

PHOTOCHEMISTRY OF UNSATURATED POLYMERS

MORTON A. GOLUB

*Ames Research Center, National Aeronautics and Space Administration,
Moffett Field, Calif. 94035, USA*

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 reviews¹⁻⁷ 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 photoinduced 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.

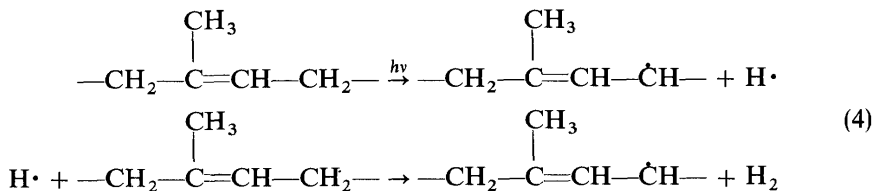
1,4-POLYBUTADIENE

The first investigation of the direct photoinduced microstructural changes in an unsaturated polymer was reported at the IUPAC Symposium on Macromolecular Chemistry in Prague⁸. That study, consisting of both near (2537 Å) and far (1236 Å) ultra-violet 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 state⁹. The latter process was attributed to excitation of the π -electrons of the double bonds to an antibonding state in which

The occurrence of a direct photoisomerization of *cis*-1,4-polybutadiene *in vacuo* at room temperature was reported also by Ho¹² in connection with a study of the photo-oxidation of this polymer.

1,4-POLYISOPRENE

Until recently the only fundamental study reported on the photolysis of 1,4-polyisoprene was the work of Bateman¹³ 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 non-condensable 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-



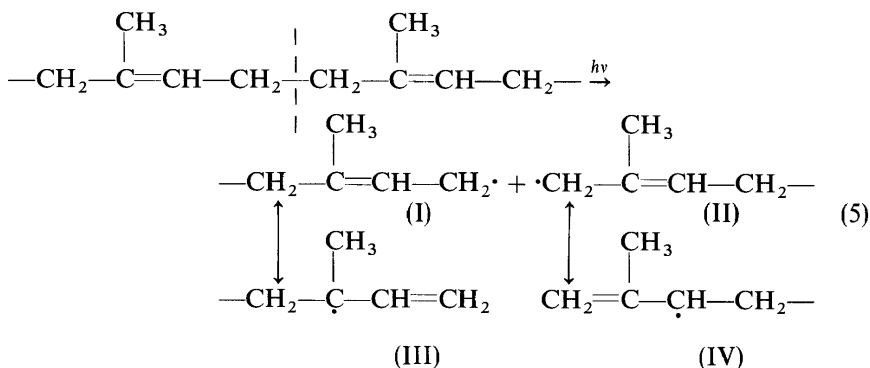
polyisoprene restricted its chemical analysis, but evidence was adduced for loss of unsaturation with a quantum yield^{13,14} approaching 0.1.

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 films¹¹. These films, although somewhat crosslinked after irradiation, were nevertheless sufficiently soluble to permit n.m.r. analysis, while infra-red 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.

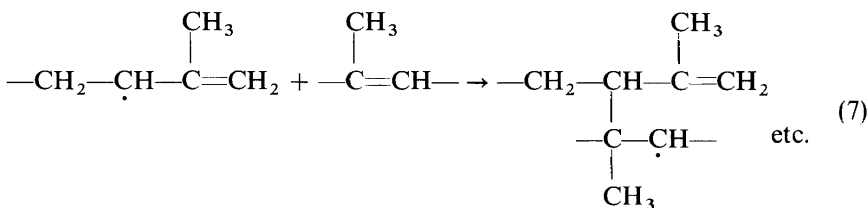
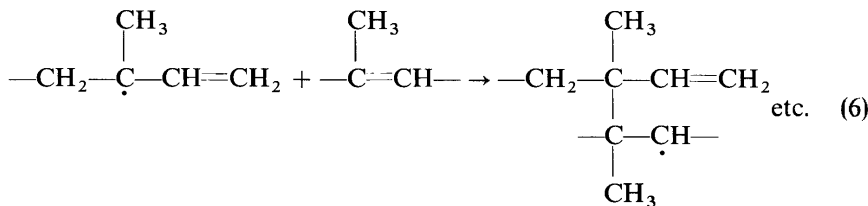
The photoisomerization of 1,4-polyisoprene, like that of 1,4-polybutadiene, has been considered¹¹ to proceed through electronically excited 1,4-double bonds (probably triplet states with ~ 74 kcal/mole) which can rotate and assume either *cis* or *trans* configuration on return to the ground state. The smooth structureless absorption tail extending to around 3000 Å (~ 95 kcal/mole) observed in the ultra-violet spectrum of the purified polyisoprene film has been associated with the trisubstituted ethylenic unit in the polymer, perhaps as a weak singlet-triplet transition¹⁵. On this basis, the polyisoprene double bonds could be excited by direct absorption of the 2537 Å photons without requiring inter- or intra-molecular energy transfer, a point of view adopted previously by Bateman¹³ and by Hart and Matheson¹⁴.

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 (reaction 5).



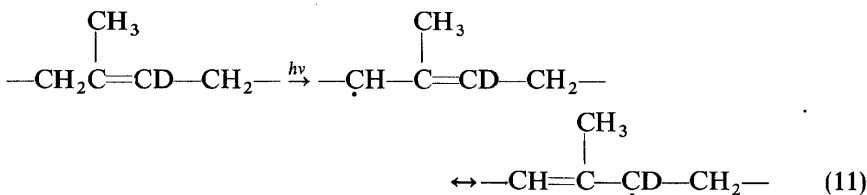
Radicals I–IV can recombine in any of four different ways or add to double bonds in the same or other macromolecular chain [reactions 6 and 7].



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* stereochemistry¹⁶. To the extent that radicals I–IV ‘polymerize’ on to 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 adapted¹¹ 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, Carstensen¹⁷, in an e.s.r. study of free radicals produced in ultra-violet-irradiated 1,4-polyisoprene, has recently proposed

absorption (*trans* —CH=CH—) in the infra-red 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- μ absorption [—C(CH₃)=CH— units] indicative of reaction 11.



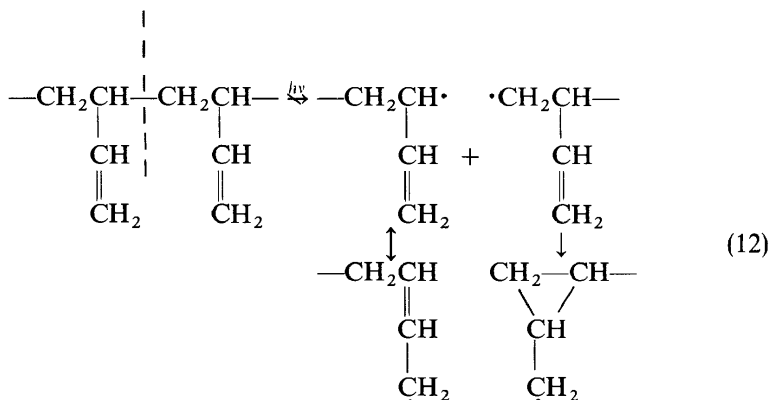
Moreover, the polyisoprenyl radicals in reactions 10 and 11 were not observed in Carstensen's e.s.r. work¹⁷. Besides radicals I and II, his e.s.r. spectra showed one additional, minor peak which was assigned to polyenyl radicals, —(CR₁=CR₂)_n—CH₂•, where R₁ and R₂ = H or CH₃, and *n* is about three.

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.

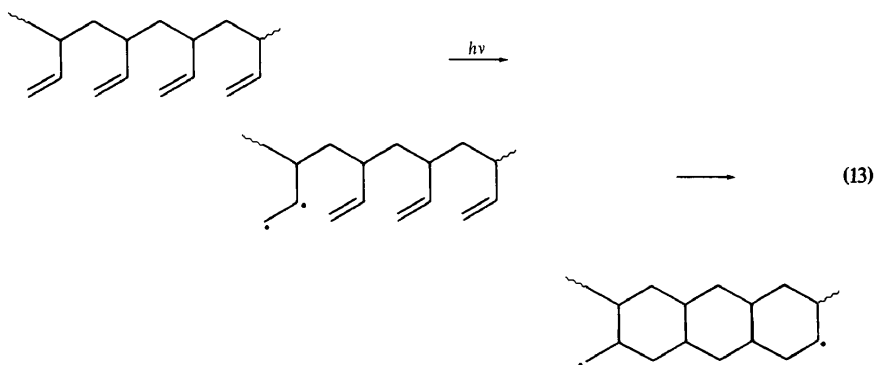
1,2-POLYBUTADIENE

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-polyisoprene²⁰. The only prior study of the photolysis *in vacuo* of a high 1,2-polybutadiene was that of a sodium-butadiene rubber (~68 per cent vinyl and ~32 per cent vinylene units) nearly twenty years ago²¹. 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 per cent hydrogen and 32 per cent methane) with a quantum yield of $\sim 2 \times 10^{-3}$. While the gas yields were not unlike those obtained by Bateman¹³, the results indicating only a small decrease in external double bonds do not carry over to 1,2-polybutadiene.

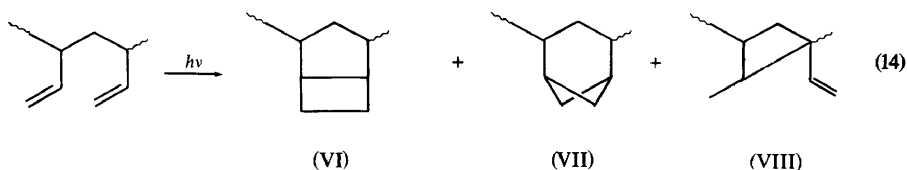
It was found more recently²⁰ that a thin film of a polybutadiene containing 91.5 per cent vinyl and 8.5 per cent vinylene double bonds, upon exposure for 90 h *in vacuo* to 2537 Å radiation, showed an 80 per cent loss of —CH—CH₂, as indicated by decreased intensities of characteristic infra-red bands. The absence of absorption at 9.8 μ 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 analogue of reactions 1 and 5 in the case of the 1,4-diene polymers] inasmuch as the characteristic 10.3- μ band for *trans* —CH=CH— was lacking in the spectrum of irradiated 1,2-polybutadiene.



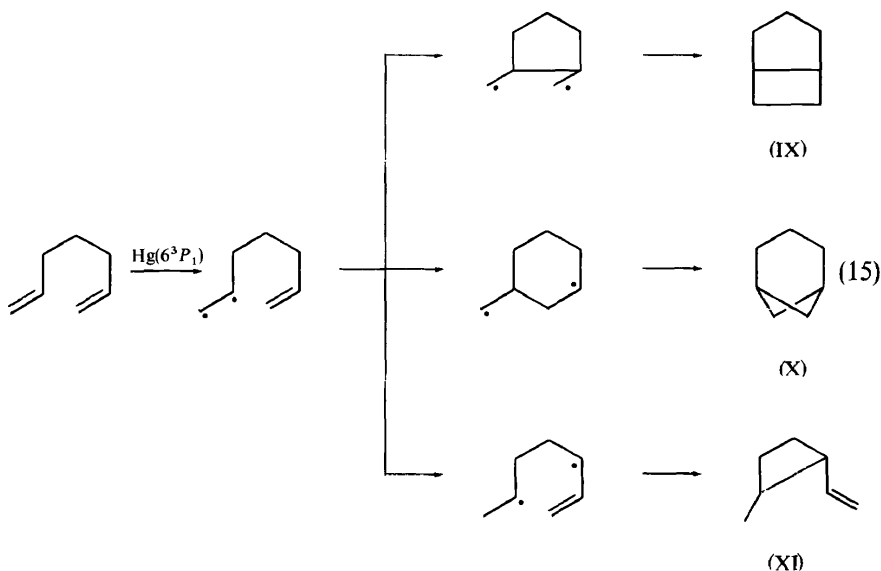
Although photocyclization of 1,2-polybutadiene could lead to fused cyclohexane rings, via reaction 13, this process was ruled out chiefly because all attempts to accomplish the *free radical* postpolymerization of 1,2-polybutadiene to a ladderlike polymer were unsuccessful²².



Instead, the photocyclization of 1,2-polybutadiene was pictured²⁰ as involving cycloaddition 14 of adjacent vinyl units to yield structures VI and VII, along with rearrangement to VIII.



VII, along with rearrangement to VIII. The precedent cited for VI and VII was the mercury-photosensitized isomerization of 1,6-heptadiene (reaction 15) in the vapour phase to the analogous bicycloheptanes IX and X^{23, 24}. The concomitant formation of methylvinylcyclobutane XI on irradiation of



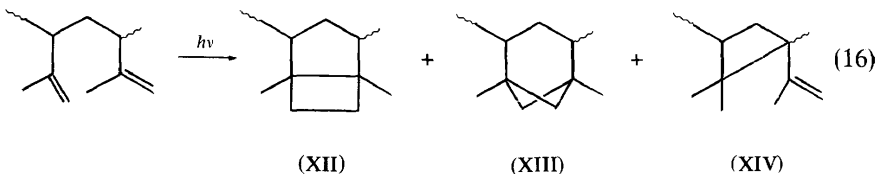
1,6-heptadiene at low pressures²⁴, though apparently not at high²³, might well find an analogue in a corresponding process in 1,2-polybutadiene, to form VIII. The latter structure could account for the appearance of a 7.3- μ (methyl) band in the spectrum of the irradiated polymer. The analogy with 1,6-heptadiene 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 cyclopolymerization, such a reaction is unknown for the unsubstituted 1,6-heptadiene²². To sum up the photolysis of 1,2-polybutadiene, it may be stated that the infra-red evidence, while not foreclosing other cyclized structures, is well represented by structures VI–VIII.

3,4-POLYISOPRENE

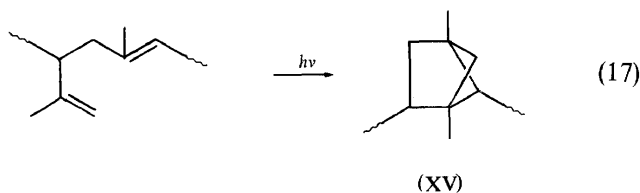
In the ultra-violet irradiation of a high 3,4-polyisoprene (65 per cent vinylidene and 35 per cent isoprenic or 1,4-double bonds)²⁰, spectroscopic data disclosed partial consumption of the two kinds of double bonds present in the polymer. The major effect was photocycloaddition of the 3,4-units analogous 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 ~ 80 per cent unsaturation in 1,2-polybutadiene, the high 3,4-polyisoprene showed, for the same radiation exposure, an overall decrease of ~ 40 per cent unsaturation [greater decrease in the 1,4- (~ 60 per cent) than in the 3,4- (~ 25 per cent) units].

The photocyclization of 3,4-polyisoprene was pictured as yielding mainly XII and XIII, rather than fused cyclohexane rings [reaction 16].

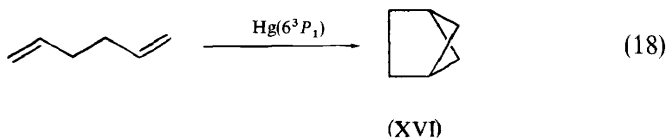
PHOTOCHEMISTRY OF UNSATURATED POLYMERS



Here again, free radical postpolymerization of 3,4-polyisoprene has never been achieved²². The formation of structure XIV, the analogue of VIII in reaction 14, was not too important since there was no observable splitting of the 7.3- μ 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 neighbouring 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 XVI²³.



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*-polypentenamers²⁵. These polymers (XVII, with head-to-tail monomer arrangement), obtained by stereospecific ring-opening polymerization of cyclopentene²⁶, are of interest here because they possess at once a vinylene unit in common with the 1,4-polybutadienes and an extra methylene group



(XVII)

in each monomer unit, which leads to a stronger C—C bond at the allyl

position. Since rupture of that particular bond in stereoregular polypentenamer yields one allyl radical compared to two in 1,4-polybutadiene, the vulnerable C—C bond in polypentenamer has a bond strength of ~ 69.5 kcal/mole, i.e. midway between that of a normal C—C bond (~ 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 polypentenamers should show photoinduced *cis-trans* isomerization similar to the 1,4-polybutadienes but with much less chain scission, and this has been observed²⁵.

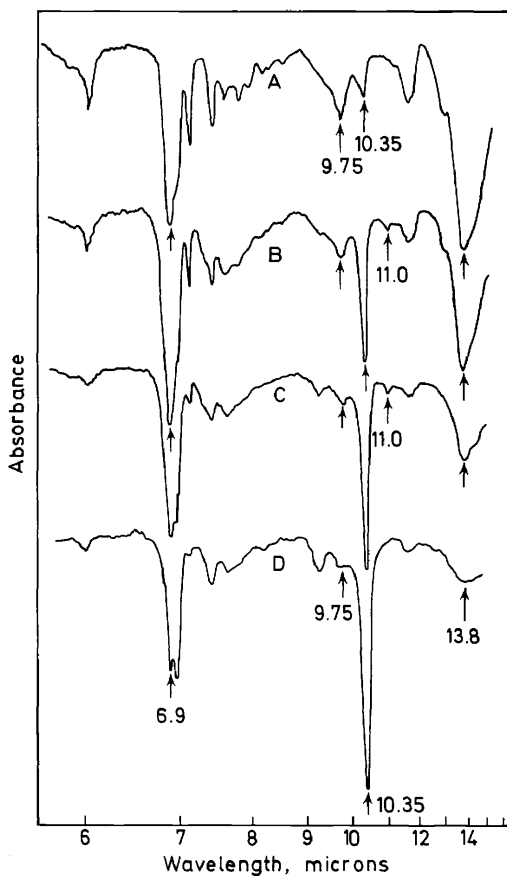


Figure 1. Typical infra-red spectra of *cis*- and *trans*-polypentenamer films before (A, D, respectively) and after (B, C) ultra-violet irradiation *in vacuo*

Infra-red spectral changes produced in thin films of purified *cis*-polypentenamer (~ 95 per cent *cis*) and high *trans*-polypentenamer (~ 80 per cent *trans*) on prolonged exposure to 2537 \AA radiation *in vacuo* are shown in Figure 1. The sharp increase in intensity of the $10.35\text{-}\mu$ band (*trans*

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 so. 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-polyisoprene¹⁷. Reactions 9a and 9b imply that a pre-requisite 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 ultra-violet 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^{10, 27} (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 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 crosslinking, 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 sidechains, 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 Centre 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.

REFERENCES

- ¹ H. H. G. Jellinek. *Pure Appl. Chem.* **4**, 419 (1962).
- ² L. A. Wall and J. H. Flynn. *Rubber Chem. Technol.* **35**, 1157 (1962).
- ³ M. B. Neiman (Ed.). *Aging and Stabilization of Polymers*, Consultants Bureau: New York (1965).
- ⁴ N. Grassie. *Encycl. Polymer Sci. Technol.* **4**, 647 (1966).
- ⁵ R. B. Fox. In *Progress in Polymer Science* (Ed. A. D. Jenkins) Vol. I, p 45, Pergamon: Oxford (1967).
- ⁶ J. F. Rabek. *Photochem. Photobiol.* **7**, 5 (1968).
- ⁷ R. B. Fox and R. F. Cozzens. *Encycl. Polymer Sci. Technol.* **11**, 761 (1969).
- ⁸ M. A. Golub and C. L. Stephens. *J. Polym. Sci.* **C16**, 765 (1967); *IUPAC Symposium on Macromolecular Chemistry* (Prague, 1965).
- ⁹ For reviews of the photo- and radiation-sensitized and other catalysed isomerizations, see: (a) M. A. Golub in *Polymer Chemistry of Synthetic Elastomers* (Ed. J. P. Kennedy and E. G. M. Tornqvist), Part II, p 939, Interscience: New York (1969); (b) M. A. Golub in *The Chemistry of Alkenes* (Ed. J. Zabicky), Vol. II, p 411. Wiley-Interscience: London (1970).
- ¹⁰ M. A. Golub. *J. Phys. Chem.* **69**, 2639 (1965).
- ¹¹ M. A. Golub and C. L. Stephens. *J. Polym. Sci. A-1*, **6**, 763 (1968); *Rev. Gen. Caout. Plast.* **45**, 749 (1968).
- ¹² T. C. Ho. *K'o Hsueh Ch'u Pan She* 365 (1963); *Chem. Abstr.* **64**, 2253h (1966).
- ¹³ L. Bateman. *Trans. Inst. Rubber Ind.* **21**, 118 (1945); *J. Polym. Sci.* **2**, 1 (1947).
- ¹⁴ E. J. Hart and M. S. Matheson. *J. Am. Chem. Soc.* **70**, 784 (1948).
- ¹⁵ C. P. Snow and C. B. Allsopp. *Trans. Faraday Soc.* **30**, 93 (1934).
- ¹⁶ C. Walling and W. Thaler. *J. Am. Chem. Soc.* **83**, 3877 (1961).
- ¹⁷ P. Carstensen. *Makromol. Chem.* **135**, 219 (1970).
- ¹⁸ S. W. Benson. Personal communication.
- ¹⁹ C. P. Pinazzi. Personal communication; results presented at the 155th American Chemical Society Meeting, San Francisco, Calif., 31 March–5 April (1968).
- ²⁰ M. A. Golub. *Macromolecules*, **2**, 550 (1969).
- ²¹ A. F. Postovskaya and A. S. Kuzminskii. *Rubber Chem. Technol.* **25**, 872 (1952).
- ²² G. B. Butler. *Encycl. Polymer Sci. Technol.* **4**, 568 (1966), and personal communication.
- ²³ R. Srinivasan and K. H. Carlough. *J. Am. Chem. Soc.* **89**, 4932 (1967).
- ²⁴ R. Srinivasan and K. A. Hill. *J. Am. Chem. Soc.* **87**, 4988 (1965).
- ²⁵ M. A. Golub. Unpublished results; NRC–NASA Research Associateship (1968–70).
- ²⁶ G. Natta, G. Dall'Asta and G. Mazzanti. *Angew. Chem.* **76**, 765 (1964); *Int. Ed.* **3**, 723 (1964).
- ²⁷ M. A. Golub and J. Danon. *Canad. J. Chem.* **43**, 2772 (1965).