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Polyisoprene Popcorn

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SUMMARY

Polyisoprene popcorn polymer has been shown to exhibit the typical properties of this class of polymers–insolubility and ability to propagate at a rate dm/dt-km. In contrast to butadiene popcorn, polyisoprene popcorn polymer (PIP) does not show marked variations in growth activity with growth generations.

Oxidation of PIP proceeds in four distinct stages: induction, acceleration, deceleration, and final periods. The growth was found to be independent of the presence or absence of an induction period, hence, the length of an induction period cannot be correlated with the number of free radical sites extant on the polymer.

When PIP oxidations are carried out in the presence of water vapor there is no change in the induction or acceleration rate curves; during the deceleration period, however, water adds to the polymer system. Secondary oxidation reactions become prominent during this stage of the reaction.

Solubility studies show that scission of most of the effective chains occurs during the very early stages of the oxidation.

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INTRODUCTION

Polyisoprene popcorn polymer (PIP) was first observed by Harries [1] who noted the formation of an insoluble mass resulting from the action of light on isoprene polymer. The ability of PIP to propagate when placed in the presence of isoprene monomer was first demonstrated by Wibaut [2]. Whitby [3] showed that PIP seeds would also propagate when placed in the presence of methyl methacrylate monomer and that the resulting PIP-MMP polymer would also grow when transferred to styrene monomer. PIP commonly occurs in commercial isoprene distillation facilities, but no systematic study of its properties has been reported in the literature.

The purpose of the present work is to characterize some of the properties of PIP and present some data on the mechanism of its oxidation. Popcorn polymers are uniquely suited to these studies due to their high purity; they are grown in the absence of air, water, inhibitors, catalysts, crosslinking agents, or other contaminating species. It is thus possible to observe features of the polymer oxidation that are obscured when other sources of polymers are used.

The effects of oxygen on natural rubber and synthetic polyisoprene and the mechanism of the oxidation reactions have been reviewed in considerable detail [4-7]. It is not the purpose of this present paper to discuss PIP oxidation mechanisms in relationship to the proposed reaction schemes for other polyisoprenes; this must be deferred until additional quantitative data are obtained. This present paper will attempt to point out some of the unique features of PIP oxidation and the preliminary conclusions that can be drawn from these observations.

EXPERIMENTAL

Approximately 0.2 g of PIP, taken from the filter of an isoprene distillation column [8], was thoroughly washed with benzene, dried in a vacuum at room temperature, and then used as the initial seed source for these experiments. The seed samples were placed on a tuft of glass wool and exposed to fresh isoprene monomer in the vapor phase. The anerobic technique has been previously described by the author [9]. All growth experiments were carried out in the darkness of an oil bath at 60°C. When a tube was almost full of popcorn (approximately 8 to 10 g) it was opened and 0.2 g samples were reseeded above fresh monomer; this process was repeated to give second generation seeds. Reseeding second generation seeds produced third generation seeds, etc. Second and third generation seeds were used for the experiments reported in this paper.

Isoprene from Matheson, Coleman, and Bell was distilled directly into the reaction tubes.

The activity of PIP seeds for growth was measured by incubating 0.200 g samples above monomer for exactly 168 hr at 60°. The weight of the resultant polymer represented the adopted standard for growth activity.

Individual sealed tube experiments were used for each point on growth rate curves. An initially weighed amount of PIP seed was propagated for a given length of time at a given temperature after which the tube was opened, the polymer evacuated for approximately 20 min to remove any sorbed monomer, and then weighed.

Solubility measurements were made using nitrogen-flushed Soxhlet extractors with benzene as the solvent. Samples were contained in previously weighed sintered-glass crucibles, and the extractions lasted for a minimum 24-hr period. Following extraction the crucibles containing the polymer were evacuated for approximately 30 min to remove solvent prior to weighing.

Polymer samples for room temperature oxidation were placed in sintered glass crucibles contained in stoppered dewars through which oxygen was passed at atmospheric pressure. The crucibles were removed at frequent intervals for weighing. For other than room temperature oxidations, the crucibles were contained in glass tubes which were mounted in a constant temperature bath maintained at the desired temperature.

RESULTS AND DISCUSSION

Two characteristics of popcorn polymers are their insolubility and their ability to propagate in a logarithmic manner; the rate of growth at any given time depends on the mass present at that time,

$$dm/dt = km$$

Figure 1 shows a plot of the final weight of 0.200 g samples of PIP as a function of time that the polymer was allowed to grow in the vapor phase above liquid monomer at temperatures of 44, 60, and 75°.

Further verification of the popcorn rate equation is shown in Fig. 2 where the growth rates of seeds of various initial masses are plotted for experiments at 60°. Within experimental error, following short induction

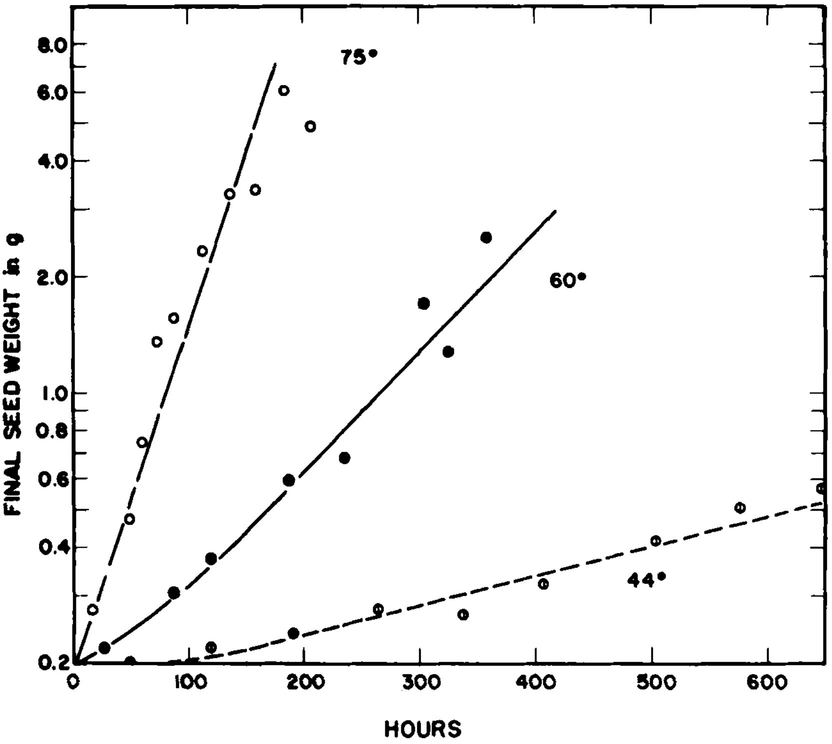


Fig. 1. Growth of polyisoprene popcorn polymer.

periods, the same slopes were obtained for initial seed sample sizes of 0.100, 0.200, and 0.400 g.

Solubility determinations of PIP after removal from the incubation tubes showed an average solubility in benzene of 2%.

It was not possible to obtain IR spectra for unoxidized PIP. Attempts to make KBr pellets using pressures up to 20,000 lb/in.^{2} failed due to the elasticity of the polymer. After removal from the die the polymer immediately expanded to its precompression volume and shattered the pellet. Thus the tacticity of the PIP is unknown.

The data of Table 1 report the standard growth activities for PIP seeds of different generations. Average activities varied from 0.476 to 0.604 g. Within experimental error, no observable trend was noted for variations in seed activity for generations three to seven. This is in contrast to butadiene popcorn polymers which show an increase in standard activity that reaches

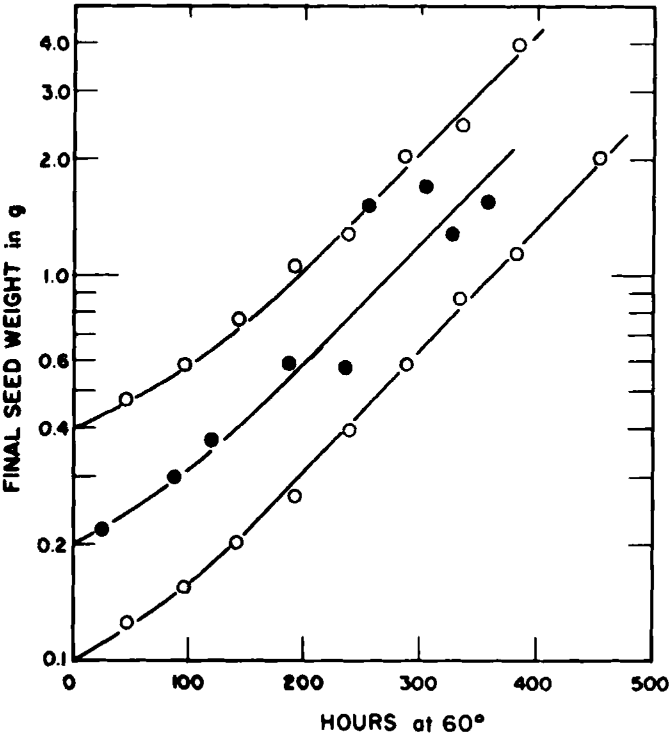


Fig. 2. Effect of seed size on growth of polyisoprene popcorn polymer.

Table 1. Variation of PIP Seed Activity with Growth Generation

Generation	Final weight of 0.200 g samples after 7 days at 60°		Average activity
3	0.478	0.475	0.476
4	0.566	0.642	0.604
5	0.575	0.609	0.592
6	0.531	0.462	0.496
7	0.517	0.540	0.528

a maximum and then decreases, the change being accompanied by an observable alteration from an amorphous popcornlike polymer to a more glassy structure [10]. No variation in the appearance of PIP was noted for samples of different generations.

Oxidation curves for PIP at temperatures of 0, 23, and 59° are illustrated in Fig. 3. Typical autoxidation curves were obtained. The ordinate

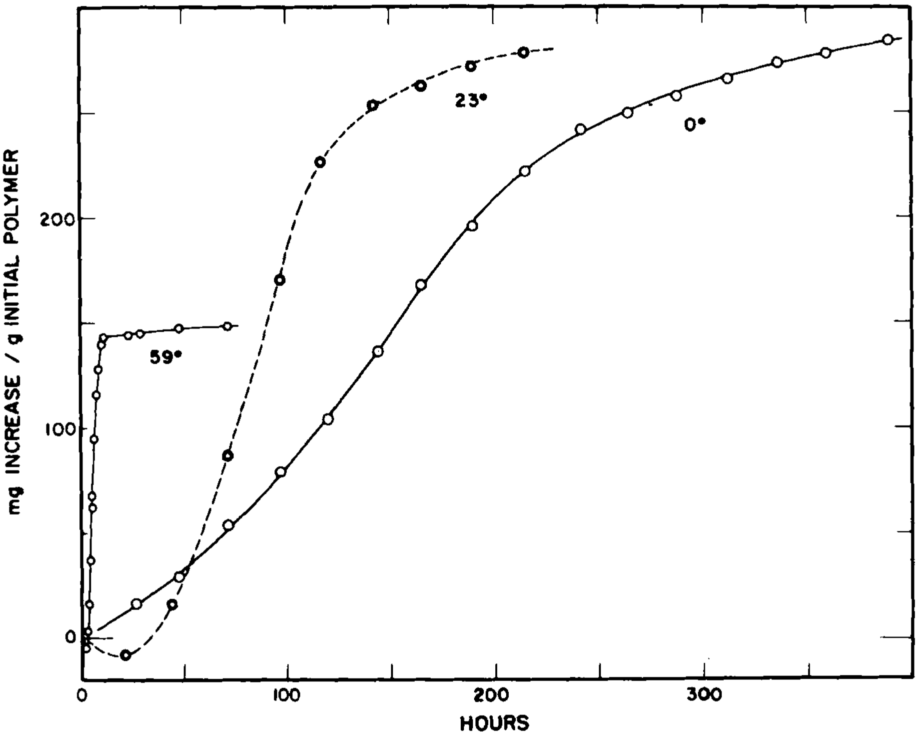


Fig. 3. Oxidation of polyisoprene popcorn polymer.

plot is the ratio of the increase in polymer mass to the mass of the initial sample and is reported as milligram increase per gram initial polymer. These curves give relative values only as the volatile by-products of the reaction were vented and not considered in the calculations. They are, however, suitable for the purpose of illustrating the behavior of the polymer. Note that several of the oxidation curves show a loss of polymer mass during the first 10 to 20 hr of oxidation, e.g., the plot for the 23° oxidation on Fig. 3.

This is due to the loss of approximately 2% dipentene which was sorbed on the polymer during polymerization.

Rate curves obtained by graphic differentiation of PIP oxidation curves show an accelerated rate which reaches a maximum; this is then followed by a deceleration period, see Fig. 7. The same general type of curve has been observed for most olefinic oxidations [11]. For discussion purposes it is convenient to divide the oxidation curves into four periods as suggested by Bauman and Maron [12]: an induction, acceleration, deceleration, and final period. Induction periods of various times were obtained by providing suitable storage conditions as discussed below. Kinetic expressions for both the acceleration and deceleration periods have been proposed [12, 13]. These theoretical expressions cannot be tested for PIP oxidations, however, until more information is obtained concerning some aspects of the reaction.

Many samples of PIP that were stored in a vacuum showed long induction periods before maximum oxidation rates were obtained. This is illustrated in Fig. 4; portions of the same initial PIP sample were used for all

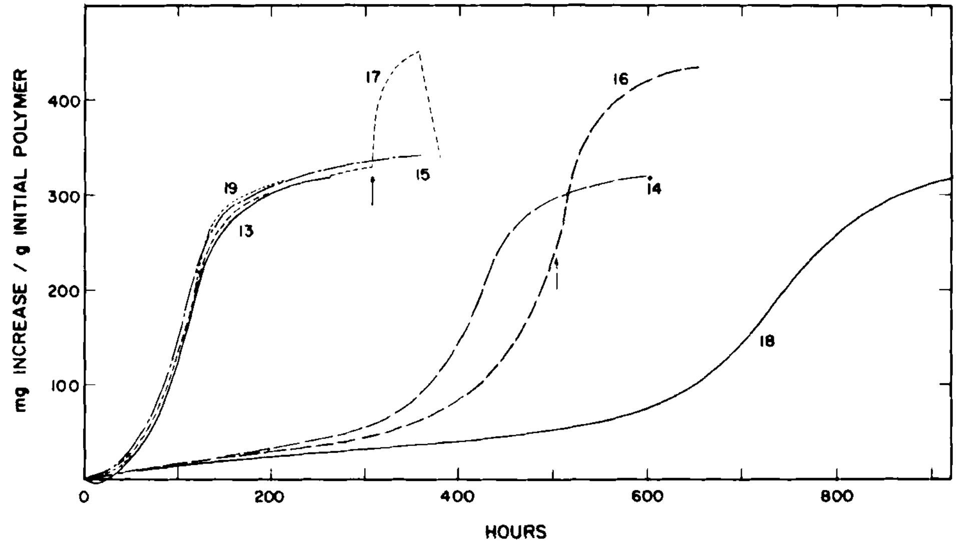
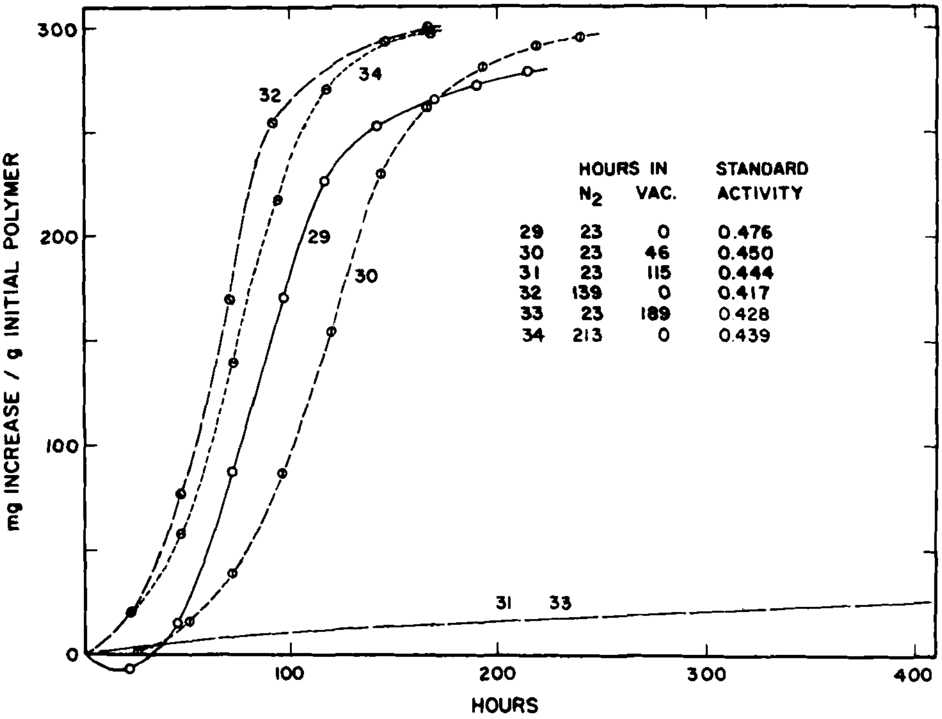


Fig. 4. Effect of storage on polyisoprene popcorn polymer oxidation induction periods. Curves 15, 17, and 19: seed stored in N_2 for 167, 314, and 529 hr; curves 13, 14, 16, and 18: seed evacuated for 18, 167 (dark), 168 (light), and 314 hr, respectively. Arrows indicate water additions.



	HOURS IN		STANDARD
	N_2	VAC.	ACTIVITY
29	23	0	0.476
30	23	46	0.450
31	23	115	0.444
32	139	0	0.417
33	23	189	0.428
34	213	0	0.439

Fig. 5. Oxidation curves and data which show that polyisoprene popcorn polymer growth activities are independent of oxidation induction periods.

oxidations. Curve 18, which shows an induction period of over 500 hr, was stored in an untrapped vacuum system (approximately 10^{-3} Torr with continuous pumping) for 314 hr; the flask was exposed to light. Similar treatment for 168 hr gave an induction period of approximately 200 hr, Curve 16. Vacuum storage for 168 hr in the dark, Curve 14, produced an induction period slightly shorter than that observed when the samples were stored for the same time period in the light. Curve 13 represents the standard oxidation rate for PIP that was oxidized without being subjected to a storage period. The other curves, 15, 17, and 19, show the oxidizibility of PIP that was kept in a stream of dry nitrogen for various lengths of time. Nitrogen storage usually resulted in slight but observable decreases in the induction period; this is undoubtedly due to the removal of sorbed dipentene.

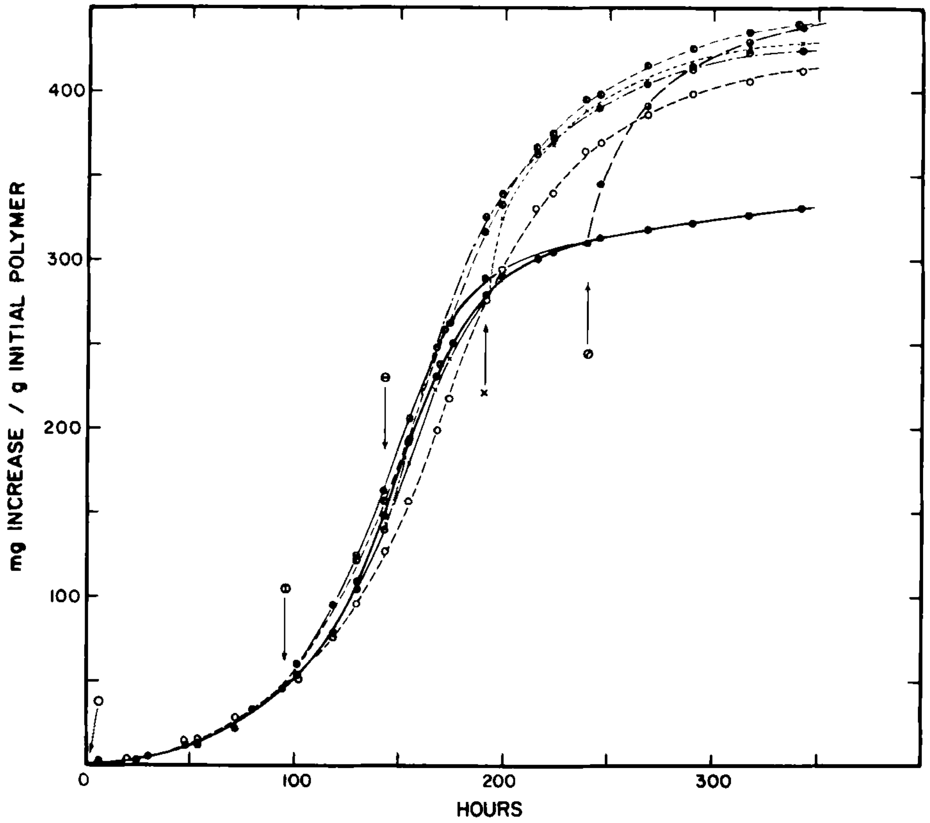


Fig. 6. Effect of water additions on the oxidation rate of polyisoprene popcorn polymer.

The cause of the induction periods produced by vacuum pumping is in doubt. They are not produced if the polymer is evacuated through a liquid nitrogen cooled trap. Since contamination by the vacuum system was suspected, another series of PIP was stored on an oil diffusion pumped, mercury and grease-free, high vacuum system (less than 10^{-6} Torr). The results are presented in Fig. 5.

Even though the cause of the induction period is in doubt, the experiments permitted us to see if there was any correlation between the induction periods and the ability of the polymer to propagate itself, i.e., its standard growth activity. These data are shown in Fig. 5. Within experi-

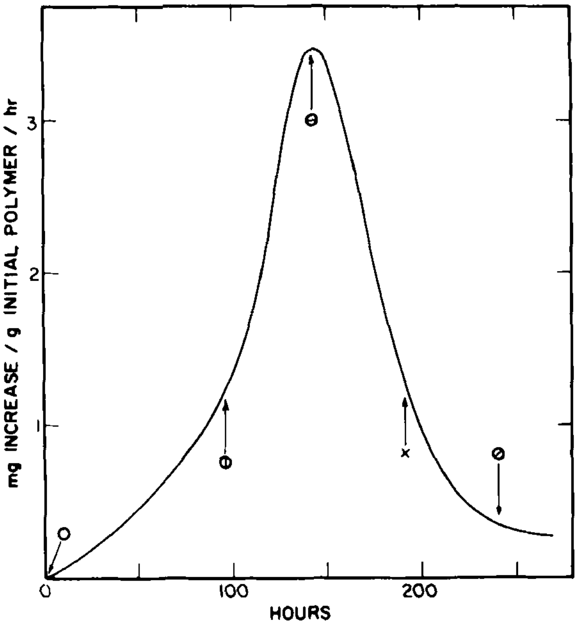


Fig. 7. Oxidation rate curve showing times at which water was introduced to the system.

mental error, the growth activity of PIP cannot be correlated with the presence or absence of the induction period.

The growing chains of PIP can terminate on standing by disproportionation or by combination of chain ends; the latter process, however, is limited and occurs to a negligible extent due to the immobility of the polymer chains. Any loss of free radical sites must therefore be correlated with an intramolecular disproportionation reaction. This would manifest itself as a loss in polymer growth activity. No such loss was noted, even for PIP samples that exhibited long oxidation induction periods.

The arrows in Fig. 4 indicate times when water was introduced into the system by allowing the oxygen to bubble through distilled water before contacting the polymer. These preliminary experiments were repeated in more detail and the results are shown in Fig. 6. Six samples of PIP were oxidized in the usual manner but water was introduced at different times during the reaction. For clarity, Fig. 7 shows the water introduction times on the corresponding rate curve. The introduction of water at the beginning of the oxidation did not produce any change in the weight of the polymer,

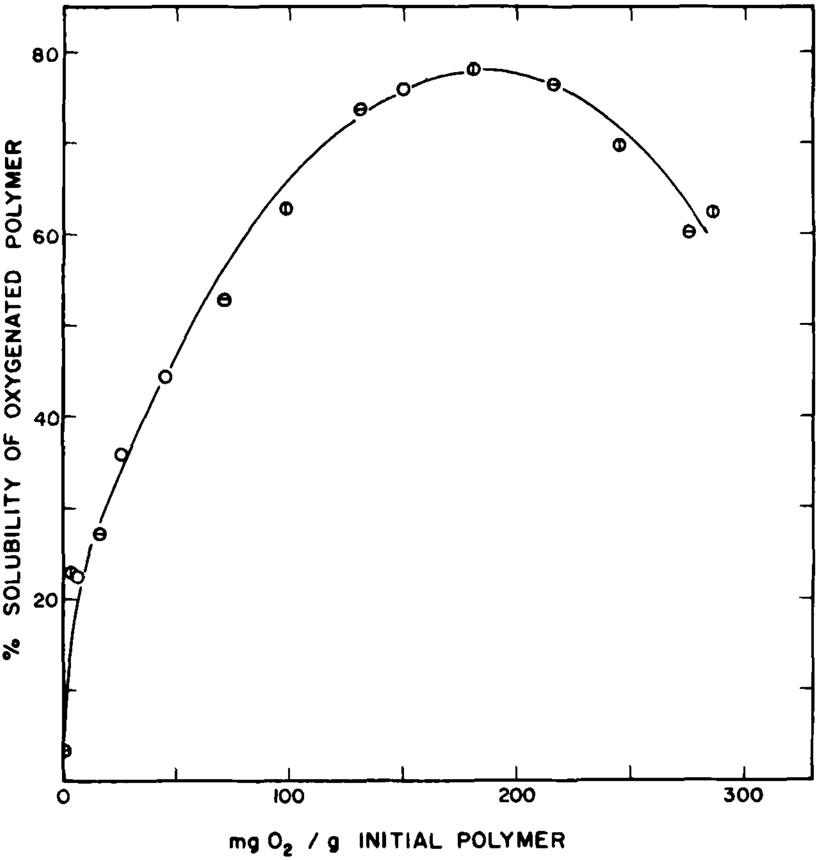


Fig. 8. Solubility of oxidized polyisoprene popcorn polymer.

i.e., there was no observable weight change due to absorption or reaction with water. Similarly, nothing happened when water was introduced during or at the peak of the acceleration period. During the deceleration period, however, water did add to the polymer system and a final relatively constant weight increase was observed for all five samples to which water had been added. These results show that there is an abrupt change in product composition; only during the deceleration period are products produced that cause water to react or be absorbed by the polymer. Once the maximum oxidation rate has been attained, secondary oxidation reactions become increasingly important.

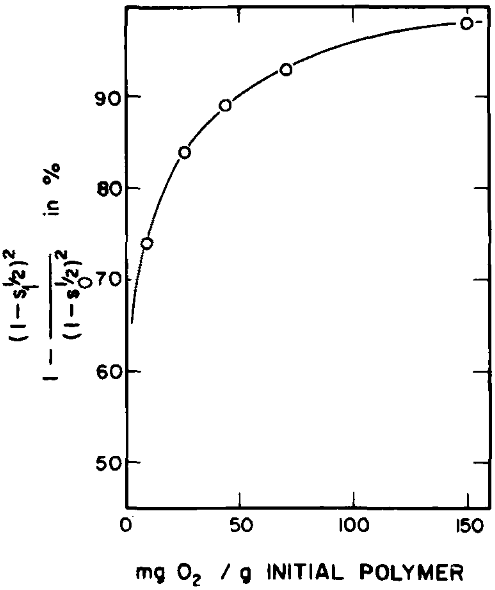


Fig. 9. Effective number of chain fractures as a function of degree of oxidation.

Horikx [14] has derived the relationship between the soluble fraction and the number of effective chains between cross-links in a three-dimensional network undergoing a scission reaction. For a degradation in which the total number of cross-links is constant, the relationship between the soluble fraction and the relative decrease in the effective number of chains is given by

$$1 - \frac{\nu_{e_2}}{\nu_{e_1}} = 1 - \frac{(1 - S_1^{\frac{1}{2}})^2}{(1 - S_0^{\frac{1}{2}})^2}$$

where ν_{e_1} and ν_{e_2} are the effective number of chains before and after degradation, respectively; S_0 and S_1 are the soluble fractions of the undegraded and degraded polymer. For popcorn polymers, S_0 is taken as equal to zero. A plot of the per cent of sol developed on oxidation of PIP vs. the relative oxygen content of the polymer (loss in weight due to any volatile fractions was neglected) is shown in Fig. 8. Maximum solubility was reached at a point in the oxidation that coincides with the attainment of the peak in the acceleration period curve; a decrease in solubility occurs during the deceleration period.

A plot of the Horikx function vs. relative oxygen content of the polymer is graphed in Fig. 9. The scission reaction is very rapid—three-quarters of the effective number of chains in the polymer are fractured during the first 10 hours of the oxidation. It appears that the scission reaction is associated with the initiation step and not the chain reaction occurring during the acceleration period. Further studies are in progress.

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