THE MECHANISM OF POPCORN POLYMER FORMATION

A Thesis

by

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INTRODUCTION

In the preparation of GR-S using the Mutual recipe considerable gel formation occurs after about 80% conversion, producing polymer of such inferior quality that the reaction must be stopped before this point has been reached. Efficient plant operation then depends upon recovery of the unchanged styrene and butadiene, which is accomplished by coagulation of the latex, evaporation of most of the butadiene at low temperature, followed by distillation of the styrene, together with about 2% of dissolved butadiene.

In both the recovered butadiene and styrene, polymerization may occur to produce a polymer, which is practically insoluble in any of the usual rubber solvents. This polymer usually occurs as a deposit in the condensers, in the styrene recovery unit, while the counterpart in the butadiene recovery occurs mainly in the rerun tower. Since the insoluble polymer formed from styrene containing small amounts of butadiene is usually white and has a cauliflower-like appearance, it is known as "popcorn" polymer. Insoluble butadiene polymer is usually glassy and brittle and varies in color from white to green or brown. Both types of popcorn show such proliferative activity that at intervals, production may have to be stopped to clean the condensers mechanically. In the recovery units of the Polymer Corporation plant at Sarnia, Canada, it has been necessary, on occasion, to cut the styrene condensers apart to remove the popcorn. The economic waste of such an operation is apparent.

It was with a view to elucidating the mechanism of formation and growth of popcorn, with the ultimate aim of completely preventing the reaction, that the present investigation was made.

A number of substances, including dimethylbutadiene[1] and chloroprene[2] are known to produce insoluble polymers under certain conditions. As early as 1932 Whitby[3] showed that after standing one to two years at room temperature dimethylbutadiene produced an insoluble, white cauliflower-like mass similar to styrene popcorn. He has described a similar polymer prepared by the spontaneous polymerization of isoprene over a period of fifteen years.[9]

Whitby and Zomlefer[4] studied the conditions under which popcorn formed in sealed tubes containing butadiene in styrene. They found that aside from the presence of butadiene, which is essential, the factors favorable to the formation of popcorn type of polymer are factors which tend to retard normal polymerization without, however, preventing it entirely. Factors such as a temperature much above 50° C, or the presence of air, and especially of oxygen, which accelerate the polymerization of unemulsified styrene are unfavorable to the formation of popcorn polymer and tend to lead to the normal, resinous polymerization of styrene. Factors which reduce the rate of normal polymerization, such as the removal of oxygen by rust formation (as may occur in the presence of water and iron), or the displacement of air by butadiene vapor, are favorable to the formation of popcorn type polymer.

The popcorn polymer first appears as insoluble nuclei in the styrene; these grow as polymerization proceeds, and later expand or "pop". A number of inhibitors including hydroquinone, ter. butyl catechol, phenol, n-propylamine, methyl iodide and methyl sulfide were found to be ineffective in preventing popcorn formation, particularly in the presence of water and iron.

Gleason et al[5] consider that butadiene popcorn is a normal polymerization product of butadiene and should be considered alongside the commonly accepted dimer and high molecular weight, soluble, rubbery polymer. Again, factors which tend to slow down formation of the two soluble types permits the popcorn variety to proliferate. They report that iron and iron compounds favor popcorn formation but are not essential, while metallic copper prevents its formation but does not arrest growth previously started. In the known absence of carbon dioxide, oxygen and/or peroxide no popcorn was formed. The presence of butadiene dimer at high concentrations (20%) prevented growth of polymer seeds in liquid butadiene.

Parrish[6] has shown that popcorn will form over a range of concentrations of butadiene in styrene from 5 to 95%. in the presence and absence of a polymerization catalyst.

Results on the initiation and growth of popcorn from pure butadiene in sealed glass ampoules at 60° C have been obtained by Welch et al.[7] They have shown that popcorn initiation requires the presence of active oxygen, and that carbon dioxide, rusty iron or other metals in the absence of active oxygen (or potentially active oxygen) do not initiate popcorn, although they may accelerate its formation when active oxygen is present. Exposure of popcorn seeds from commercial stills to air for a few weeks at ordinary temperatures removed their power of growth in monomer. They found that popcorn seeds show an approximately logarithmic growth which is the same in both the liquid and gas phases. A later report[8] by Beckwith and Robey on the formation and growth of butadiene popcorn substantiates the above conclusions. They found further that the presence of an interface of liquid water also appears to have a promoting influence. There appeared to be no relation between the formation of soluble tacky polymer and popcorn formation, although both were catalyzed by peroxides. Growth of popcorn seeds was found to occur in the absence of any known catalyst.

Popcorn polymer has been produced from mixtures of 2% butadiene in methyl methacrylate,[10] but the substitution of either isoprene or dimethylbutadiene for butadiene in solutions of styrene or methyl methacrylate will not produce popcorn polymer. This leads to the view that butadiene is more prone than its homologs to undergo branching and cross linking during polymerization.

Whitby et al[11,12] have shown that popcorn seeds, either of the butadiene or butadiene-styrene types, will grow to produce cauliflower-like material in a variety of monomers, including styrene, dimethylbutadiene and methyl methacrylate. The same has been found to be true using popcorn seed formed by the spontaneous polymerization of isoprene.[9] It has been found,[12] further, that in second generation growth, 5% of butadiene-styrene popcorn polymer will bring about popping of the whole when it is incubated in styrene at 55° C, and that 5% of the second generation polymer will similarly grow in a third generation, yielding popcorn polymer containing only 1 mole of butadiene per 40 moles of styrene.

A number of workers[7,13] have reported that both butadiene and butadiene-styrene popcorn lose their activity for growth in monomers on being exposed to the atmosphere for a number of days. Whitby[14] states that isoprene popcorn increases rapidly in weight when allowed to stand in air at room temperature, and still more rapidly when heated in air at 55° C. When exposed to air at room temperature, the polymer gradually falls off in proliferative activity, although it will still grow after 72 days. Heating butadiene-styrene popcorn polymer for a fairly long period in air at 55° C causes complete deactivation while heating for 27 hours at 100° C is insufficient.[14]

Whitby and Zomlefer[14] have tested a variety of popcorn polymer samples with Pratesi's reagent, the results indicating that their vigor of growth is directly related to their peroxide content. The data are considered to be qualitative only, since the reagent is extremely sensitive to the presence of peroxides. The pyrolytic decomposition of popcorn polymer made from styrene containing 2% butadiene gave the same products as regular, soluble polystyrene, which seems to indicate that its molecules are composed mainly of long chains of styrene monomers, which have grown on an insoluble, cross linked nucleus. It is considered that two factors are necessary for the occurrence of popcorn polymerization: first, an insoluble nucleus; second, catalytically active centers on the nucleus. To produce the insoluble nucleus requires the presence of at least a proportion (which may be small) of conjugated diene. The insolubility may arise as a result of cross linking, during polymerization in the absence of air, on an originally soluble, diene-containing polymer. The catalytically active centers are apparently peroxidic in nature. Popcorn polymerization is considered to involve essentially polymerization <u>on</u> an insoluble nucleus (or seed) of monomer imbibed by it, under the catalytic influence of peroxides <u>in</u> the seed.

Kharasch[15] has postulated a theory similar to that of Whitby for the growth of popcorn seed. He considers that active seed growth is associated with the following two factors:

1. The active seed must be a material insoluble in organic solvents (benzene or styrene) but must nevertheless, swell in them; 2. the active seed must contain a relatively large number of peroxide groups (or hydroperoxides) attached to the insoluble polymer. To substantiate this theory Kharasch has shown that the ability of seeds to grow in pure styrene is directly related to their peroxide content, as measured by a method similar to that of Roby and Wiese.[16] It is also indicated that successive generations of popcorn grown in styrene show a marked decrease in proliferative activity, which is attributed to dilution of the peroxides on the original seed. When popcorn seed is exposed to air, especially under the action of a strong light, the proliferative activity first increases and then decreases, corresponding to the measured changes in hydroperoxide content. Similar changes in the peroxide content have been observed by Farmer[17] during peroxidation of a number of compounds containing double linkages, and he has offered a mechanism to explain the effect. Kharasch has succeeded in producing active seeds, capable of growth in styrene to popcorn polymer, by strong peroxidation of linseed oil, tung oil and GR-S polymers. When so peroxidized these compounds prove to be quite insoluble in styrene and thus satisfy the first condition of the above hypothesis.

Attempts, made at Johns Hopkins,[18] to evaluate popcorn activity from physical properties have met with little success. Samples showing a considerable variation in proliferative activity were obtained from a number of plants, and contained from 7-42% butadiene. The refractive index was always about 1.60, and thus did not serve to indicate the composition. After standing in air they contained 150 to 5000 ppm of active oxygen, as determined by a method similar to that of Roby and Wiese.[16] Extraction of the popcorns with hot benzene seemed to proceed indefinitely, the samples not reaching a constant weight. Surface area determinations by absorption methods seemed to indicate that popcorn is not filled with fine pores similar to those existing in charcoal.

This report seems to represent the first, for the styrene-butadiene system, in which curves are given for the amount of popcorn growth as a function of the time, although, unfortunately, the amount of popcorn present was measured by the height to which the seed had grown in the tube, and as such the measurements cannot be considered as giving more than an approximate relation between weight of popcorn polymer and time. However, it seems apparent that an initial induction period followed by an increasing growth rate occurs in solutions containing 2% butadiene in styrene. In a general way the rate of popcorn growth increased with the active oxygen content and with the butadiene content of the popcorn.

Also, the maximum height to which popcorn expanded in about 18 times its weight of monomers increased with the butadiene or active oxygen content of the popcorn.

An extremely large number of possible inhibitors of popcorn formation have been tried in what has been, in view of the doubts concerning the mechanism of the reaction, a completely expirical fashion. Early experiments were made to discover inhibitors capable of preventing popcorn initiation, and a large number of compounds were found to be effective in this capacity, even when iron and water were present[6,8,10,19,20,21,22]. With seeded samples it was found, however, that most of these compounds were quite ineffective, particularly in the presence of water and iron.[9,12,14]

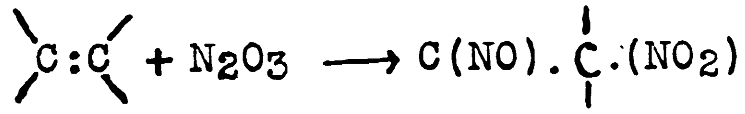
Kharasch[23] has obtained evidence to show that when copolymerizations are terminated by methods now in use, the products still contain considerable amounts of free radicals. He has shown that active popcorn contains free radicals, the activity of which can be quenched with nitric oxide, so that the popcorn, when introduced into styrene, no longer possesses proliferative properties.

He has shown[24] that nitric oxide completely inhibits copolymerization when added to the Mutual formula, at the beginning of the reaction, in amounts equivalent to 50% of the mercaptan used. Nitric oxide[25,26] was found to inhibit also the polymerization of butadiene by sodium hydride, GR-S copolymerization and the bulk polymerization of styrene.

Bloomfield and Jeffrey[27] have investigated the reaction between nitric oxide and various olefinic compounds including solutions of rubber, dihydromyrcene, 1-methlcyclohexene and cyclohexene. The reaction exhibited the characterististics of a free-radical mechanism possessing an induction period of 15-30 minutes. Nitrogen was formed, which on admixture with the nitric oxide caused the reaction to cease. The following overall reactions explain the formation of some of the products:

(a) $RH + 4NO \longrightarrow RNO_2 + N_2 + HNO_2$

$2HNO_2 \longrightarrow H_2O + N_2O_3$

(b) 

(c) $2RH + 10NO \longrightarrow 2RNO_2 + 3N_2 + 2HNO_2$

The Theory of Polymerization

It is now widely accepted that addition polymerization such as occurs with a large variety of monomers, including most of the vinyl type, differs fundamentally from condensation polymerization. In the latter type of polymerization stepwise addition of monomer occurs, the products of each step being then similar in ability to react with further monomer. Such a reaction leads to a polymer having a chain length which increases directly with increasing time. The polymers produced by addition polymerization, however, possess molecular weights essentially independent of the time of reaction.

This approximate constancy of molecular weight in the products of addition polymerization has been adequately explained by a mechanism, now widely accepted, involving three fundamental steps: initiation, which produces active monomer molecules; propagation, during which monomer molecules add to the initial active molecules, the activity being maintained at the end of the growing chain; and termination by which the active growing chains become deactivated.

Initiation: $M \longrightarrow M^*$

Propagation: $M^* + M \longrightarrow M_2^* \rightarrow \rightarrow \rightarrow Mn^*$

Termination: $2M_n^* \longrightarrow M_{2n}$

In general the propagation reaction will be considerably faster than either the initiation or termination so that fairly long chains will develop and be terminated in a very short time. The effect of very small amounts of various substances in catalyzing or inhibiting polymerizations of this type is evidence for this mechanism.

A number of methods for initiating chains are known to exist. It seems fairly definite that purely thermal activation of the double bond can produce active molecules of styrene.[28,29] Photochemical activation has been studied by a number of workers,[30] and in general takes place with a rate proportional to $\sqrt{\text{Intensity}}$, indicating that the photo-activated monomer can either return to the inactive state or grow into a chain. A variety of substances have been found capable of catalyzing polymerization reactions. In certain cases (free radicals, alkali metals, peroxides, ozonides) the catalyst acts by producing a free radical, in other instances (BF_3, $AlCl_3$, $SnCl_4$) association of the catalyst with the monomer takes place. Radical catalyzed polymerization of vinyl- and acryl-derivatives has been studied by Abere[31], Alyea[32] Bolland[33], Goldfinger[31], Naidus[31], Norrish[34], Price[35], Raff[36] and Schulz[37].

It has been shown from independent evidence that a number of substances capable of initiating polymerization reactions do in fact decompose to form free radicals[30,37,38-40] in solution. Price et al[40,41,42] have shown that samples of polystyrene and polymethyl methacrylate, polymerized in the presence of a number of different organic peroxides, contain fragments of the peroxides used. In one case the concentration of activating radicals was measured directly by the color of the solution and it was found that the initial rate of monomer consumption is proportional to this concentration. The initial rate of disappearance of monomer is found in many cases to be proportional to the square root of the concentration of the catalyst, which is to be expected on the basis of the dissociation of catalyst into free radicals, assuming a first order decomposition of catalyst and a second order termination by reaction of two radical chains.

Eyring[43] has developed equations for the rate of overall polymerization as a function of the monomer and radical concentration. Assuming that propagation consists of the rapid addition of monomer molecules to polymer radicals the velocity of propagation is:

(1) $V\text{prop.} = k_2AC^*$ where C^* is the concentration of radicals and A is the concentration of monomer.

If propagation is much faster than initiation the overall rate is given by:

(2) $-\frac{dA}{dt} = k_2AC^*\left[1 + \frac{V\text{init}}{V\text{prop}}\right]$ where the second term is small.

If now we assume that a steady state exists such that the rate of initiation is equal to the rate of termination, we have:

(3) $\frac{V\text{init.}}{V\text{prop.}} = \frac{V\text{term.}}{V\text{prop.}} = \frac{1}{\gamma}$ where γ is the kinetic chain length of the reaction.

The termination can only involve the reaction between two free radicals, since only in this case will free radicals disappear. Thus:

(4) $V \text{ term.} = k_3 C^{*2}$

Combining this with the steady state assumption:

(5) $C^* = (V \text{ init.}/k_3)^{\frac{1}{2}}$

Substituting this value for C^* in (2) we have:

(6) $-\frac{dA}{dt} = k_2 \, (V\text{init.}/k_3)^{\frac{1}{2}} . \, (A + \frac{1}{Y})$

By comparing this equation with the overall rate expression observed experimentally it is possible to decide the mechanism of the initiation step. The second order overall rate observed[28,29] in the uncatalyzed polymerization of styrene, both in solvent and as pure liquid, requires second order initiation. The three-halves-order rate observed in the polymerization catalyzed by benzoyl peroxide requires an initiation which is first order in monomer. The half order dependence on catalyst requires initiation to be first order in benzoyl peroxide. The unimolecular overall rate observed by Price[44] in the benzoyl peroxide catalyzed polymerization of d-s-butyl-α-chloroacrylate requires initiation independent of monomer concentration. A generalization can be made by writing:

$V\text{init.} = k_1 \, AB$

where B is equal to the benzoyl peroxide concentration in the catalyzed case and equal to A, the concentration of monomer, in the uncatalyzed case. With unimolecular overall rate, $\mathbf{A}$ is equal to unity, and B is equal to the catalyst concentration. We then have from (3) and (6):

$$(7)\quad \frac{1}{\gamma} = \frac{(k_1 k_3 B)^{\frac{1}{2}}}{k_3 \mathbf{A}^{\frac{1}{2}}} \qquad C^* = \left[\frac{k_1 \mathbf{A} B}{k_3}\right]^{\frac{1}{2}}$$

$$(8)\quad -\frac{d\mathbf{A}}{dt} = k_2 . \left[\frac{k_1 B}{k_3}\right]^{\frac{1}{2}} . \mathbf{A}^{3/2} . (1 + \frac{1}{\gamma})$$

From equation (7) it follows that the degree of polymerization, assuming it to be the same as γ, the kinetic chain length, should be proportional to the square root of the monomer concentration when catalyst is present. The data of Schulz and Husemann[28(a)] for the polymerization of styrene is not in agreement, however, with this conclusion. For the uncatalyzed polymerization of styrene, equation (7) predicts that the degree of polymerization should be independent of the concentration of monomer, a fact which is in complete disagreement with the data of various investigators,[28(b),29(a),29(b)] since it depends not only on the monomer concentration but also on the particular solvent used.

Flory[45] proposed that "Chain Transfer" involving the transfer of the odd electron from the chain to either a monomer or solvent molecule, could take place. In this way the chain would be terminated, leaving the free radical still in solution, and thus allowing polymerization to continue at its normal rate. The true degree of polymerization can then be expressed by:

$$P = \frac{V_{prop}}{V_{term} + V_{transfer}}$$

an equation which has been found to agree well with experiment.

Assuming that a steady state exists and that the velocity of initiation is a function only of the catalyst and monomer concentration it follows that the rate of polymerization should be either a constant or decreasing function of the time showing an initial maximum value. Schulz et al[46] have shown that the polymerization of methyl methacrylate under the influence of oxygen or peroxide proceeds with a steadily increasing velocity, until finally, after an induction period of variable length, monomer reacts violently, with a 90° rise in temperature. The induction period may last for hours. They demonstrated that the explosive reaction is due to branching of the reaction chains rather than to poor heat transfer due to an increase in viscosity as the reaction proceeds. Norrish and Smith[34] consider, however, that the increase in reaction rate can be accounted for completely by poor heat transfer due to viscosity of the solution. Norrish and Brookmann[47] have explained in a similar manner the increase in reaction rate with time observed in the peroxide and ozonide catalyzed copolymerization of methyl methacrylate.

Medvedev et al[48] have observed that chloroprene polymerization, catalyzed by tetralin hydroperoxide, proceeds at a rate which increases with time. Considering that initiation of active centers may take place by decomposition of catalyst into free radicals, by purely thermal activation, and by opening of the double bonds in the reaction chains already produced, that is by branching, they derived the following equation for the amount of polymerized chloroprene:

$$x = (k_1C + k/k_2) . (e^{k_2t} - 1)$$

where k is the thermal uncatalyzed rate constant, k_1 that for the catalyzed linear polymerization and k_2 that for the lateral branching reaction. C is the concentration of hydroperoxide. This equation was found to represent very well the experimental results over a range of hydroperoxide concentrations from 0 to 3% at temperatures from 30-50°. k, k_1 and k_2 at 30° were calculated to be 0.03, 0.17 and 0.017, while the activation energies E_k, E_{k1}, and E_{k2} were 20.2, 10.5 and 28.2 kcals. After long polymerization the insoluble μ polymer was formed.

In a later paper Medvedev et al[49] have shown that the polymer formed during the polymerization of chloroprene retains free radicals even after it has been removed from the reacting medium, while measurements prove that the number of such radicals may greatly exceed the number initially present potentially, in the catalyst added. The addition of polymer, stored in vacuo for long periods, catalyzes the polymerization of monomer, so that the reaction proceeds at the same rate as had occurred when the monomer was removed from the polymer, providing the polymer concentration is the same in both cases. Such has been found to be true for other polymers, particular for the copolymer of butadiene and vinyl cyanide. In general a linear relation existed between the rate of polymerization and the number of free radicals present. It is considered that the exponential increase in reaction rate is caused, firstly, by branching of growing chains, and secondly, by hindered recombination of radicals due to an increase in viscosity of the system. Branching takes place by the opening of a double bond in a reacting chain, due to the occasional accumulation of energy from monomer addition in the particular bond which breaks. In illustrating the effect of viscosity upon the termination reaction Medvedev assumes that the solution is heterogeneous, the polymer particles being extremely large compared with monomer molecules. The motion of the large particles will be greatly dependent on viscosity, while the velocity of monomer molecules will be relatively unaffected, so that the propagation reaction will not diminish greatly in speed as the reaction process continues, while the rate of termination, which must involve collisions between polymer particles possessing active free radicals, will be considerably decreased.

Copolymerization

Considerable attention has been focussed in recent years on the mechanism of copolymerization, since evaluation of this problem is not only of great theoretical interest, but of practical importance in the preparation of synthetic rubbers such as GR-S. Norrish and Brookmann[47] were perhaps the first to propose a reasonable mechanism for copolymerization reactions; that is, reactions in which both types of monomer enter each growing chain. They assumed that two types of growing free radical chains exist in solution, depending upon which monomer exists at the end of the chain possessing the odd electron. It is then possible to set up four equations representing the propagation reactions.

$$A^* + A \xrightarrow{k1} A^*$$

$$A^* + B \xrightarrow{k2} B^*$$

$$B^* + A \xrightarrow{k3} A^*$$

$$B^* + B \xrightarrow{k4} B^*$$

where A and B refer to the two types of monomer molecules, and A^* and B^* refer to growing chains ending in the respective monomers.

By then assuming a steady state wherin the rate of formation of A^* and B^* are equal solution of the kinetic equations give the overall rate expression:

$$\frac{dp}{dt} = \frac{a + b[A] + c[A]^2}{1 + k[A]} \cdot n$$

where n refers to the steady state number of active centers.

The equation is only applicable to the initial stages of the reaction since it was assumed that the polymerization is of zero order with respect to monomer.

Evidence was given to show that this type of equation does conform with their experiments on the copolymerization of styrene and methyl methacrylate. Studies based upon the above type of reasoning have been made by a number of investigators.[50-58] Mayo and Lewis[56] have developed an equation relating the composition of the copolymer to initial concentrations of monomers and to the time. Two constants, characteristic of the monomer pair, and equal to the ratios k_1/k_2 and k_4/k_3 in the above equations, appear in the resulting equation and can be evaluated experimentally. The equation was applied to the copolymerization of styrene and methyl mathacrylate and values of the two constants for these monomers were obtained. This equation has been applied to GR-S polymerization by Nicholls[59] and the values of k_1/k_2 and k_4/k_3 found to be 0.44 and 1.59 respectively, where A and B in the above equations refer to styrene and butadiene respectively. This indicates that butadiene will react faster than styrene with either type of chain, although it has been shown that reaction with A^* is faster than with B^*.

Alekseeva et al [55] have examined by ozonolysis, the copolymer of butadiene and styrene and have assigned a structure to it. Branson and Simha[52,58] have developed equations applicable to any number of monomer components in the system.

Because of the difficulties owing to popcorn formation in the plant, and because of the comparative lack of data concerning the mechanism of the reaction, the Associate Committee on Rubber Research of the National Research Council at Ottawa has considered further work in this field advisable.

The present investigation has been confined principally to a study of popcorn prepared in solutions of butadiene in styrene, since the reactions involving pure butadiene popcorn are being investigated by another worker in this laboratory. Since few results have been published on the bulk copolymerization of these monomers to form soluble polymer, and because of the obvious possibility of a relation existing between the formation of popcorn and soluble polymer kinetic experiments were also made with the normal copolymerization catalyzed by benzoyl peroxide.

EXPERIMENTAL AND RESULTS

Styrene was supplied by Sarnia and was similar to that used in the plant, the principal impurity being t-butyl catechol. Purification was effected by vacuum distillation through a small column packed with glass helices, agitation in the distillation flask being attained by bubbling through a slow stream of air. The styrene thus purified showed no significant variation in the reaction kinetics, from batch to batch. It was stored in a refrigerator at 0° C, for periods usually not exceeding two weeks.

The butadiene used was also supplied by Sarnia, and like the styrene was of commercial grade containing t-butyl catechol as a polymerization inhibitor. It was purified, stored and measured into the reaction tubes in an apparatus constructed entirely of Pyrex. Purification was effected by bubbling the gas through two absorbers, each containing N/1 sodium hydroxide, to remove any t-butyl catechol carried over in the stream, and after drying by passing through two tubes containing calcium chloride, the butadiene was condensed with a dry ice-acetone mixture into the storage vessel. The preliminary use of phosphorus pentoxide as a drying agent was unsuccessful since considerable polymerization of the butadiene occurred on the surface of the reagent. The condensed butadiene was stored at -78° C out of contact with oxygen, and at no time during the course of one and one half years was any residue of polymer found in the storage vessel.

The benzoyl peroxide was labelled "Kahlbaum" and was used without further purification. It was found to give results in the polymerization of styrene, identical with those obtained after recrystallization, and with those obtained using Merck CP material.

Nitric oxide was prepared by the action of a nitric acid-sulphuric acid mixture (approximately 1:1 by volume) on mercury in a simple nitrometer. The gas initially was colore slightly with nitrogen dioxide, but on shaking it over mercur it became completely colorless. Both acids used were labelle C. P.

Except where otherwise specified pyrex reaction tubes were used which, when sealed off, were 16 cms. in lengt and 1.5 cms. in diameter. Before the reagents were added these tubes were fitted with female ground glass joints such that the overall length was 24 cms. Since most polymerizatio reactions are extremely sensitive to traces of impurities considerable care was observed in cleaning the reaction vessels. They were filled first with boiling chromic acid, then washed out well with distilled water and finally dried in an oven at 100° C. With this treatment the results obtained were usually quite reproducible.

In earlier experiments a known volume of a solution of benzoyl peroxide in redistilled acetone was then added with a pipette, and the acetone was evaporated under reduced pressure. This method proved troublesome, however, owing to occasional bumping, and in later experiments the benzoyl peroxide was weighed into a flask and dissolved in a measured volume of styrene.

In certain experiments it was necessary to vary the butadiene concentration while keeping the benzoyl peroxide concentration constant. Since density data on the styrene-butadiene system were not available it was assumed, as a first approximation, that the specific volumes of the two components were additive. Since the largest butadiene concentration used was only about 10% (by weight), the error is probably not serious.

Popcorn seed, if required for the experiment, was weighed to the nearest 0.1 mgms. and transferred to the reaction tubes, which were then constricted to facilitate sealing off, and styrene (or the styrene solution of benzoyl peroxide) added with a pipette. The samples were immediately frozen in a dry ice-acetone mixture and the butadiene added.

Butadiene was evaporated from the storage vessel into a calibrated volume system containing a manometer and connected, (by means of a glass joint) through a stopcock, with the reaction tube cooled to -78° C. After observing the initial pressure in the system the required amount of butadiene was condensed into the reaction mixture and the residual pressure noted.

The reaction tube was sealed off and, after the reaction mixture was melted, was placed in a thermostat controlled to within 0.1° C. In general, six identical samples were prepared for each experiment.

From the known volume and initial and final pressures in the system the weight of butadiene added was calculated, assuming the ideal gas law to be true, a correction being applied for the change in volume owing to the change in the height of mercury in the manometer. A correction was also made for the amount of gas remaining in the sealed off portion of the tube. The maximum probable error in the measurement of butadiene is estimated at 1×10^{-3} gms., which is equal to 1% or less for most of the experiments made.

After removing the reaction tubes from the thermostat the reaction was stopped by freezing in a dry ice-acetone mixture and the time recorded. The tube was then opened and the contents washed into a flask with approximately 50 ml. of benzene. After digesting 3-4 hours the insoluble popcorn was filtered through a weighed sintered-glass crucible and, after washing well with benzene, was dried to constant weight at 70° C. The drying was accomplished in two days; heating for longer periods produced a yellow discoloration in the popcorn, (which was invariably pure white initially) probably indicating considerable peroxidation. The effect was more marked with popcorn prepared in solutions of high butadiene content, and from seeds containing large amounts of butadiene.

To determine the amount of soluble polymer formed the filtrate and washings were collected and diluted with 3 to 4 times their volume of methanol. The mixture, sometimes containing considerable colloidal polymer, was allowed to stand overnight at 0° C to effect coagulation, and the supernatant liquor was filtered through a weighed sintered-glass filter. Fresh methanol was added to the polymer and the whole was refluxed 2 to 3 hours on a steam bath. This was found necessary to remove benzene from the polymer so that it could be dried in vacuo in reasonable time. The polymer was then filtered through the original filter and was dried to constant weight in a vacuum desicator at room temperature, this being accomplished usually within two days.

Since a fairly large number of different seeds were used in this work a summary of their preparation and butadiene concentrations will be given here rather than with the results to follow. The concentration of butadiene in the seed, (and in the solution) is always expressed as the number of moles of butadiene per mole of styrene (written m/m), and is assumed to be the same as that of the solution from which it was prepared. The true values cannot be greater than calculated, since in all samples, the monomers were converted to popcorn in nearly 100% yields. Assuming that popcorn is a true copolymer the values reported are probably at least proportional to the true values since, in no case was heterogeneity in a given sample observed. (No special sampling procedure was used, and the popcorn consisted in many samples of quite large particles.)

With the exception of A and B (below) all samples were prepared in the absence of benzoyl peroxide, while all but A were prepared by the growth of added seed. The procedure followed in preparing a sample was similar to that described for the ordinary experiments, and in all cases the reactions took place at 48.9° C. After complete reaction (usually about one week) the popcorn was removed, digested three to four hours in benzene, filtered and washed with benzene until dilution of the filtrate with methanol showed no precipitated soluble polymer. The popcorn seed was then dried at room temperature under a hi-vac for approximately 24 hours, when it was divided into one gram lots and sealed in tubes under vacuum, and stored at 0° C in the dark. This procedure was followed with all seeds except A, which was used with soluble polymer present.

The butadiene concentrations in the seeds are given below:

A - 0.0409 m/m
B - 0.0404 m/m
C - 0.0422 m/m
D - 0.267 m/m
E - 0.00991 m/m
F - 0.1463 m/m
G - 0.439 m/m
H - 0.1001 m/m
I - 0.2080 m/m
J - ∞ m/m
K - 0.262 m/m

Seed J consists of pure butadiene popcorn polymer taken from the butadiene rerun column at Sarnia.

Analyses of the seeds for carbon and hydrogen proved to be practically worthless, since the experimental error was comparable to the differences sought. Nothing more than a general trend could be obtained, following approximately the calculated values.

Preliminary studies were begun on the initiation of popcorn in unseeded samples, containing 2% butadiene by weight in styrene, at 50° C and without added benzoyl peroxide. The results showed little reproducibility, traces of insoluble polymer first making their appearance after periods varying from 6 to 12 days. In view of the relatively large effect of oxygen on the reaction reported ny Whitby[4], and since this seemed to be the only variable impurity in the system, it seemed likely that traces of this gas, were responsible for the unsatisfactory results obtained, It was hoped that measurements of the weight of popcorn in these experiments might be extrapolated to zero time to obtain a value for the initiation period, but the rate of growth of the popcorn nucleus, once visible, proved to be so great in comparison with the initial induction period, that even the slightest variation in oxygen content made such measurements hopelessly inaccurate.

For this reason experiments were made under conditions similar to those above, except that weighed amounts of popcorn were added at the outset, and the growth of these seeds was examined. Again, however, poor reproducibility was obtained, and was attributed to the presence of traces of oxygen in the system. Control of the concentration of oxygen in the system was therefore sought by adding benzoyl peroxide in small amounts, and by this method satisfactory results were obtained.

Results are given in Table I for the growth of 0.1 gms. of seed"A" with three different concentrations of of added benzoyl peroxide. Although traces of soluble polymer were present in the seed the values serve to indicate the nature of the results to be expected.

Table I

Effect of Benzoyl Peroxide on Soluble and Insoluble Polymer Formation

Weight of styrene - 4.515 gms.
Weight of butadiene - .0950 gms.
Ratio butadiene: styrene in solution - 0.0405 m/m)
Ratio butadiene: styrene in seed - "A" (0.0409 m/m)
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Benzoyl Peroxide (gms.)	Time (mins.)	Weight of Popcorn (gms.)	Yield Popcorn (%)	Weight Soluble Polymer (gms.)	Yield Soluble Polymer (%)
0.02392	1050	0.131	0.67	0.443	9.61
0.02392	2485	0.322	4.82	1.144	24.8
0.02392	2966	0.358	5.60	1.267	27.4
0.02392	3922	0.913	17.6	2.101	45.6
0.02392	5346	1.094	21.6	3.731	81.0
0.00957	990	0.118	0.39	0.264	5.73
0.00957	2429	0.429	7.15	0.633	13.7
0.00957	2759	0.521	9.14	0.740	16.1
0.00957	3712	1.723	35.2	1.238	26.8
0.00957	4108	2.924	61.4	1.973	42.8
0.04784	1192	0.121	0.46	0.704	15.3
0.04784	1675	0.161	1.32	0.928	20.2
0.04784	2638	0.201	2.20	1.712	37.2
0.04784	3033	0.230	2.82	1.938	41.8

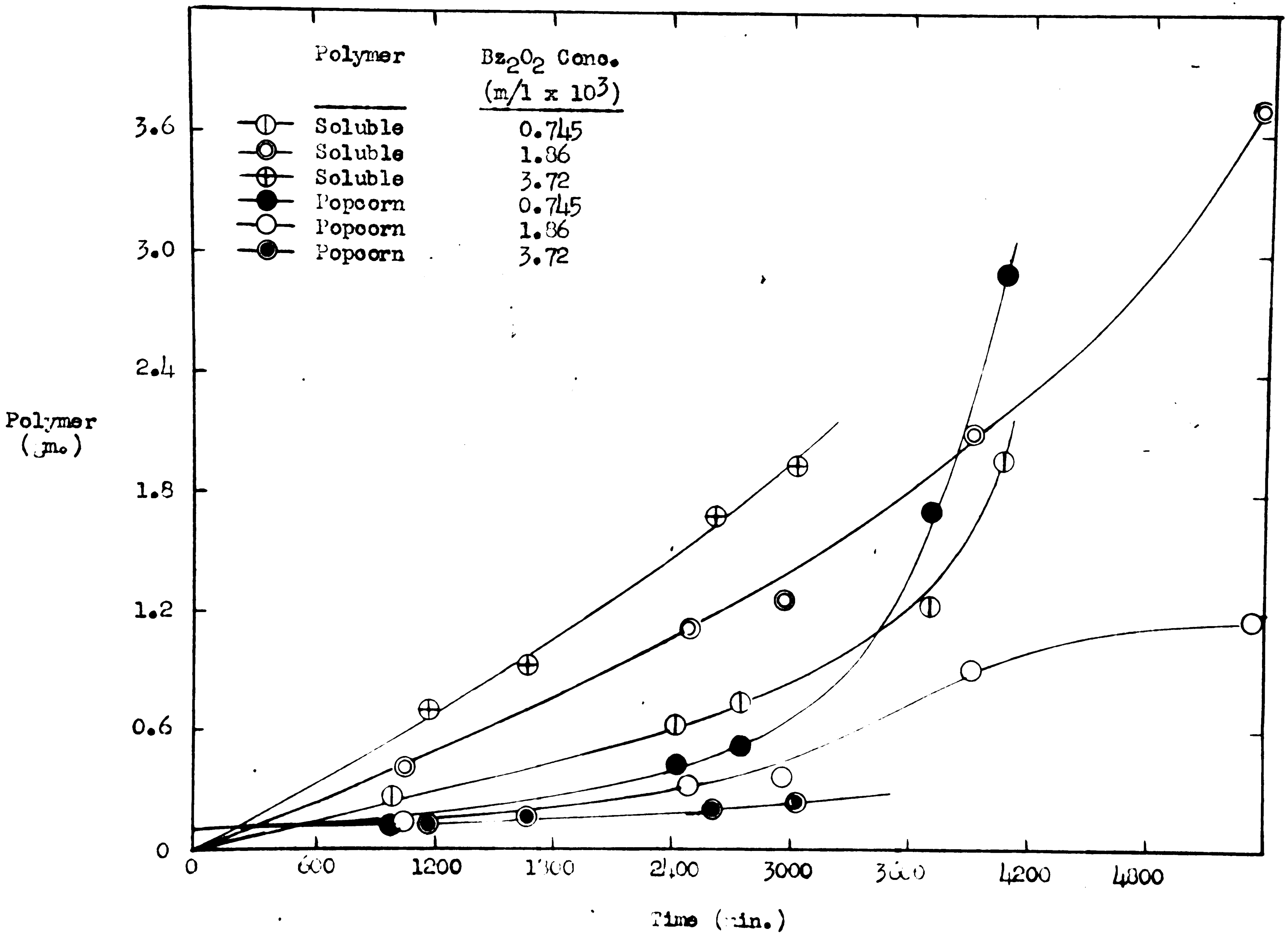


Fig. 1. Rate of Growth of Seed "A" (0.0409 m/m) and Soluble Polymer Formation in Butadiene: Styrene (0.0405 m/m) at 48.9° C

The results of Table I are plotted in fig. 1 and indicate that a pronounced induction period, lasting for 1200-1500 minutes, occurs in the growth of popcorn seed. Increasing the benzoyl peroxide concentration considerably slows down popcorn growth, but increases the rate of formation of soluble polymer.

Soluble polymer is formed at a rate which is initially linear, but which after larger times, increases markedly.

To determine what, if any, was the role of butadiene in the growth of popcorn seeds, experiments were made in pure styrene containing only benzoyl peroxide. The results are shown in Table II.

Table II

Growth of Seed "B" (0.0404 m/m) in Pure Styrene

Weight of Styrene - 4.515 gms.
Weight of Seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Benzoyl Peroxide (gms. $\times 10^3$)	Time (mins.)	Weight of Popcorn (gms.)	Yield Popcorn (%)	Weight Soluble Polymer (gms.)	Yield Soluble Polymer (%)
0.800	1342	0.160	1.33	0.176	3.90
0.800	3151	0.248	3.28	0.364	5.85
0.800	4319	0.302	4.48	0.529	11.7
0.800	5944	0.347	5.47	0.711	15.8
0.800	7148	0.398	6.61	0.879	19.5
0.800	8757	0.407	6.80	1.138	25.2
2.000	1340	0.149	1.09	0.216	4.79
2.000	2650	0.235	2.99	0.449	9.95
2.000	4463	0.343	5.39	0.789	17.5
2.000	5632	0.352	5.59	1.021	22.6
2.000	7272	0.434	7.41	1.514	33.6
2.000	8472	0.426	7.22	1.797	39.8
20.00	1734	0.139	0.87	0.879	19.5
20.00	3546	0.189	1.97	1.997	44.2
20.00	4714	0.241	3.12	3.038	67.4
20.00	6340	0.198	2.18	4.152	92.1
20.00	7545	0.197	2.15	4.085	90.6
20.00	9153	0.197	2.15	4.325	95.9

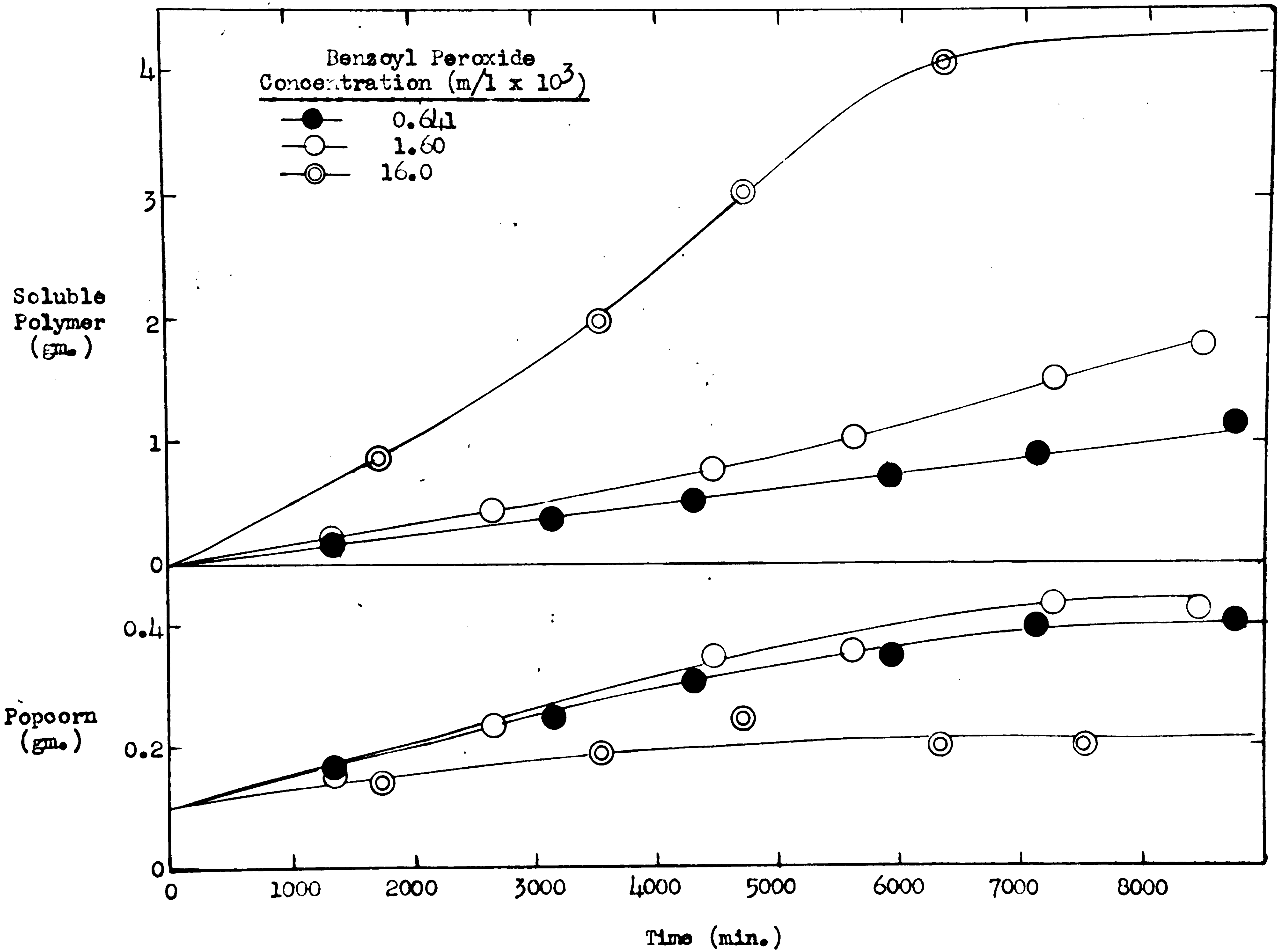


Fig. 2. Rate of Growth of Seed "B" (0.0404 m/m) and Soluble Polymer Formation in Styrene at 48.9° C.

The results of Table II are plotted in fig. 2, and show considerably different characteristics from those of fig. 1. Seed growth is essentially linear, finally ceasing before complete conversion of styrene to insoluble and soluble polymers occurs. The curves showing the formation of soluble polymer are essentially similar to those previously obtained with butadiene present, although it is to be noted that the rate still increases with time even after popcorn growth has practically ceased.

To determine further the effect of varying the butadiene concentration in the styrene, experiments were made using 0.01, 0.04 and 0.14 m/m of butadiene at several benzoyl peroxide concentrations. The results indicated an increasing induction period, followed by an increasing rate of growth with increasing butadiene concentration, but were of qualitative value only, since the time during which growth took place, at the highest butadiene concentration, was only a small fraction of the length of the induction period, so that small errors in preparing the solutions were considerably magnified in the weight of popcorn formed. Since no induction period was observed in the formation of soluble polymer these results were considered to be quite accurate and are shown in Table III. In all experiments no appreciable growth of popcorn occurred within the first 3500 minutes.

Table III

Formation of Soluble Polymer In Seeded Samples

Weight of Styrene - 4.515 gms.
Weight of Butadiene - 0.332 gms.
Ratio Butadiene: Styrene in Solution - 0.1417 m/m.
Temperature 48.9°.

Weight of Benzoyl Peroxide (gms.x 10^3)	Time (mins.)	Weight of Soluble Polymer (gms.)	Yield Soluble Polymer (%)
0.800	407	0.027	0.56
0.800	1462	0.080	1.65
0.800	3943	0.195	4.02
0.800	4793	0.232	4.79
2.000	1042	0.091	1.88
2.000	3608	0.265	5.46
20.00	3309	0.711	14.7

Comparison of the results in Tables I and II for the formation of soluble polymer and popcorn indicate that the former is not an intermediate in the formation of insoluble polymer.

To determine whether the presence of seed influenced the formation of soluble polymer experiments were made using unseeded samples. The results are shown in Tables IV and V.

Table IV

Formation of Soluble Polymer

In Unseeded Samples

Weight of Styrene - 4.515 gms.
Weight of Butadiene - .0942 gms.
Ratio Butadiene: Styrene in solution - 0.0402 m/m.
Temperature - 48.9° C.

Weight of Benzoyl Peroxide (gms.x 10^3)	Time (mins.)	Weight of Soluble Polymer (gms.)	Yield Soluble Polymer (%)
0.800	928	0.032	0.70
0.800	3516	0.253	5.50
0.800	5695	0.402	8.74
0.800	7123	0.503	10.9
0.800	8188	0.579	12.6
0.800	9747	0.708	15.4
2.000	789	0.042	0.91
2.000	5539	0.585	12.7
2.000	6958	0.792	17.2
2.000	8018	0.926	20.1
2.000	9567	1.523	33.0
8.00	634	0.054	1.17
8.00	3206	0.615	13.4
8.00	5384	1.230	26.7
8.00	6812	1.809	39.2
8.00	7879	2.336	50.6
8.00	9438	3.314	71.9

Table V

Formation of Soluble Polymer In Unseeded Samples

Weight of Styrene - 4.515 gms.
Weight of Butadiene - Nil.
Temperature - 48.9° C.

Weight of Benzoyl Peroxide (gms.x 10^3)	Time (mins.)	Weight of Soluble Polymer (gms.)	Yield Soluble Polymer (%)
0.800	1194	0.138	3.06
0.800	2787	0.301	6.66
0.800	3791	0.412	9.14
20.00	1051	0.513	11.4
20.00	2071	0.989	21.9
20.00	2641	1.247	27.6
20.00	3640	1.782	39.4

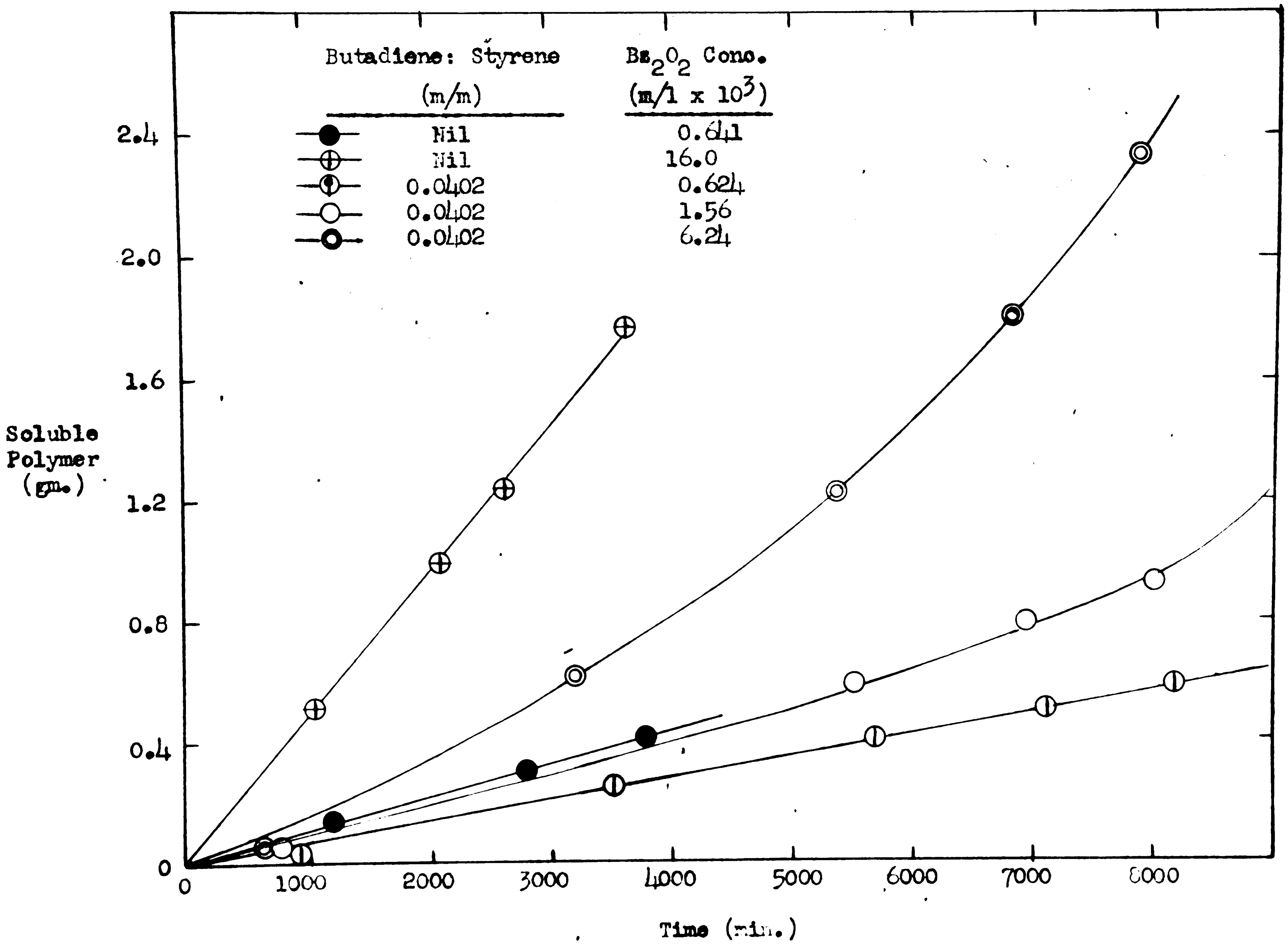


Fig. 3. Rate of Soluble Polymer Formation in Unseeded Samples at 48.9° C

The results of Tables IV and V are plotted in fig. 3 and indicate that even in the absence of popcorn, the initially linear rate of soluble polymer formation increases with time, particularly at large concentrations of benzoyl peroxide and with butadiene present.

Considering the formation of soluble polymer in the light of the equations developed by Eyring[43], it is evident that plotting the initial rates against the square root of benzoyl peroxide should produce a straight line. Initial slopes, obtained from the results of Tables I, II, III, IV and V, are given, with the corresponding peroxide concentrations, in table VI.

The initial rates plotted against the square root of benzoyl peroxide concentration are shown in fig. 4 for both seeded and unseeded samples at three different butadiene concentrations in the solution. As predicted by theory a linear relation exists, which seems to depend but little on the presence of seed. With pure styrene the seed may show a slight catalytic activity.

Table VI

Initial Rates of Soluble Polymer Formation At Various Butadiene Concentrations

Initial Rate (gms./mins.)	Benzoyl Peroxide Concentration (m/l)	Square Root of Bz_2O_2 Concentration	Ratio Butadiene:Styrene (m/m)
x $2.62x10^{-4}$	$7.45x10^{-3}$	0.0863	0.0405
x $4.36x10^{-4}$	$1.86x10^{-2}$	0.136	0.0405
x $6.03x10^{-4}$	$3.72x10^{-2}$	0.193	0.0405
$0.70x10^{-4}$	$6.24x10^{-4}$	0.0250	0.0402
$1.16x10^{-4}$	$1.56x10^{-3}$	0.0395	0.0402
x $1.24x10^{-4}$	$6.41x10^{-4}$	0.0254	0.0000
x $1.75x10^{-4}$	$1.60x10^{-3}$	0.0400	0.0000
x $5.06x10^{-4}$	$1.60x10^{-2}$	0.126	0.0000
$1.10x10^{-4}$	$6.41x10^{-4}$	0.0254	0.0000
$4.88x10^{-4}$	$1.60x10^{-2}$	0.126	0.0000
$4.80x10^{-5}$	$5.77x10^{-4}$	0.0240	0.1417
$7.50x10^{-5}$	$1.44x10^{-3}$	0.0380	0.1417
$2.15x10^{-4}$	$1.44x10^{-2}$	0.120	0.1417

x Seeded Samples.

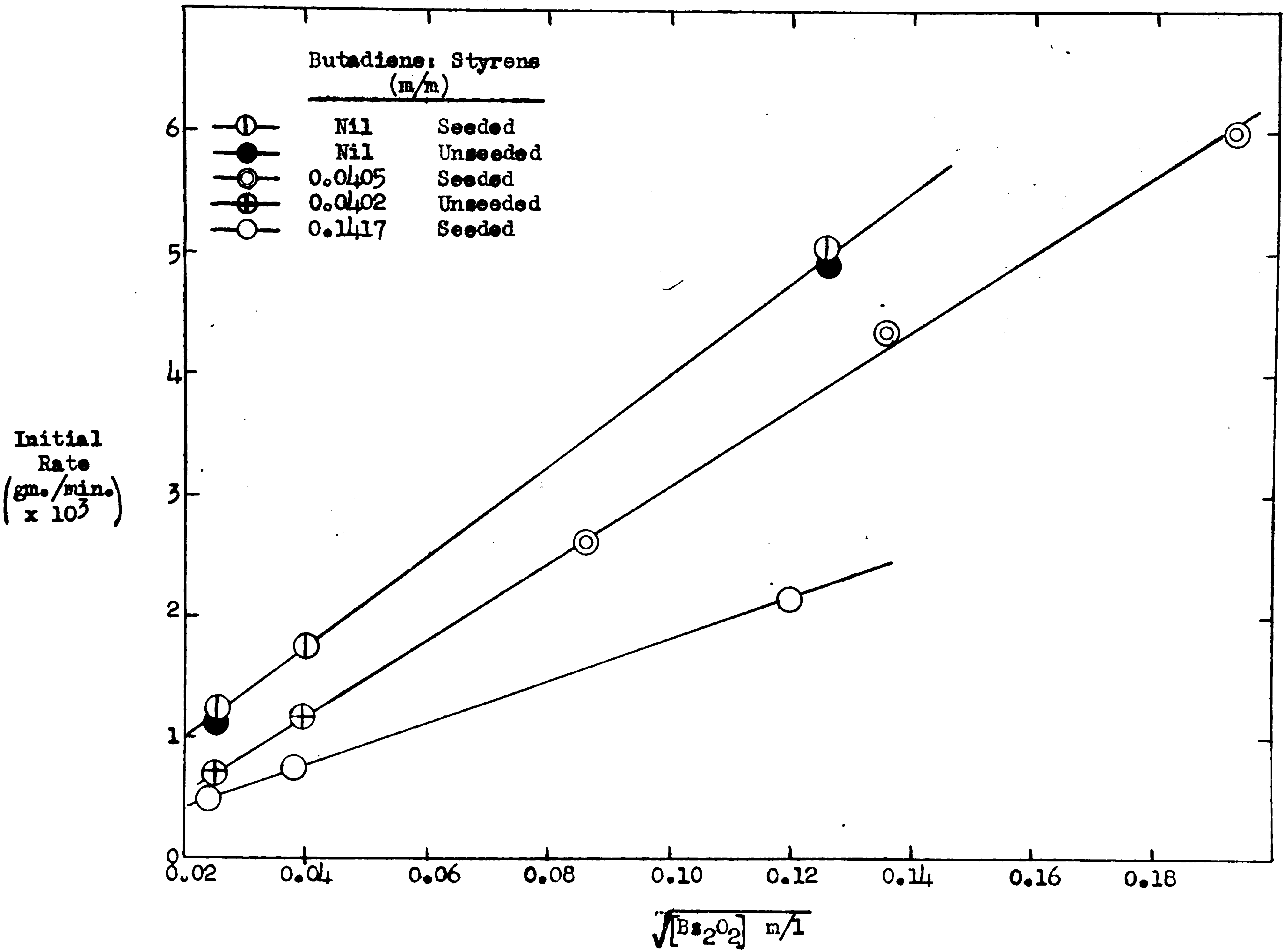


Fig. 4. Dependence of Initial Rate of Soluble Polymer Formation on Benzoyl Peroxide Concentration at 48.9° C

To establish whether the reaction to form popcorn takes place on the seed or in solution the following experiment was devised. The reaction was stopped by cooling, after a time late in the induction period, and the solution in three of the samples was replaced by fresh monomers and benzoyl peroxide in concentrations similar to those initially used. After resealing, the reaction vessels were again placed in the thermostat and the samples allowed to react for various periods of time. If reaction takes place in solution to build up some intermediate which reacts to form, or precipitates as popcorn a new induction period should occur in those samples to which fresh monomers were added. The results are shown in Table VII.

The values given in Table VII are plotted in fig. 5, and clearly indicate that the reaction is little affected by replacement of the solution by fresh monomers. The induction period observed must be due to changes taking place on the seed rather than in the solution.

Table VII

Replacement of Solution by Fresh Monomers After Partial Reaction

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0952 gms.
Ratio butadiene: styrene in solution = 0.0406 m/m
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Initial weight of seed - 0.1000 gms.
Ratio butadiene: styrene in seed "B" - 0.0404 m/m.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.196	2075	2.08
0.283	3181	4.02
1.474	4408	30.2
x 0.333	3079	5.11
x 1.294	4269	26.2
x 3.609	5525	77.0

x Fresh Monomers added after 2100 minutes.

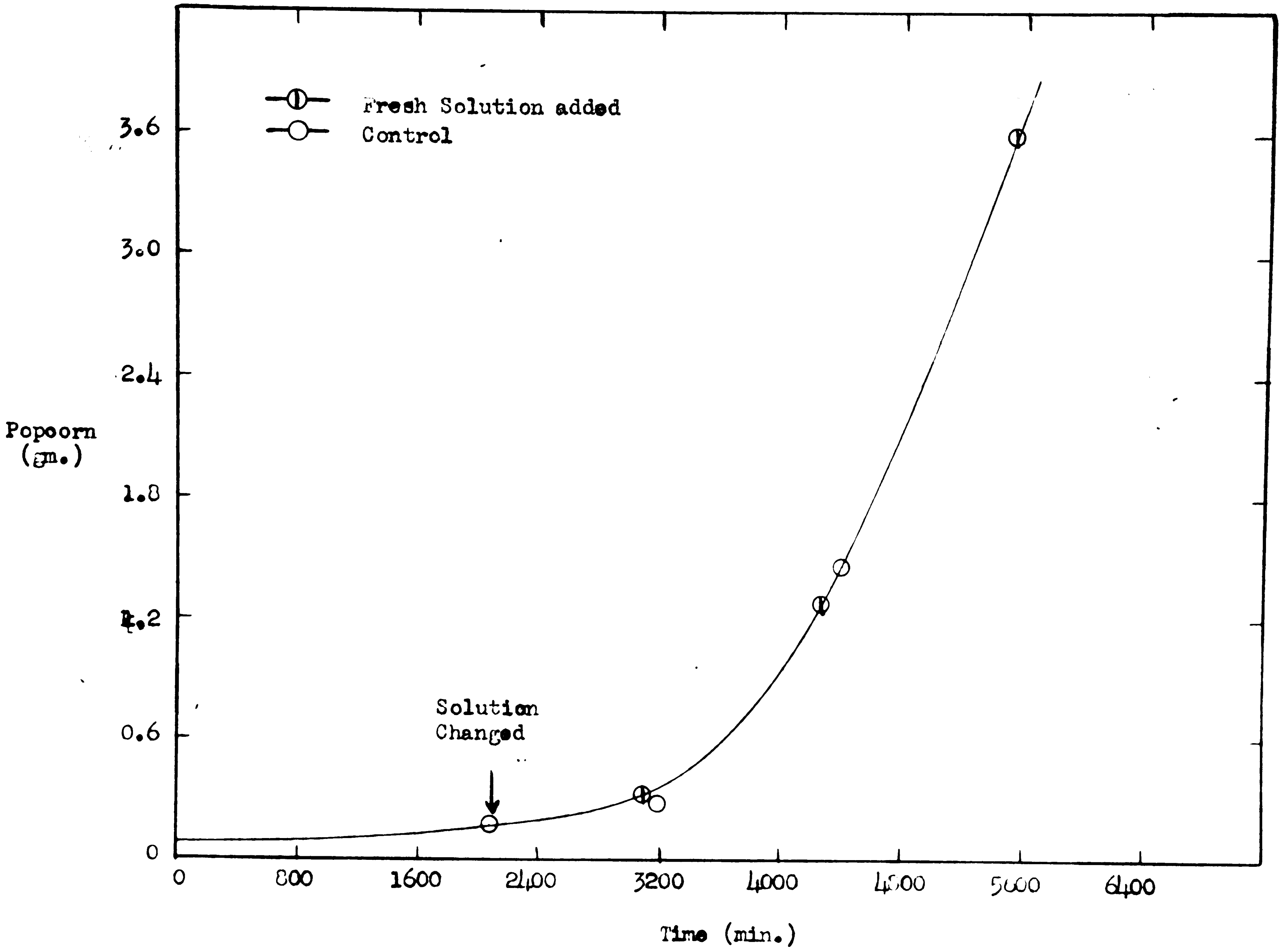


Fig. 5. Growth of Seed "B" (0.0404 m/m) in Butadiene: Styrene (0.0404 m/m) – Solution Replaced after Partial Reaction

Preliminary experiments made using seed prepared from solutions containing 0.27 m/m of butadiene indicated that growth proceeded considerably more rapidly than with the seed used in previous experiments, complete "popping" with the former occurring within approximately twelve hours in a solution containing 0.04 m/m butadiene. A number of seeds were prepared from solutions containing various concentrations of butadiene, rate curves for popcorn growth being determined for each in a solution containing 0.04 m/m of butadiene. The results of the experiments are shown in Tables VIII, IX, X, XI, XII, XIII, XIV and XV.

Table VIII

Growth of Popcorn Seed "E" (0.00991 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0942 gms.
Amount of benzoyl peroxide - 8.00×10^{-3} gms.
Ratio butadiene: styrene in solution - 0.0402 m/m.
Initial weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.117	617	0.37
0.155	1139	1.19
0.317	2774	4.71
0.469	3281	8.01
0.788	3546	14.9
1.071	3906	21.0

Table IX

Growth of Popcorn Seed "C" (0.0422 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0962 gms.
Ratio butadiene: styrene in solution - 0.0411.m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.346	1475	5.34
0.431	1574	5.02
0.510	1705	8.91
0.717	1940	13.4
0.950	2197	18.4
1.126	2295	22.2

Table X

Growth of Popcorn Seed "F" (0.1463 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0956 gms.
Ratio of butadiene: styrene in solution - 0.0408 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.107	179	0.15
0.247	395.5	3.18
0.530	512	9.33
0.567	627	10.1
0.879	737	16.9
1.013	774	19.8

Table XI

Growth of Popcorn Seed "I" (0.2080 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0955 gms.
Ratio of butadiene: styrene in solution - 0.0407 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.179	196	0.17
0.463	321	7.88
0.768	422	14.5
1.048	513	20.6
1.548	606	31.4
2.393	833	49.8

Table XII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0957 gms.
Ratio of butadiene: styrene in solution - 0.0408 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.170	133	0.15
0.422	260.5	6.98
0.929	387	18.0
1.053	424	20.6
1.403	483	28.2
1.666	539	33.9

Table XIII

Growth of Popcorn Seed "G" (0.439 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0952 gms.
Ratio of butadiene: styrene in solution - 0.0406 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.191	296	1.97
0.127	106.5	0.59
0.371	582	5.88
0.855	758	16.4
0.844	842	16.1
1.106	969	21.8

Table XIV

Growth of Popcorn Seed "J" (Polybutadiene)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0952 gms.
Ratio of butadiene: styrene in solution - 0.0406 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.306	1289	4.46
0.652	1697	12.0
0.764	1888	14.0
0.846	1953	16.2
1.294	2222	25.9
1.484	2302	30.0

Table XV

Growth of Popcorn Seed "H" (0.1001 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0956 gms.
Ratio of butadiene: styrene in solution - 0.0408 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Temperature - 48.9° C.
Weight of seed - 0.1000 gms.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.119	278	0.41
0.331	660	5.01
0.463	758	7.88
0.763	994	14.4
0.841	1157	16.1
0.984	1379	19.2

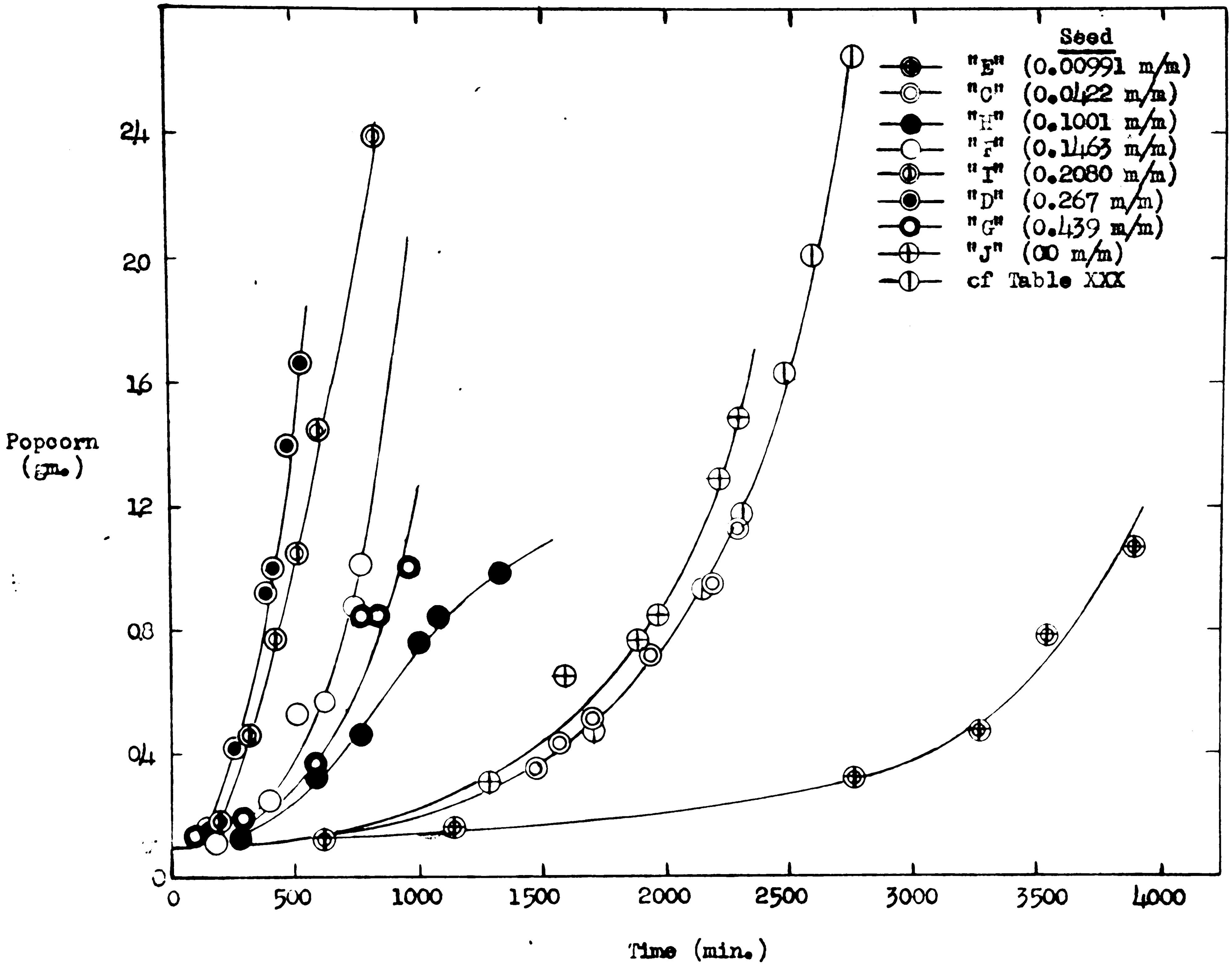


Fig. 6. Rate of Seed Growth in Butadiene: Styrene (0.040 m/m)

The results of the seven tables are plotted in fig. 6, and serve to indicate the importance of the butadiene concentration, in the seed, as a factor in determining the rate of popcorn formation. It is evident from the curves that the overall rate plotted against the concentration of butadiene in the seed shows a very sharp maximum at approximately 0.27 m/m.

The measurement of soluble polymer formation using seed containing 0.262 m/m offers an opportunity to determine whether popcorn growth influences the former rate, since from fig. 2 a linear relation holds for periods much longer than the 700 minutes required for popping in this case. The results of soluble and insoluble polymer formation using a seed containing 0.262 m/m are shown in Table XVI.

The results shown in Table XVI are plotted in fig. 7. It is evident that the growing popcorn does accelerate appreciably the formation of soluble polymer, which shows here a slight induction period (so small that it does not appear in the previous longer experiments). The slope of the approximately straight line immediately after the induction period is 2.8×10^{-4} gms./min., as compared with the slope of 2.5×10^{-4} gms./min., obtained from fig. 4 for the same peroxide concentration, while in the latter stages of the reaction the rate of soluble polymer formation increases to 7.2×10^{-4} gms./min.

Table VI

Formation of Soluble Polymer in Seeded Samples "K" (0.262 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0956 gms.
Ratio of butadiene: styrene in solution - 0.0408 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Time (mins.)	Weight of Popcorn (gms.)	Yield of Popcorn (%)	Weight of Soluble Polymer (gms.)	Yield of Soluble Polymer (%)
120	0.101	0.22	0.026	0.56
273	0.190	1.95	0.068	1.47
411	0.511	8.90	0.109	2.36
501	0.968	18.8	0.140	3.04
582	1.246	24.8	0.189	4.10
618	1.641	33.4	0.218	4.72

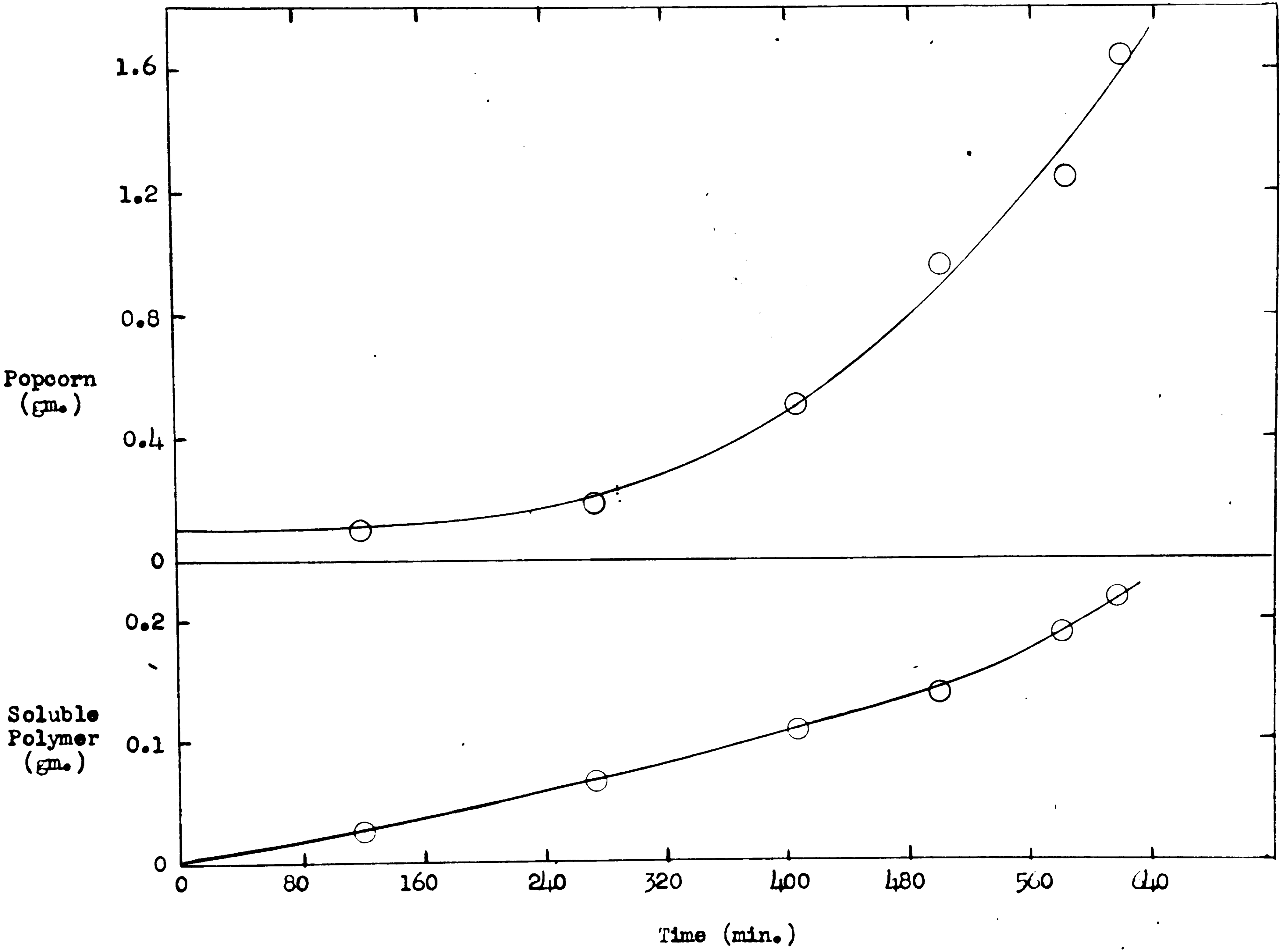


Fig. 7. Rate of Growth of Seed "K" (0.262 m/m) and Soluble Polymer Formation in Butadiene: Styrene (0.0408 m/m)

Experiments were also made using seed prepared by growth of 0.1 gms. of seed containing 0.04 m/m of butadiene in 45 gms. of pure styrene, but the induction period was so large that no growth occurred before the monomers were completely converted to soluble polymer. At low concentrations of peroxide "popping" did occur after periods approximately equal to the initiation period normally required in unseeded samples.

To study further the effect of butadiene in solution on the rate of seed growth, experiments were made using seed containing 0.267 m/m of butadiene. Since this seed showed only a small induction period, the difficulties previously encountered with the slower growing seed were minimized.

Results were obtained using three different concentrations of butadiene in styrene and in pure styrene, and are shown in Tables XVII, XVIII and XIX. The weight of benzoyl peroxide was chosen to give the constant concentration 5.48×10^{-3} m/m assuming that the volumes of butadiene and styrene are additive.

Table XVII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - nil.
Weight of benzoyl peroxide - 7.74×10^{-3} gms.
Weight of Seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.247	155	3.26
0.403	227	6.72
0.798	364	15.5
1.157	480	23.4
1.389	613	28.6
2.281	1288	48.4

Table XVIII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0229 gms.
Ratio of butadiene: styrene in solution - 0.00976 m/m.
Weight of benzoyl peroxide - 7.80×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.155	89	1.21
0.213	144	2.50
0.315	193	4.75
0.705	286	13.3
0.906	329	17.8
1.018	361	20.2

Table XIX

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.238 gms.
Ratio of butadiene: styrene in solution - 0.1013 m/m.
Weight of benzoyl peroxide - 8.36×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.152	118.5	1.20
0.252	262.5	3.52
0.414	336.5	7.26
0.877	471	18.0
1.142	606	24.2

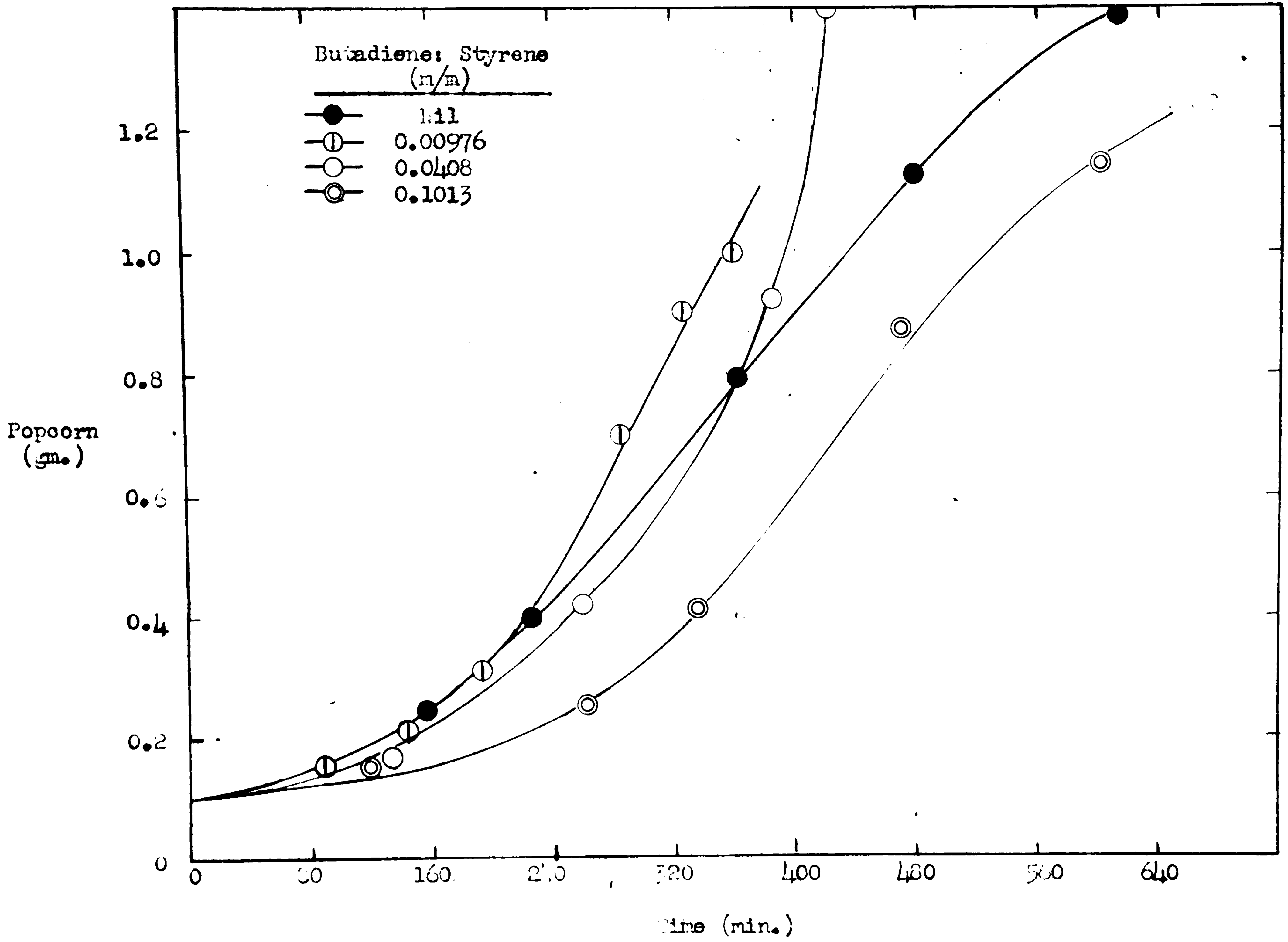


Fig. 8. Rate of Growth of Seed "D" (0.287 m/m)

The results of these tables together with those of Table XIII are plotted in fig. 8. With pure styrene there is a decided falling off in rate after a comparatively short initial rise, producing the familiar "S" shaped curve characteristic of consecutive reactions. With butadiene present the decrease in rate is less pronounced and in general the rate, after a given amount of popcorn has been formed decreases with increasing butadiene concentration. This is contrary to the qualitative results, previously discussed, for the growth of seed of low butadiene content, since in that case, although the induction period was larger at higher butadiene concentrations in the solution, thus causing an apparent decrease in overall rate, the actual rate after the induction period for a given weight of popcorn formed, increased with increasing butadiene concentration.

As a further check on the qualitative results previously observed another series of experiments was made using seed containing 0.0422 moles of butadiene per mole of styrene. With improved technique it was found possible to obtain fairly reproducible results under these conditions, although the values given for the highest concentration of butadiene in the solution are subject to considerable error. The results for three concentrations of butadiene are given in Tables XX, XXI and XXII, and as in the previous experiments the weight of benzoyl peroxide was adjusted to a concentration of 5.48×10^{-3} m/l (excepting Table XXI) assuming additivity of the volumes of butadiene and styrene.

The results shown in the Tables together with those appearing in Table IX are plotted in fig. 9. As previously observed, the character of the results obtained differs considerably from those obtained with seeds showing a large rate of growth. At a butadiene concentration of 0.00976 m/m in the solution the curve is essentially linear, while at higher values the rate increases with time after a pronounced induction period. There appears to be little change in the rate (after the induction period) on increasing the butadiene concentration from 0.1007 m/m to 0.208 m/m, and although there is a small difference in peroxide concentration, it is hardly sufficient to produce an appreciable effect.

The results in Table I indicate the importance of benzoyl peroxide in determining the rate of seed (0.04 m/m) growth. Since the effect of butadiene in solution is dependent upon the butadiene content of the seed, it became of interest to determine whether variations in benzoyl peroxide concentration influence the growth of seeds containing various amounts of butadiene in a similar manner. For this reason a series of experiments was made using seed containing 0.267 m/m and various concentrations of benzoyl peroxide. The results are shown in Tables XXIII and XXIV.

Table XX

Growth of Popcorn Seed "C" (0.0422 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0229 gms.
Ratio of butadiene: styrene in solution - 0.00976 m/m.
Weight of benzoyl peroxide - 7.80×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.201	651	2.22
0.326	1208	4.98
0.447	1765	7.65
0.576	2280	10.5
0.635	2622	11.8
0.790	3180	15.2

Table XXI

Growth of Popcorn Seed "C" (0.0422 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.236 gms.
Ratio of butadiene: styrene in solution - 0.1007 m/m.
Weight of benzoyl peroxide - 8.36×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
x 0.259	1781	3.34
x 0.673	2106	12.0
x 2.132	2468	42.8
0.292	1907	4.04
0.380	1988	5.90
0.963	2220	18.2
1.131	2311	21.8
1.486	2348	29.2
1.754	2401	13.8

x These values were obtained at a different time, using the same seed, and serve to indicate the reproducibility obtained in different experiments under similar conditions.

Table XXII

Growth of Popcorn Seed "C" (0.0422 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.489 gms.
Ratio of butadiene: styrene in solution - 0.208 m/m.
Weight of benzoyl peroxide - 8.74×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.
Concentration of benzoyl peroxide - 5.36×10^{-3} m/l.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.142	2937	0.84
0.282	4793	3.64
0.934	5250	16.7
1.418	5368	26.3
1.478	5492	27.5
1.211	5554	22.2

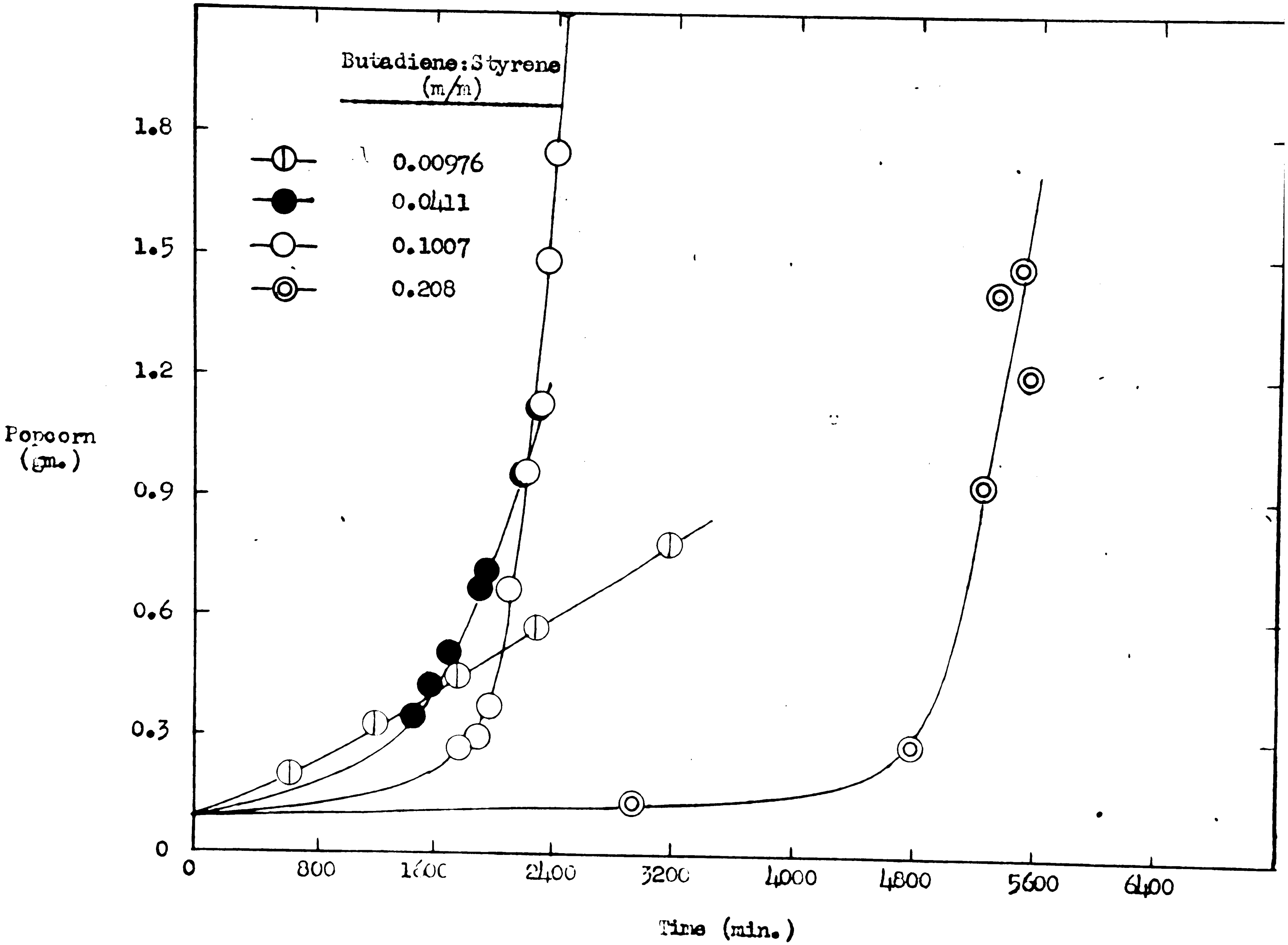


Fig. 9. Rate of Growth of Seed "C" (0.0422 m/m)

Table XXIII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0961 gms.
Ratio of butadiene: styrene in solution - 0.0410 m/m.
Weight of benzoyl peroxide - 4.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.132	81	0.70
0.189	143	1.93
0.358	238	5.60
1.234	437	24.6
1.801	589	37.0
2.547	675	53.2

Table XXIV

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0958 gms.
Ratio of butadiene: styrene in solution - 0.0408 m/m.
Weight of benzoyl peroxide - 16.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.172	120	1.57
0.370	222	5.86
0.651	316	11.9
1.026	411	20.1
1.853	670	38.0
1.949	763	40.1

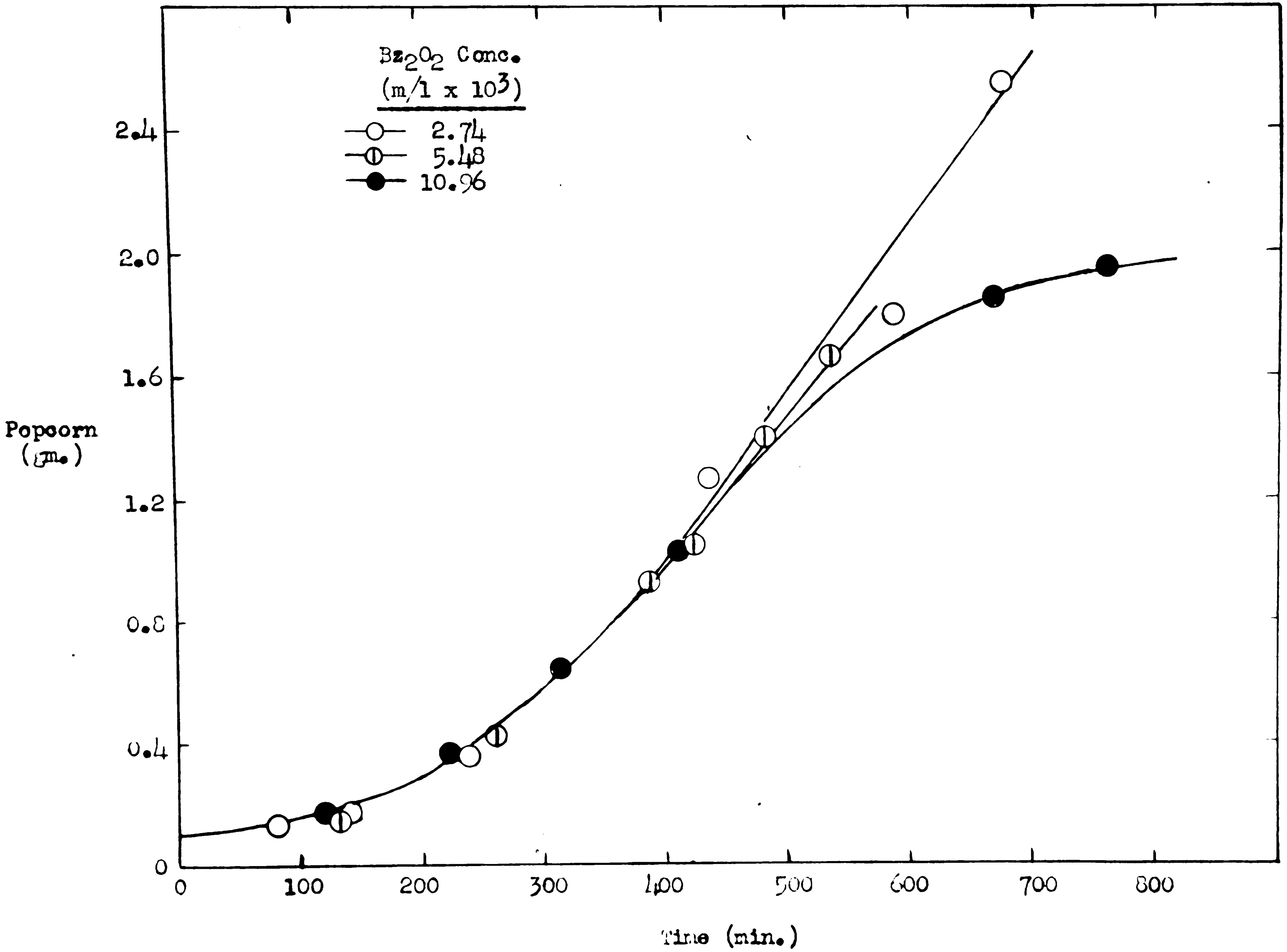


Fig. 10. Rate of Growth of Seed "D" (0.267 m/m)

The results of Tables XII, XXIII and XXIV are plotted in fig. 10, and indicate that benzoyl peroxide has only a slight effect on the growth of this seed. The rate of growth apparently falls off somewhat in the later stages of the reaction, the decrease commencing at lower conversions with the higher concentrations of benzoyl peroxide.

Similar experiments were made with seed containing 0.1001 m/m, that is, intermediate between the two butadiene concentrations already used. The results are shown in Tables XXV and XXVI.

The results together with those of Table XV, plotted in fig. 11, are similar to those obtained using seed containing 0.267 m/m, increase of benzoyl peroxide concentration again lowering the conversion at which the rate begins to decrease. The earlier stages of the reaction appear to be independent of benzoyl peroxide concentration over the range studied.

Since the importance of benzoyl peroxide as a reaction variable seems to depend somewhat upon the type of seed used, further experiments were made using pure butadiene popcorn seed, to have a complete picture of the effect over the entire range of seeds. The results are given in Tables XXVII and XXVIII.

Table XXV

Growth of Popcorn Seed "H" (0.1001 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0951 gms.
Ratio of butadiene: styrene in solution - 0.0405 m/m.
Weight of benzoyl peroxide - 4.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.125	305	0.54
0.250	515	3.26
0.570	818	10.2
0.715	910	13.3
0.742	975	13.9
1.017	1234	19.9

Table XXVI

Growth of Popcorn Seed "H" (0.1001 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0960 gms.
Ratio of butadiene: styrene in solution - 0.0409 m/m.
Weight of benzoyl peroxide - 16.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.276	575	3.82
0.367	655	5.80
0.464	816	7.90
0.596	980	10.8
1.288	2104	25.8

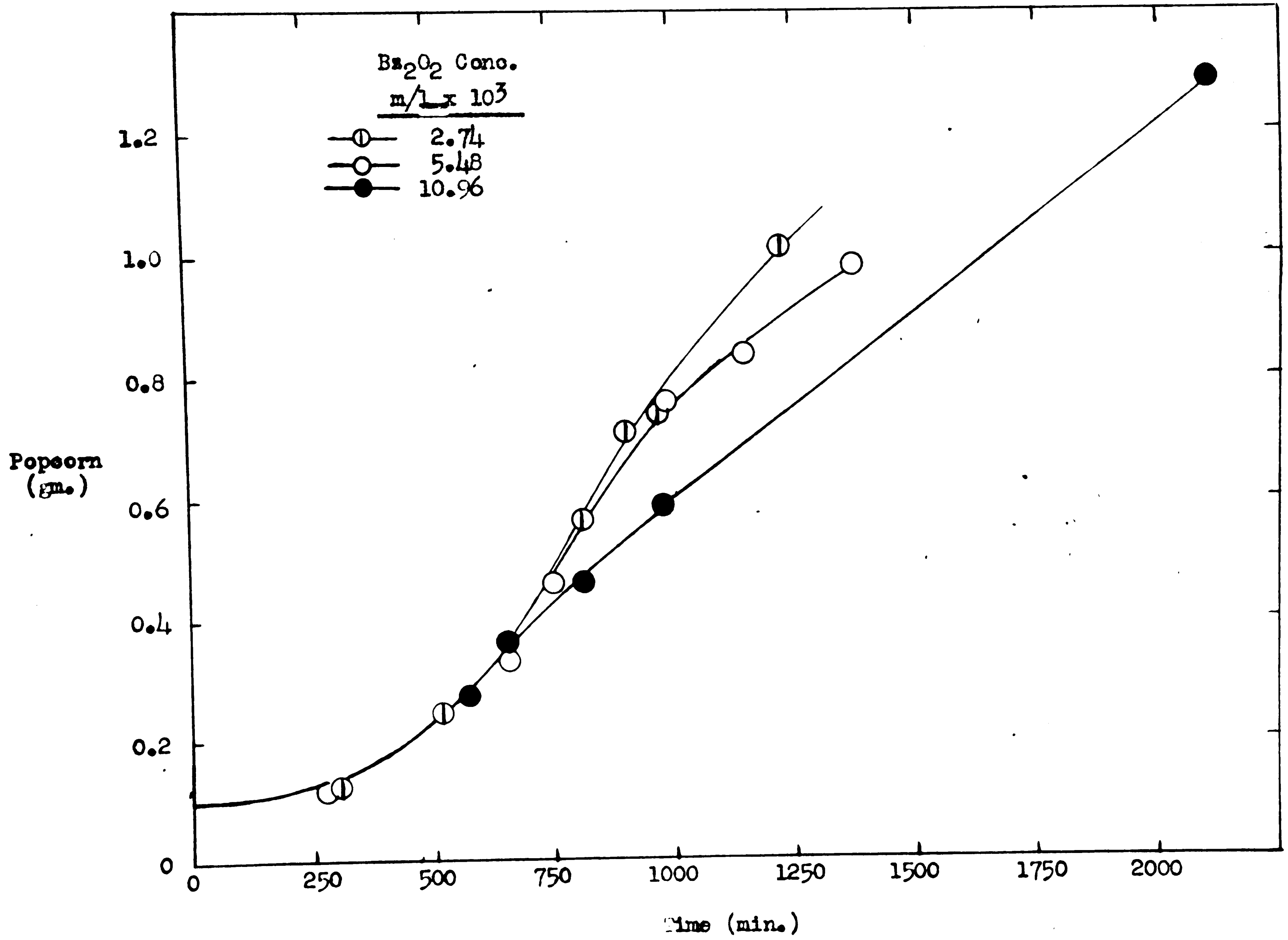


Fig. 11. Rate of Growth of Seed "H" (0.1001 m/m)

Table XXVII

Growth of Popcorn Seed "J" (Polybutadiene)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0951 gms.
Ratio of butadiene: styrene in solution - 0.0405 m/m.
Weight of benzoyl peroxide - 4.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.305	1256	4.44
0.489	1571	8.44
0.897	1914	17.3
1.069	2062	21.0
1.492	2243	30.2
1.802	2413	36.9

Table XXVIII

Growth of Popcorn Seed "J" (Polybutadiene)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0951 gms.
Ratio of butadiene: styrene in solution - 0.0405 m/m.
Weight of benzoyl peroxide - 16.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.199	923	2.15
0.304	1235	4.42
0.524	1576	9.21
0.844	1903	16.1
1.022	2130	20.0
1.536	2356	31.2

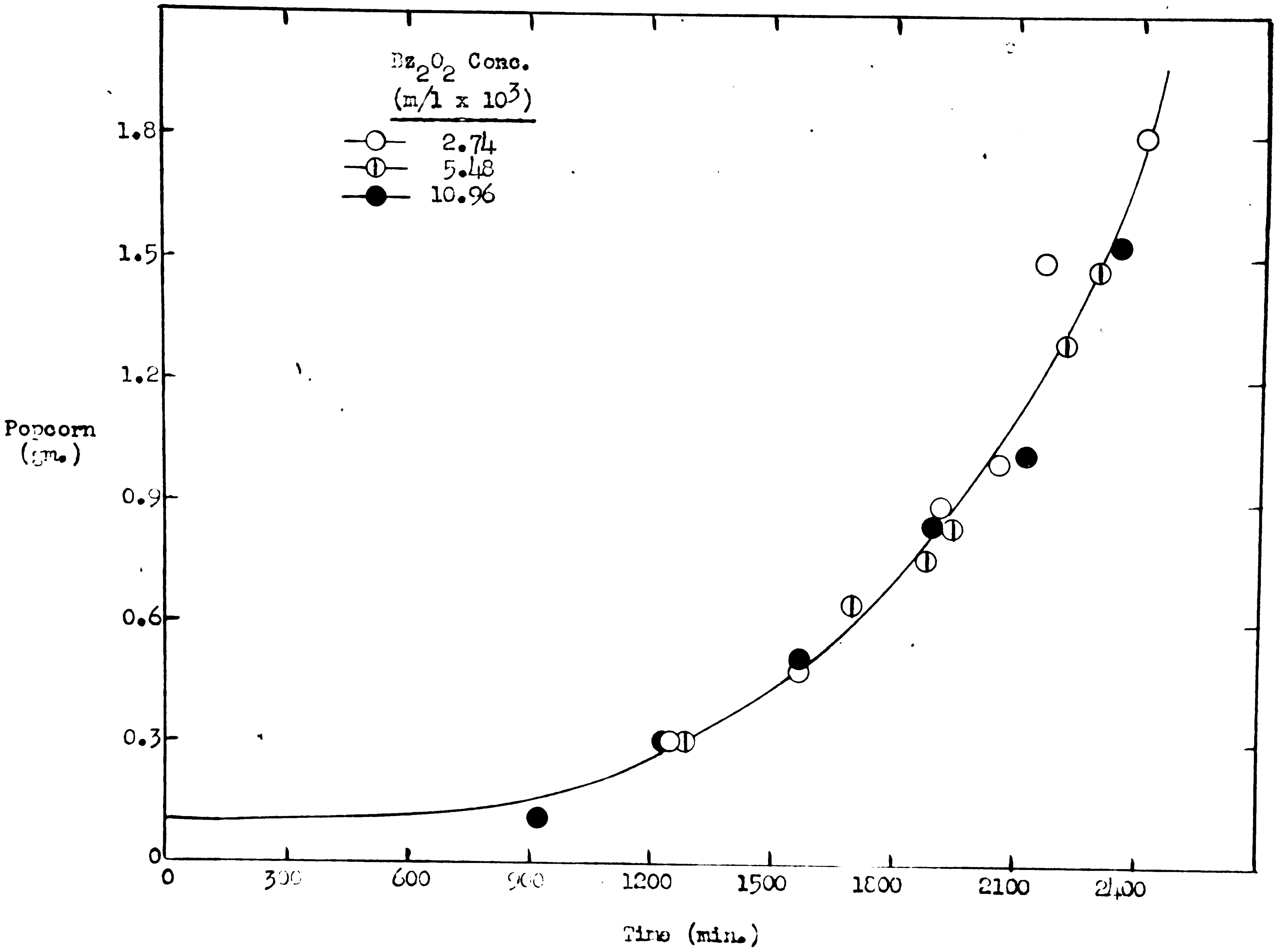


Fig. 12. Rate of Growth of Seed "J" (Polybutadiene)

The results shown in Tables XXVII and XXVIII together with those in Table XIV are plotted in fig. 12. Over this range of benzoyl peroxide concentration with pure butadiene popcorn seed, there seems to be no variation in the rate of seed growth, and the decrease in rate observed with seeds containing 0.1001 m/m and 0.267 m/m of butadiene does not occur up to a conversion of 37%.

According to the theory proposed by Kharasch[15] peroxide or hydroperoxide present on the seed decomposes to form free radicals which then add monomer molecules in the normal propagation reaction, and which must be removed by some termination process. Such a theory predicts that a decrease in rate must occur, due to the decrease in the number of peroxides, as the reaction proceeds. The point at which the rate begins to fall off should, obviously, be independent of the actual amount of monomers present (at a given concentration of reagents) and should be a function only of the number of peroxide on the seed. To determine whether this was true for the growth rate of seed containing 0.267 m/m of butadiene an experiment was made using twice the normal quantities of styrene, butadiene and benzoyl peroxide, but the same weight of seed. The results are shown in Table XXIX.

Table XXIX

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 9.030 gms.
Weight of butadiene - 0.1917 gms.
Ratio of butadiene: styrene in solution - 0.0409 m/m.
Weight of benzoyl peroxide - 16.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.372	243	2.94
0.680	313	6.29
0.978	411	9.53
1.542	482	15.6
1.841	583	18.9
2.823	709	29.6

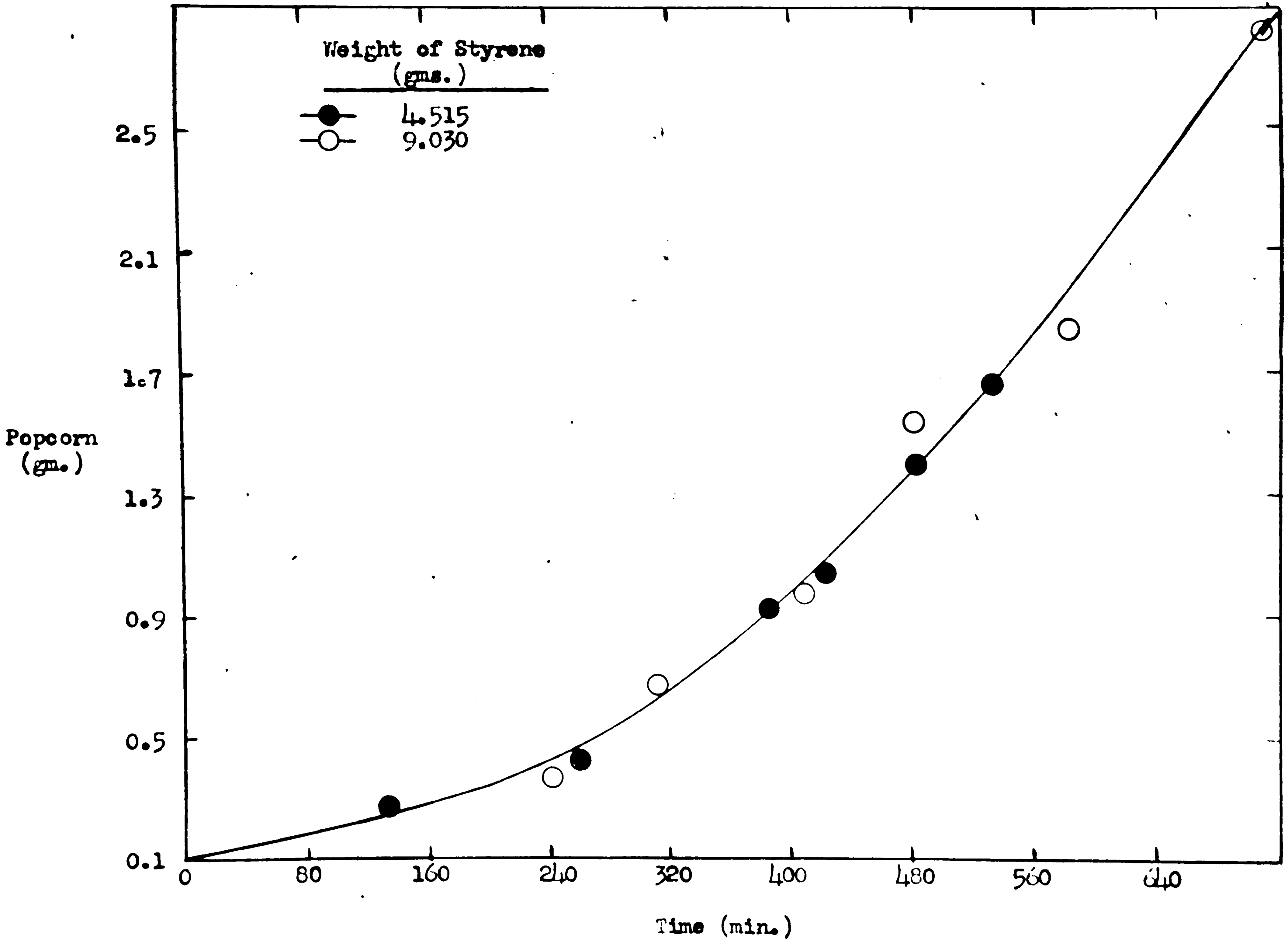


Fig. 13. Rate of Growth of Seed "D" (0.267 m/m)

The results together with those shown in Table XII, are plotted in fig. 13. It is apparent that the use of a larger amount of monomers has prevented any decrease in rate until about 2.8 gms. of popcorn (which in this experiment represents a conversion of 30%) has been formed, and that the falling off must be due at least in part, to the changing concentrations of reactants as the reaction proceeds.

A similar experiment was made using seed containing 0.0422 m/m of butadiene and the results, shown in Table XXX, agree well with those obtained (Table IX) with the smaller amounts of monomer, indicating that changing concentrations of reactants, due to the formation of polymers, has little effect, in this case, on the rate of seed growth. The results are plotted together with those of Table IX in fig. 13.

In general, it seems true, that the decrease in rate at higher conversions, when butadiene is present, is a secondary effect, as is the apparent variation with benzoyl peroxide concentration. In the absence of butadiene in solution, however, the magnitude of the effect is so great as to indicate that changes in the reagent concentrations, with increasing conversion cannot completely account for the decrease in rate (fig. 8), or, indeed, complete stopping of the growth (fig. 2).

Table XXX

Growth of Popcorn Seed "C" (0.0422 m/m)

Weight of styrene - 9.030 gms.
Weight of butadiene - 0.1921 gms.
Ratio of butadiene: styrene in solution - 0.0410 m/m.
Weight of benzoyl peroxide - 16.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.488	1716	4.21
0.939	2152	9.10
1.177	2306	11.7
1.631	2485	16.6
2.098	2596	21.6
2.646	2765	27.6

Table XXXI

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0941 gms.
Ratio of butadiene: styrene in solution - 0.0402 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.0500 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.118	198	1.60
0.363	358	7.35
0.570	448	12.2
0.761	532	16.7
1.115	627	25.0
1.195	711	26.8

It is evident that if the theory proposed by Kharasch[15] is correct an increase in growth rate should accompany an increase in the weight of seed, since thereby the number of peroxides capable of decomposing will be larger. Accordingly, experiments were made in which the initial weight of seed was varied, the results being shown for three different values in Tables XXXI, XXXII and XXXIII.

These results, together with those shown in Table XII, are plotted in fig. 14 and indicate that an increase in the rate of popcorn formation with increasing weight of seed, does in fact, occur. There seems to be little doubt, therefore, that at least a fraction of the chains started are initiated on the surface of the seed.

Table XXXII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0953 gms.
Ratio of butadiene: styrene in solution - 0.0406 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.2000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.296	127	2.08
0.621	229	9.13
0.936	279	16.0
1.254	329	22.8
1.529	364	28.8
2.018	412	39.4

Table XXXIII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0954 gms.
Ratio of butadiene: styrene in solution - 0.0406 m/m.
Weight of benzoyl peroxide - 8.00x10^{-3} gms.
Weight of seed - 0.4000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.473	86	1.58
0.776	176	8.15
1.296	226	19.5
1.446	260	22.6
2.264	326	40.4

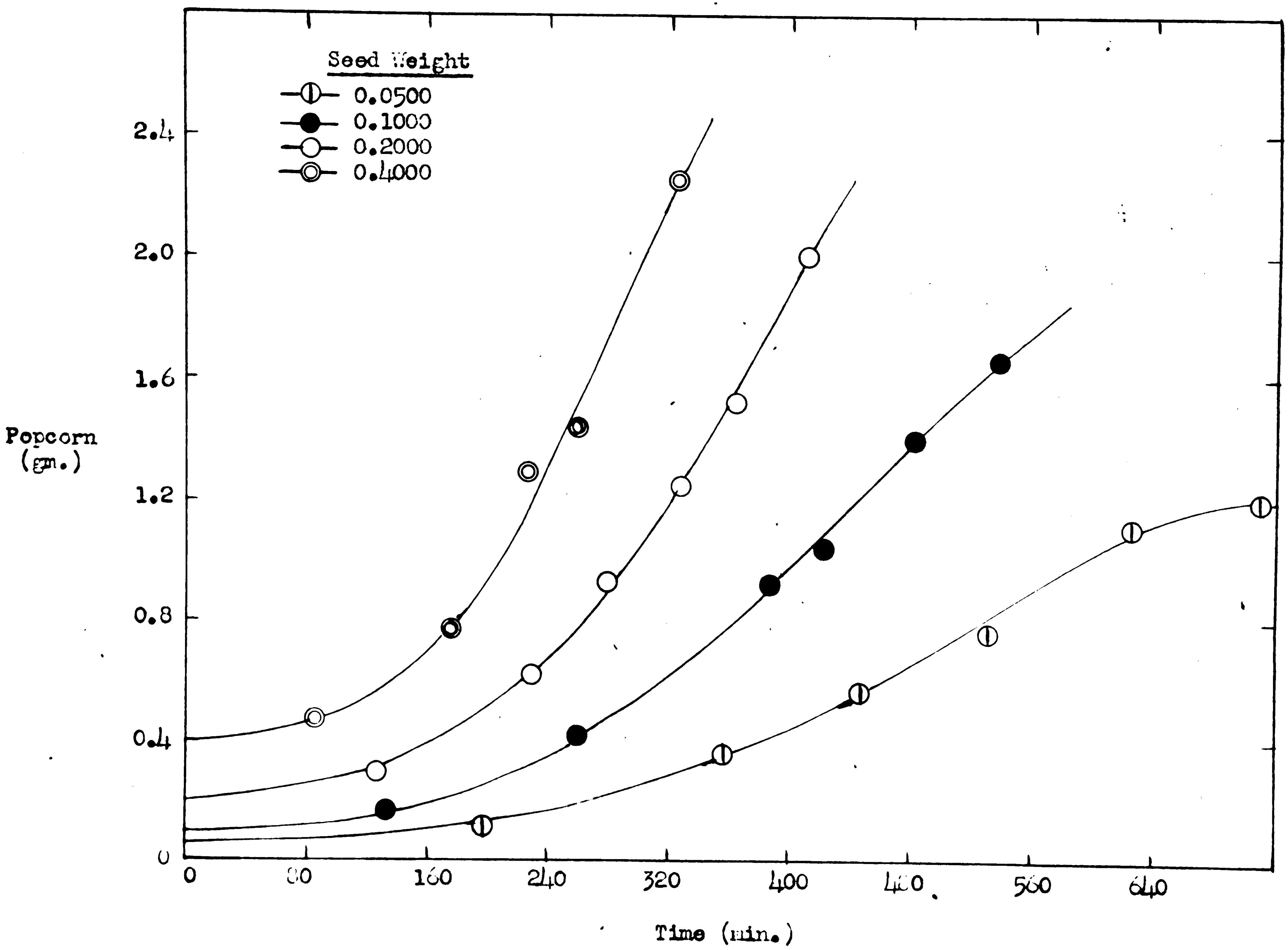


Fig. 14. Rate of Growth of Seed "D" (0.267 m/m)

Preliminary experiments on the growth of seed containing 0.0422 m/m of butadiene indicated that, at 75° C, with a concentration of 0.04 m/m in solution, the monomers were completely converted to soluble polymer before appreciable growth occurred. At room temperature the induction period was much longer (about three weeks), but practically complete "popping" occurred. Preliminary experiments using seed containing 0.26 m/m of butadiene indicated that measurable rates under the above conditions could be obtained over a temperature range from 20° to 100° C. The results of quantitative experiments over this range are shown in Tables XXXIV, XXXV, XXXVI and XXXVII.

In fig. 15 these results together with those of Table XII are plotted, and indicate a rather surprising temperature coefficient for the overall reaction. Between 65° and 85° C the reaction appears to be independent of temperature, while below 65° the induction period increases very rapidly, although growth once started soon reaches a rate comparable to that occurring at higher temperatures. The effect of temperature serves to emphasize the complexity of the overall reaction, and the necessity of considering it as the result of a number of different steps.

Table XXXIV

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0951 gms.
Ratio of butadiene: styrene in solution - 0.0406 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 39.0° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.431	1910	7.17
0.833	2032	15.9
1.264	2131	25.2
1.582	2195	32.2
2.069	2290	42.6
2.178	2333	45.0

Table XXXV

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0944 gms.
Ratio of butadiene: styrene in solution - 0.0403 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 64.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.144	67	0.96
0.587	210	10.6
0.710	266	13.2
0.897	299	17.3

Table XXXVI

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0943 gms.
Ratio of butadiene: styrene in solution - 0.0402 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 74.7° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.123	40	0.51
0.206	93	2.34
0.442	159	7.58
0.623	224	11.6
0.847	277	16.6
0.908	309	17.9

Table XXXVII

Growth of Popcorn Seed "D" (0.267 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.0941 gms.
Ratio of butadiene: styrene in solution - 0.0401 m/m.
Weight of benzoyl peroxide - 8.00×10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 85.1° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
0.212	98	2.43
0.400	161	6.51
0.526	204	9.25
0.676	241	12.5
0.792	289	15.0
1.034	328	20.2

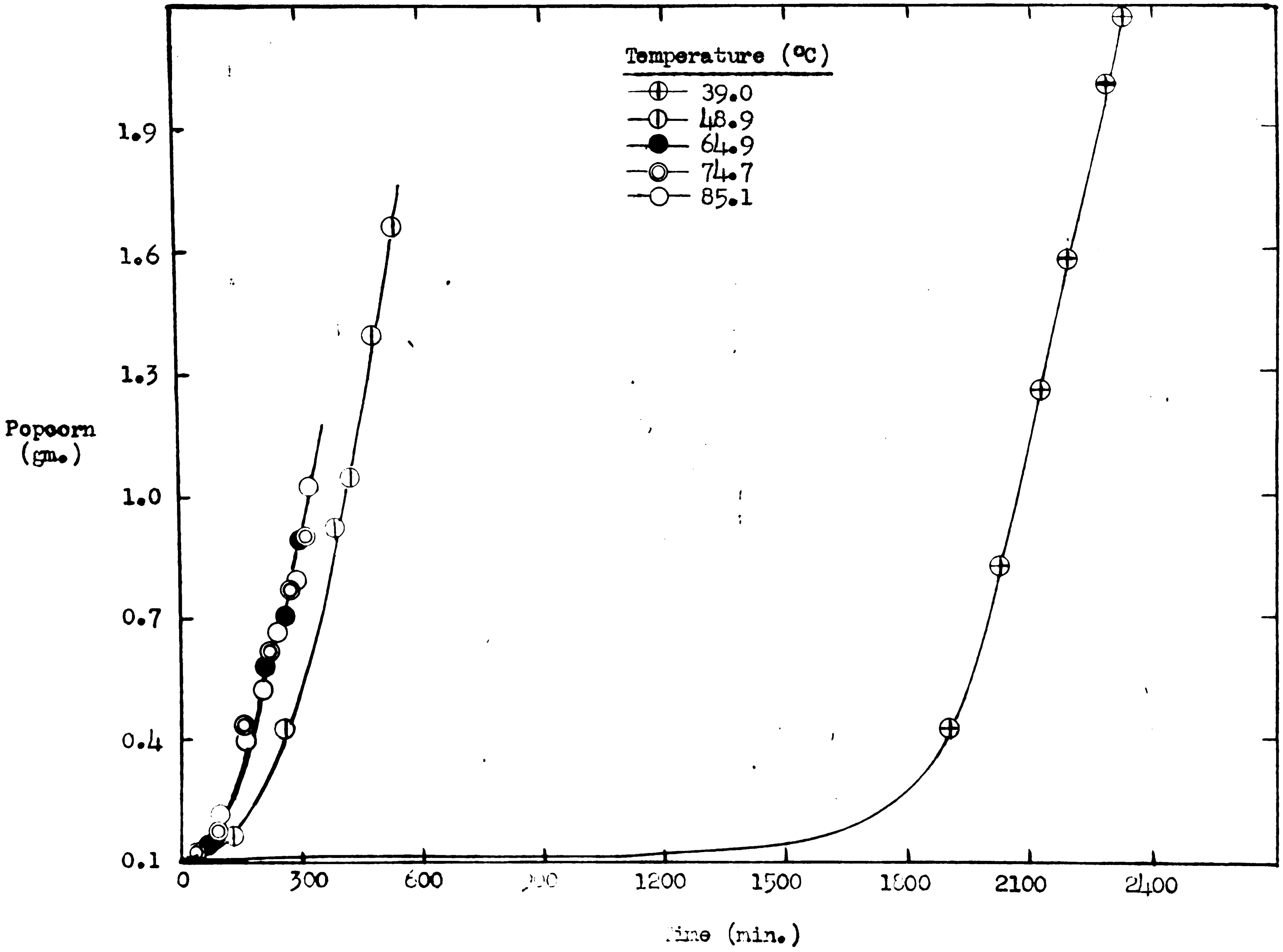


Fig. 15. Rate of Growth of Seed "D" (0.267 m/m)

Preliminary experiments in which the concentration of styrene was varied by diluting the system with benzene (the concentration of the butadiene being kept constant) indicated that this variable was important in determining both the induction period and rate of growth of seed "B" (0.0404 m/m). With 1 vol. of benzene and 4 vols. of styrene (20 gms./liter of butadiene) "popping" occurred in ten days, while with 3 vols. of benzene and 2 vols. of styrene a period of approximately thirty days was required. The induction period was considerably lengthened, and growth, once started, was much slower in the system diluted with benzene.

Changes in pressure during the growth of seed were measured to determine the rate of disappearance of butadiene. A manometer (constructed of capillary tubing) was sealed to the reaction tube and the pressure recorded during the reaction.

With seed "C" (0.0422 m/m) in a solution containing 0.040 m/m of butadiene and 0.1 m/1 of benzoyl peroxide the pressure decreased only 8% with a 15% conversion to popcorn, while during further "popping" it decreased in an approximately exponential manner to the final zero value. The curves are not reproduced here since temperature control during the reactions was poor, and the results cannot be compared directly with those obtained in the above growth experiments.

Interpretation of the results on a quantitative basis is difficult since departures from Raoult's law are probably great, although there appears to be little doubt that the butadiene concentration remains essentially constant during the early part of the reaction (up to 15% conversion to popcorn).

Initiation of Popcorn Polymer

As previously mentioned, preliminary experiments on the initiation of popcorn in unseeded samples indicated that traces of oxygen in the system exerted considerable influence on the rate of the reaction. Addition of benzoyl peroxide has been shown to overcome this effect in seeded samples, although, since the induction period in unseeded samples is so great, addition of benzoyl peroxide in comparatively small quantities is sufficient to cause complete polymerization to soluble polymer before nuclei of popcorn appear. It was found possible, however, by the introduction of small enough quantities of benzoyl peroxide, to obtain complete "popping" after fairly reproducible periods of time.

Qualitatively the results were similar to those reported by Whitby[4]. After an induction period lasting approximately one week (at 48.9° C) a small nucleus of popcorn was observed at the bottom of the tube, but not attached to the glass surface. The surrounding liquid varied in viscosity at this point, from that of a heavy syrup to that of the original monomers, depending upon the concentration of benzoyl peroxide or of oxygen added. In some samples the nuclei formed were unable to grow further before the whole had been converted to glassy soluble polymer. After the nucleus had appeared growth usually occurred at a relatively rapid rate, polymerization being completed in one to two days, although the degree of "popping", that is, the amount of popcorn formed, varied with the soluble polymer content at the end of the induction period. Occasionally small amounts of popcorn were found at the top of the reaction tube, in the vapor phase, particularly in those samples containing large amounts of oxygen and in which "popping" was only partially completed. As reported by Whitby[4], it was found that the introduction of rusty iron and water usually catalyzed the initiation slightly.

To determine the effect of butadiene and the influence of benzoyl peroxide on popcorn growth, experiments were made in which the concentrations of these reagents were varied. The time taken for the nucleus to appear was used as a measure of the initiation period and the results are of only semi-quantitative value, being probably correct to within 10-20%. Reproducibility, within these limits, is fairly good in those samples containing added benzoyl peroxide, but considerable variation occurred in samples not so treated. In such samples considerable care was taken to remove free oxygen from the system by flushing out repeatedly with nitrogen. The results of these experiments are shown in Tables XXXVIII, XXXIX and XL.

Table XXXVIII

Initiation of Popcorn in Unseeded Samples

Weight of styrene - 4.515 gms.
Weight of benzoyl peroxide - 2.80×10^{-3} gms.
Temperature - 48.9° C.

Weight of Butadiene (gms.)	Concentration of Butadiene (m/m)	Time for Nucleus Appearance (days)	Time for Complete "Popping" (days)
0.095	0.0405	6.5	Solidified
0.095	0.0405	6.5	Solidified
0.240	0.102	5.3	6.5
0.240	0.102	5.0	5.9
0.624	0.266	8.0	9.8
0.624	0.266	6.6	8.5

Table XXXIX

Initiation of Popcorn in Unseeded Samples

Weight of styrene - 4.515 gms.
Weight of benzoyl peroxide - 5.40×10^{-4} gms.
Temperature 48.9° C.

Weight of Butadiene (gms.)	Concentration of Butadiene (m/m)	Time for Nucleus Appearance (days)	Time for Complete "Popping" (days)
0.095	0.0405	7.2	10
0.095	0.0405	6.4	8.8
0.240	0.102	5.3	6.3
0.240	0.102	4.9	6.3
0.624	0.266	10.0	11.3
0.624	0.266	10.0	11.3

Table XL

Initiation of Popcorn in Unseeded Samples

Weight of styrene - 4.515 gms.
Weight of benzoyl peroxide - nil.
Temperature - 48.9° C.

Weight of Butadiene (gms.)	Concentration of Butadiene (m/m)	Time for Nucleus Appearance (days)	Time for Complete "Popping" (days)
0.095	0.0405	11.7	13.8
0.095	0.0405	11.7	13.8
0.240	0.102	9.6	11.7
0.240	0.102	6.3	8.7
0.624	0.266	ca. 25	-
0.624	0.266	ca. 25	-

It is clear from these results that an optimum concentration of butadiene exists in the initiation of popcorn at a concentration near 0.1 m/m of butadiene. The presence of small amounts of peroxides apparently promotes the formation of the insoluble polymer, although the results of Tables XXXVIII and XXXIX indicate that an optimum at low concentrations exists, above which little further catalytic activity occurs. The results are not sufficiently extensive to determine whether the presence of traces of peroxides are necessary for popcorn initiation, since such traces probably were present in the styrene used.

Because of the catalytic activity of the seed and of such solid substances as rusty iron, it appeared possible that nucleus formation requires the presence of a surface, taking place by some mechanism involving adsorption. To determine whether such heterogeneity was involved powdered Pyrex was added to the system, containing no benzoyl peroxide, and the reaction rate was evaluated in the normal fashion. It was found that considerable air, which could not be completely removed by flushing with nitrogen or by evacuation, was occluded on the powdered glass so that some correction must be applied for this factor. The results are shown in Table XLI.

Table XLI

The Effect of Powdered Glass on Popcorn Initiation

Weight of styrene - 4.515 gms.
Weight of benzoyl peroxide - nil.
Weight of powdered glass - 3.00 gms.
Temperature - 48.9° C.

Weight of Butadiene (gms.)	Concentration of Butadiene (m/m)	Time for Nucleus Appearance (days)	Time for Complete "Popping" (days)
0.095	0.0405	4.3	8.3
0.095	0.0405	8.3	9.3
0.240	0.102	5.3	6.9
0.240	0.102	4.3	5.3
0.624	0.266	ca. 14	-
0.624	0.266	ca. 14	-

Comparison of these results with those shown for samples containing no added surface indicate that little catalytic activity occurs. The rate is generally greater than that observed in the normal reaction containing no benzoyl peroxide, but is comparable to that occurring in samples containing added peroxide, being somewhat slower at the higher butadiene concentrations. If initiation were taking place at the glass surface, however, a very large increase in rate would be expected, since the surface is enormously increased by the added glass. The slight catalytic effect observed can probably be adequately accounted for by the occluded oxygen introduced into the system.

Inhibition of Popcorn Growth

Considerable evidence (e.g. Tables VII , XXXI-XXXIII) has been accumulated indicating that polymerization occurs on the added seed, causing apparent growth. In view of the evidence presented by Medvedev[49] that free radicals exist on the surface of polymers after polymerization is completed, and by Kharasch[23] who has expressed similar ideas concerning popcorn polymer, experiments were designed to determine whether growth of a popcorn seed did occur by a propagation reaction on free radicals present on the seed. McClure et al[60] have shown that benzoyl peroxide decomposes to form free radicals, which should, if the surface does contain radicals, deactivate the seed to a marked extent. Weighed quantities of seed containing 0.0404 m/m of butadiene were treated for fourteen hours with an acetone solution of benzoyl peroxide at a temperature of 48.9° C, control experiments being made simultaneously on similar seeds treated only with pure acetone. After the above treatment the acetone was evaporated from the seeds, fresh benzoyl peroxide was added to the untreated samples, and the monomers were finally introduced. The results of these experiments are shown in Table XLII.

Table XLII

Growth of Seed "B" (0.0404 m/m)

Treated with Benzoyl Peroxide

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.095 gms.
Ratio of butadiene: styrene in solution - 0.0405 m/m.
Weight of benzoyl peroxide - 2.00x10^{-3} gms.
Weight of seed - 0.1000 gms.
Temperature - 48.9° C.

Weight of Popcorn (gms.)	Time (mins.)	Yield of Popcorn (%)
x 0.139	2653	0.85
x 0.597	4426	10.8
0.194	2597	2.04
0.550	4364	9.75

x Pretreated with an acetone solution of benzoyl peroxide (1.46x10^{-3} m/l).

Considerable difficulty was experienced in evaporating the acetone, due to bumping, so that the experimental error was quite high. The results serve to show, however, that no marked deactivation of the seed occurred by treatment with benzoyl peroxide, thus indicating that free radicals initially present on the surface do not contribute appreciably to the growth of the seed.

A large volume of evidence has been accumulated indicating that nitric oxide, reacts very quickly with most types of free radicals, probably because it itself possesses an odd electron. Assuming that popcorn polymerization, like most polymerizations of this type, is of a free radical nature, it is to be expected that nitric oxide should exert a profound inhibitory influence on the reaction. Experiments have indicated this to be true. With 0.2% (by weight) of nitric oxide present in six samples containing 0.0405 m/m of butadiene and 8.00×10^{-3} m/l of benzoyl peroxide, complete inhibition of the growth of seeds containing 0.040 m/m of butadiene and the formation of soluble polymer has occurred for a period greater than six months at 48.9° C. In all samples a color change to pale yellow occurred shortly after the introduction of nitric oxide.

Further experiments were made using varying amounts of nitric oxide and in the presence of rusty iron and water, since these materials are present in the plant recovery system. The results of these experiments are shown in Table XLIII.

Shortly after addition of 0.1% nitric oxide to the sample containing iron and water the solution acquired a pronounced red color, indicating reaction probably between the iron and nitric oxide. It is interesting to note that after growth had started, (that is, after it had become visible) complete "popping occurred in one to two days, or at approximately the normal rate.

There seems to be little doubt that nitric oxide is an effective inhibitor for the growth of popcorn polymer, and that it would prove effective in the plant in extremely small concentrations, since the time during which styrene is in contact with the seed is relatively short.

Table XLIII

The Influence of Nitric Oxide on Seed Growth "C" (0.0422 m/m)

Weight of styrene - 4.515 gms.
Weight of butadiene - 0.095 gms.
Ratio of butadiene: styrene in solution - 0.0405 m/m.
Weight of benzoyl peroxide - nil.
Weight of Seed - 0.1000 gms.
Temperature - 48.9° C.

% Nitric Oxide (Weight)	Results
0.1	No growth after 80 days
0.05	" " " 80 "
0.01	" " " 80 "
0.002	Popped after 46 days
x 0.1	" " 36 "
x 0.01	" " 12 "

x Contained 1 ml. of water and rusty iron.

Experiments were made to determine the solubility of nitric oxide in styrene as a first step in evaluating its usefulness in the plant. The apparatus used was of the static type and consisted of a manometer, a bulb (which could be shaken) containing styrene, and a reservoir, the volume of which could be varied by raising or lowering the height of mercury in it. After the introduction of nitric oxide the manometer indicated a fairly rapid initial absorption, after which the rate of gas disappearance became very slow. On raising the pressure in the system (by decreasing its volume) absorption again speeded up for a time and again the rate gradually decreased, and by still a third increase in pressure the rate curve followed a similar pattern. It was found by this method that the rate of gas disappearance was lower after an increase in pressure than was the initial rate, the actual pressure being lower in this latter case. This indicated that a reaction was occurring, one of the products of which was an inert gas, serving to dilute the nitric oxide in the system. Absorption, in a ferrous sulphate solution, of the gas remaining in the system after reaction, showed that at least one quarter of it consisted of an inert gas, (probably nitrogen). This is in agreement with the results reported by Bloomfield and Jeffrey[27] for similar reactions. Lowering the pressure in the system, after considerable absorption had taken place, did not result in nitric oxide coming out of solution, further indicating that a chemical reaction was involved. Finally, a number of color changes occurred in the styrene; first, from colorless to pale blue, then to colorless, with the deposition of a white crystalline material and finally to yellow which deepened gradually to brown and was accompanied by the disappearance of the deposited crystals. The yellow solution was found to inhibit markedly the normal polymerization of styrene.

Kharasch[23] has reported that popcorn seed may be deactivated by the action of nitric oxide, which he attributed, at the time, to free radicals existing on the surface of the seed. Experiments have been made using 0.0405 m/m seed treated with nitric oxide for five minutes under pressures ranging from 24 to 76 cms., and under a pressure of 76 cms. for periods of time ranging from two to fifteen minutes. After a removal of the NO by evacuation 0.1 gm. samples of these seeds were added to the normal reaction mixture containing 0.0405 m/m of butadiene and 8×10^{-3}gms. of benzoyl peroxide and were incubated at 48.9° C. In all cases the growth of seed was considerably retarded, although approximately 0.5 gms. of popcorn formed before the monomers were completely used up in forming soluble polymer. It seems likely that if free radicals existed on the surface, and were responsible for growth, complete deactivation should occur in the time allowed. The reaction of peroxides with nitric oxide, however, is known to be relatively slow, so that, if these were responsible for free radicals which could then grow by normal propagation, only partial deactivation would be expected.

Nitrogen dioxide was found to react violently with styrene, the reaction being sufficiently exothermic, with no external cooling, to cause ignition. By dropwise addition of N_2O_4 to styrene cooled to -78° C the reaction could be controlled, the product being a viscous brown oil, distilling at 175° C under atmospheric pressure. The distillate possessed an odor similar to that of benzaldehyde or nitrobenzene. This product was found to inhibit strongly the normal polymerization of styrene. Whitby has since reported that it shows marked inhibitory properties in popcorn polymerization.

DISCUSSION OF RESULTS

There seems to be little doubt that the formation of popcorn, like that of soluble polymer, takes place by a free radical mechanism. The results of Whitby[14] on the pyrolytic decomposition of popcorn formed from styrene solutions containing 2% butadiene showed products similar to those obtained from soluble polystyrene, thus indicating that the two polymers are essentially similar. It is difficult to conceive of any other mechanism which will account for the large inhibitory influence of traces of nitric oxide, (well known for its ability to break free radical chains) on both the formation of popcorn and of soluble polymer.

Accepting this fact, it becomes evident that the formation of popcorn must be considered in the light of the three fundamental steps, previously outlined, involving production of free radicals, growth of the chains thus initiated, and termination by reaction with the terminal radicals on the growing chains. Any assumption regarding the nature of these steps must account for the somewhat unusual nature of the reaction kinetics, which involve a marked induction period, followed by a rapidly increasing rate of growth.

The formation of soluble polymer, at least in the initial stages of the reaction, appears to occur independently of the presence of popcorn seed in the solution, practically no induction period being observed. After popcorn growth has begun the rate of soluble polymer formation increases to values considerably greater than those observed in samples containing no insoluble polymer, and it is apparent by comparing the results shown in figs. 1 and 7 that there is no relation between the weight of popcorn formed and the weight of soluble polymer present. For example, from fig. 1, although 0.4 gm. of soluble polymer is present the amount of popcorn which has been formed is only 0.06 gm., while from fig. 7, in a similar solution one gram of popcorn has been formed while less than 0.2 gm. of soluble polymer is present. It is apparent, further, that while benzoyl peroxide catalyzes the formation of soluble polymer, it has an inhibitory influence on the popcorn growth. Thus there appears to be little possibility that soluble polymer is an intermediate in the formation of popcorn, and that precipitation of the former from a saturated solution, or addition of active chains (of soluble polymer) to the seed, do not contribute appreciably to popcorn growth.

The results (Table VII) of the experiment in which the solution over the seed was renewed after partial reaction (no new induction period being thereby produced) offers further conclusive evidence that popcorn polymer is not produced from soluble polymer, acting as an intermediate.

It is also evident from this that the removal of impurities, or of butadiene from the solution is not necessary to cause reaction to begin; that is, the induction period cannot be attributed to these factors, but must occur because of changes taking place only on the seed. The experiment indicates also that the rise in rate cannot be attributed to a rise in temperature due to an increase in viscosity of the system, as was found to be true for the polymerization of methyl methacrylate[34], since if this were true, removal of the soluble polymer should result in a further induction period, during which more soluble polymer should be formed.

It is thus apparent that popcorn growth (at least with seeded samples) must occur on the added seed, and therefore, that free radicals must either be present on the seed initially or must be formed by reaction with the components in solution.

Assuming then that popcorn growth takes place as a reaction distinct from the formation of soluble polymer, not involving impurities in the solution, with a free radical mechanism, and at constant temperature, it is evident that the following relation should be representative of the rate.

$$\frac{dp}{dt} = kn$$

Where p is the weight of popcorn at time t, n is the number of free radicals present as growing chains, and k is a number involving the monomer concentrations.

Assuming further, that the formation of popcorn involves true copolymerization, taking place by a series of reactions similar to those discussed by Norrish and Brookmann[47] (cf. page 19), k should be expressible as a function of the monomer concentrations, similar to that given by these authors. From their relation, and from the fact that butadiene polymerizes much more slowly than styrene, it is evident that k should decrease with increasing butadiene concentration. In applying this relation, of course, it is assumed that a steady state involving active butadiene and styrene chain ends exists throughout the reaction, an assumption which can only be true if the rate of initiation of chains is slow compared with the rate of growth of the chains. Since the overall reaction rate is comparatively slow this condition must be satisfied.

Measurements of the change in pressure in the system have indicated that the butadiene concentration, and thus k, is essentially constant for the early stages, and decreases during the latter stages of the reaction. The results shown in fig. 9 indicate that the increase in rate with time cannot be accounted for by a decrease in butadiene concentration, since a decrease in the initial concentration actually produces a decrease in rate (after the induction period, during which the butadiene concentration is constant).

The changes in growth rate with time can, therefore, only be explained on the basis of changes in the number of free radicals, n, on the seed.

There is little possibility that free radicals, existing initially on the seed do, by a propagation reaction, produce popcorn polymer. The results of treating the seed with nitric oxide or with a solution of benzoyl peroxide indicate this to be true. Furthermore, in all cases, the initial rate of popcorn growth is zero, a fact which could not be true, were free radicals present on the seed at the outset of reaction.

Reaction of the seed with benzoyl peroxide could lead to an intermediate which would decompose to form free radicals. The actual inhibitory effect of benzoyl peroxide on popcorn growth observed, however, indicates that such an effect must be small.

The results of Welch[7] on the growth of polybutadiene seed in pure butadiene have indicated that a relation of the type

$$\frac{dP}{dt} = k_1 P$$

exists. Such an equation may be derived assuming that purely thermal activation of the double bonds in the popcorn present could produce the free radicals necessary for polymerization, since in this case the number of radicals (to which the rate of polymerization is proportional) may be proportional to the weight of popcorn present. The relation indicates that the logarithm of the weight of popcorn plotted against the time should produce a straight line.

The data given in Tables IX, XX, XXI, XXII and XXX for the growth of 0.0422 m/m seed "C" in solutions of various butadiene concentrations are plotted in this way in fig. 16, and show that after an induction period the growth does, in fact, become logarithmic for butadiene concentrations (in the solution) between 0.04 m/m and 0.2 m/m. The slopes of the straight lines produced should equal the values of $k_1/2.3$ above if the equation is correct, and may, as observed, increase with increasing butadiene concentration, since the number of double bonds which may be broken is thus increased. However, it is difficult to explain why, at butadiene concentrations below 0.01 m/m, growth is no longer logarithmic (see also fig. 2) and further, why growth should show such a pronounced induction period, even when the butadiene concentrations in the seed and in the solution are the same.

The results given in Tables XII, XVII, XVIII and XIX for the growth of 0.267 m/m seed "D" are plotted logarithmically in fig. 17, and indicate that, in this case, the equation given above does not conform with experiment. It is evident further, that the slopes of the middle portions of each curve (which might be considered linear) actually decrease slightly with increasing butadiene concentration.

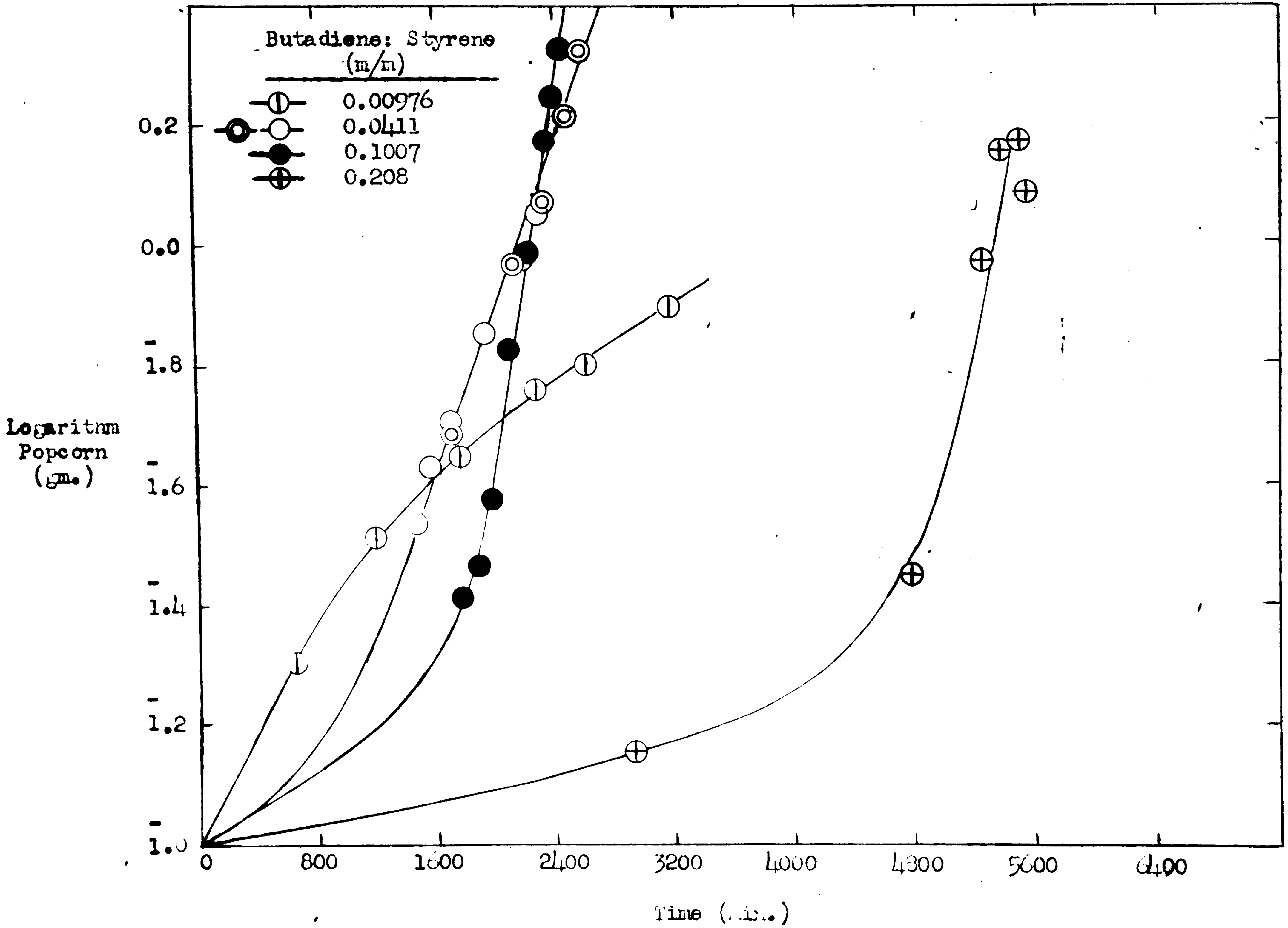


Fig. 16. Logarithmic Growth Rate of Seed "C" (0.0422 m/m)

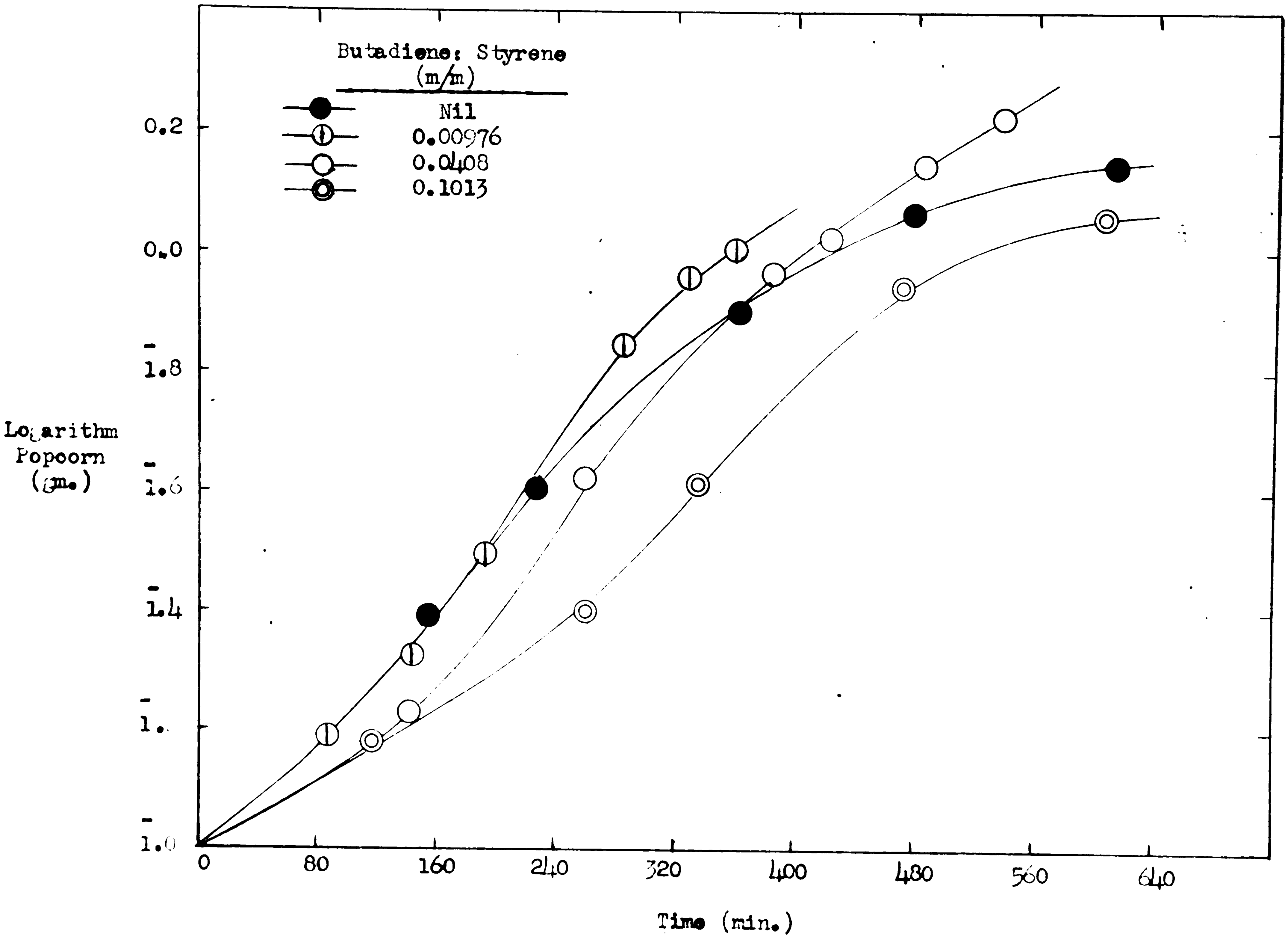


Fig. 17. Logarithmic Growth Rate of Seed "D" (0.267 m/m)

Comparison of this value of k, (7.0×10^{-3}/min.) with that for the 0.04 m/m seed, (1.29×10^{-3}/min.) (in both cases for a butadiene concentration in solution of 0.04 m/m) shows a difference which is difficult to explain on the above hypothesis, since it is to be expected that once growth has proceeded somewhat k should become mainly dependent upon the butadiene concentration in solution, the factor which controls the composition of the popcorn formed.

It thus appears evident that the hypothesis outlined above, while explaining the results in part, is inadequate to account for all of the effects observed.

The importance of peroxides on the seed in determining the growth rate has been emphasized by Whitby[14] and Kharasch[15]. The latter has attributed the non-linear rate curves observed by Welch[7] to a rate of initiation (decomposition of the peroxides on the seed) greater than the rate of termination of chains.

Assuming, therefore, that the free radicals necessary for seed growth are produced entirely by the decomposition of peroxides (or hydroperoxides) on the seed it is possible to set up an equation representing the number of growing chains as a function of the time. It is difficult to conceive of such an initiation rate being other than first order with respect to the number of peroxides on the seed, although the decomposition may require a reaction with one or both of the monomers present. The rate of initiation may therefore be expressed:

$$\frac{dn}{dt} = k_1 c_0 e^{-k_1 t}$$

where c_0 is equal to the initial number of peroxide groups (which will react) on the seed, and k_1 is the rate constant in which has been incorporated the monomer concentrations, assuming them to be constant.

Termination of the growing chains may take place in a number of different ways. Reaction between two growing chains could deactivate both with the formation of a covalent bond. Such a reaction would lead to a rate of termination proportional to n^2. Growing chains might react with free radicals in solution, probably present as growing chains of soluble polymer. This reaction would give rise to a termination rate proportional to n and to the number of free radicals in solution, a function of the benzoyl peroxide concentration. Chain transfer reactions, similar to those proposed by Flory[45] if occurring on popcorn seed, would result in actual termination with the production of a new growing chain in solution. Reactions of this type, possibly involving both benzoyl peroxide and monomer molecules, would lead to a rate of termination proportional to n.

Thus, following the above assumptions concerning popcorn growth, the following equation may be written for the number of growing chains as a function of the time:

$$\frac{dn}{dt} = k_1c_0e^{-k_1t} - k_2n - k_3n^2$$

where k_2 is a composite rate constant including radical termination and transfer reactions, and k_3 is the rate constant for reaction between two chains growing on the seed.

It is evident from this equation that the maximum value of $\frac{dn}{dt}$ must occur at zero time, at which point it is equal to k_1c_0. Since $\frac{dP}{dt} = kn$, values of $\frac{dP}{dt}$ plotted against time should give a curve proportional to the relation between n and t. Values of $\frac{dP}{dt}$ obtained from the curves shown in figs. 8 and 9 are plotted in figs. 18 and 19 as a function of the time. From fig. 18, representing the growth of seed "D" (0.267 m/m), it is evident that, while in pure styrene the initial slope, that is, $\frac{dn}{dt}$, is a maximum, and the curve is typical of that for the formation of an intermediate in consecutive reactions, with butadiene present this is no longer true, a point of inflection actually occurring before n reaches a maximum value. The increase in $\frac{dn}{dt}$ with increasing time is even more apparent in the curves shown in fig. 19, representing the growth of seed "C" (0.0422 m/m). There thus appears to be an induction period not only in the formation of popcorn, but also in the initiation of radical chains, when butadiene is present in the solution.

A possible explanation for the role of butadiene in producing an induction period in the formation of radicals lies in assuming that butadiene reacts with peroxides

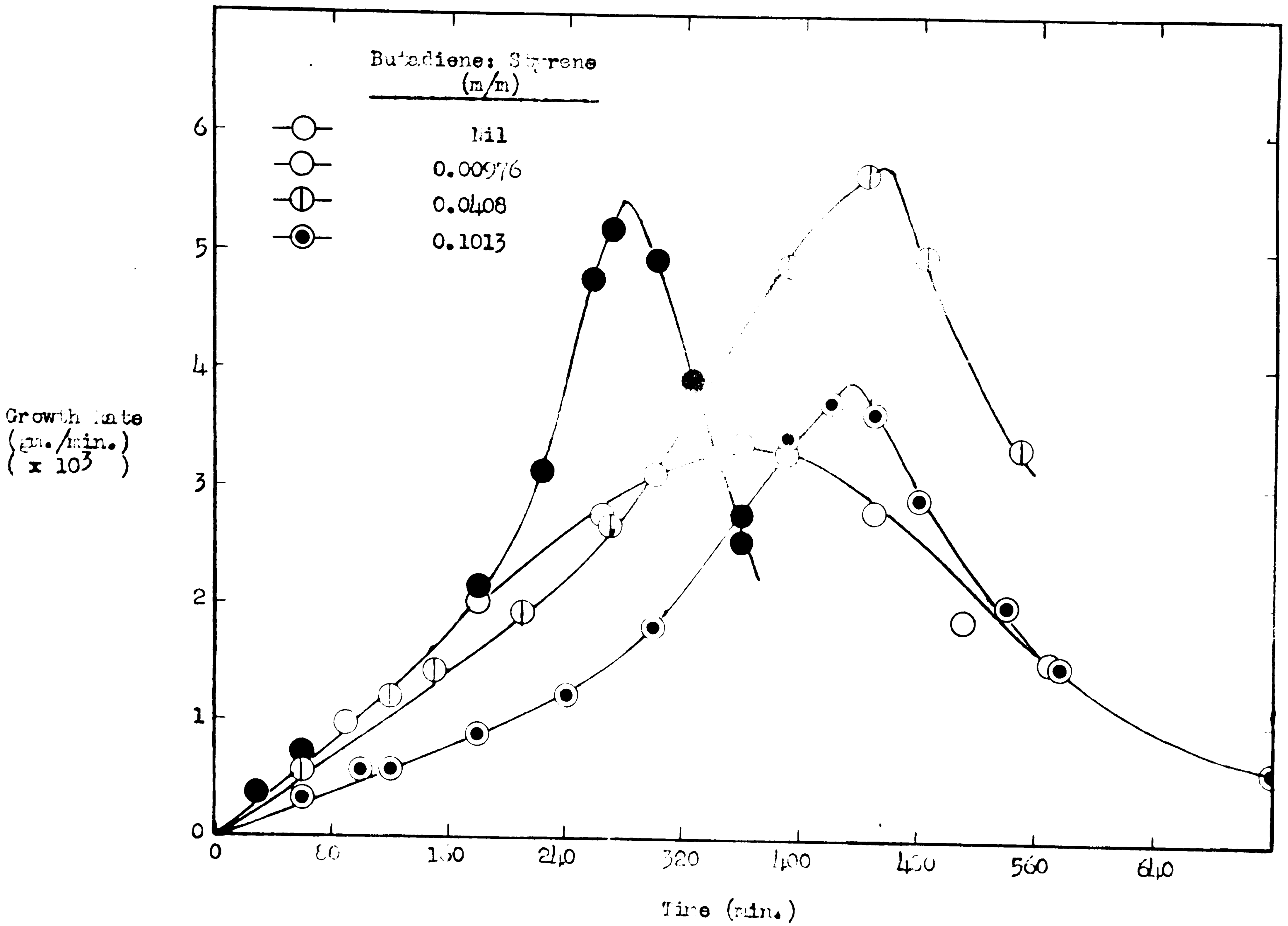


Fig. 18. Rate of Growth of Seed "D" (0.207 m/m) as a Function of Time

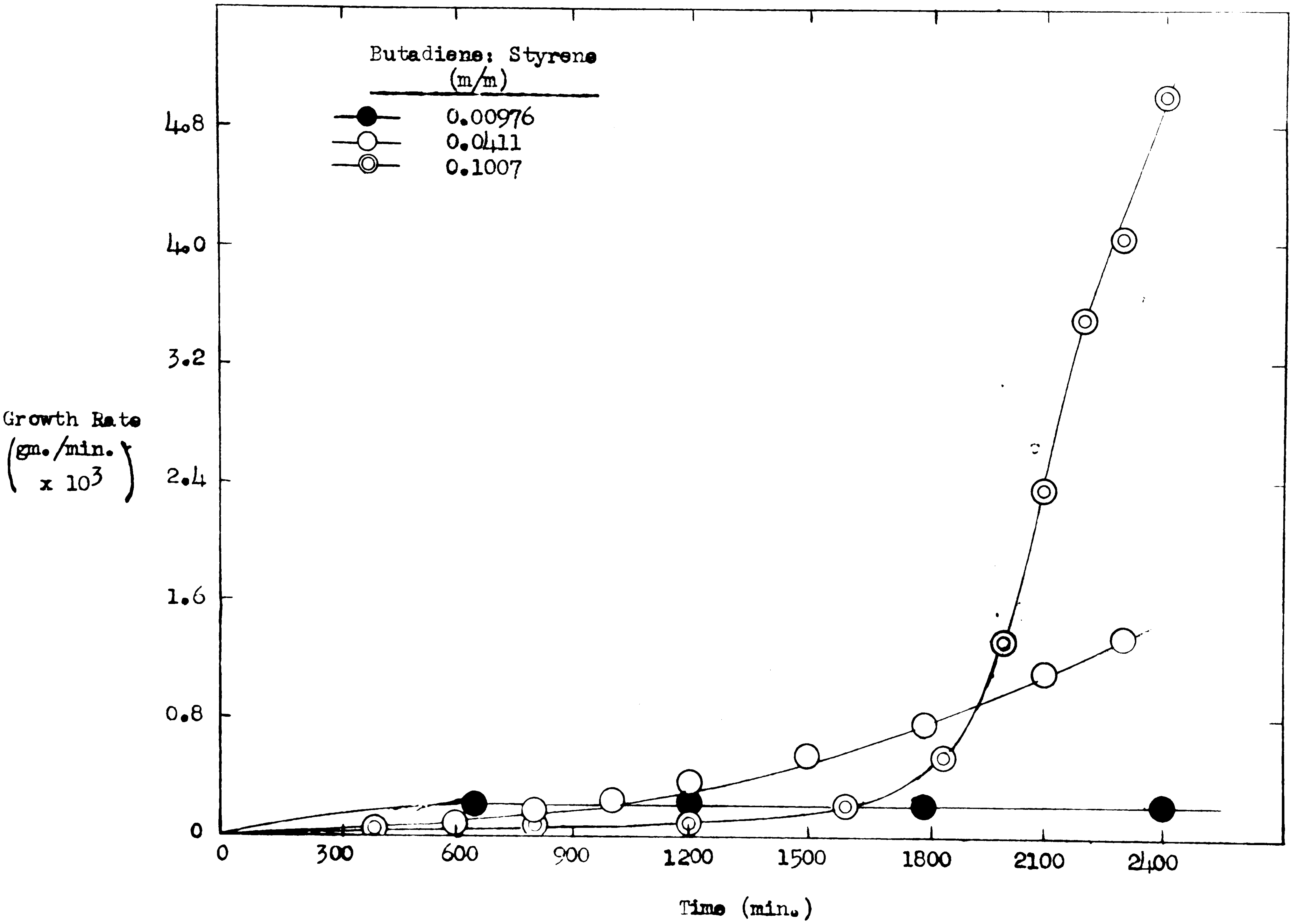


Fig. 19. Rate of Growth of Seed "C" (0.0422 m/m) as a Function of Time

to form an intermediate which then decomposes to form free radicals. Such an assumption leads to the following equation:

$$\frac{dn}{dt} = k_1c + k_5X - k_2n - k_3n^2$$

where $$C = c_oe^{-(k_1 + k_4 [Bd])t} = c_oe^{-Kt}$$

and $$X = \frac{k_4 [Bd] c_o}{k_5 - K} \cdot \left[e^{-Kt} - e^{-k_5t} \right]$$

X is the number of molecules of peroxide-butadiene intermediate on the seed.

[Bd] represents the concentration of butadiene in the solution.

k_4 is the rate constant for the formation of intermediate.

k_5 is the rate constant for the decomposition of intermediate to form free radicals.

Although this equation indicates that an induction period in the formation of radicals should exist, it predicts that $\frac{dn}{dt}$ plotted against time should give a curve having a maximum slope at zero time. Although this may be true for the growth of seed "D" (0.267 m/m) (fig. 18) it is evident on examination of the curves shown in fig. 19 for the growth of seed "C" (0.0422 m/m) that, particularly at the higher concentrations of butadiene, the curve showing $\frac{dn}{dt}$ as a function of time possesses a pronounced induction period.

To explain the results obtained it appears necessary to introduce another reaction by which free radicals can be formed, which is not dependent upon decomposition of any molecular species on the seed surface. A reaction similar to that postulated by Medvedev[49] in the polymerization of chloroprene, which involves opening the double bond in a reacting chain, could produce free radicals in the manner sought. Opening double bonds in the deactivated popcorn chains formed has already been discussed (above) and shown to be inadequate. The most logical assumption appears to be that the energy released by monomer addition to the *growing* chain will distribute itself along the chain (as vibrational and rotational energy), and that, occasionally, sufficient energy will concentrate in a double bond (of a butadiene unit) to open it. If collision with a monomer molecule occurs at this point before the activated bond can return to its normal state a new growing chain (actually two) will then be started. Such an hypothesis explains the importance of butadiene in the "popping" reaction.

Assuming, then, the following reactions:

1. $c + M \xrightarrow{k_1} n$ Initiation.
2. $n \xrightarrow{k_2} 3n$
3. $n + M \xrightarrow{k_3} n$ Propagation.
4. $n + r \xrightarrow{k_4} m$ Termination.
5. $2n \xrightarrow{k_5} m$

where c represents a peroxide group on the surface of the seed, M represents a monomer molecule,

n represents a growing chain,

r includes all types of molecules or radicals (other than n) capable of causing termination,

m is an inactive chain,

it follows that

$$\frac{dn}{dt} = k_1c + k_2n - k_4n - k_5n^2$$

where concentrations of monomer, and of r, as well as the factor of 2 occurring in reaction 2 have been included in the respective rate constants. In this equation c and n represent the number (on the seed) of peroxide groups and free radical chains respectively.

Since this equation is non-linear its solution is difficult to obtain, but as a first approximation, the last term may be neglected. The error may not prove serious, since the movement and thus the possibility of collisions between chains growing on the seed is considerably hindered. The equation thus becomes:

$$\frac{dn}{dt} = k_1c_0e^{-k_1t} + kn \qquad (1)$$

where k is equal to k_2-k_4

Integration gives:

$$n = \frac{k_1c_0}{k+k_1}\left[e^{kt} - e^{-k_1t} \right] \qquad (2)$$

where we have assumed that at $t = o$ $n = o$

Substituting this value for n in the equation of propagation

$$\frac{dP}{dt} = k_3n$$

and integrating:

$$P - P_0 = \frac{k_3k_1c_0}{k + k_1} \left[\frac{1}{k} \left(e^{kt} - 1\right) + \frac{1}{k_1} \left(e^{-k_1t} - 1\right)\right] \qquad (3)$$

where P represents the weight of popcorn at time t and P_0 represents the initial weight of seed.

It is evident from this treatment that an induction period may occur in $\frac{dn}{dt}$, and should be especially pronounced at low values of c_0.

Since the only quantity involving the seed which appears in this equation is c_0, it is clear (if the treatment is correct) that the variations in induction period and growth rate observed in fig. 6 with seeds containing various butadiene: styrene ratios must be explained by assuming that the number of peroxide groups per gram of seed depends upon this ratio. It is apparent then that the concentration of peroxides in the seed increases sharply to a maximum at a molar ratio of butadiene: styrene of 0.27 m/m, while at higher molar ratios it decreases to the value existing in polybutadiene popcorn.

The surface area per gram of popcorn probably decreases as its butadiene content increases, since, while popcorn containing small amounts of butadiene appears to be quite porous and is of the "cauliflower" type, polybutadiene popcorn is glassy and brittle. Between these two extremes the properties of the popcorn vary in porosity and hardness, It has been shown[61] that the rate of growth of polybutadiene popcorn in butadiene vapor increases as the seed is more finally divided, thus indicating that in this case the surface available to peroxidation, and thus growth, depends upon the state of subdivision of the polymer. No such effect has been noted with seed containing small concentrations of butadiene.

Farmer and Sutton[17] in an investigation of the reaction of oxygen with low molecular weight polyisoprenes have concluded that oxygen forms hydroperoxides on the methylene carbon atoms as a primary step, the unsaturation of the compounds being unaffected. Secondary autoxidative changes, spontaneous or promoted by heat and light, and involving interaction of hydroperoxide groups at the double bonds, thus producing saturation, also take place. A third reaction involving fission of the chain at single and double bonds also occurs.

Thus, increasing the butadiene: styrene ratio in the seed, while increasing the concentration of double bonds and thus the possibility of peroxidation by atmospheric oxygen, may decrease the concentration of hydroperoxides (assuming only these decompose to form free radicals) owing to interaction with the double bonds. These factors together with the decrease in the number of hydroperoxides available for reaction, owing to the decrease in specific surface area at higher butadiene: styrene ratios, may explain the observed maximum in the rate curves (fig. 6).

The value of c_0 is important in determining not only the rate of the reaction but also the shape of the rate curves. If c_0 is relatively large, then most of the radicals necessary for a given amount of seed growth (eg. 2 gms.) may be produced in the early stages of the reaction principally by the decomposition of the peroxides. This implies that throughout the early stages of the reaction the second term in equation 3, which involves radical formation from hydroperoxides, will be comparable to the first, which involves radical formation by branching. If, however, c_0 is sufficiently small, complete decomposition of the peroxides may not produce enough radicals to give an appreciable weight of popcorn after the chains, thus started have reacted and terminated. In this case, during the early stages of the reaction, an induction period will occur, while in the later stages the radicals responsible for growth will be produced principally by the branching reaction, and popcorn formation will be logarithmic, as can be seen from equation 3 in which the second term, as well as the numeral 1 appearing in the first term will be negligible in comparison with the value of e^{kt}. The equation then explains why, with 0.267 m/m seed the relation between the weight of popcorn and time is not logarithmic (fig. 17), while with 0.04 m/m seed, for reaction, owing to the decrease in specific surface area at higher butadiene: styrene ratios, may explain the observed maximum in the rate curves (fig. 6).

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To predict the effect of changing butadiene concentration in the solution on the growth of seed, it is necessary to determine how the values of the constants given in the equation are affected. Obviously, k_2 will be zero in pure styrene, and will increase as butadiene is added, since the number of double bonds capable of opening will increase. Increase of butadiene concentration may decrease the value of k_2, however, in two ways: the rate at which monomer molecules add to the chain decrease in a manner similar to that described above (Norrish and Brookman[47]), and thus the rate at which energy is supplied to the chains, and so to the double bonds, becomes smaller; there is a possibility that resonance between two butadiene links adjacent in the chain may stabilize the double bonds and prevent opening. Thus it seems not unlikely that at high butadiene concentrations a decrease in the branching rate may occur, and that an optimum butadiene concentration exists.

The variation of k_4 with changing butadiene concentration is difficult to predict, since the actual termination processes involved are uncertain.

To explain the observed results it is necessary to assume that hydroperoxides react with styrene, to produce free radicals. Thus, increasing the butadiene concentration in the solution will decrease the value of k_1, since this constant contains a factor representing the styrene concentration. It seems likely that adsorption of butadiene on the seed enhances this effect, since otherwise the concentration of styrene is little changed by relatively small changes in butadiene concentration.

It is thus apparent that for seed having a small value of c_0 increasing the butadiene concentration in solution should increase the induction period, since k_1 (as well as k_3) is decreased, and should increase the logarithmic growth rate, after the induction period, since k, the rate of branching, is increased. It is evident that at a low concentration of butadiene k_2 may become equal to k_4, that is, the rate of branching may become equal to the rate of termination, and k is zero. In this event equation 3 becomes:

$$P - P_0 = k_3C_0\left[t + \frac{1}{k_1} \left(e^{-k_1t} - 1\right) \right]$$

and it is evident that, after an induction period, growth should become linear. Reference to the curves shown in fig. 9, indicate that the above results are correct, and that at a concentration of 0.00976 m/m of butadiene growth does in fact become linear. It is evident also from these curves that k changes only slightly between 0.1 m/m and 0.2 m/m of butadiene. Since k_2 becomes zero in pure styrene, it becomes obvious why (fig. 2) popcorn growth in this medium ceases before complete conversion of monomers is effected.

With seed having a large value of c_0 and in which considerable growth occurs from radicals produced directly from hydroperoxides, increasing the butadiene concentration may decrease the rate of "popping", since both k_1 and k_3 decrease. Comparison of the curves shown in fig. 8 indicate that with seed "D" (0.267 m/m) such an effect is observed. Growth of this seed takes place during that portion of the curve corresponding to the induction period in the growth of seed "C" (0.0422 m/m). It is interesting to note that, as predicted by equation 2, in which, for pure styrene, k becomes $-k_4$, the curve showing n (or $\frac{dP}{dt}$) as a function of the time (fig. 18) is similar to that for the formation of an intermediate in consecutive reactions.

From equation 3 it is seen that plotting $\frac{P-P_0}{c_0}$ as a function of the time should give (for a solution of given composition) a curve independent of the weight or type of seed. Assuming that c_0 is proportional to the weight of seed it is evident that plotting $\frac{P-P_0}{P_0}$ against time should give a single curve for all experiments in which only P_0 was varied. The results shown in Tables XII and XXXI-XXXIII are plotted in this manner in fig. 20, and indicate these predictions to be correct.

The inhibitory effect of benzoyl peroxide, especially in the growth of seed "A" (0.0409 m/m) (fig. 1), indicates that the free radicals produced in solution may react with and thus terminate growing chains on the popcorn. Since the

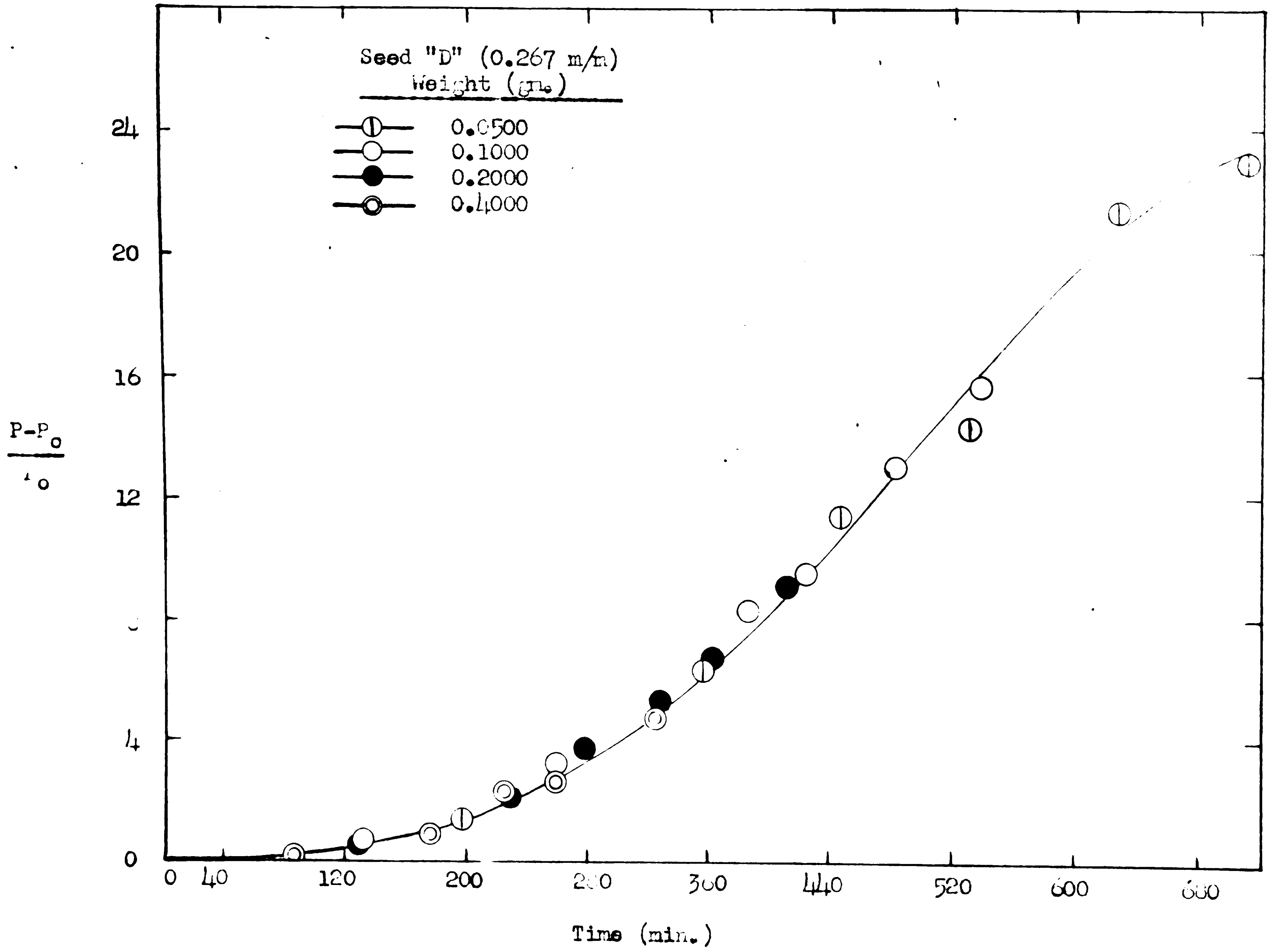

Fig. 20. Ratio Popcorn Formed: Seed Weight as a Function of Time

effect is very much smaller in the growth of seeds containing a larger concentration of hydroperoxides, (figs. 10, 11 and 12), it seems probable that other reactions such as chain transfer contribute considerably to chain termination. The decrease in rate at higher conversions for some of the seeds may be accounted for by the relatively large increase in benzoyl peroxide concentration occasioned by the removal of monomers from the solution as insoluble polymer. In general, the effects of benzoyl peroxide observed appear somewhat inconsistent and further work is necessary to elucidate its role in the reaction mechanism.

Calculations of the constants appearing in equation 3 have been made in an approximate manner. Expanding the exponentials in equation 2 by Taylor's theorem it is evident that for small values of t

$$\frac{dP}{dt} = k_3k_1c_0t$$

and thus that the rate of popcorn formation should be a linear function of the time in the early stages of the reaction. This is seen to be approximately true in figs. 18 and 19. From the slopes of these straight lines, in a solution containing 0.041 m/m of butadiene and $5.48\text{x}10^{-3}$ m/l of benzoyl peroxide, values of $k_3k_1c_0$ have been calculated for seeds "C" (0.0422 m/m) and "D" (0.267 m/m), and found to be $1.00\text{x}10^{-7}$ gm./min.^{2} and $1.00\text{x}10^{-5}$ gm./min.^{2} respectively. Thus it is apparent that the ratio of initial peroxide concentrations in the two seeds is 1/100. Assuming that in the later stages of the growth of seed "C" radicals are produced exclusively by branching, it is evident that the slope of the straight line obtained by plotting the logarithm of popcorn weight against time is equal to k/2.3. The value of k thus obtained for growth in a solution containing 0.041 m/m of butadiene is 1.29×10^{-3}/min. From equation 3 it can be seen that the intercept of this line at zero time is equal to log $\frac{k_3 k_1 c_0}{k(k + k_1)}$, so that by substitution of the above values of k and $k_3 k_1 c_0$, k_1 can be calculated. By this method it is found to have a value of 1×10^{-4}/min. It should be emphasized, however, that the above values are only approximate since the values of the initial rates are subject to large errors. Furthermore, the quantitative application of equation 3 is limited to the initial portion of the reaction, since it has been assumed that the concentration of monomers and of benzoyl peroxide is constant, and since changes in the viscosity of the system will undoubtedly affect the course of the reaction. It is to be remembered, also, that in deriving the equation termination by interaction between growing chains on the seed has been neglected. Using the above calculated values of the constants equation 3 is plotted for the two seeds "C" and "D" in fig. 21. The experimental points taken from Tables IX, XII and XXX are shown in the figure and indicate

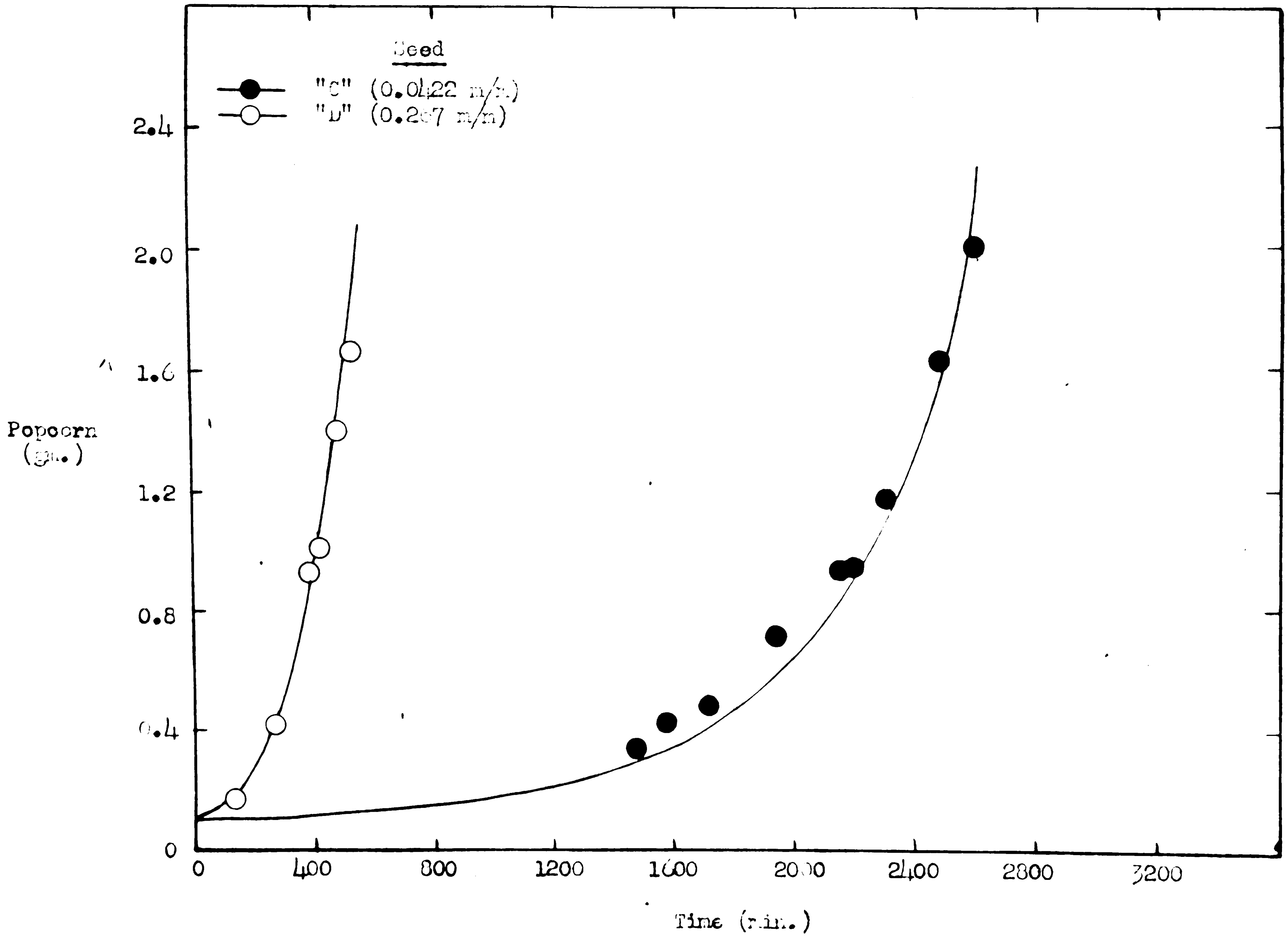

Fig. 21. Comparison of Observed Growth Rate with Theoretical Curves

that the agreement is quite good, especially in view of the experimental errors involved in the calculation of the constants.

The production of free radicals by branching of growing chains offers an explanation for the fact that popcorn (in unseeded samples) after nucleus formation has occurred, forms at rate approximately equal to that in seeded samples, even though oxygen has been rigorously excluded from the system. It is clear that in the formation of a nucleus, oxygen may play a role, since this must be accomplished by branching of chains existing initially as soluble polymer. Thus, since oxygen (or peroxides) in solution catalyzes the formation of soluble polymer it must catalyze to some extent, the initial formation of a nucleus, although once this is present it appears that reaction proceeds completely by the formation of radicals by the branching process, and that oxygen acts as an inhibitor, probably by termination of the growing chains.

The maximum initiation rate at a butadiene concentration of 0.1 m/m may occur because of an optimum in the rate of branching (as observed in seeded samples) at this concentration. Further increase in the butadiene concentration will lower considerably the rate at which propagation occurs, thus increasing the initiation time.

The effectiveness of nitric oxide as an inhibitor of seed growth is readily understood in the light of the above suggestions, since this reagent combines readily with free radicals. Thus, as long as the concentration of nitric oxide is sufficient to ensure that the rate of radical termination is greater than that of branching and peroxide initiation, little growth will occur. When the concentration has dropped below this value (because of reaction with radicals) growth will become logarithmic, the consumption of the nitric oxide remaining will increase rapidly, and the "popping reaction will soon reach its normal rate. It is thus possible to explain why, in samples containing nitric oxide, even after an induction period of several months, growth of the seed once started occurs at approximately the normal rate. It is further evident that reagents capable only of destroying peroxides on the seed cannot prevent popcorn formation.

The use of nitric oxide in the plant promises fruitful results in preventing popcorn formation as well as further growth of that already present. Its reaction with styrene is slow so that most of the gas would be carried through the distillation columns in which popcorn formation is most troublesome. The results indicate that only traces of nitric oxide are required to prevent the reaction completely for periods of several weeks, so that in the plant, where the styrene is in contact with seed for only a short time, very small concentrations indeed should suffice, even in the presence of water and iron.

The principal objection at present to the use of nitric oxide as a popcorn inhibitor is its inhibitory effect on normal polymerization. Since it was observed that nitrogen dioxide inhibits normal polymerization also, it is doubtful whether oxidation of the nitric oxide would alleviate the problem. It is possible, however, that the very small concentrations necessary to prevent popcorn formation in the plant may not affect normal polymerization appreciably.

Since, however, branching of radical chains appears to give rise to popcorn formation, it is evident that only such a reagent as nitric oxide, capable of directly destroying free radicals, and not only peroxide groups, can be effective in the prevention of the reaction.

It appears quite probable that branching, similar to that involved in the formation of popcorn, may occur in the emulsion copolymerization of butadiene and styrene. The formation of gel may then be accounted for by branching of actively growing chains in the system as well as by cross linking of inactive polymer. The function of the modifier is readily understandable, then, since by decreasing the length of the chains the probability of branching becomes smaller. This process of gel formation should be distinguished from that induced by the action of heat and oxygen (Kolthoff[62]), which probably occurs by peroxidation of inactive chains leading thus to crosslinking.

SUMMARY

The kinetics of popcorn formation in samples containing added popcorn seed and in unseeded samples has been studied. In both types of reaction poor reproducibility was eliminated by the addition of small amounts of benzoyl peroxide, indicating that traces of oxygen in the system greatly influence the polymerization.

Initial experiments were made using 0.1 gms. of seed (prepared by allowing a solution containing 0.04 moles of butadiene per mole of styrene to polymerize to popcorn polymer at 48.9° C) in 4.6 gms. of a butadiene solution in styrene (0.04 m/m). A pronounced induction period (1200 minutes) was followed by approximately logarithmic, growth of the seed. Soluble polymer formed at the same rate as in unseeded samples during the induction period, although during the later seed growth the rate of normal polymerization increased, probably owing to the increase in benzoyl peroxide concentration as monomers were removed from the solution as popcorn. Comparison of the rate curves for popcorn and soluble polymer formation indicate the latter is not a precursor in seed growth.

The rate of popcorn formation depended markedly upon the butadiene: styrene ratio in the seed (assuming this to be the same as the solution from which it was prepared), a sharp maximum occurring at a ratio of 0.27 m/m. Growth

rates of seeds having molar ratios between 0.01 and ∞ (polybutadiene) were investigated, and indicated that with the faster growing seeds a logarithmic relation no longer existed. Replacement of the solution over the seed after partial reaction by fresh monomers and benzoyl peroxide produced no new induction period, indicating that growth occurs through reactions taking place on the seed, rather than in solution.

Increasing the concentration of benzoyl peroxide decreased the rate of popcorn formation, particularly in the later stages of the reaction, at the same time increasing the rate of normal polymerization to form soluble polymer. The magnitude of the effect (on seed growth) depends specifically upon the butadiene: styrene ratio in the seed.

In the growth of seed containing 0.04 m/m of butadiene increasing the concentration of butadiene in solution produced a pronounced increase in induction period. The logarithmic growth rate increased with increases in butadiene: styrene ratios in solution from 0.01 to 0.1 m/m, although an increase to 0.2 m/m produced no further change. The growth rate in pure styrene was small, finally ceasing before complete conversion of monomer to popcorn and soluble polymer occurred. With seed containing 0.27 m/m of butadiene the growth rate (after the induction period) decreased with increasing butadiene concentration in the solution (0.01 to 0.1 m/m).

Increasing the seed weight (0.27 m/m) from 0.05 to 0.4 gms. showed a marked increase in growth rate in solutions containing 0.04 m/m of butadiene. The growth rate of seed (0.27 m/m) in solution containing 0.04 m/m of butadiene showed a rather surprising temperature coefficient. Decreasing the temperature from 64.9 to 39.0° C produced a very large increase in the induction period, although growth, once started reached a rate comparable to that at the higher temperature. Between 64.9 and 85.1° C the reaction appears to be practically independent of temperature.

Experiments were made with unseeded samples at 48.9° C. Small concentrations of benzoyl peroxide (less than 7×10^{-4} m/l) catalyze initiation of popcorn slightly, although larger values have little further effect. At large concentrations the whole of the monomers may be converted to normal soluble polymer before popcorn appears. There appears to be an optimum butadiene: styrene ratio (0.1 m/m) in popcorn initiation. The addition of powdered glass had little effect on the time required for popcorn formation, indicating that the reaction does not take place on the walls of the vessel.

The addition of traces of nitric oxide has been found to greatly inhibit the growth of seed (0.04 m/m) in solutions containing 0.04 m/m of butadiene at 48.9° C. Under these conditions "popping" has been completely prevented by 0.2% of nitric oxide by weight for more than six months, and delayed for 46 days by 0.002%.

The effectiveness of nitric oxide is considerably reduced in the presence of rusty iron and water. Treatment of seed (0.04 m/m) with nitric oxide for periods of several minutes reduces its rate of growth, but does not completely prevent it.

Nitric oxide has been found to react slowly with styrene, an inert gas (probably nitrogen) being formed. A white crystalline compound has been isolated.

A mechanism for the reaction has been developed. Peroxides on the seed decompose to form free radicals which then grow into chains by the normal mechanism of propagation, and terminate, probably by reaction with free radical chains in solution and by a chain transfer mechanism with monomers. Production of new radicals by the opening of double bonds in a <u>growing</u> chain on the seed takes place. Activation occurs by the occasional concentration of energy, released by the propagation reaction, in the double bond. An equation has been developed giving the weight of popcorn as a function of the time, and indicates satisfactory agreement between theory and experiment.

CLAIMS TO ORIGINAL RESEARCH

1. A kinetic study of the formation of popcorn in solutions of butadiene in styrene has been made. The addition of small amounts of popcorn catalyzes the reaction, the magnitude of the effect being dependent upon the weight of seed and the ratio of butadiene: styrene in it. An optimum catalytic effect occurs with seeds containing 0.27 m/m of butadiene.
2. With seeded samples it has been shown that popcorn formation takes place by a reaction distinct from that involved in the formation of soluble polymer, although both apparently take place by a free radical mechanism. Increasing the concentration of benzoyl peroxide catalyzes the latter reaction, but inhibits the former.
3. The rate of formation of popcorn in seeded solutions containing 0.04 m/m of butadiene, after a pronounced induction period, increases as the reaction proceeds. The increase is approximately logarithmic with seeds showing a large induction period, but with seeds showing rates near the optimum this is no longer true. In pure styrene the growth of the former seeds reaches a small constant rate which finally decreases to zero before the monomer is completely polymerized. Butadiene apparently is necessary for "popping" with this type of seed. The faster growing seeds show a decrease in rate with

increasing butadiene concentration. The effect of temperature on seed growth indicates the complexity of the reaction.

4. The initiation of popcorn in unseeded solutions of butadiene in styrene has been studied. The time required for the formation of a popcorn nucleus is dependent upon the butadiene: styrene ratio in the solution, being a minimum at 0.1 m/m. Small amounts of benzoyl peroxide or oxygen catalyze initiation, although larger amounts produce no further effect. The reaction apparently does not occur at the walls of the vessel.
5. Nitric oxide inhibits markedly the formation of popcorn in seeded samples, a concentration of 0.2% (by weight) completely preventing it for more than six months. Treatment of the seed with nitric oxide reduces its proliferative activity. A slow reaction occurs between nitric oxide and styrene.
6. A mechanism is postulated for the formation of popcorn in seeded samples and is extended to initiation when seed is absent. The free radicals, on the seed, necessary for polymerization may be produced by decomposition of hydroperoxide groups as well as by branching of chains, thus started, at double bonds opened through thermal activation by the energy released from the propagation reaction. An equation

showing the rate of seed growth has been developed and found to agree well with experiment.

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