Notes

Photocyclization of 1,2-Polybutadiene and 3,4-Polyisoprene[1]

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Recently, the ultraviolet irradiation under vacuum of thin films of purified 1,4-polybutadiene and 1,4-polyisoprene has been shown[3,4] to result in extensive *cis–trans* isomerization and loss of 1,4 unsaturation, the latter process being accompanied by the formation of new external double bonds (vinyl units in the polybutadiene, and vinyl and vinylidene units in the polyisoprene) and also, quite surprisingly, by the novel formation of cyclopropyl groups. As an extension of our prior work on the photoinduced microstructural changes in these 1,4-polymers, the present note is concerned with reporting the corresponding changes produced in 1,2-polybutadiene and in a high 3,4-polyisoprene. Apparently, only one previous study of the photolysis under vacuum of a high 1,2-polybutadiene has been reported, that of a sodium–butadiene rubber (~68% vinyl and ~32% vinylene units) some 17 years ago,[5] but no such study has been reported for 3,4-polyisoprene.

Results and Discussion

1,2-Polybutadiene. Figure 1 shows the infrared spectral changes produced in a thin film of 1,2-polybutadiene (obtained from Phillips Petroleum Co., and having initial unsaturation of 91.5% vinyl, 7.0% *cis*-vinylene, and 1.5% *trans*-vinylene) on exposure for 90 hr under vacuum to 2537-Å radiation, following the procedure described previously.[4] The sharp decrease in the intensities of the 11.0-, 10.1-, 7.1-, 6.1-, and 3.3-μ absorption bands[6] attests to the pronounced loss of $-CH{=}CH_2$ units, amounting to ~80% of the original 1,2 unsaturation, which attends the ultraviolet irradiation of 1,2-polybutadiene. Further indication of the loss of unsaturation is the observation that the minor peaks at 7.8 and 5.5 μ in Figure 1A, likewise associated with vinyl units, and the peak at 7.5 μ, which is probably also due to these same units, are all absent from Figure 1B. The resulting saturation of the $-CH{=}CH_2$ units is revealed by the markedly enhanced absorption at 6.9 μ and the broadening of the 3.5-μ band. The peak at 7.3 μ in Figure 1B indicates the formation of some methyl groups in the saturation process (estimated at about one per nine monomer units), although much less than that observed in the acid-catalyzed cyclization of 1,2-polybutadiene.[7-9]

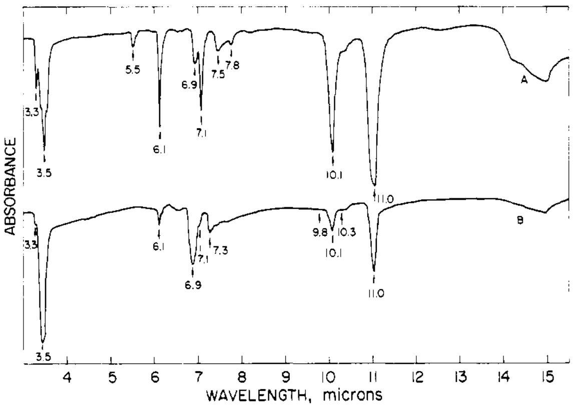
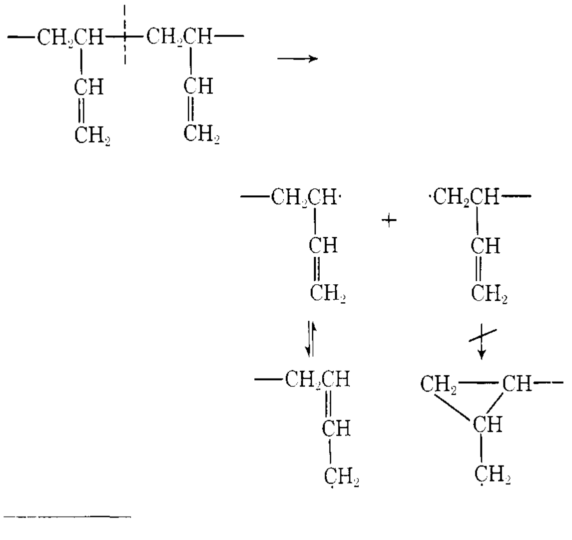


Figure 1. Infrared spectra of 1,2-polybutadiene before (A) and after (B) extensive ultraviolet irradiation under vacuum.

Since the 1,2-polybutadiene film is rapidly crosslinked on ultraviolet irradiation, it was not possible to examine the photoinduced microstructural changes in this polymer more fully with the aid of nmr analysis, as was done previously for 1,4-polyisoprene.[4] However, the infrared data, which reveal the formation of no new unsaturation or other new structures (besides methyls, and saturated vinyl groups) in the photochemical transformations of 1,2-polybutadiene, can be accounted for entirely by cyclization. Thus, the changes in infrared spectra noted here are similar to those observed in the cationic cyclization of various diene polymers.[7-10] On the other hand, the absence of absorption at 9.8 μ (Figure 1B) indicates that the formation of cyclopropyl groups (as observed in the photolysis of 1,4-polybutadiene or 1,4-polyisoprene) is not one of the cyclization possibilities. Furthermore, chain scission of the type



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(3) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Part C*, **16**, 765 (1967).

(4) M. A. Golub and C. L. Stephens, *ibid., Part A-1*, **6**, 763 (1968); *Rev. Gen. Caout. Plast., Ed. Plast.*, **45**, 749 (1968).

(5) A. F. Postovskaya and A. S. Kuzminskii, *Rubber Chem. Technol.*, **25**, 872 (1952).

(6) For assignment of these and other infrared bands mentioned in this note, see H. A. Szymanski, "Interpreted Infrared Spectra," Vol. 1, Plenum Press, New York, N. Y., 1964.

(7) J. Kiji and M. Iwamoto, *J. Polym. Sci., Part B*, **6**, 53 (1968).

(8) J. L. Binder, *ibid., Part B*, **4**, 19 (1966).

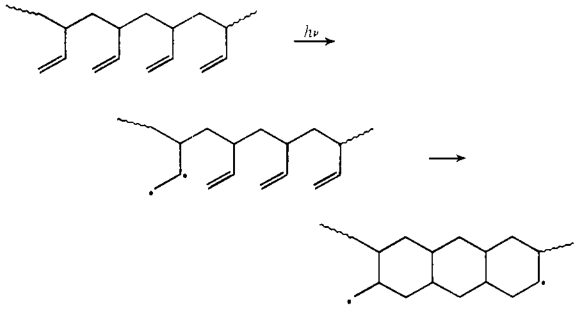
(9) A. Carbonaro and A. Greco, *Chim. Ind.* (Milan), **48**, 363 (1966); *Chem. Abstr.* **65**, 5536*h* (1966).

(10) M. A. Golub in "Polymer Chemistry of Synthetic Elastomers," Part II, J. P. Kennedy and E. G. M. Törnqvist, Ed., Interscience Publishers, New York, N. Y., 1969, Chapter 10B.

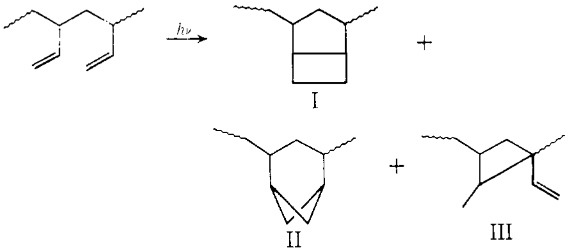
(analogous to the rupture of the carbon–carbon bond connecting two consecutive monomer units in the 1,4 polymers[3,4]), which would result in some vinyl units being replaced by vinylene units, cannot be important inasmuch as Figure 1B shows no absorption at 10.3 μ (*trans*-CH=CH-).

The ease with which 1,2-polybutadiene undergoes insolubilization and loss of unsaturation on ultraviolet irradiation had been anticipated by the earlier work on sodium–butadiene rubber,[5] but the detailed infrared spectra were not shown, nor were the implications of photocyclization considered.

Although the photoinduced cyclization of 1,2-polybutadiene could involve the following process leading to the formation of fused cyclohexane rings this process is considered very unlikely.

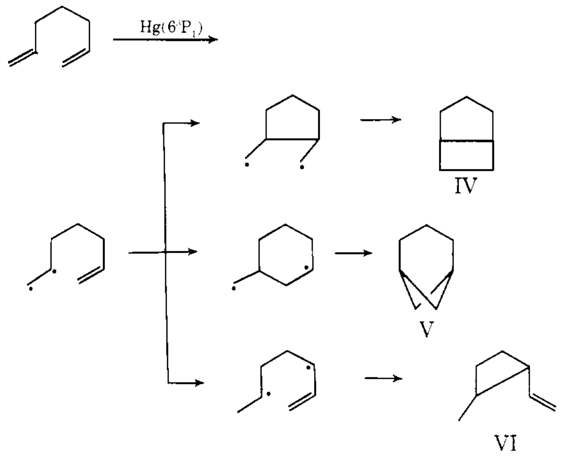


Thus, all attempts to achieve the free-radical postpolymerization of 1,2-polybutadiene to a ladderlike polymer have been unsuccessful.[11] Also, the *cationic* cyclization of 1,2-polybutadiene,[9] in contrast to that for 1,4- and 3,4-polyisoprenes and 1,4-polybutadiene,[10] results in the formation of isolated six-membered rings (or *monocyclic* structures) rather than fused rings (or polycyclic structures). Morever, in the ultraviolet irradiation of 1,4-polyisoprene, very few, if any, of the original double bonds are involved in cyclization other than cyclopropyl ring formation.[4] Instead, the photocyclization of 1,2-polybutadiene probably involves cycloaddition of adjacent vinyl groups to yield structures I and II, along with rearrangement to structure III. Very good precedent for I and II is found in the mercury photosensitized isomerization of 1,6-heptadiene in the vapor phase to the analogous bicycloheptanes IV and V.[12,13]



The concomitant formation of methylvinylcyclobutane VI (Scheme I) from 1,6-heptadiene on irradiation at low pressures,[13] though apparently not at high,[12] might well find an analog in a corresponding process in 1,2-polybutadiene, to form III, which would account for the methyl absorption (7.3 μ) in Figure 1B.

Scheme I



Likewise, the formation of dimer in the 1,6-heptadiene system[12] apparently has a counterpart in the photoinduced cross-linking of 1,2-polybutadiene. Summing up the situation with this polymer, we may state that structures I–III, as well as cross-links, are fully compatible with the spectrum of irradiated 1,2-polybutadiene. While the spectral data do not foreclose other cyclized structures, the arguments against the occurrence of fused cyclohexane rings appear rather compellent.[14] At any rate, the remarkable result of this work is the very facile photocyclization of 1,2-polybutadiene which cannot be duplicated by any (nonphotochemical) free-radical process.

3,4-Polyisoprene. The ultraviolet irradiation of a high 3,4-polyisoprene (polymer sample kindly supplied by Dr. R. J. Angelo, Du Pont Experimental Station, Wilmington, Del., and having initial unsaturation of 65% vinylidene and 35% isoprenic (1,4) double bonds), using the previous procedure,[4] produced a photocyclization which was similar to that of 1,2-polybutadiene, though less efficient. Since the high 3,4-polyisoprene experienced relatively little photoinduced cross-linking, it was possible to examine its microstructural changes by means of both nmr and infrared analysis.

The significant changes observed in the infrared spectra of the high 3,4-polyisoprene were diminution of the intensities of the 11.3- and 6.1-μ bands (associated with the 3,4 or -C(CH$_3$)=CH$_2$ units), a decrease in absorption in the 11.5–12.0-μ region (associated with the 1,4 or -C(CH$_3$)=CH- units), and the appearance of a weak peak at 9.8 μ (presumably the result of cyclopropyl groups formed directly from some of the 1,4 units, as in the case of 1,4-polyisoprene[4]). There were no indications in the infrared for the formation of vinylene or vinyl double bonds, or any other new structures besides the cyclopropyl groups and those arising from saturation of some of the 3,4 and 1,4 double bonds originally present. The nmr spectra (Figure 2) provided definite evidence for the partial loss of original unsaturation, but little or no additional information on the resulting structures other than the fact that they are sat-

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(11) G. B. Butler, *Encycl. Polym. Sci. Technol.*, **4**, 568 (1966), and personal communication.

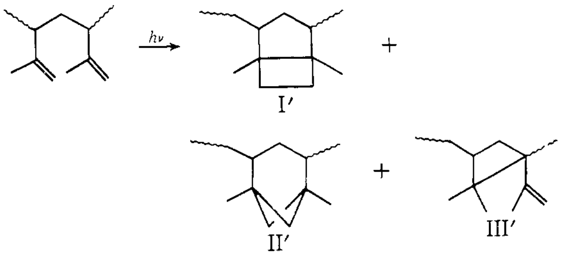
(12) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

(13) R. Srinivasan and K. A. Hill, *ibid.*, **87**, 4988 (1965).

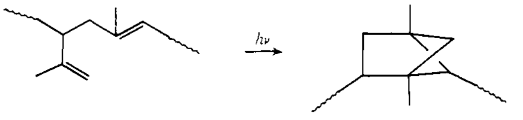
(14) This conclusion is further strengthened by the fact that, although certain substituted 1,6-heptadienes (*e.g.*, 2,6-diphenyl-1,6-heptadiene) can undergo free-radical cyclopolymerization, such a reaction is unknown for the unsubstituted 1,6-heptadiene.[11]

urated. Thus, the nmr spectrum of irradiated 3,4-polyisoprene showed decreases in the τ 5.1 ($-CH=$), 5.4 ($>C=CH_2$), 8.1 ($-CH_2C(=)-$) and 8.4 ($-C(CH_3)=$) peaks, an increase in the 8.8 ($-CH_2C<$) peak, the development of a new peak at 9.1 ($CH_3C<$), and the appearance of barely detectable peaks at 9.5 and 10.0 (CH_2 in cyclopropyl groups).[15] By way of comparison to the photoinduced loss of ~80% unsaturation in 1,2-polybutadiene, the high 3,4-polyisoprene for the same radiation exposure showed an over-all decrease of ~40% unsaturation (greater decrease in the 1,4 (~60%) than in the 3,4 (~25%) units).

By analogy to the photolysis of 1,2-polybutadiene, we visualize the photocyclization of 3,4-polyisoprene as involving mainly pairs of neighboring vinylidene groups (yielding I′ and II′) rather than the formation of fused cyclohexane rings. Here again, it was not possible to achieve a free-radical postpolymerization of 3,4-polyisoprene.[11] The formation of structure III′, the polyisoprene analog of III, if it occurs, is not important enough to cause splitting of the 7.3-μ band (*gem*-dimethyls) in the infrared spectrum of irradiated 3,4-polyisoprene. The fate of the 1,4 units in the high 3,4-polyisoprene, in view of prior work,[4] would be to produce some cyclopropyl groups, additional 3,4 units, and some vinyl units (which would rapidly disappear through photocyclization); in addition, the 1,4 units could also undergo photocyclization with neighboring 3,4 units (to yield a structure such as VII). The latter process is formally analogous to the mercury-sensitized photocyclization of 1,5-hexadiene to yield preferentially the bicyclohexane VIII.[12]



I′ II′ III′



VII

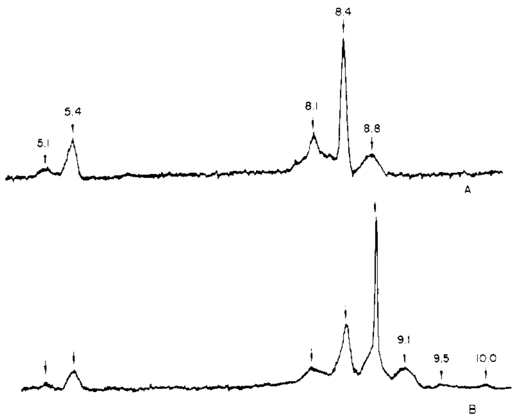
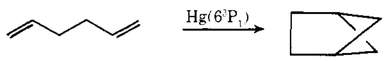


Figure 2. Nmr spectra of a high 3,4-polyisoprene before (A) and after (B) extensive ultraviolet irradiation under vacuum.



VIII

Mechanism. In common with the spectra of 1,4-polyisoprene,[4] the ultraviolet spectra of 1,2-polybutadiene and 3,4-polyisoprene showed smooth, structureless, absorption tails extending to around 3000 Å, and having about 5–15% absorption at 254 mμ. As in the case of the 1,4 polymers,[4] it is thought that the source of the photochemistry in 1,2-polybutadiene and 3,4-polyisoprene is direct absorption of 2537-Å photons by the double bonds themselves, and not an inter- or intramolecular energy transfer process from some adventitious impurity.[16] The processes depicted for the photocyclization of the latter polymers are presumed to involve the intermediacy of biradicals ensuant on excitation of the respective double bonds. As such, these processes are the counterparts of the process leading to cyclopropyl formation in the case of the 1,4 polymers.[4]

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(15) The observed broadening of the peaks near τ 8.1 and 8.4 in Figure 2B might be due to methylene protons in certain cyclobutyl structures.[12]

(16) This point of view is in accord with that invoked by L. Bateman [*J. Polym. Sci.*, **2**, 1 (1947)] and by E. J. Hart and M. S. Matheson [*J. Amer. Chem. Soc.*, **70**, 784 (1948)] to account for the effect of ultraviolet light on pure polyisoprene films.