,3-d<sub>2</sub> [(-CH<sub>2</sub>CD=CDCH<sub>2</sub>-)<sub>n</sub>] showed that formation of trans -CH=CH- in ordinary cis-1,4-polybutadiene was due to cis-trans isomerization and not to a double bond migration posing as an isomerization (3).



The occurrence of a direct photoisomerization of cis-1,4-polybutadiene in vacuo at room temperature was reported also by Ho<sup>12</sup> in connection with a study of the photooxidation of this polymer.

#### 1,4-POLYISOPRENE

Until recently the only fundamental study reported on the photolysis of 1,4-polyisoprene was the work of Bateman<sup>13</sup> over twenty-five years ago. He showed that irradiation of degassed, purified Hevea rubber films in the wavelength range 2300-3650 Å resulted in gas evolution, mostly hydrogen, with a quantum yield of  $\sim 4 \times 10^{-4}$ . The largest relative yield, at 2350-2850 Å, was about 2.5 times this value, indicating an upper limit of  $\sim 10^{-3}$  for efficiency of noncondensable gas formation. Hydrogen was assumed to originate through reaction (4), while the resulting polymeric radicals combine to form

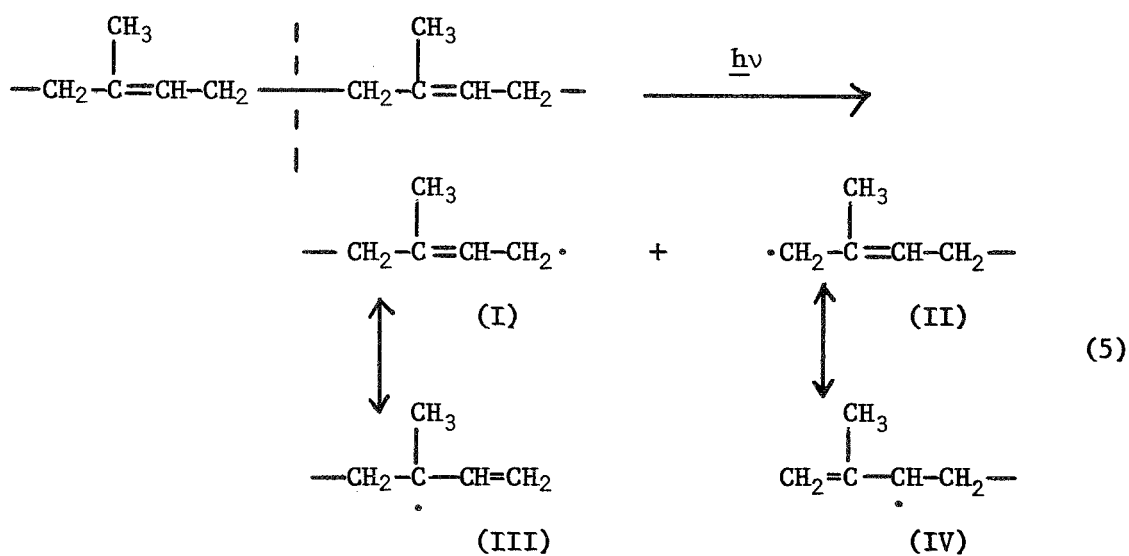


crosslinks. The attendant insolubilization of the irradiated 1,4-polyisoprene restricted its chemical analysis, but evidence was adduced for loss of unsaturation with a quantum yield<sup>13,14</sup> approaching 0.1.

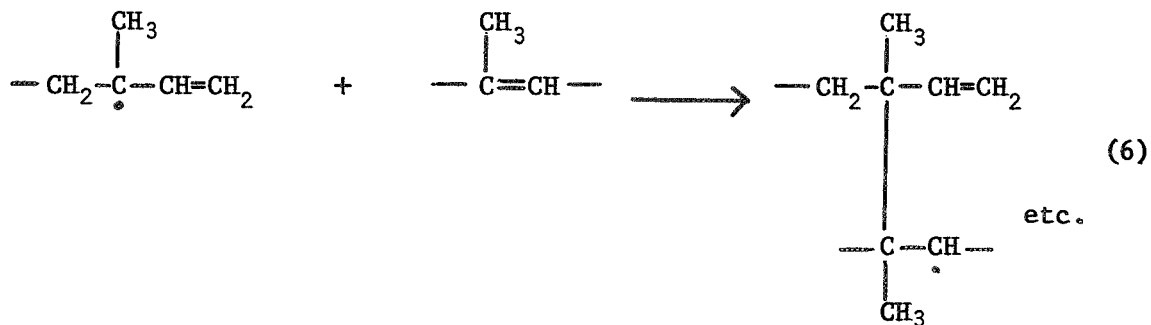
As a follow-up to Bateman's pioneering work, we carried out a detailed spectroscopic study of the photoinduced microstructural changes in 1,4-polyisoprene films<sup>11</sup>. These films, although somewhat crosslinked after irradiation, were nevertheless sufficiently soluble to permit n.m.r. analysis, while infrared analysis was performed on the films before and after irradiation. As with the 1,4-polybutadienes, 2537-Å-irradiation of 1,4-polyisoprene films in vacuo resulted in cis-trans isomerization (with a photostationary cis-trans ratio in the range 70:30 to 50:50), loss of 1,4-double bonds, formation of cyclopropyl groups, and the appearance of new external double bonds (vinylidene and vinyl units). Quantum yields for the first three of these processes were estimated at 0.041, 0.083 and 0.018, respectively.

The photoisomerization of 1,4-polyisoprene, like that of 1,4-polybutadiene, has been considered<sup>11</sup> to proceed through electronically excited 1,4-double bonds (probably triplet states with  $\sim 74$  kcal/mole) which can rotate and assume either cis or trans configuration on return to the ground state. The smooth structureless absorption tail extending to around 3000 Å ( $\sim 95$  kcal/mole) observed in the ultraviolet spectrum of the purified polyisoprene film has been associated with the trisubstituted ethylenic unit in the polymer, perhaps as a weak singlet-triplet transition<sup>15</sup>. On this basis, the polyisoprene double bonds could be excited by direct absorption of the 2537 Å photons without requiring inter- or intramolecular energy transfer, a point of view adopted previously by Bateman<sup>13</sup> and by Hart and Matheson<sup>14</sup>.

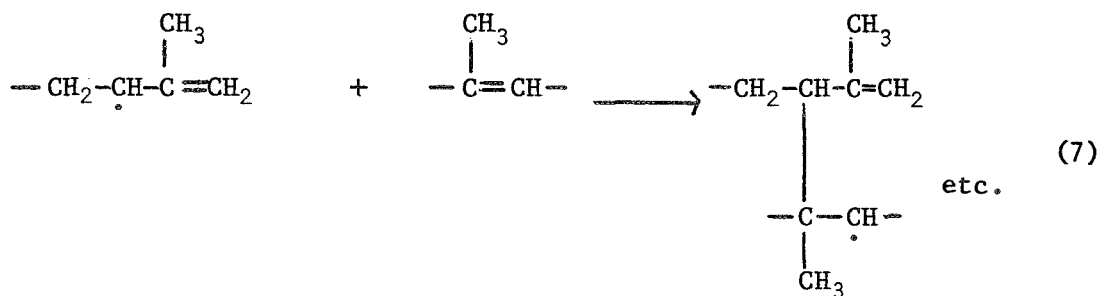
Some of the energy absorbed by the double bonds is undoubtedly diverted into rupturing C-C bonds connecting successive isoprene units. That particular bond is the 'weak link' in the chain with a strength (~55 kcal/mole) which is lowered from the normal C-C bond strength by the resonance energy of the two allyl radicals formed on chain scission (5).



Radicals I-IV can recombine in any of four different ways or add to double bonds in the same or other macromolecular chain [reactions (6) and (7)].

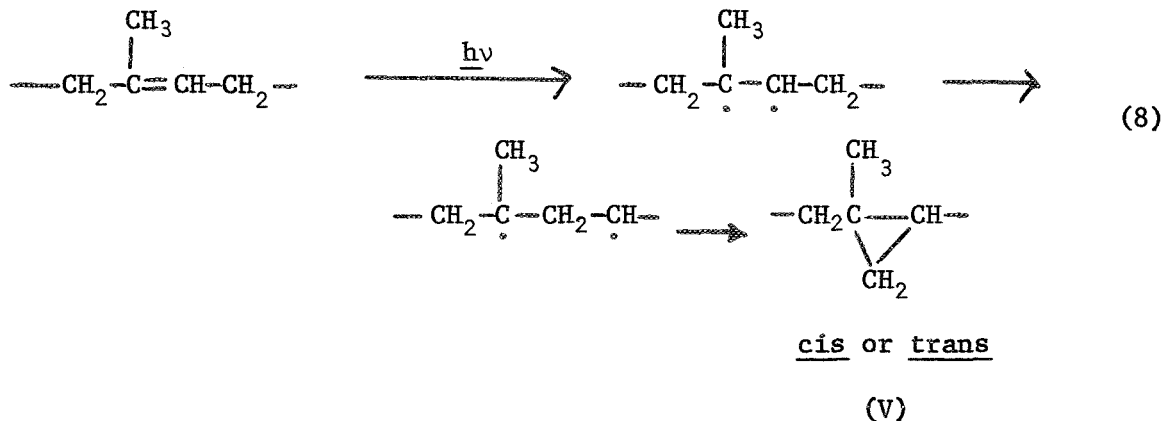




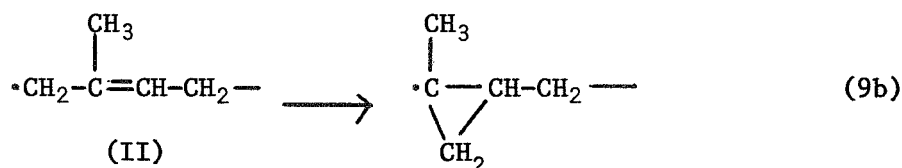
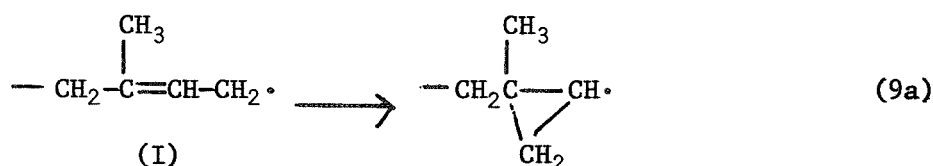


The overall effect is to create vinylidene and vinyl double bonds as well as some endlinks (or crosslinks) in the irradiated 1,4-polyisoprene. Since the resulting vinylidene content was three to five times the vinyl content, radical IV is that much more reactive than III, while I and II on subsequent reaction preserve the original 1,4-double bonds, with probable retention of cis-trans stereochemistry<sup>16</sup>. To the extent that radicals I-IV "polymerize" onto nearby double bonds to form endlinks, there is an added loss of double bonds over and above those which are transformed into vinylidene, vinyl or cyclopropyl structures.

The mode of excitation of double bonds which leads to cis-trans isomerization was adapted<sup>11</sup> to explain the appearance of cyclopropyl groups, namely, formation of a biradical followed by 1,2-hydrogen migration and then ring closure [reaction (8)]. However, Carstensen<sup>17</sup>, in an e.s.r. study of free radicals produced in ultraviolet-irradiated 1,4-polyisoprene, has



recently proposed an alternative route to cyclopropyl groups: if radicals I and II formed on chain scission possess excess energy they might undergo ring closure [reaction (9a) or (9b)]; the resulting cyclopropyl radicals

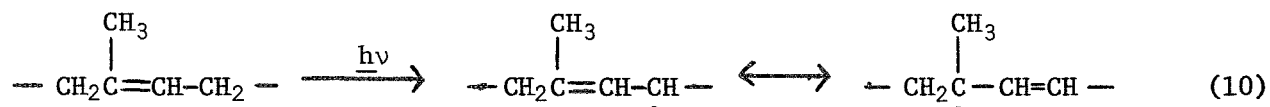


could then recombine with the counterpart radicals II and I (or their allylic resonance forms, IV and III), respectively. For this mechanism to hold, the radicals in (9a) or (9b) must have enough energy to overcome the endothermicity of the cyclopropyl ring closure, *i.e.*,  $\sim 26$  kcal/mole<sup>18</sup>. That such 'hot' radicals might arise in the photolysis of 1,4-diene polymer films is indicated by the large energy difference between the 2537 Å photons ( $\sim 112$  kcal/mole) and the strength ( $\sim 55$  kcal/mole) of the C-C bond leading to radicals I and II.

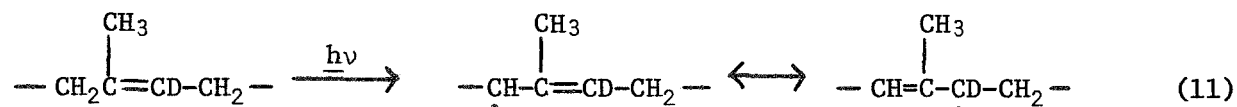
It is interesting to note that the spectroscopic evidence advanced for cyclopropyl groups in ultraviolet-irradiated 1,4-polyisoprene and 1,4-polybutadiene<sup>11</sup> (9.8- $\mu$  infrared absorption, and 9.6- and 10.0- $\tau$  n.m.r. peaks in the former polymer and 9.4- and 10.3- $\tau$  peaks in the latter) was confirmed

by Pinazzi<sup>19</sup> who reported practically the same infrared and n.m.r. data for model compounds of 1,4-polyisoprene containing structure V.

That double bond migration (10) is not a significant reaction in the photolysis of 1,4-polyisoprene was shown by the absence of 10.3- $\mu$



absorption (trans -CH=CH-) in the infrared spectrum of the irradiated polymer. Likewise, double bond migration in the opposite direction can be neglected, as seen in the fact that irradiated polyisoprene-3-d did not reveal 12- $\mu$  absorption [-C(CH<sub>3</sub>)=CH- units] indicative of reaction (11).



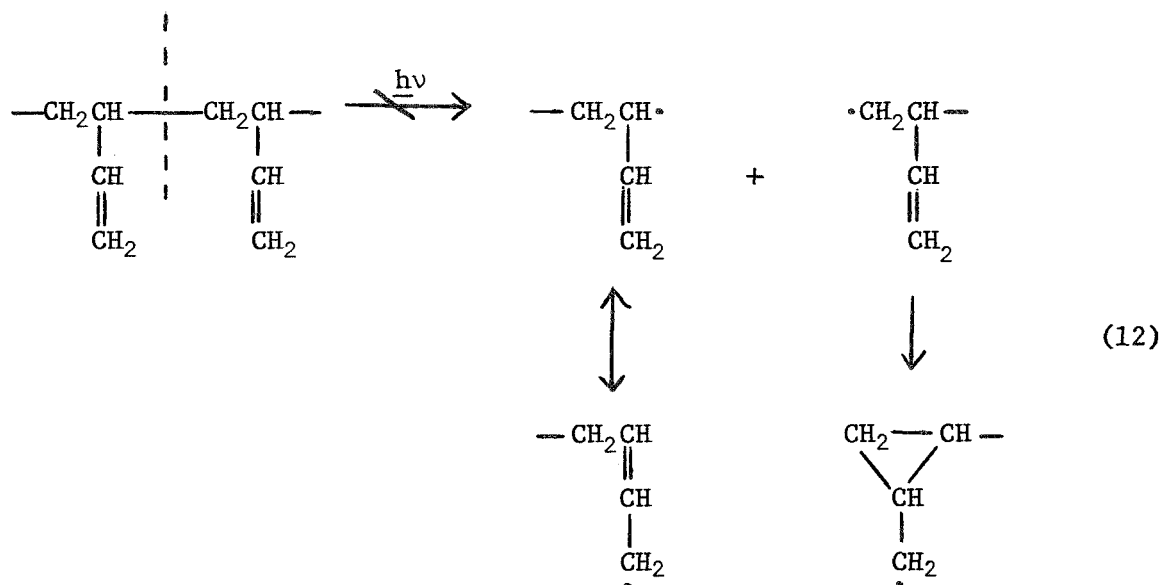
Moreover, the polyisoprenyl radicals in reactions (10) and (11) were not observed in Carstensen's e.s.r. work<sup>17</sup>. Besides radicals I and II, his e.s.r. spectra showed one additional, minor peak which was assigned to polyenyl radicals, -(CR<sub>1</sub>=CR<sub>2</sub>)<sub>n</sub>-CH<sub>2</sub>·, where R<sub>1</sub> and R<sub>2</sub> = H or CH<sub>3</sub>, and n is about 3.

These considerations reinforce the conclusion, based on quantum yield data, that reaction (4) is unimportant relative to photoinduced cis-trans isomerization or loss of unsaturation; as noted above, quantum yields for the latter processes are some 40-80 times as large as that for hydrogen production.

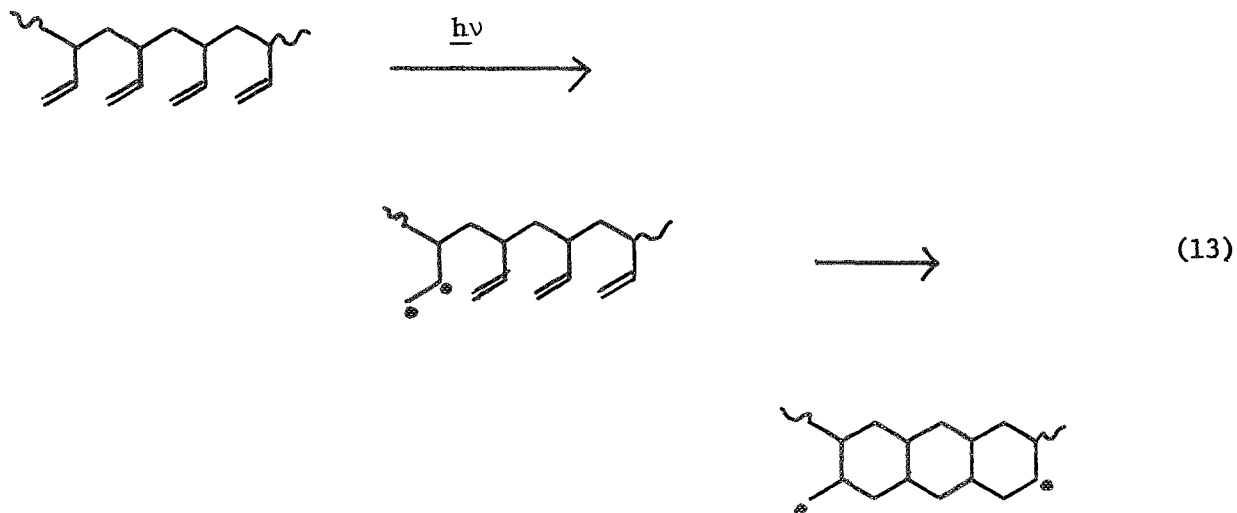
### 1,2-POLYBUTADIENE

As an extension of work on the photoinduced microstructural changes in the 1,4-diene polymers, where the double bonds are in the main chain, a study was made of the corresponding changes in two unsaturated polymers where the double bonds are external to the main chain, namely, 1,2-polybutadiene and 3,4-polyisoprene<sup>20</sup>. The only prior study of the photolysis in vacuo of a high 1,2-polybutadiene was that of a sodium-butadiene rubber (~68% vinyl and ~32% vinylene units) nearly twenty years ago<sup>21</sup>. In that work the polymer displayed a sharp drop in unsaturation (quantum yield of 0.73), the loss of double bonds occurring primarily in the main chain. In addition, there was evolution of gas (~64% hydrogen and 32% methane) with a quantum yield of  $\sim 2 \times 10^{-3}$ . While the gas yields were not unlike those obtained by Bateman<sup>13</sup>, the results indicating only a small decrease in external double bonds do not carry over to 1,2-polybutadiene.

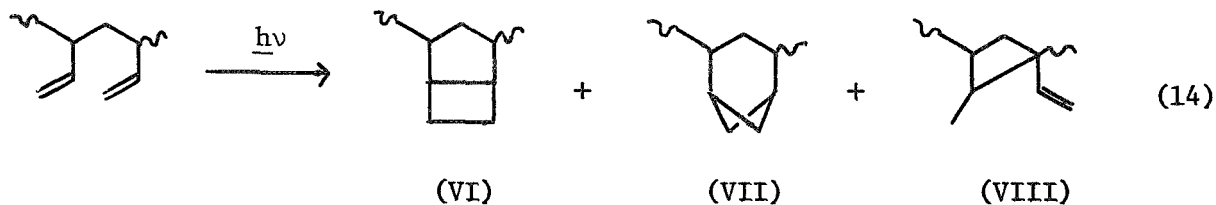
It was found more recently<sup>20</sup> that a thin film of a polybutadiene containing 91.5% vinyl and 8.5% vinylene double bonds, upon exposure for 90 hr in vacuo to 2537 Å radiation, showed an 80% loss of  $-\text{CH}=\text{CH}_2$ , as indicated by decreased intensities of characteristic infrared bands. The absence of absorption at 9.8  $\mu$  implied that formation of cyclopropyl groups was not one of the photocyclization possibilities. Nor was there chain scission of the type shown in reaction (12) [the analog of reactions (1) and (5) in the case of the 1,4-diene polymers] inasmuch as the characteristic 10.3- $\mu$  band for trans  $-\text{CH}=\text{CH}-$  was lacking in the spectrum of irradiated 1,2-polybutadiene.



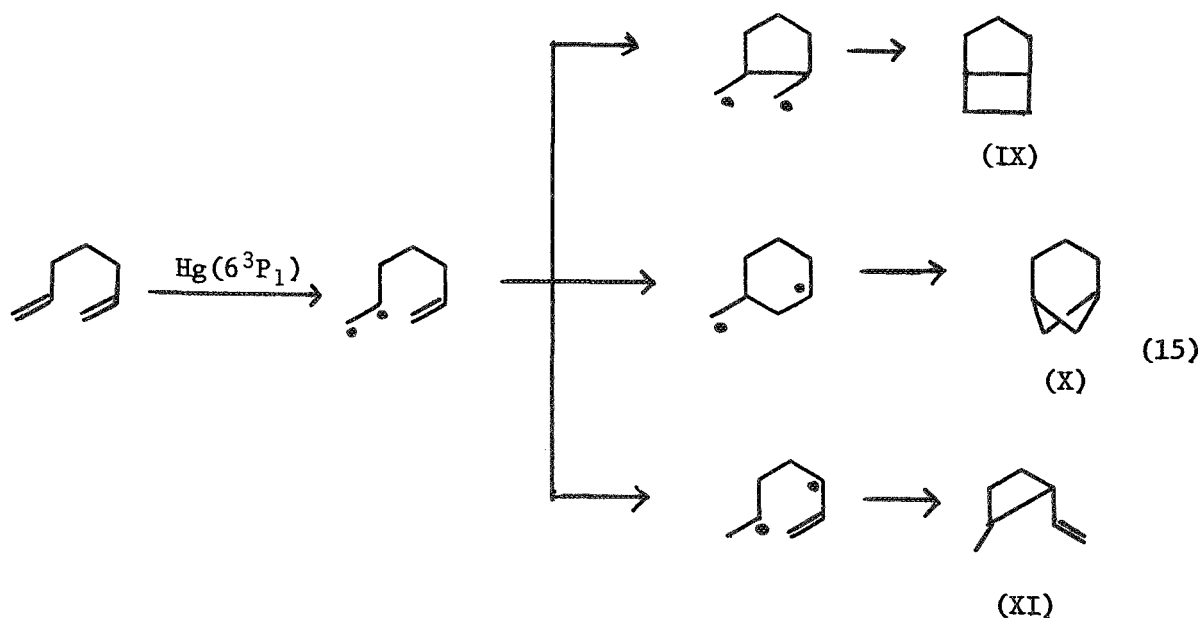
Although photocyclization of 1,2-polybutadiene could lead to fused cyclohexane rings, via reaction (13), this process was ruled out chiefly because all attempts to accomplish the free radical postpolymerization of 1,2-polybutadiene to a ladderlike polymer were unsuccessful<sup>22</sup>.



Instead, the photocyclization of 1,2-polybutadiene was pictured<sup>20</sup> as involving cycloaddition (14) of adjacent vinyl units to yield structures



VI and VII, along with rearrangement to VIII. The precedent cited for VI and VII was the mercury-photosensitized isomerization of 1,6-heptadiene (15)



in the vapor phase to the analogous bicycloheptanes IX and X<sup>23,24</sup>. The concomitant formation of methylvinylcyclobutane XI on irradiation of

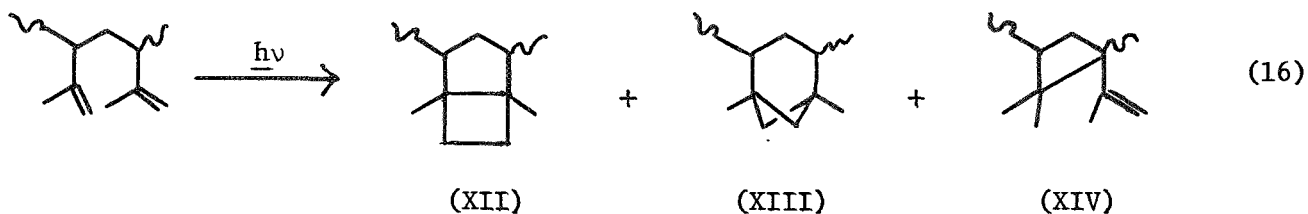
1,6-heptadiene at low pressures<sup>24</sup>, though apparently not at high<sup>23</sup>, might well find an analog in a corresponding process in 1,2-polybutadiene, to form VIII. The latter structure could account for the appearance of a 7.3- $\mu$  (methyl) band in the spectrum of the irradiated polymer. The analogy with 1,6-heptadiene affords a further argument against fused cyclohexane rings in irradiated 1,2-polybutadiene: although certain substituted 1,6-heptadienes (e.g., 2,6-diphenyl-1,6-heptadiene) can undergo free radical cyclo-polymerization, such a reaction is unknown for the unsubstituted 1,6-heptadiene<sup>22</sup>. To sum up the photolysis of 1,2-polybutadiene, it may be stated that the infrared evidence, while not foreclosing other cyclized structures, is well represented by structures VI-VIII.

### 3,4-POLYISOPRENE

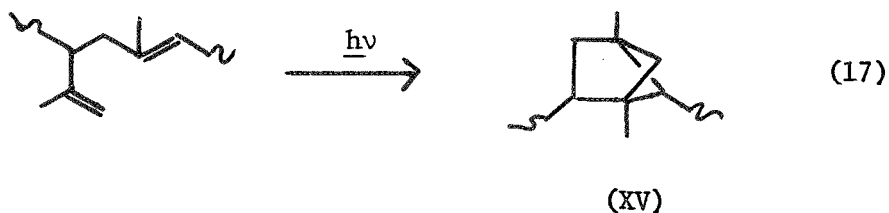
In the ultraviolet irradiation of a high 3,4-polyisoprene (65% vinylidene and 35% isoprenic or 1,4-double bonds)<sup>20</sup>, spectroscopic data disclosed partial consumption of the two kinds of double bonds present in the polymer. The major effect was photocycloaddition of the 3,4-units analogous to that discussed above for the vinyl units in 1,2-polybutadiene. At the same time, some of the 1,4-units were transformed into cyclopropyl groups in the manner described for 1,4-polyisoprene. In comparison to the photoinduced loss of  $\sim$ 80% unsaturation in 1,2-polybutadiene, the high 3,4-polyisoprene showed, for the same radiation exposure, an over-all decrease of  $\sim$ 40% unsaturation [greater decrease in the 1,4- ( $\sim$ 60%) than in the 3,4- ( $\sim$ 25%) units].

The photocyclization of 3,4-polyisoprene was pictured as yielding

mainly XII and XIII, rather than fused cyclohexane rings [reaction (16)].

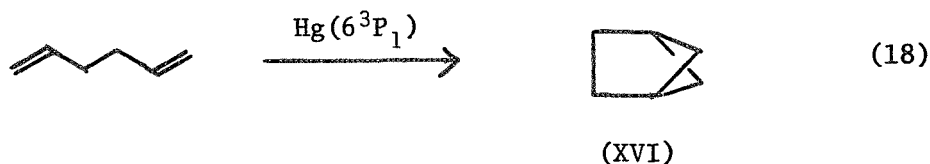


Here again, free radical postpolymerization of 3,4-polyisoprene has never been achieved<sup>22</sup>. The formation of structure XIV, the analog of VIII in reaction (14), was not too important since there was no observable splitting of the 7.3- $\mu$  band (gem-dimethyls) in the spectrum of irradiated 3,4-polyisoprene. The 1,4-units in the high 3,4-polyisoprene, apart from forming cyclopropyl groups (and perhaps some vinyl and vinylidene units as well), would likely be involved in photocyclization with neighboring 3,4-units to yield a structure such as XV. Reaction (17) is analogous to the mercury-



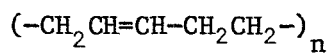
sensitized photocyclization of 1,5-hexadiene to yield preferentially the bicyclohexane XVI<sup>23</sup>.





### POLYPENTENAMERS

Having reviewed the published work on the direct photochemical transformations of diene polymers, we now consider the corresponding changes taking place in two additional unsaturated polymers, cis- and trans-poly-pentenamers<sup>25</sup>. These polymers (XVII, with head-to-tail monomer arrangement), obtained by stereospecific ring-opening polymerization of cyclopentene<sup>26</sup>, are of interest here because they possess at once a vinylene unit in common with



(XVII)

the 1,4-polybutadienes and an extra methylene group in each monomer unit, which leads to a stronger C-C bond at the allyl position. Since rupture of that particular bond in stereoregular poly-pentenamer yields one allyl radical compared to two in 1,4-polybutadiene, the vulnerable C-C bond in poly-pentenamer has a bond strength of  $\sim 69.5$  kcal/mole, i.e., midway between that of a normal C-C bond ( $\sim 82$  kcal/mole, as in polyethylene) and that of the corresponding bond in 1,4-polybutadiene (82 minus twice the allyl resonance energy of 12.5, or 57 kcal/mole). Consequently, the poly-pentenamers should show photo-induced cis-trans isomerization similar to the 1,4-polybutadienes but with



in Figure 5 of ref. 8), the vinyl content in spectrum B or C in Figure 1 here is estimated to be  $\approx 1.6$  double bonds per 100 monomer units<sup>†</sup>.

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<sup>†</sup>The estimated vinyl contents are based on the relative values of the absorbance ratio,  $A_{11.0}/A_{6.9}$ , where the 6.9- $\mu$  band ( $\text{CH}_2$  bending vibration) is an approximate internal standard. The above estimate for 1,4-polybutadiene, which constitutes a revision of an earlier one (5 to 8 vinyl double bonds per 100 monomer units)<sup>8</sup>, is similar to the combined vinylidene-vinyl content of a comparably irradiated 1,4-polyisoprene (15.3 external double bonds per 100 monomer units)<sup>11</sup>.

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The absence of distinct 9.8- $\mu$  absorption in the infrared spectra of irradiated polypentenamers indicates that there is little or no photo-induced formation of cyclopropyl groups in these polymers, in contrast to the 1,4-diene polymers. To be sure, there is absorption at 9.75  $\mu$  in spectra B and C in Figure 1, but this is related to the cis configurations in the polymer backbone since the initial cis polypentenamer (spectrum A) has a moderately strong band at that wavelength. As the cis content decreases from top to bottom in Figure 1 so also does the intensity of the 9.75- $\mu$  band. While this fortuitous absorption would obscure the development of a new weak peak at 9.8  $\mu$ , such a development clearly cannot be significant: the relative intensity at 9.75  $\mu$  in B and C not only reflects the cis contents in these spectra but it is also substantially lower than the relative intensity of the 9.8- $\mu$  cyclopropyl peak in a similarly irradiated 1,4-polybuta-

diene<sup>8</sup>. Unfortunately, n.m.r. analysis could not be applied to the cyclopropyl question here inasmuch as the polypentenamer films were completely insoluble after irradiation.

Since cyclopropyl structures are presumably not formed in the photolysis of polypentenamers<sup>†</sup>, the mechanism proposed originally<sup>11</sup> for

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<sup>†</sup>Further support for this argument is provided by irradiations performed on films of a high trans-polyheptenamer  $[(-CH_2CH=CHCH_2CH_2CH_2CH_2-)]_n$ <sup>25</sup>. An irradiated film having an infrared spectrum resembling a composite of B and C in Figure 1, so far as the 10.35-, 11.0- and 13.8- $\mu$  bands are concerned, showed scarcely any absorption at 9.8  $\mu$  and, therefore, negligible cyclopropyl formation, despite pronounced trans  $\rightarrow$  cis isomerization. The trans-polyheptenamer film also showed the same small production of vinyl units that polypentenamer exhibited.

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the formation of such groups in the 1,4-diene polymers requires revision. For that mechanism to be valid, a process analogous to that given in reaction (2) or (8) would have to occur in the polypentenamers but this is evidently not the case. The inference may therefore be drawn that whereas cis-trans isomerization in both 1,4-diene polymers and polypentenamers necessarily involves photoexcited vinylene units, cyclopropyl formation probably does not.

At this time, the only route to cyclopropyl structures which appears plausible is the one mentioned above in connection with Carstensen's e.s.r.

work on irradiated 1,4-polyisoprene<sup>17</sup>. Reactions (9a) and (9b) imply that a prerequisite for photoinduced formation of cyclopropyl groups in an unsaturated macromolecule is its ability to undergo chain scission with concomitant formation of 'hot' allyl radicals. Polypentenamer, which generates photochemically few vinyl double bonds and hence experiences little chain scission, consequently yields negligible cyclopropyls. This also offers a rationale for the failure of 1,2-polybutadiene to form cyclopropyl groups on ultraviolet irradiation: even though  $-\text{CH}=\text{CH}_2$  units are excited photochemically, resulting in a different kind of cyclization [reaction (14)], no main chain scission occurs and so no allyl radicals form which can undergo ring closure to cyclopropane structures. It is worth mentioning that this criterion also accounts for the absence of cyclopropyls in the radiolysis of the 1,4-diene polymers<sup>10,27</sup> (in contrast to their photolyses). Thus, despite the facile cis-trans isomerization and loss of unsaturation induced by ionizing radiation, there is negligible production of vinyl units in the 1,4-diene polymers and therefore no main chain scission or transitory allyl radicals to give rise to cyclopropyl groups.

#### CONCLUSION

From the foregoing discussion it is clear that the particular unsensitized photochemical transformations occurring in unsaturated polymers depend on whether the C=C bonds are predominantly of the internal or external type. In polymers with internal double bonds the photochemical processes are further influenced by whether scission produces one or two allyl radicals per chain

rupture. Thus, in 1,4-polybutadiene and 1,4-polyisoprene (which yield two allyls per rupture) the important reactions observed are cis-trans isomerization, loss of unsaturation, production of new double bonds and cyclopropyl formation. However, in cis- and trans-polypentenamers (which yield but one allyl per chain rupture) the principal microstructural change is cis-trans isomerization with very little vinyl production and negligible cyclopropyl formation. On the other hand, in 1,2-polybutadiene and 3,4-polyisoprene, polymers having external unsaturation, cycloaddition of adjacent double bonds is the major photochemical process. Although the above reactions are accompanied by gas evolution (mostly hydrogen) and cross-linking, the latter two processes are relatively unimportant on a quantum yield basis. In future work it will be of interest to see how these generalizations apply to the photochemistry of still other unsaturated polymers, such as those having vinylene units in the side chains, or different distributions of double bonds along the main chain.

#### Acknowledgement

Support for the original research on the direct photolysis of 1,4-polybutadiene films by the National Aeronautics and Space Administration (during 1964) while the author was at Stanford Research Institute, and the opportunity to carry out the polypentenamer work at Ames Research Center in the course of a National Research Council Resident Research Associateship, 1968-1970, are gratefully acknowledged. The author wishes to thank Dr. Gino Dall'Asta of Montecatini Edison, Milan, Italy, for kindly supplying the samples of polypentenamers and polyheptenamer used in this work.

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LEGEND OF FIGURE

Figure 1. Typical infrared spectra of cis- and trans-polypentenamer films before (A, D, respectively) and after (B, C) ultraviolet irradiation in vacuo.

