Oxidation of Polyisoprene Popcorn Polymer. IV. Effect of Polymer Purity on Carbon Dioxide and Water Yields

Glenn H. Miller[a]

[a] Department of Chemistry, University of California, Santa Barbara, California

PLEASE SCROLL DOWN FOR ARTICLE

Oxidation of Polyisoprene Popcorn Polymer. IV.
Effect of Polymer Purity on
Carbon Dioxide and Water Yields

GLENN H. MILLER

Department of Chemistry
University of California
Santa Barbara, California, 93106

ABSTRACT

Recent oxidation studies on polyisoprene popcorn polymer
have shown that the yields of volatile products are a function
of the presence or absence of residual isoprene dimers on
the polymer. In contrast to previously reported data, no
carbon dioxide is detected when highly purified polymer is
used. Also, the yields of water drop to approximately half
the previously reported values. Quantitative data are
presented for the production of water during the early stages
of autoxidation. The reported data emphasize the possible
errors that can occur when oxidation reaction mechanisms
are based on the stoichiometry of volatile products produced
from impure polymer samples.

INTRODUCTION

In the course of conducting experiments on the oxidation of poly-
isoprene popcorn polymer (PIP), it has become apparent that the

analytical results obtained for the yields of volatile oxidation products depend on the pretreatment given to the polymer prior to its oxidation. Dimeric species and several lower-molecular-mass compounds are present on PIP as artifacts of the 60° sealed-tube polymerization technique used to produce the polymer. The presence of these compounds can cause marked differences in the relative yields of volatile oxidation products.

In this work, a helium-flush technique has been employed to obtain PIP samples of high purity. When these samples are oxidized, the condensed volatile products form a homogeneous, aqueous liquid sample. This is in contrast to the two layers, aqueous and oil, present when less pure polymer is oxidized. Also, no carbon dioxide can be detected as a product when the helium-flushed polymer is oxidized.

This paper presents a comparison of the data obtained for carbon dioxide production from PIP samples that received various treatments prior to being oxidized. In addition, more precise data are presented for the production of water during the early stages of the autoxidation reaction. The reported data point out the errors that might occur when a reaction mechanism for oxidative degradation of a polymer is based on the stoichiometry of volatile oxidation products whose yields may be a function of impurities present in the polymer as a result of the polymerization procedure.

EXPERIMENTAL

Preparation and Purification of PIP

The third generation PIP used in these experiments was grown anerobically at 60° in the manner previously described [1]. Dried isoprene monomer (Matheson, Coleman, and Bell) was distilled directly into the reaction tubes. All handling of the polymer was done in the inert atmosphere of a glove box that was continuously flushed with dry nitrogen.

Volatile impurities, dimers, and other artifacts of the 60° polymerization were removed by flushing the polymer for an extended period of time with a stream of dry helium. The flow system used for both the helium flush and the oxidation is diagrammed in Fig. 1. The gases were dried by passage through two P_4O_{10} drying tubes and then through a U-tube filled with glass beads maintained at -78° The polymer was contained in a 250-ml glass-stoppered flask equipped with Rotaflo Teflon stopcocks. Volatile products were collected in a Rotaflo-stopcock-equipped trap maintained at -78°. Sections of the apparatus were connected by 12/5 ground-glass joints.
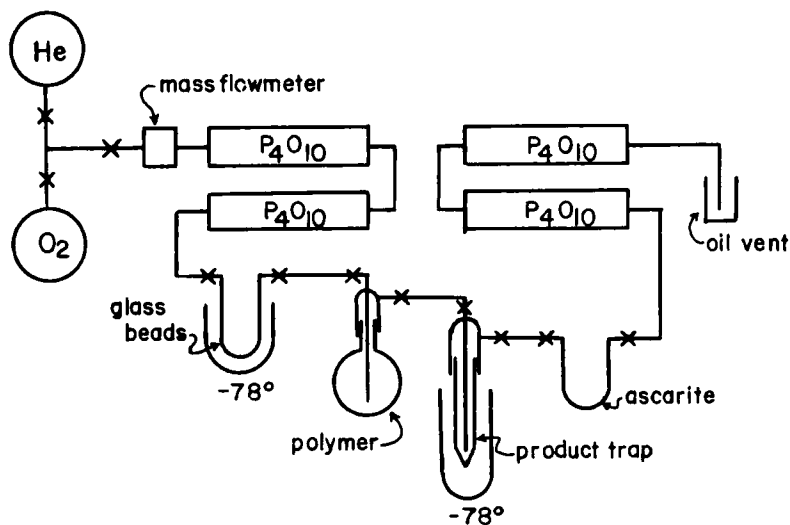
FIG. 1. Flow system used for polyisoprene popcorn oxidations.

Partial data for three series of polymer oxidations are reported in this work. One PIP sample was evacuated for 21.6 hr and flushed with helium for 390 hr; the second sample was flushed for 380 hr and the third for 316 hr. Polymer samples from 20 to 25 g were used. The helium flow rate was 50 ml/min.

Oxidation Procedure

The helium-flushed polymer-containing flask, a helium-flushed collection trap, and the helium-flushed ascarite trap were weighed before being connected to the flow apparatus. A 50-ml/min flow of oxygen was then passed through the system for a definite period of time, usually 3 or 4 hr. Following this, the oxygen valve was closed and the helium valve was opened, and the system was flushed with helium for an 18 to 20 hr period. In this manner the volatile oxida- tion products were flushed from the polymer and collected. Follow- ing this flush period, the polymer flask, ascarite tube, and a replacement helium-flushed trap were placed back on the system for another 3 or 4 hr oxidation period. Again the polymer was flushed with helium for 18 to 20 hr and the procedure repeated. In this manner the change in polymer weight, total weight of volatile products, and the amount of carbon dioxide formed were determined following each 3 or 4 hr oxidation period. All oxidations were at room temperature.

Analytical Method

Each of the volatile product samples was analyzed by vapor phase chromatography. Since the amounts of sample were small following these short oxidation periods, the product collection traps were rinsed with four 50-μl aliquots of absolute ethanol. Ten microliter portions of this alcohol solution were then used for each VPC analysis. A minimum of three analyses was made for each sample and the average result used.

Chromatographic separations were made on a Hewlett-Packard model 7620A research chromatograph using a Poropak QS column as previously described [2]. The oven temperature was programmed as follows: 100° for 2 min; increased 30°/min to 130° and held for 2 min; increased 30°/min to 180° and held for 2 min; and then increased 30°/min to 240° and held for 20 min.

RESULTS AND DISCUSSION

The three samples of PIP used in this work lost from 5.0 to 6.7% by mass as a result of the helium flush procedure. The VPC spectrum of the volatile compounds removed during the first 96 hr is shown in Fig. 2. During this time, 4.3% of the sample volatilized and seven products were noted. The major product is the dimer dipentene (1-methyl-4-isopropenylcyclohexene). The minor products other than isoprene have not yet been identified. The material collected during the remaining helium flush time of 220 hr resulted in a further loss of 0.7%. Only dipentene and traces of a higher boiling dimer were given off during this period. These hydrocarbons probably resulted from the slow thermal degradation of the polymer at the 60° temperature maintained during the polymerization process. Studies on the thermal degradation of PIP are now in progress.

Brock and Hackathorn [3] have studied the structure of polyisoprenes using thermal degradation data. From their results one can conclude that, since the primary dimeric species obtained from the helium-flushed PIP samples in this work is dipentene, the polymer must consist primarily of 1,4-structures with small percentages of 1,2- and/or 3,4-linkages.

Miller and Leung [4] reported water and carbon dioxide yields for the oxidation of three similar PIP samples that had received different treatments before being oxidized. Some of their results are shown in Fig. 3. One sample was evacuated for 46 hr prior to oxidation, and another was extracted with benzene for 212 hr and then evacuated for 1 hr prior to the oxidation. Both of these gave carbon dioxide yields which averaged 0.020 to 0.022 mole of carbon dioxide per mole of oxygen reacted.
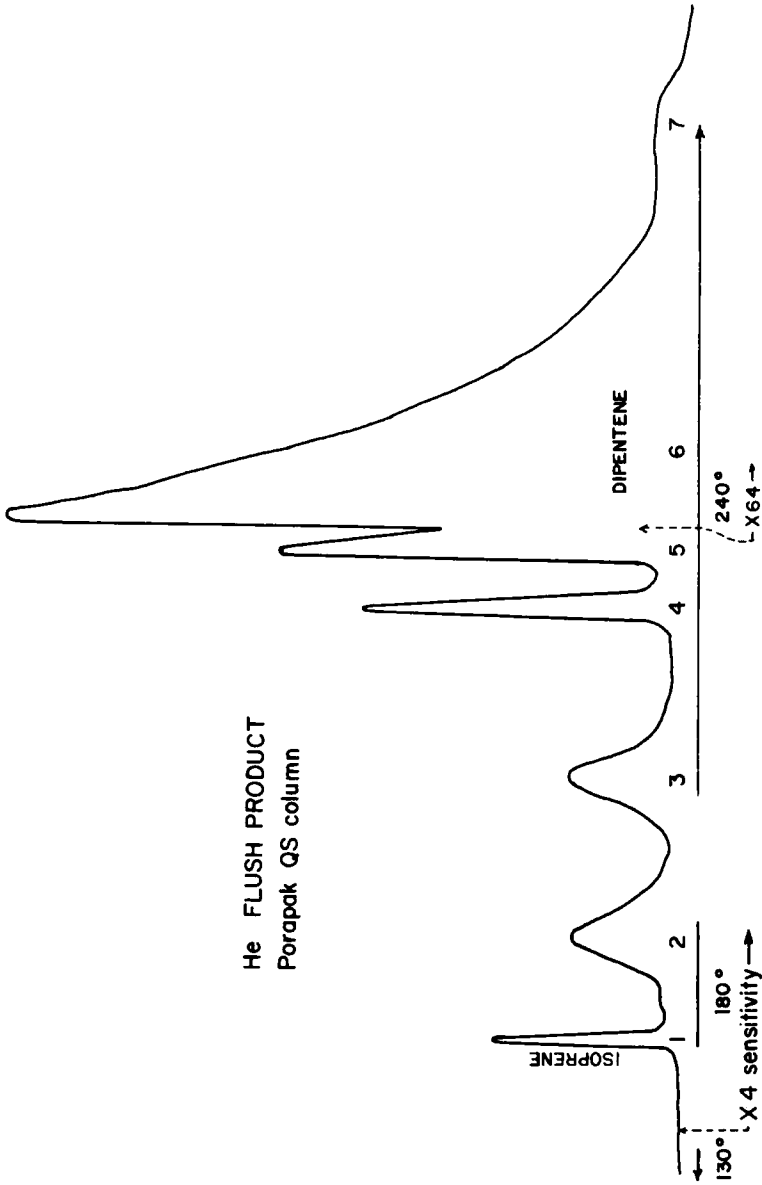
He FLUSH PRODUCT
Porapak QS column

ISOPRENE

DIPENTENE

130°

180°
X 4 sensitivity →

240° →
X64 →

1   2   3   4   5   6   7

FIG. 2. Chromatograph of volatile products flushed from polyisoprene popcorn polymer.
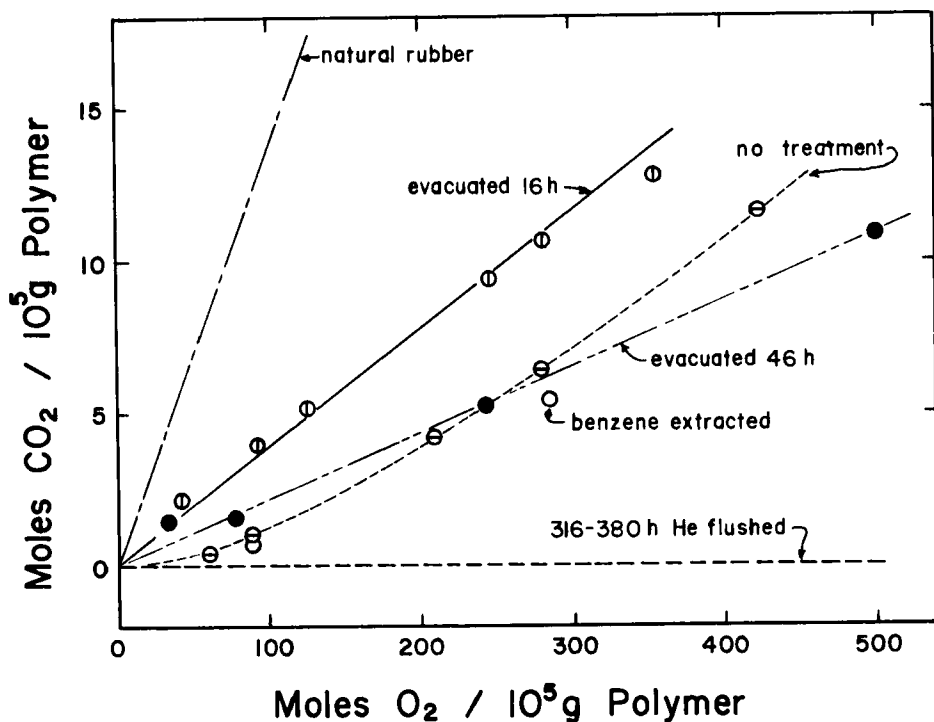
FIG. 3. Rates of carbon dioxide formation for polyisoprene pop-corn polymers that had received various treatments prior to the oxidation.

A second set of experiments, using the same PIP polymer, was reported by Miller and Lu [2]. Here the oxidations were performed on PIP that had been evacuated for 16 hr prior to the oxidation. Carbon dioxide yields averaging 0.038 mole per mole of oxygen reacted were obtained. These results are shown as vertical-line circles in Fig. 3.

For natural rubber, Bevilacqua [5] obtained much higher yields of carbon dioxide, 0.108 mole carbon dioxide per mole of reacted oxygen. The data in Fig. 3 are plotted as moles per 10^5 g of original polymer so that the results can be compared directly to those reported by Bevilacqua. His data are indicated by the line labeled "natural rubber."

The horizontal dashed line in Fig. 3 represents the data obtained from helium-flushed polymer samples; no carbon dioxide could be detected. In order to verify these results, since slightly different

experimental techniques were used in the previous experiments, an oxidation experiment was performed on the identical apparatus used for the helium-flushed PIP oxidations. The polymer used received no treatment prior to the oxidation. The results are shown in Fig. 3 by the horizontal dash circles. The amount of carbon dioxide found compared favorably with the amounts found previously for PIP samples that had been evacuated for 46 hr or that had received the benzene extraction treatment.

From these results it appears that the rate of carbon dioxide production during the early stages of polyisoprene oxidation is a function of the amount of dipentene remaining on the polymer. A 46-hr evacuation or a benzene extraction is sufficient to remove all the lower-boiling hydrocarbons present following the polymerization, but neither is sufficient for the removal of all the higher-boiling dipentene.
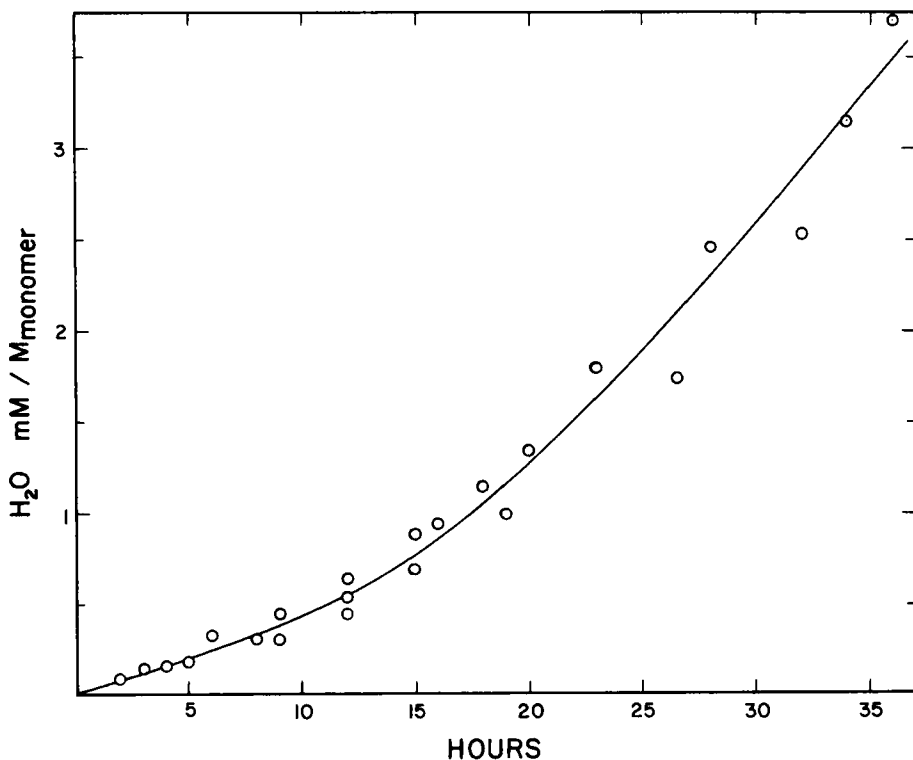

FIG. 4. Rate of water production during the early stages of polyisoprene popcorn polymer autoxidation.
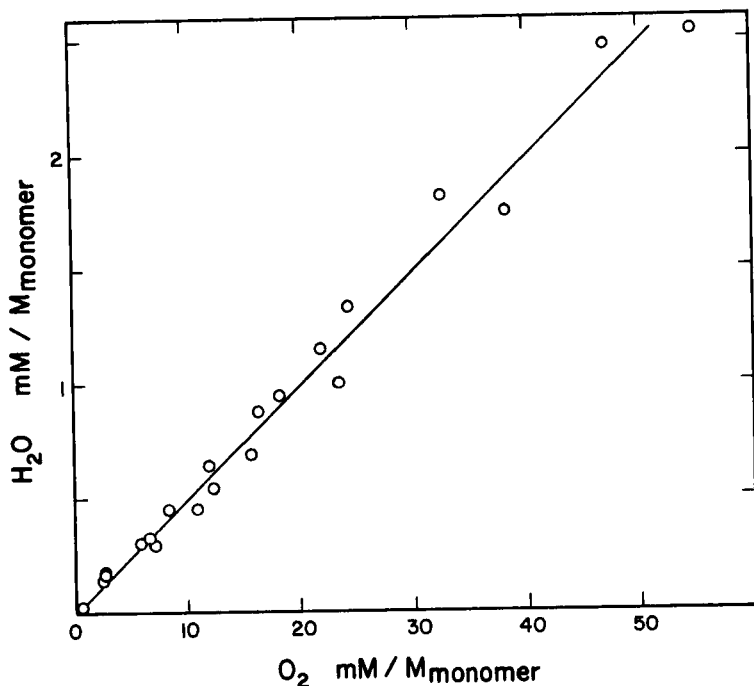
FIG. 5. Rate of water formation as a function of oxygen consumed during the early stages of polyisoprene popcorn polymer autoxidation.

If these conclusions are correct, then it is possible that the higher rate of carbon dioxide formation observed from the oxidation of natural rubber or synthetic polyisoprenes is due to the presence of hydrocarbon impurities and does not result from any primary polymer oxidation reaction. Alternatively, the carbon dioxide found as a product from natural rubber oxidation may result from the oxidation of already produced oxidation products. It is difficult to remove volatile compounds trapped in natural rubber or the synthetic polyisoprenes, and their rate of removal is probably diffusion controlled. This is not the case for popcorn polymers, however, for complete accessibility to the polymer is maintained at all times. The latter assumption must be made to account for the logarithmic growth of these polymers [6]. It is clear, nevertheless, that the dependability of any reaction mechanism based on the stoichiometry of carbon dioxide production must be questioned.

   As previously reported [4], water is the main volatile product

from the oxidation of PIP. Using helium-purified PIP, it was possible to obtain quantitative data for the rate of water production during the very early stages of the autoxidation. Figure 4 is a plot of the water yields as a function of time; the yields are reported as millimoles of water per mole of monomer units present in the original unoxidized polymer, $mM/M_{monomer}$. A more informative plot is shown in Fig. 5 where the water yield is plotted as a function of the amount of oxygen reacted. Approximately 0.0495 mole of water is formed for every 1.00 mole of oxygen reacted, or about 20 moles of oxygen per 1 mole of water produced. These data must be considered to be more accurate than those previously reported. For example, Miller and Lu [2] reported water yields of 0.098 mole of water per mole of reacted oxygen, almost twice the amount found in this work. The difference can be attributed to the presence of the dipentene dimer that was not completely removed in the earlier work.

Quantitative data for other major volatile reaction products are being obtained for the early stages of PIP autoxidation. Further discussion of the significance of the water yields will be deferred until these data are completed.

ACKNOWLEDGMENT

REFERENCES

[1] G. H. Miller and H. Leung, J. Macromol. Sci.—Chem., A4, 1705 (1970).
[2] G. H. Miller and Shih-chen Lu, Ibid., A7, (1973).
[3] M. J. Hackathorn and M. J. Brock, J. Polym. Sci., B, 8, 617 (1970).
[4] G. H. Miller and W. J. Leung, J. Macromol. Sci.—Chem., A5, 443 (1971).
[5] E. M. Bevilacqua, Rubber Chem. Technol., 30, 667 (1957).
[6] G. H. Miller, R. L. Alumbaugh, and R. J. Brotherton, J. Polym. Sci., 9, 453 (1952).