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### Oxidation of Polyisoprene Popcorn Polymer. V. Raman Spectra of Polyisoprene Popcorn Polymer Following Oxidation

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## **Oxidation of Polyisoprene Popcorn Polymer. V. Raman Spectra of Polyisoprene Popcorn Polymer Following Oxidation**

**THOMAS W. T. CAMPBELL, IBRAHIM SAID ABDUL-BARI, and  
GLENN H. MILLER**

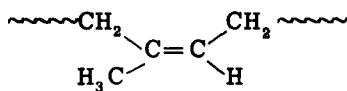
Department of Chemistry  
University of California  
Santa Barbara, California 93106

### **ABSTRACT**

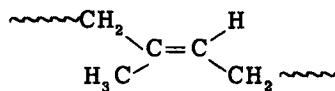
From Raman spectral data, no decrease in the double-bond content of polyisoprene popcorn polymer was detected following various periods of oxidation. No conclusion could be made concerning the fate of the 1,2 or 3,4 vinyl-group attachments.

The Raman spectral assignments for polyisoprene polymers were presented by Cornell and Koenig [1]. They found that only Raman bands for total 1,4 content and total vinyl content could be observed. Both the *cis*-1,4 (I) and the *trans*-1,4 (II) polymers give strong characteristic bands at  $1662\text{ cm}^{-1}$  due to the 1,4 carbon-carbon double bond stretching frequency. The 1,2 (III) and 3,4 structures (IV) give C=C stretching frequencies at  $1643$  and  $1641\text{ cm}^{-1}$ , respectively. By comparing the spectra of polymer samples before

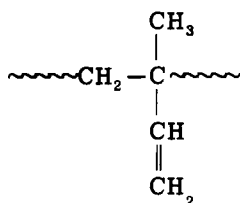
and after various degrees of oxidation, it should be possible to gain some information concerning the fate of the double bonds during the autoxidation reaction. Pure samples of polyisoprene popcorn polymer were used in this work.



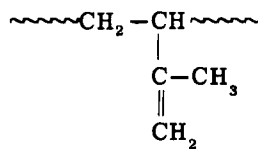
I



II



III



IV

## EXPERIMENTAL

The techniques used for the preparation of extremely pure polyisoprene popcorn polymers, methods for handling, and the helium flushing techniques have been presented [2, 3].

Raman spectra were obtained on a Cary Model 82 Raman spectrograph equipped with a Spectra Physics model 164-03 argon-ion laser. An excitation wavelength of 4880 Å was used at a power level of 0.200 W. All spectra were obtained from solid polymer samples.

## EXPERIMENTAL RESULTS AND CONCLUSIONS

The Raman spectrum of an unoxidized sample of polyisoprene popcorn polymer is shown in Fig. 1. The major peak at  $1662 \text{ cm}^{-1}$  indicates a high degree of 1,4 double bond structure which is undoubtedly trans. The shoulder on the  $1662 \text{ cm}^{-1}$  peak at  $1641\text{--}1643 \text{ cm}^{-1}$  indicates a small percentage of 1,2 and/or 3,4 double bond structure. This is in substantial agreement with the work of Brock [4]. He found a polyisoprene popcorn polymer sample to contain 86.4% 1,4, 6.1% 1,2, and 7.5% 3,4 content by means of an analysis based on the structure of the dimers produced from thermal degradation [5].

In order to determine the effect of oxidation on the double bond structure of polyisoprene, four different samples of the popcorn polymer were oxidized for 20-hr periods. Raman spectra were obtained at the

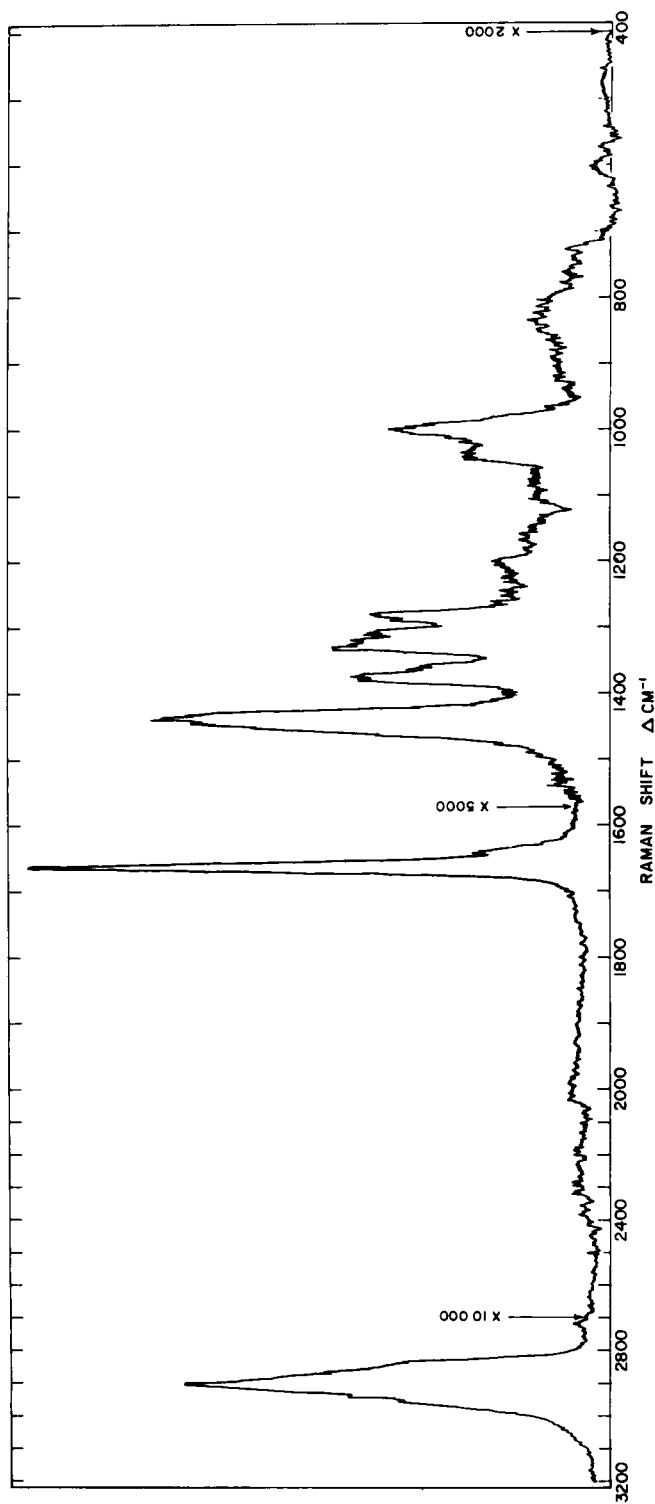


FIG. 1. Raman spectrum of unoxidized polyisoprene popcorn polymer.

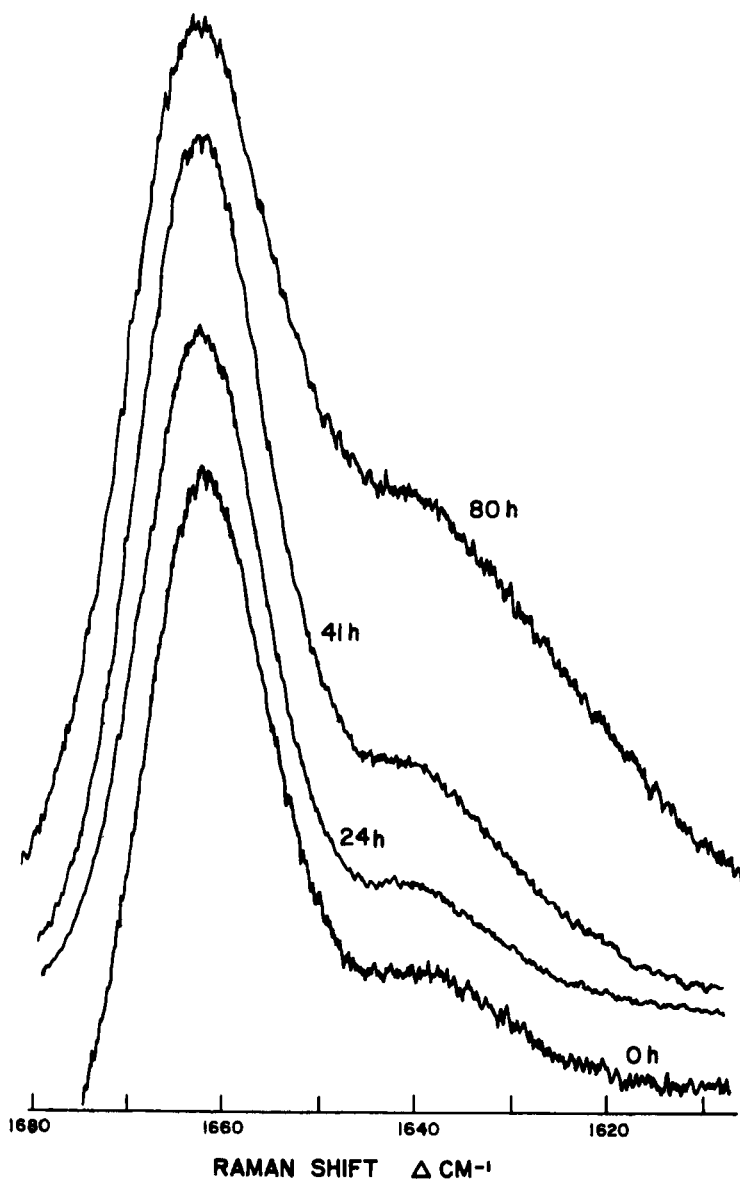
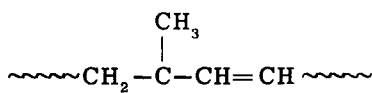


FIG. 2. Spectra showing the change in the  $1641\text{-}1643 \text{ cm}^{-1}$  peak for polyisoprene after various oxidation periods.

start of the oxidations and at 4-hr intervals. The  $1662\text{ cm}^{-1}$  peak heights were measured and normalized to the  $1434\text{ cm}^{-1}$  peak ( $\text{CH}_2$  deformation vibration, a strong peak). Within experimental error, no decrease in the concentration of the double-bond content of the polymer was noted. During the 20-hr oxidation periods, 25 mmoles of oxygen reacted per mole of monomer units in the initial sample.

A comparison of the heights of the  $1662\text{ cm}^{-1}$  (1,4 content) peak to the  $1641\text{-}1643\text{ cm}^{-1}$  (1,2 and 3,4 content) peak should give an indication of the fate of the dangling vinyl groups relative to the trans double bonds when the polymer is oxidized. Following the 20-hr oxidation periods used for the above-mentioned four samples, no change in the ratio of the two peaks was noted. To verify this, another sample of polymer was oxidized for a longer period of time. The Raman spectral peaks of interest are shown in Fig. 2 for samples that were oxidized for 0, 24, 41, and 80 hr, respectively. From these data it is apparent that the  $1641\text{-}1643\text{ cm}^{-1}$  peak increases in intensity rather than decreases. This is undoubtedly due to the superposition of spectral peaks resulting from carbonyl bands. The shoulder could not be resolved into distinct peaks. One must therefore conclude that this technique is unsuitable for monitoring the fate of the dangling vinyl groups.

The Raman spectral data do, however, support the previously suggested reaction mechanisms which locate the attacking oxygen at 1) a free-radical site on the polymer, 2) the site of a tertiary hydrogen, or 3) the site of a hydrogen alpha to a double bond, and not at the double bond. The most likely position for the initial attack on polyisoprene popcorn polymer is the free-radical allylic structure



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