Polyisoprene Popcorn Polymer. VII. Nuclear Magnetic Resonance Study of the Oxidized Polymer

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ABSTRACT

The NMR spectra of the soluble portion of oxidized polyisoprene popcorn polymer has been examined. No single structure can be assigned to the oxidized polymer that is attributable to any particular oxidation mechanism. A 30-h oxidized sample showed a double bond content of approximately 40% cis, 57% trans, and 3% 3,4-addition. There was a very large increase in the content of $-\overset{|}{\underset{|}{C}}-O(O)R$ or $-\overset{|}{\underset{|}{C}}-O(O)H$ and $CH_3-\overset{|}{\underset{|}{C}}-$ units as the oxidation time was increased from 30 to 60 h. The presence of, and the large increase in the content of $CH_3-\overset{|}{\underset{|}{C}}-$ units, none of which were observed for nonpopcorn polyisoprenes, can probably be attributed to the increased importance of $R^{\bullet}$ radical reactions in the oxidation of the highly cross-linked popcorn polymer structures.

INTRODUCTION

Determinations of the microstructures of popcorn polymers have been difficult due to the insolubility of the polymers. By means of analyses based on the dimers produced from the thermal degradation of polyisoprene popcorn polymer (PIP), Brock [1] found a typical

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sample to contain 86.4% of the 1,4-addition polymer, 6.1% of the 1,2-, and 7.5% of the 3,4-. An examination of the Raman spectra of PIP confirmed the presence of small amounts of 1,2- and/or 3,4-structures [2]. Neither of these techniques, however, was able to give any data on the presence of cis-1,4- structural units in what has been assumed to be primarily an all-trans-1,4- polymer.

The autoxidation of polyisoprene has been reviewed by numerous authors [3-6]. An NMR study of the thermal oxidation of polyisoprene polymers and the model compounds squalene and dihydromyrcene was made by Golub, Hsu, and Wilson [7]. Their study of the spectra showed a loss of original –C(CH₃)=CH– double bonds and the formation of cyclic peroxy structures accompanied by epoxy, peroxide, hydroperoxide, and alcohol groups on the oxidized polymer. They ruled out the occurrence of cis-trans isomerism during the course of the oxidation.

Since PIP becomes partially soluble when oxidized, it is possible to obtain NMR spectra for the dilute solutions of the soluble portion of the oxidized polymer. The primary purpose of this work was to study the NMR spectra of the soluble fraction of PIP that had been oxidized for 30 and 60 h in an attempt to elucidate both the microstructure of the polymer and the mechanism of the oxidation.

EXPERIMENTAL

The procedure for the preparation of PIP has been described [8, 9]. All volatile artifacts of the polymerization, i.e., monomer and dimers, were removed by flushing the polymer with dry helium for 336 h. The helium flow was 20 mL/min. The apparatus used for both the helium flush and oxidations has been described [8].

PIP samples were oxidized at room temperature in a stream of dry oxygen flowing at the rate of 20 mL/min for 30- and 60-h intervals. Each oxidation interval was followed by a 24-h helium flush to remove volatile oxidation products.

All handling of the polymer samples was done in the inert atmosphere of a glove box that was continuously flushed with dry nitrogen.

Samples of the oxidized PIP for NMR analysis were placed in sealed glass tubes with CD₃Cl solvent. As much polymer as possible was dissolved. The 30-h oxidation sample was 16.6% soluble by mass, and the 60-h sample was 34.3% soluble. The solutions were transferred to standard NMR tubes, and spectra were obtained on a Varian XL-100 instrument utilizing Fourier-Transform averaging.

RESULTS AND DISCUSSION

Figure 1 shows the ¹H NMR spectra for the soluble portions of PIP after 30 and 60 h of oxidation. The presence of 3,4-addition polymer
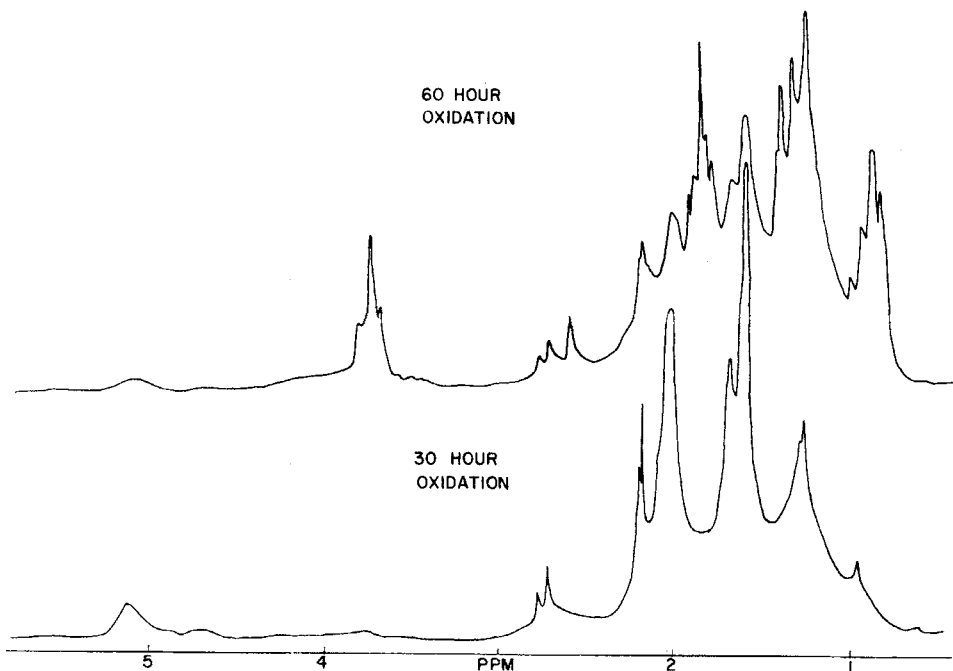
FIG. 1. ^{1}H NMR spectra of the soluble portion of polyisoprene popcorn polymer following 30 and 60 h of oxidation.

structure is confirmed by the 4.71 ppm resonance ($-\overset{|}{C}=CH_2$). Estimates based on the integrations of the spectral peaks indicate a 3 to 5% 3,4- content. This compares favorably with the 7.5% found by Brock in a sample of unoxidized PIP determined by a study of the dimers produced on thermal degradation.
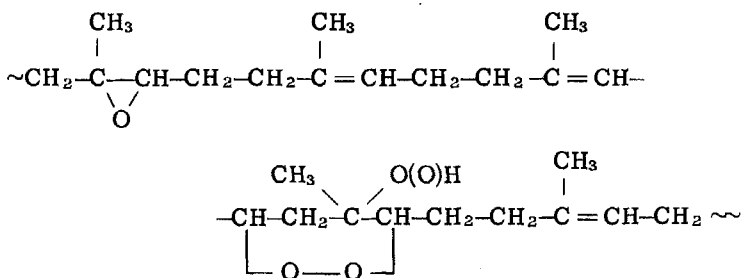
The resonances at 1.61 ppm (trans-$CH_3-\overset{|}{C}=\overset{|}{C}-$) and 1.68 ppm (cis-$\overset{|}{C}H_3-\overset{|}{C}=\overset{|}{C}-$) for the 30-h oxidation sample indicate the unsaturation to be approximately 40% cis and 57% trans. After 60 h of oxidation, the approximate percentages were 29% cis and 66% trans. The apparent decrease in the cis-trans ratio does not mean that cis-trans isomerization has occurred. Golub [7] found no evidence for cis-trans isomerization in their study of the thermal oxidation of 1,4-polyisoprene. For PIP, it is possible that preferential oxidation occurred at the cis configuration sites.

The resonances centered at 1.31 ppm ($C\underline{H}-\overset{|}{\underset{|}{C}}-O-$) were very prominent in the spectrum of the 30-h oxidation sample and increased in the

60-h sample where they appeared as four distinct peaks. If the 1.31 peak is assigned to CH_3–C–O–, then the integrations show approximately two CH_3–C–O– for every three CH_3–C=C– units.

Integration of the 2.72 ppm (–C—CH–) peak indicates one epoxide for every 5.4 –C = C– units.

Data for the 30-h oxidized sample of PIP are in partial agreement with the Bolland-type, 5-monomer structure discussed by Golub [7]:

$$\sim CH_2-\underset{\underset{O}{\diagdown\diagup}}{\overset{\overset{CH_3}{|}}{C}}{-}CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-$$

$$-CH-CH_2-\underset{\underset{O——O}{\diagdown\;\;\;\diagup}}{\overset{\overset{CH_3}{\diagdown}\;\;\;\overset{O(O)H}{\diagup}}{C}}-CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2 \sim$$

The negligible 5.5-5.6 ppm (–CH=CH–) resonance observed is consistent with such a structure, but the 5.12 ppm (–C=CH–) and the 3.74 ppm (–C–O(O)H peaks are insufficient to account for three double bonds and one –O(O)H unit, respectively.

Only a broad minor resonance at 3.74 ppm (–CH–O(O)R or –C–O(O)H) was observed following 30 h of oxidation. Integration of the peaks show an approximate ratio of one –CH–O(O)R or –C–O(O)H unit for every 20 CH_3–C–O– units. The picture changes, however, following 60 h of oxidation. Here the integrations indicate an approximate one-to-one ratio for the –C–O(O)H and the CH_3–C–O– structural units. The increase in the magnitude of the resonances centered around 3.74 is one of the most dramatic changes observed when comparing the 30- and 60-h oxidation spectra.

The 60-h oxidation data do not fit, even approximately, the Bevilacqua, Bolland, or Mayo [10] structures.

The 0.95 ppm resonance shown for the 30-h oxidation sample can be partially assigned to the methyl hydrogens on tertiary carbon atoms involved in cross-linking (CH_3–C–). The presence of this 0.95 peak, however, is no real indication of the extent of cross-linking. Following

the next 30 h of oxidation it increased markedly and was accompanied by additional peaks in the 0.8 to 1.0 region. The increase cannot be assigned to additional cross-linking for the reaction is one of degradation.

Part of the initial 0.95 peak might be attributed to $CH_3-\overset{|}{\underset{|}{C}}-$ units resulting from 1,2-addition. The small peak at 5.63 ppm ($CH_2=CH-$), however, indicates a 1,2-addition content of considerably less than 1%.

Morand [11] has tabulated 26 compounds produced as by-products from polyisoprene oxidation. Of these 26, only propanol would be expected to give resonance peaks in the 0.8-1.0 ppm range. The large increase in these resonances therefore cannot be attributed to small molecule fragments adhering to the polymer.

One possible explanation for the 0.8-1.0 ppm resonances would be the occurrence of cyclization. Binder [12], in his study of cyclic structures in diolefin polymers, assumed the resonances he observed near 1.0 ppm to be due to methyls attached to fused cyclohexane rings. These results were questioned by Chen [13] who attributed the observed resonances to satellite peaks from the intense peaks of methyl and methylene groups in uncyclized polymer. There is no convincing evidence for the formation of fused cyclohexane or cyclohexene rings in PIP oxidation.
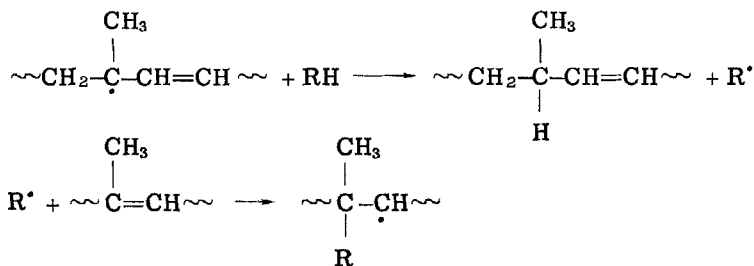
Another type of cyclization was proposed by Colclough and Tidd [14] who cited evidence for the structure
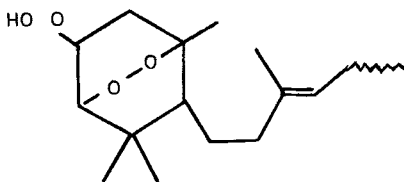
in their study of the oxidation of squalene. For PIP oxidation, however, gem-dimethyls could only be produced at one end of the polymer chain and other $CH_3-\overset{|}{\underset{|}{C}}-$ groups could only result from this type of cyclization if there were a considerable number of tail-to-tail structures in the PIP structure.

Golub [7] found no 0.8-1.0 ppm resonances in the cis-1,4-polyisoprene spectra either before or after oxidation. He attributed this to the fact that the loss of double bonds proceeds almost entirely through ROO' radicals rather than R' radicals. The oxidation of dihydromyrcene, however, did show a small 0.89 ppm resonance. Using Golub's reasoning, it appears that the best presently available explanation for the large 0.8-1.0 ppm peaks in oxidized PIP is that, in contrast to nonpopcorn polyisoprene, the R' radicals become as

important as the RO· radicals. The following reactions could explain the observed increase in the CH_3-$\overset{|}{C}$- structural units in oxidized PIP:

$$\overset{\displaystyle CH_3}{\underset{\displaystyle \cdot}{\overset{|}{\underset{|}{\sim\sim CH_2-C-CH=CH \sim\sim}}}} + RH \longrightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{\sim\sim CH_2-C-CH=CH\sim\sim}}}} + R\cdot$$

$$R\cdot + \overset{\displaystyle CH_3}{\overset{|}{\sim\sim C=CH\sim\sim}} \longrightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle R}{\overset{|}{\underset{|}{\sim\sim C-\underset{\cdot}{C}H\sim\sim}}}}$$

ACKNOWLEDGMENT

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