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. III. Further Studies on Water and Carbon Dioxide Production

Glenn H. Miller[a]; Shih-Chen Lu[a]
[a] Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California

To cite this Article Miller, Glenn H. and Lu, Shih-Chen(1973) 'Oxidation of Polyisoprene Popcorn Polymer. III. Further Studies on Water and Carbon Dioxide Production', Journal of Macromolecular Science, Part A, 7: 3, 753 — 763
To link to this Article: DOI: 10.1080/00222337308061168
URL: http://dx.doi.org/10.1080/00222337308061168

J. MACROMOL. SCI.—CHEM., A7(3), pp. 753-763 (1973)

Oxidation of Polyisoprene Popcorn Polymer. III. Further Studies on Water and Carbon Dioxide Production

GLENN H. MILLER and SHIH-CHEN LU

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

ABSTRACT

The volatile products resulting from polyisoprene popcorn polymer oxidation were analyzed quantitatively for carbon dioxide and water, and semiquantitatively for formaldehyde. The production of these three products was a linear function of the amount of oxygen consumed in the reaction. For every mole of oxygen reacted, 0.098 mole of water, 0.038 mole of carbon dioxide, and > 0.016 mole of formaldehyde were formed. Twenty-four products were detected after extensive oxidation; the major ones being water, carbon dioxide, formaldehyde, formic acid, 2,5-hexanedione, and acetic acid. No levulinaldehyde was identified in the products.
A tentative oxidation mechanism is discussed.

INTRODUCTION

The effect of oxygen on natural rubber and synthetic polyisoprenes has been reviewed in considerable detail [1-4]. The various oxidation mechanisms proposed for polyisoprenes are based on the scheme originally presented by Bolland and Hughes [5] for the oxidation of squalane. This involves the formation of one six-membered cyclic peroxide ring and a hydroperoxide group for every two molecules of oxygen involved in the initial oxidation step.

Polyisoprene popcorn polymer (PIP) was characterized and some preliminary data on its oxidation were presented in the first paper of this series [6]. The amounts of water, carbon dioxide, and condensable condensate produced during the oxidation of PIP were previously determined by a gravimetric procedure [7]; that is, water was determined by absorption on silica gel. Since it is not known whether products other than water are absorbed by this reagent, the rate of water production has been redetermined in this work by a more exact technique in which the condensable fraction was first extracted with ether, and the aqueous layer then analyzed by gas chromatography. The results obtained differ considerably from those previously reported.

Approximately 24 compounds were detected in the volatile fraction collected from PIP oxidation. Of these, the following were identified: carbon dioxide, water, formic acid, formaldehyde, acetone, methyl formate, butanone, butenone, acetaldehyde, acetic acid, 2,5-hexanedione, and a dipentene. Most of these products were also among those identified by Bevilacqua [8] in his analyses of the products of cis-polyisoprene oxidation. The important difference, however, is the appearance of 2,5-hexanedione, and the fact that no levulinaldehyde could be detected in the PIP oxidation products. Levulinaldehyde has been assumed to be a major intermediate product and many of the presently accepted reaction mechanisms are based on its formation [5].

A tentative reaction mechanism for PIP oxidation is discussed that does not involve the intermediate formation of levulinaldehyde.

EXPERIMENTAL METHOD

The fifth generation polyisoprene popcorn (PIP) seeds used for these experiments were grown anerobically at 60° in the manner previously described [9]. Isoprene monomer was from Matheson, Coleman, and Bell. Seeds were evacuated for 16 hr before being oxidized.

PIP samples for oxidation were contained in round-bottom, 250-ml flasks equipped with Teflon Rotaflo stopcocks. P_4O_{10}-dried oxygen was passed through the flask at the rate of 25 ml/min. All oxidations were done at ambient temperatures.

After exiting from the reaction flask, the product-containing oxygen stream passed through a cold trap cooled to -78°, and then through a U-tube filled with Ascarite for carbon dioxide determinations.

The cold trap for product collection was equipped with Rotaflo stopcocks. It was weighed prior to the oxidation experiment and was removed, warmed to room temperature, and weighed at various time intervals. After weighing, one of the stopcocks was opened and the volatile gases were allowed to escape and the trap was then reweighed. Mass spectrographic analyses of the vented gas showed it to be primarily formaldehyde with small amounts of higher aldehydes. This vented gas was considered as formaldehyde for the calculations reported.

The consensed products separated into an aqueous and an oil layer. The oil layer was removed by ether extraction and the remaining aqueous layer was weighed. A typical vapor-phase chromatogram of the aqueous layer is shown in Fig. 1. The composition of the aqueous layer was 80 to 98% water; the exact amounts were determined by integration of the chromatogram peak areas and comparing with known samples.

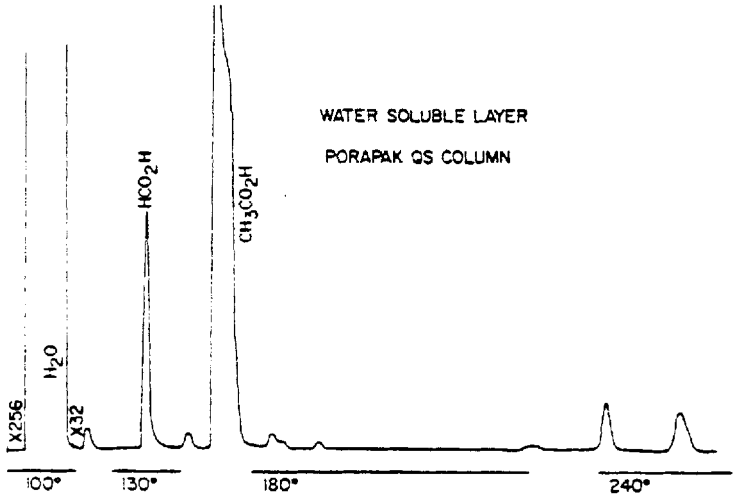


FIG. 1. Typical chromatograph of oxidation products in aqueous layer.

Chromatographic separations were done on a Hewlett-Packard model 7620A research chromatograph apparatus equipped with 10 ft, 1/8 in. copper tubing columns filled with Porapak QS (80-100 mesh). 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 8 min; and then increased 30°/min to 240° and held for 20 min.

EXPERIMENTAL RESULTS

Product Separation and Identification

Quantitative analytical data were obtained for water and carbon dioxide, and semiquantitative data for formaldehyde production. Approximately 24 products were detected. Of these, the following were identified: carbon dioxide, water, formic acid, acetic acid, formaldehyde, acetaldehyde, acetone, methyl formate, butanone, butenone, 2,5-hexanedione, and a dipentene. The major products were water, carbon dioxide, formic acid, 2,5-hexanedione, and acetic acid.

Only two higher-boiling products were produced in moderate amounts. These were both isoprene dimers. No products boiling higher than dipentene, and no levulinaldehyde, were detected.

Quantitative Results

The rate of oxygen consumption by the polymer is graphed in Fig. 2. This curve is similar to those obtained previously; the rate of oxygen consumption is most rapid during the early stages of the oxidation and the peak rate of oxygen consumption occurs after approximately 100 hr for room temperature oxidations.

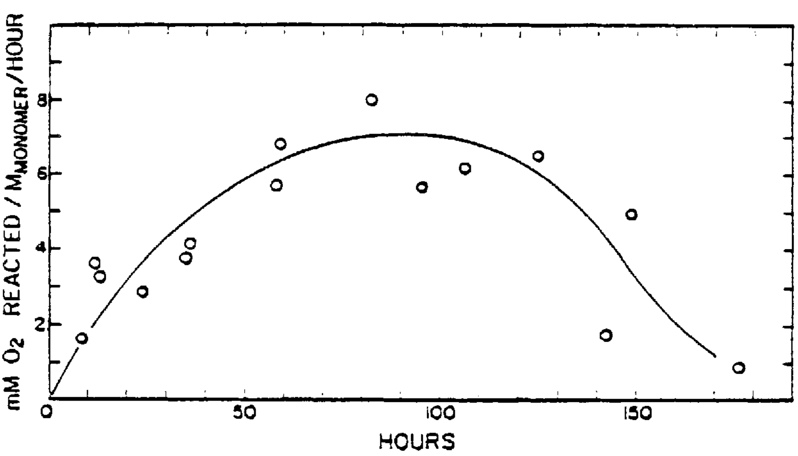


FIG. 2. Rate of polyisoprene popcorn oxidation.

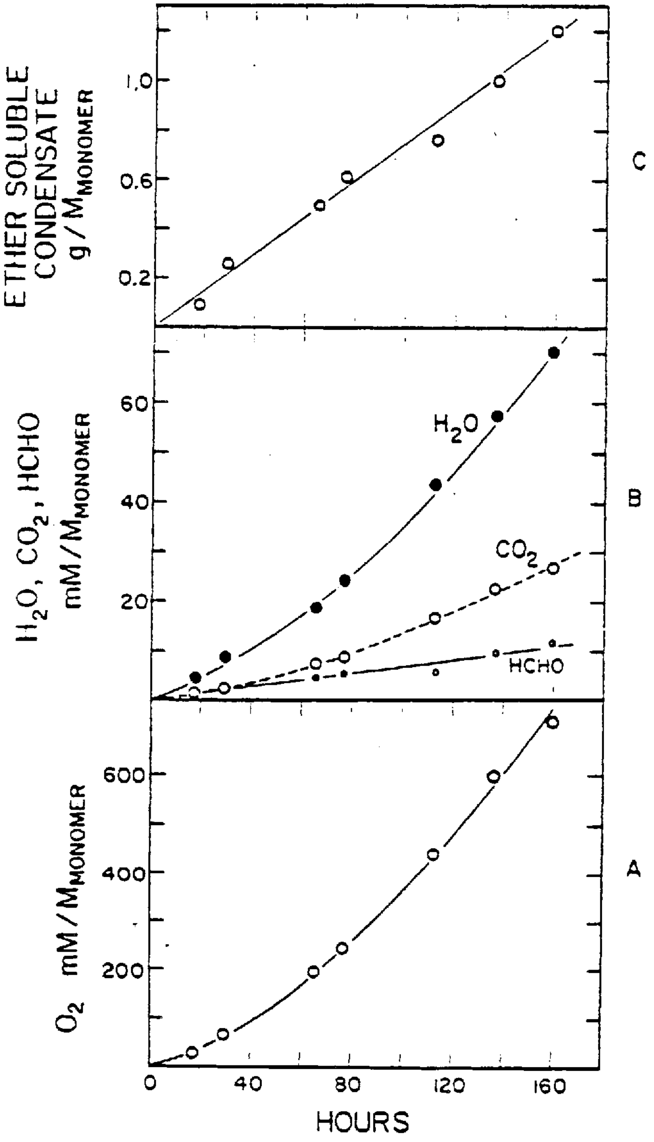


FIG. 3. (A) Amount of oxygen reacted. (B) Yields of H_2O, CO_2, and HCHO. (C) Yields of ether-soluble condensate.

Figure 3 summarizes the quantitative data obtained. All yields are plotted as a function of hours of oxidation at room temperature. Figure 3A is a plot of the amount of oxygen reacted in mM per M_M (millimoles per mole of monomer unit present in the original polymer before oxidation); Fig. 3B gives the yield data for water, carbon dioxide, and formaldehyde. Fig. 3C is a plot of the total mass of the ether-soluble condensate in g/M_M.

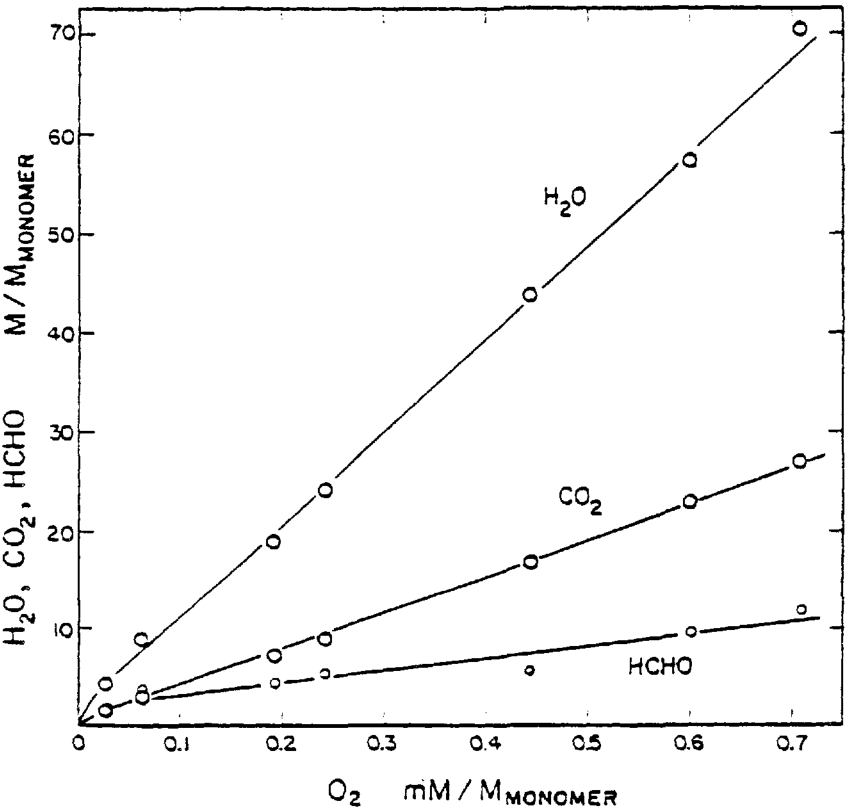


FIG. 4. Yields of H_2O, CO_2, and HCHO as a function of the amount of oxygen reacted.

The data can best be interpolated by reference to Fig. 4. Here the yields of the three products, carbon dioxide, water, and formaldehyde, are plotted as a function of the amount of oxygen reacted. Except for the slightly increased rates during the initial stages of oxidation, the rates of product formation appear to be linear functions of the total amount of oxygen consumed. Approximately 0.098 mole of water and 0.038 mole of carbon dioxide are produced for every mole of oxygen reacted.

The rate of formaldehyde production shown on Fig. 3 represents a minimum value. The plotted data were obtained by measuring the loss in mass when the Dry-Ice-cooled, cold trap was warmed to room temperature and the gases vented. Mass spectrographic analyses showed the gas to consist of formaldehyde with some traces of higher aldehydes. Some formaldehyde was undoubtedly oxidized to formic acid and some was lost in the formation of other secondary reaction products. Approximately 0.016 mole of formaldehyde was found per mole of oxygen reacted.

Figure 5 is a plot of the water yield vs the carbon dioxide yield. 2.56 moles of water were produced for every mole of carbon dioxide.

DISCUSSION AND CONCLUSIONS

The oxidation product produced in greatest yields from PIP oxidation is water. The rate of water production found in the present work,

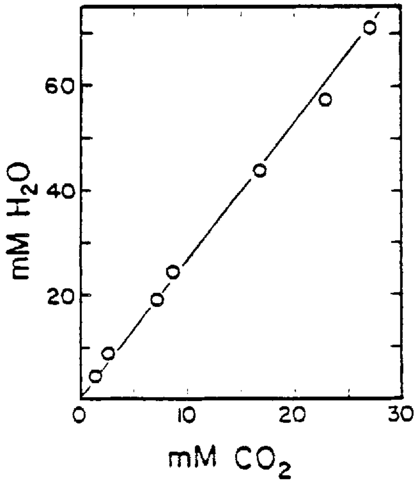


FIG. 5. Comparison of H_2O and CO_2 production.

0.098 mole per mole of reacted oxygen, is only half of that found previously when a silica gel absorption method was used for water determination. This difference is readily accounted for, however, since products other than water are undoubtedly absorbed by the silica gel. The rate of water production per mole of reacted oxygen is linear during the early stages of the reaction.

The yields of carbon dioxide found in this work were considerably higher than those found previously; 0.038 mole/mole of reacted O_2 compared to 0.02 mole/mole O_2. Both of these values, however, are much lower than that reported by Bevilacqua for natural rubber—0.108 mole/mole O_2.

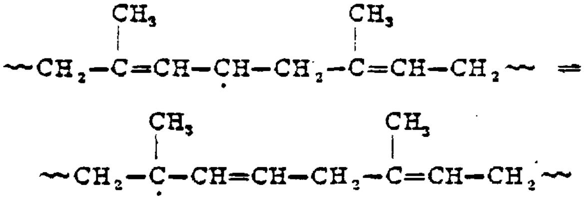
The rate of formaldehyde production amounted to 0.016 mole/mole of reacted oxygen. This represents a minimum, however, since some formaldehyde was oxidized to formic acid and some was lost in the formation of esters and other secondary products.

The above results, although quantitative for the system studied, cannot be considered reliable for the purpose of devising a reaction mechanism based on the stoichiometry of the reaction products. The three products—carbon dioxide, water, and formaldehyde—account for only approximately 10% of the total amount of oxygen that reacted with the polymer. Most of the reacted oxygen remains on the polymer, probably as cyclic peroxide links, hydroperoxide, ether, carbonyl, or alcohol groups. The same conclusion was reached for the oxidation of polyisoprene in solution [10].

Most of the 24 volatile products detected were successfully separated on a Porapak chromatography column. These columns proved satisfactory for this work since water is one of the first components eluted. Several compounds appearing in the ether-extract layer, however, with retention times close to that of acetic acid, were not resolvable. Acetic acid, 2,5-hexanedione, and formic acid were found in appreciable quantities. Many of the minor products remain unidentified.

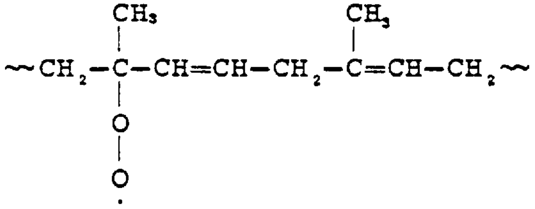
The reaction mechanisms previously proposed for polyisoprene oxidations do not appear completely suitable for the oxidation of PIP. The reasons are twofold. First, water must be accounted for as the major reaction product, and second, levulinaldehyde cannot be considered as a reaction product intermediate. A possible reaction mechanism follows.

It is not necessary to present a mechanism for the formation of the initial free radical sites on PIP. It has been shown that popcorn polymers, due to the absence of termination reactions, contain relatively high concentrations of free radicals [11].



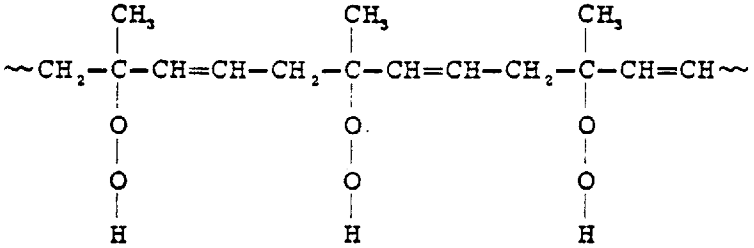
$$\sim CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\underset{\bullet}{CH}-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \;\rightleftharpoons\; \sim CH_2-\overset{CH_3}{\overset{|}{\underset{\bullet}{C}}}-CH=CH-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\sim \qquad (1)$$

Molecular oxygen first adds to the free radical site



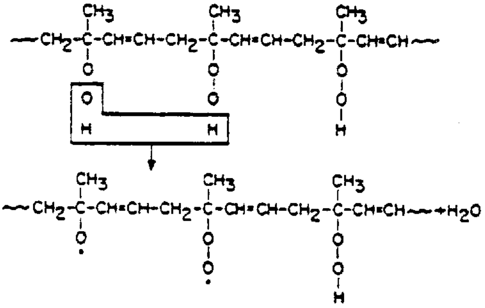
$$\sim CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\\cdot}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{C}{=}CH-CH_2\sim \qquad (2)$$

The peroxy radical could be located at various sites along the chain, but the tertiary position shown in Eq. (2) is the most stable, and the molecule could be expected to isomerize to this configuration. A hydrogen atom is then abstracted to produce a hydroperoxide group, leaving another free radical site on the chain. After isomerization, this adds the next oxygen molecule to form a peroxy linkage. This chain process is repeated to give the structure



$$\sim CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH\sim \qquad (3)$$

Water is then eliminated to give peroxy and alkoxy radicals

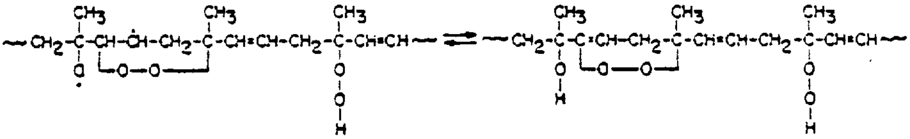


$$\sim CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH\sim$$

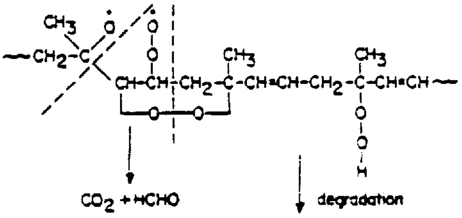
$$\downarrow$$

$$\sim CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\\cdot}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\\cdot}}{C}}-CH{=}CH-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\O\\|\\O\\|\\H}}{C}}-CH{=}CH\sim + H_2O \qquad (4)$$

This rearranges to give



Further addition of oxygen leads to scission and degradation.



This mechanism does not require a stoichiometrical balance to exist between the moles of water produced and the moles of carbon dioxide or formaldehyde produced. It does, however, indicate a one-to-one ratio for carbon dioxide and formaldehyde. The carbon dioxide to formaldehyde ratio found in this work, 0.038/0.016, appears to be reasonable since all the one-carbon atom products such as formic acid, and methyl formate must be considered as originating from formaldehyde.

Most of the oxygen remains on the polymer as cyclic peroxide linkages, keto, alcohol, acid, or aldehyde groups. Each scission produces one polymer-bound keto group and an aldehyde group in agreement with the data of Barnard and Percy [4].

Parts of this suggested mechanism correspond to those previously proposed by other investigators. The important distinction, however, is that this scheme does not involve the intermediate formation of the compound levulinaldehyde and accounts for the formation of water as a major product.

The two- and three-carbon atom products, such as acetaldehyde, acetic acid, and acetone, are probably the result of oxidation of 1,2- or 3,4-polyisoprene sequences in the polymer.

REFERENCES

[1] D. Barnard, L. Bateman, J. I. Cunneen, and J. F. Smith, in <u>The Chemistry and Physics of Rubber-like Substances</u> (L. Bateman, ed.), Maclaren, London, 1963, Chap. 17.

[2] E. M. Bevilacqua, in Autoxidation and Antioxidants, Vol. 2 (W. O. Lundberg, ed.), Wiley (Interscience), New York, 1962 Chap. 18.
[3] E. M. Bevilacqua, Rubber Age (N. Y.), 80, 271 (1956).
[4] J. L. Cunneen, Rubber Rev., 41, 182 (1968).
[5] J. L. Bolland and H. Hughes, J. Chem. Soc., 1949, 492.
[6] G. H. Miller and H. Leung, J. Macromol. Sci.—Chem., A4(8), 1705 (1970).
[7] G. H. Miller and W. J. Leung, J. Macromol. Sci.—Chem., A5(2), 443 (1971).
[8] E. M. Bevilacqua, E. S. English, J. S. Gall, and P. M. Norling, J. Appl. Polym. Sci., 8, 1029 (1964).
[9] G. H. Miller, R. L. Alumbaugh, and R. J. Brotherton, J. Polym. Sci., 9, 453 (1952).
[10] F. R. Mayo, K. Egger, and K. C. Irwin, Rubber Chem. Technol., 41, 271 (1968).
[11] G. H. Miller, D. Chock, and E. P. Chock, J. Polym. Sci., Part A, 3, 3353 (1965).

Received for publication October 10, 1972