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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Oxidation of Polyisoprene Popcorn Polymer. II. Gravimetric Analysis

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**To cite this Article** Miller, Glenn H. and Leung, Wai Jong(1971) 'Oxidation of Polyisoprene Popcorn Polymer. II. Gravimetric Analysis', *Journal of Macromolecular Science, Part A*, 5: 2, 443 – 452

**To link to this Article:** DOI: 10.1080/00222337108069390

**URL:** <http://dx.doi.org/10.1080/00222337108069390>

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## Oxidation of Polyisoprene Popcorn Polymer. II. Gravimetric Analysis

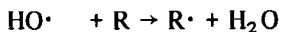
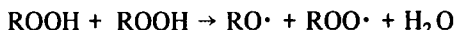
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### SUMMARY

Water, carbon dioxide, and condensable condensate produced during the oxidation of polyisoprene popcorn polymer were determined gravimetrically. For pure polyisoprene popcorn polymer from which 4.6% soluble polymer and volatiles were removed, the rates of water and carbon dioxide production during the early stages of the autoxidation were linear and amounted to approximately 2 moles of water and 0.2 moles of carbon dioxide for every 10 moles of oxygen reacted.

The generally accepted scheme for polyisoprene oxidation must be modified to account for the water production. Two possible routes for its synthesis are:



### INTRODUCTION

Polyisoprene popcorn polymer (PIP) oxidizes rapidly when exposed to air or oxygen at room temperature. Typical S-shaped autoxidation curves

are obtained which exhibit induction, acceleration, deceleration, and final periods; the induction period, however, may be absent depending on the pretreatment or storage conditions for the polymer [1].

Characterization of PIP and some preliminary data on its oxidation were presented in the first paper of this series [1]. No product analyses or product distribution data have been presented for oxidation of PIP.

The effect of oxygen on natural rubber and synthetic polyisoprenes has been reviewed in considerable detail [2-5] and a reaction mechanism has been proposed based on product analysis and distribution [5].

The purpose of the present paper is to present some data obtained by gravimetric analysis of the water, carbon dioxide, and condensate produced by PIP oxidation.

## EXPERIMENTAL

The fourth generation PIP seeds used for these experiments were grown anaerobically in the darkness of an oil bath at 60° in the manner previously described [1]. Isoprene from Matheson, Coleman, and Bell was distilled directly into the reaction tubes.

PIP samples for oxidation were contained in weighed sintered-glass crucibles which were suspended in a vertical tube through which  $P_4O_{10}$ -dried oxygen was passed at the rate of 25 ml/min. All reported oxidations were at room temperature. The exit gases passed through a silica gel U-tube for water sorption, a -78° cold trap for condensate collection, and finally an Ascarite-filled U-tube for carbon dioxide determination. Dry oxygen was allowed to flow through the system for a day in order to bring the system to equilibrium prior to the introduction of the PIP. The rates of water, condensate, and carbon dioxide production were then determined by periodically weighing the collection traps.

The amount of oxygen which reacted with the polymer was determined by weighing the PIP sample, adding to this the weights of the materials collected, and then subtracting the weight of the original unoxidized PIP. Any uncollected gaseous products such as carbon monoxide, if any, were ignored in the calculations.

PIP for Oxidation 37 (2.91 g) was placed in the oxidation chamber immediately after removal from the tube in which it was grown; it received no pretreatment. For Oxidation 38, the PIP was first pumped on a mercury-free high vacuum system (Teflon stopcocks, oil diffusion pump) for 46 hr. During this time the polymer sample lost 4.6% of its original mass due to

the loss of volatiles, probably dipentene, which formed during the polymerization; a 2.68 g sample was used. The PIP for Oxidation 39 was extracted with benzene in a nitrogen-flushed Soxhlet extractor for 212 hr; 6.4% of the original sample was soluble. This polymer (2.33 g) was then oxidized following a 1-hr evacuation to remove solvent.

## RESULTS AND DISCUSSION

The oxidation rate curves are shown in Fig. 1; no induction periods were noted for any of the three samples. The oxidation rate during the acceleration period was greatest for Sample 39 from which both soluble polymer and dipentene were removed; the next fastest rate was for PIP from which only dipentene was removed, 38, and the slowest rate was observed for polymer that was oxidized directly with no removal of soluble polymer or volatiles. These data indicate that the oxidation proceeds most rapidly if the cross-linked polymer is free of dimer and short-chain soluble polymer;

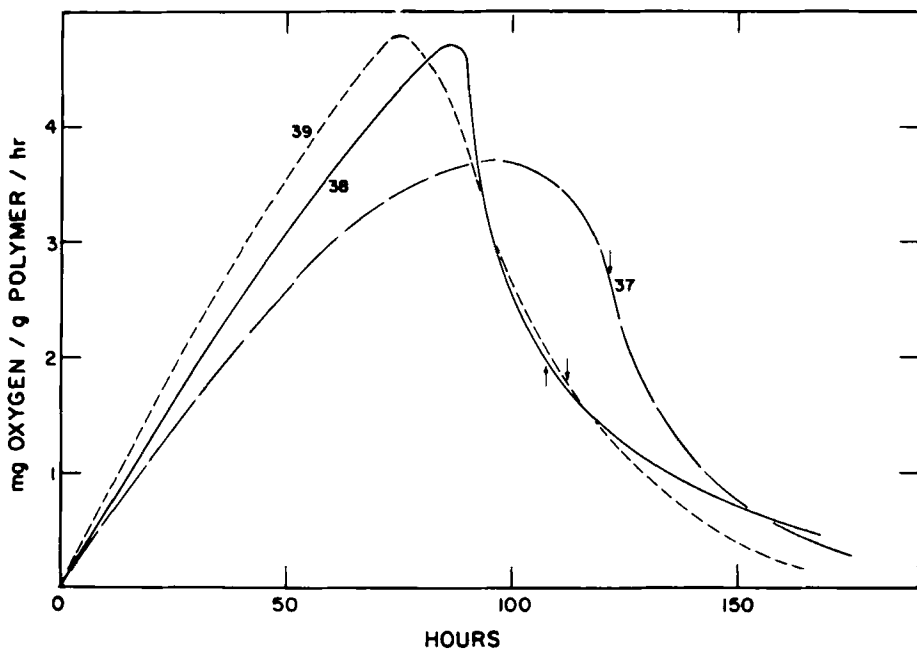


Fig. 1. Oxidation rates for polyisoprene popcorn polymer.

both of the latter are probably devoid of free radical sites and hence exhibit slower initial oxidation rates.

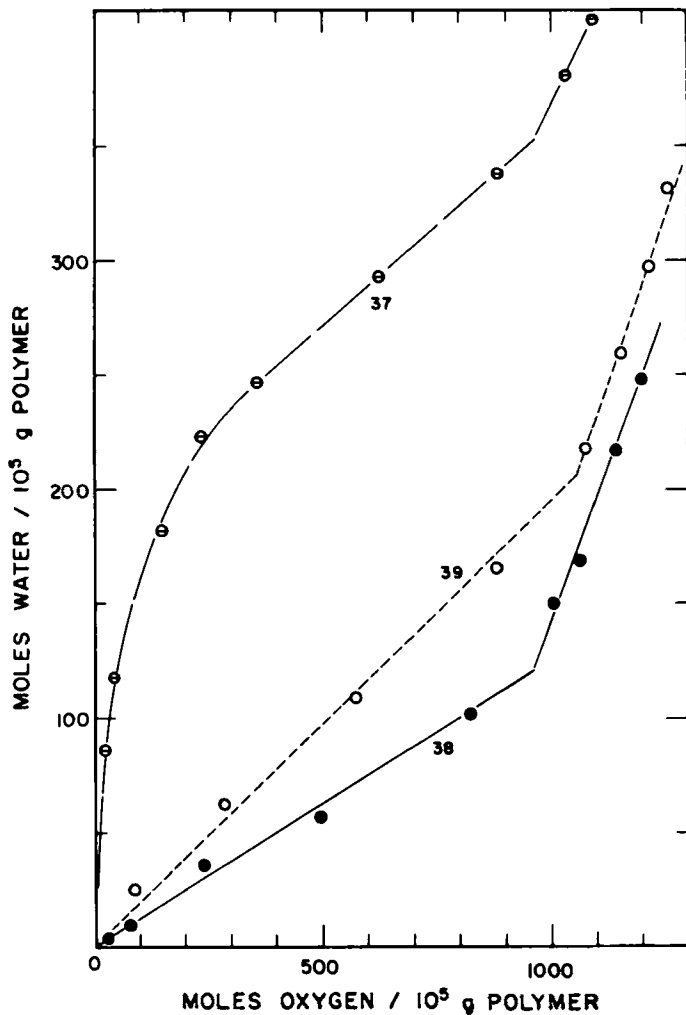


Fig. 2. Rate of water formation in PIP oxidations.

Figure 2 is a plot of the moles of water produced as a function of the moles of oxygen reacted (the data are reported as moles per  $10^5$  g of polymer so that the figures can be compared to those of Bevilacqua [6]).

The apparent production of water per mole of oxygen reacted for PIP 37 increased very rapidly during the early stages of the reaction. Comparing Curves 38 and 39, it is seen that the amount of water produced was greater per mole of oxygen consumed for the PIP which had the soluble polymer removed by extraction; 1.96 moles water per 10 moles oxygen versus 1.26 moles water for PIP 38.

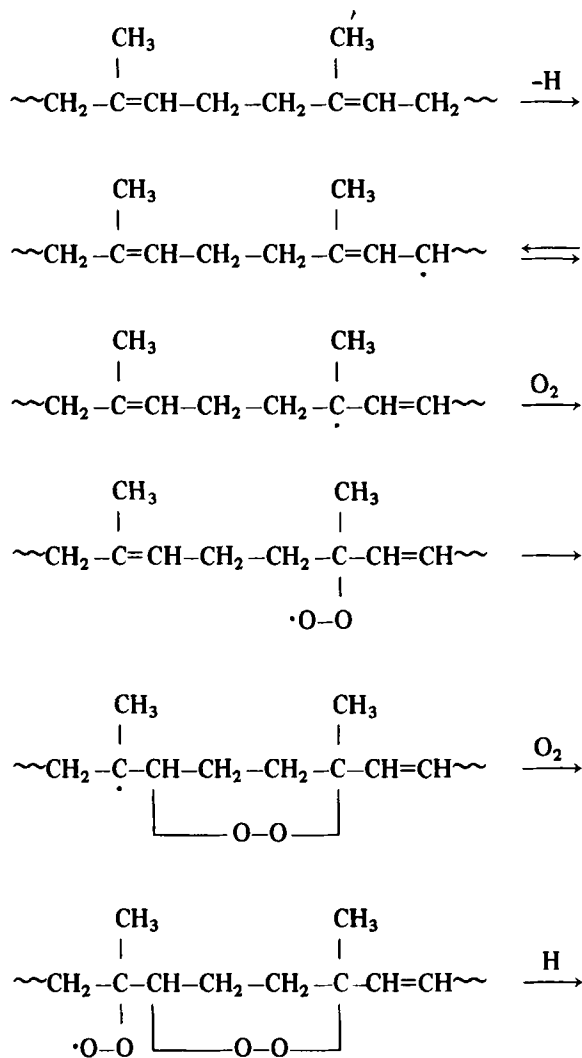
During the latter stages of the rate deceleration period there is a marked and sudden increase in the rate of water production per mole of oxygen consumed as shown by the breaks in the curves of Fig. 2. The arrows on Fig. 1 indicate the times for which these changes in slope occurred in each of the water production curves. The sudden appearance of a greater amount of reacted oxygen in the form of water is undoubtedly due to the onset of reactions involving further oxidation of oxidation products already produced. Unexplained, however, is the fact that at the same time more water is being produced per mole of oxygen consumed, there is also a sudden uptake of water by the oxidized polymer, water than can be recovered reversibly by pumping the oxidized polymer [1]. Actually, therefore, the slopes of the water production curves should be steeper to account for the water trapped by the polymer sample at this point in the oxidation. One clear conclusion from these data, however, is that any discussion of the mechanism of polyisoprene oxidations must be based on product distributions and analyses prior to this stage of the oxidation.

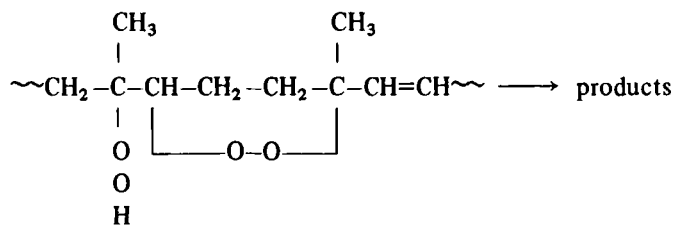
Figure 3 is a graph of the moles of carbon dioxide produced per mole of oxygen reacted. Approximately the same slope was obtained for all samples, a small induction period being noted for the PIP still containing dipentene. The unlabeled dashed line, slope 0.135, represents the carbon dioxide production rate noted by Bevilacqua [6] for natural rubber; this is many orders of magnitude greater than that obtained for PIP. This can probably be explained by the fact that natural rubbers are already partially oxidized and the more rapid production of carbon dioxide undoubtedly results from oxidation of previously formed reaction products. There is no apparent break in the carbon dioxide curve to correspond to the observed breaks in the water production curves. This would indicate that the carbon dioxide is not produced in the same reaction sequence that is responsible for the sudden more rapid production of water which occurs during the deceleration period.

The mass of condensate collected as a function of oxygen reacted is graphed in Fig. 4. The composition of this condensate is as yet not completely known, although preliminary analyses indicate that it consists

of acetone, acetaldehyde, formic acid, acetic acid, butanone, butenone, and several other components not yet identified.

Although the gravimetric procedures used in these experiments have obvious limitations, an important conclusion can be deduced; that is, water is an important primary product. A presently accepted oxidation scheme for polyisoprenes is as follows [2]:





Cunneen's modification is similar but involves decomposition via an alkoxy radical [5].

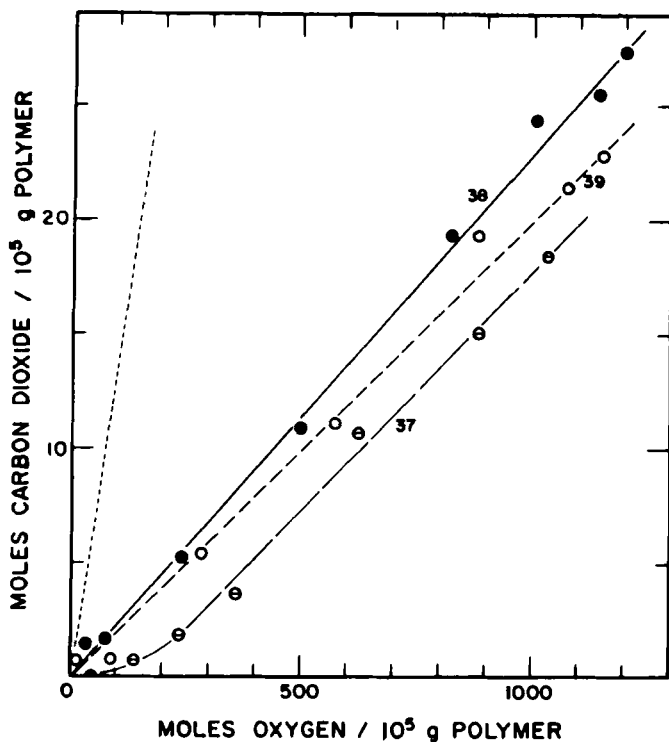
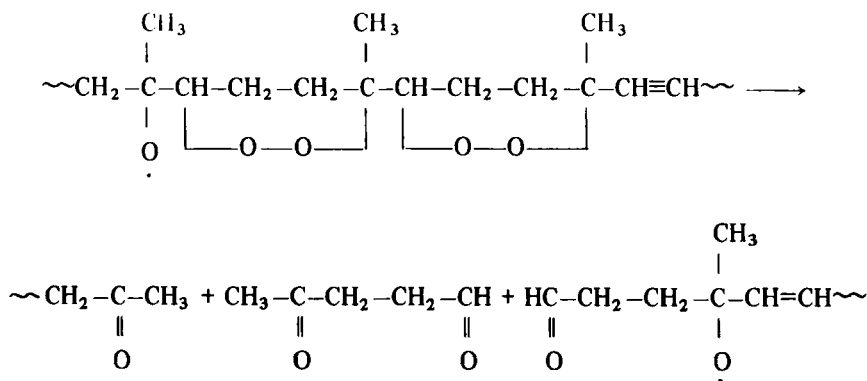


Fig. 3. Rate of CO<sub>2</sub> formation in PIP oxidations.





These schemes are based on a careful consideration of the main products produced during the reaction. Water, per se, is not included in these schemes. Water was not undetected as a reaction product, however, as

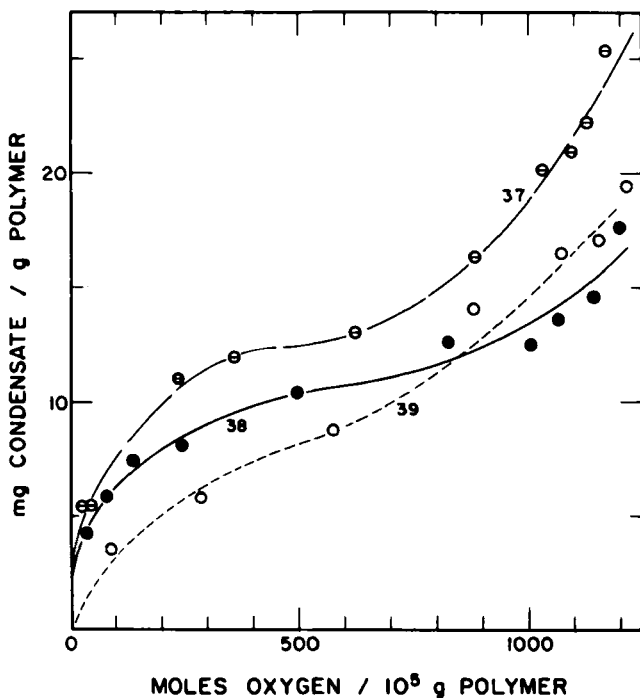


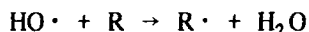
Fig. 4. Rate of formation of condensate other than H<sub>2</sub>O in PIP oxidations.

Bevilacqua [7] reported water yields as high as 80% for his Hevea oxidation experiments; Farmer and Sundralingham [8] characterized the yields of water as "small but not negligible." Prior to this present work on PIP it is safe to conclude that all polyisoprenes studied contained water as an artifact of the polymerization techniques used. This is not true for PIP, for these polymers are grown in the absence of both air and water, and water is definitely a major oxidation product.

Many reaction schemes can be written to account for the production of water as a reaction product. Any acceptable scheme, however, must include the formation of initial hydroperoxy groups alpha to the double bonds, and should also, in view of the work of Mayo [9] and Cunneen [5], include the formation of alkoxy groups. Two possibilities are:



or



These reactions are not new; they have been proposed as steps in numerous hydrocarbon oxidation schemes [10].

Further discussion of PIP oxidation mechanisms must await the results of additional quantitative experiments. These are now in progress.

#### ACKNOWLEDGMENT

The authors wish to thank the National Science Foundation, Grant GP19663, for financial assistance.

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*Accepted by editor August 12, 1970*

*Received for publication August 14, 1970*