

THE KINETICS OF COPOLYMERIZATION OF BUTADIENE AND STYRENE IN HOMOGENEOUS SOLUTIONS

- Part I Copolymerization of 75 weight percent butadiene and 25 weight percent styrene
- Part II- Copolymerization in homogeneous solution at constant free radical concentration

A Thesis

by

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followed by rupid successive additions of monomer molecules to the active

The Theory of Addition Polymerization

Although high polymers represent a comparatively new field of physicochemical study, their technical importance has led to a rapid accumulation of both empirical and theoretical knowledge of their behaviour. Earlier attempts (1-6) to establish the mechanism of polymer formation were followed in 1934 by the suggestion of Chalmers (7) that alternative mechanisms of polymerization were possible: (1) The step-wise synthesis of long chains by a succession of similar steps (polycondensation);

(2) A chain mechanism consisting of a slow primary reaction followed by rapid growth (addition polymerization). It is now generally accepted that, as a rule, the process of addition polymerization differs fundamentally from condensation polymerization. Polycondensations involve monomers which are so constructed that the condensation process is capable of indefinite repetition. This results in a material that steadily increases in molecular weight throughout the course of the reaction. In addition polymerizations the polymer mole-

cules formed in the initial stage are essentially of the same molecular weight as those formed later. Thus each polymer molecule grows rapidly to an average size and becomes stabilized. This indication of a chain mechanism is supported by the susceptibility of the reactions to catalysis and inhibition. Thus addition polymerization can be said to proceed by means of chain reactions which involve activation of the monomer (initiation) followed by rapid successive additions of monomer molecules to the active centre (propagation) until the polymer becomes stabilized (termination).

Eyring et al (8) developed a general theory for vinyl polymerization as follows:

On the basis of a free radical mechanism the following rate relations hold:

Initiation:
$$M \xrightarrow{k_1} M^{\bigstar}$$
Propagation: $M^{\bigstar} + M \xrightarrow{k_2} M_2^{\bigstar} \xrightarrow{k_2} M_3^{\bigstar} \xrightarrow{k_2} M_n^{\bigstar}$ Termination: $M_n^{\bigstar} + M_r^{\bigstar} \xrightarrow{k_3} M_{n+r}$ 

 $M^{\bigstar}$  represents an active centre.

Assuming that propagation consists of the rapid addition of monomer molecules to polymer radicals the velocity of propagation is:

 $V_{prop} = k_2 [R] M - - - - - - - - - - - (1)$ where [R] is the concentration of active centres and M is the concentration of monomer.

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

$$\frac{-dM}{dt} = k_2 [R] M (1 + \frac{V_{init}}{V_{prop}}) - - - - - - (2)$$

where the second term is small. This must be true if long polymers are to be formed.

If it is assumed that the rate constants for reactions of the active radicals ( $k_2$  and  $k_3$ ) are large compared with the rate constant of their formation  $k_1$ , a steady state will soon be reached such that the rate of initiation is equal to the rate of termination, when

where  $\delta$  is the kinetic chain length of the reaction or in other words the average number of monomer units bound in a polymer molecule.

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

where 
$$\delta = \frac{V_{\text{prop}}}{V_{\text{init}}} = \frac{k_2 M}{(k_3 V_{\text{init}})^{\frac{1}{2}}}$$
 -----(7)

Abere et al (9) have developed the equations for rates of polymerization and  $\delta$  for all possible initiation processes.

Expressions are now available for the overall rate of polymerization and the average degree of polymerization which can be compared directly with experimental data. However, these are not sufficient to determine unambiguously the individual rate constants of the different elementary steps, having only two equations and at least three unknowns. Other expressions are required which combine these same unknowns with directly measurable quantities. One of these is the distribution function of the polymer formed after different lengths of time under various experimental conditions. Attempts have been made in this direction by Ginell and Simba (10) and Eyring et al (8).

Ginell and Simha succeeded in integrating the differential equations for the consumption of inactivated monomer, the formation and consumption of activated monomer, the formation and consumption of active chain molecules of arbitrary degree of polymerization n and the accumulation of the stable molecules of general type  $m_n$ . Sets of formulae which describe the course of the reaction have been developed. They find that the final number distribution of the polymer is:

$$m_n = m_1^o \left(\frac{k_3}{k_2}\right)^2 \left(\frac{k_2}{k_2 + k_3}\right)^{n-1}$$
 -----(8)

 $m_1^{\circ}$  being the amount of monomer originally present and, accordingly, the final weight distribution function is

$$w_n = m_1^{\circ} \cdot n(\frac{k_3}{k_2})^2 (\frac{k_2}{k_2 + k_3})^{n-1} - - - - - - - - (9)$$

This expression contains the rate constants of propagation and termination and combines them with the experimentally accessible quantity, the weight fraction  $w_{n}$ .

No systematic investigation has yet been published which combines equations (6), (7) and (9). However, Abere et al (9) have combined the results of Alfrey (11) and Bartovics (12) for the weight fraction distribution curves for polystyrene, prepared with benzoyl peroxide at  $60^{\circ}$ , 120° and 180°C, with the kinetic data of other authors (13,14). They found the rate constants  $k_1$  (first order initiation),  $k_2$  and  $k_3$  to be characterized by the following frequency factors and activation energies:

 $k_1$ A  $\doteq 10^{11}$ E = 24.0 kcal. per mol. $k_2$ A  $\doteq 10^5$ E = 5.0 kcal. per mol. $k_3$ A  $\doteq 10^4$ E = 5.0 kcal. per mol.

#### Activation:

A number of methods of initiating chains are known to exist. It seems fairly definite that purely thermal activation of the double bond can produce active molecules of styrene (15,16). Photochemical activation has been studied by a number of workers (17) and in general takes place with a rate proportional to  $\sqrt{\text{intensity}}$ , indicating that the photoactivated 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<sub>3</sub>, AlCl<sub>3</sub>, SnCl<sub>4</sub>) association of the catalyst with monomer takes place.

The uncatalyzed polymerization of styrene was found to have an activation energy of about 23,000-25,000 cal. per mole and a collision factor between  $10^{4}$  and  $10^{6}$ . A second order overall rate was observed both in solution and in bulk polymerizations showing that the initiation process is second order with respect to monomer.

The radical catalyzed polymerization of vinyl and acryl derivatives has been studied by Abere et al (13), Alyea (18), Bolland (19), Norrish (20), Price (21), Raff (22) and Schulz (23). Proof for a free radical activation was found in three ways:

(1) Independent evidence showed that a number of substances capable of initiating polymerization reactions decompose in solution to form free radicals (16,23,24,25,26). If it is assumed that such free radicals lead to a propagation reaction, the resulting polymer would contain fragments from the catalyst as end groups. Price et al (26,27,28) have shown that samples of polystyrene and polymethyl methacrylate, polymerized in the presence of a number of different organic peroxides, do in fact contain at least one catalyst fragment per molecule.

(2) In one case the concentration of activating radicals was measured directly by the colour of the solution and it was found that the initial

rate of monomer consumption was proportional to this concentration.

(3) Kinetic data also point to a free radical activation. Assuming that the rate of initiation is first order with respect to the catalyst equation (6) becomes

$$-\frac{\mathrm{dA}}{\mathrm{dt}} = k_2 \left(\frac{k_1 c}{k_3}\right)^{\frac{1}{2}} \left(M + \frac{1}{\delta}\right) = k_2 \left(\frac{k_1 c}{k_3}\right)^{\frac{1}{2}} M$$

since  $\frac{1}{X}$  is very small. The rates of benzoyl peroxide catalyzed polymerization of vinyl 1- $\beta$ -phenylbutyrate and d-s-butyl  $\ll$  chloroacrylate (29,30) in dilute solution were first order with respect to the monomer as well as half order with respect to the catalyst. Investigations of peroxide catalyzed polymerizations of styrene (15b), methyl methacrylate (8) and vinyl acetate (31) all clearly indicated a rate dependent upon the square root of the catalyst concentration. This offers substantiation for the free radical mechanism. However, the investigators found a three-halves-order dependence of rate on monomer concentration for peroxide catalyzed polymerizations of styrene and vinyl acetate using high concentrations of monomer. Equation (6) shows that an initiation which is first order in monomer is required to explain this. Several reports on the kinetics of the decomposition of benzoyl peroxide have shown that the reaction is actually a first order process. However, Price (28) and Bartlett (32) found that the rate of benzoyl peroxide decomposition increased several fold in the presence of styrene. A possible explanation may be that in the thermal decomposition only that portion of the decomposition which leads to an alkyl radical and carbon dioxide is measured since the acyloxy radicals may recombine to form the peroxide. In the presence of monomer which will react with the acyloxy as well as the alkyl radicals, reversion to peroxide will be inhibited and the overall rate of

disappearance of peroxide will increase.

Eyring (8) has suggested that in free radical reactions the activation of the ethylene bond consists in lifting the two "unsaturation" electrons into a state of identical spin so that they occupy repulsive orbits (i.e. a singlet-triplet transition occurs). If this point of view is adopted, catalysts of the radical type accelerate the initiation reaction by increasing the frequency factor rather than decreasing the activation energy. The uncoupling of the spins of the unsaturation electrons becomes much more probable in the presence of atoms, radicals or molecules containing an odd electron. Uncatalyzed polymerization has been observed to have an activation energy of 23.0 kcal. and a collision factor of  $10^5$ while the catalyzed polymerization has E = 23.0 kcal. and A equal to  $10^{\circ}$ .

Williams (33), Thomas et al (34) and Wasserman (35) have studied the polymerization catalyzed by polarization of the double bond. The polymerization of isobutylene with BF3 and of styrene with SnCl<sub>4</sub> gave initial rates of monomer consumption which were directly proportional to the concentration of the catalyst as was expected. Eyring pointed out that in these reactions the heteropolar elevated state of the double bond is probably responsible for the activation (singlet-singlet transition).

This type of catalysis accelerates the reaction by decreasing the activation energy necessary to bring the molecule into the first activated singlet state (approx. 40 kcal.) down to values between 20 and 25 kcal. per mole. The collision factor  $(10^{11})$  is not noticeably changed by the catalyst.

#### Propagation:

(1) The simplest propagation reaction is the normal chain growth, which

seems to take place rapidly. Observations of Schulz (15a,d) and others indicate that the average lifetime of a growing polystyrene chain of about 1000 monomers is between  $10^{-3}$  and  $10^{-2}$  seconds if the radical mechanism is involved. On the other hand, Melville (17) has observed that methyl methacrylate can grow over a very long period of time without being effectively terminated. The same has been found true for chloroprene by Medvedev (36) and for butadiene by Gunning and Steacie (37).

(2) Chain Transfer was postulated to explain some experimental results which are inconsistent with the formal theory.

If it is assumed that the degree of polymerization is equal to  $\delta$ , the kinetic chain length of the reaction, then for the catalyzed polymerization of styrene the degree of polymerization should be proportional to the square root of the monomer concentration (equation (7) where  $V_{init} = k_{l}cM$ ). The data of Schulz and Huseman (15a) are not in agreement with this (8). For the uncatalyzed polymerization of styrene, 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 (15b,16) since it depends not only on the monomer concentration but also on the particular solvent used. This indicates the occurrence of some reaction which deactivates the growing polymer without terminating the reaction chain.

Such reactions were proposed by Flory (38) and termed "chain transfer" reactions. The growing polymer molecule stabilizes itself by transferring its activity to some other molecule, monomer, solvent or polymer. These reactions may be formulated thus:

$$M_{\mathbf{X}}^{\bigstar} + M \xrightarrow{k_{t}} M_{\mathbf{X}} + M^{\bigstar}$$

$$M_{\mathbf{X}}^{\bigstar} + S \xrightarrow{k_{t}'} M_{\mathbf{X}} + S^{\bigstar}$$

$$S^{\bigstar} + M \xrightarrow{k_{S}} M^{\bigstar} + S$$

The true degree of polymerization of the polymer formed during any small amount of reaction is then given by:

$$\overline{P_n} = \frac{V_{\text{prop}}}{V_{\text{term}} + V_{\text{trans.}}} = \frac{k_2 \text{RM}}{k_3 \text{R}^2 + k_1 \text{MR} + k_1 \text{SR}} = - - - - (10)$$

$$= (k_1 \text{cM})^{\frac{1}{2}} \text{ for the catalyzed polymerization}$$

where  $R = \frac{(k_1 c_M)}{k_3 c_2}$  for the catalyzed polymerization.

Substituting this value in (10) and inverting:

$$\frac{1}{R_{h}} = \frac{kt'S}{(k_{2}+k_{t})M} + \frac{(k_{1}k_{3}c)^{\frac{1}{2}}}{(k_{2}+k_{t})M^{\frac{1}{2}}} + \frac{k_{t}}{k_{2}+k_{t}} - - - - - (11)$$

The only important transfer process was found to be reaction with the solvent (i.e.  $k_t$  is zero) for styrene polymerization (8).

In the absence of catalyst (12) becomes:

These equations hold only for the polymer formed when the monomer concentration is constant, i.e. at the beginning of the reaction. They have been shown to hold for the polymerization of styrene in various solvents (8) and it should be noted that the true kinetic chain length was found to be essentially independent of the solvent used. It is therefore probable that the solvent has no specific chemical action in chain initiation or in chain propagation except as it may alter the thermodynamic activities of the initial and activated states.

(3) Branching is another propagation process which was introduced into the discussion of styrene polymerization by Raff (22), Schulz (15d) and Staudinger (39) to explain characteristic discrepancies between degrees of polymerization obtained from osmotic pressure and viscosity measurements. This argument has lost strength in view of more recent data (40). In fact there is great doubt of the existence of branching in pure polystyrene. However, Medvedev et al (36,41) have shown that branching does occur in isoprene. 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 a decreasing function of the time showing an initial maximum value. Medvedev et al (36) have observed that chloroprene polymerization catalyzed by tetralin hydroperoxide proceeds at a rate which increases with time. Considering that initiation of active centres 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:

 $X = (k_1c + k/k_2) (e^{k}2t_1) - - - - - - - - - (14)$ 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 the experimental conditions very well.

In a later paper Medvedev et al (41) showed that the polymer formed during the polymerization of chloroprene contains 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 potentially present from the catalyst decomposition.

### Termination:

Radical chain termination evidently occurs if two growing chains collide or if one chain collides with the dissociation product of the catalyst.

Abkin (42), Bolland (19), Medvedev (41) and Melville (17) have studied the termination of growing chains of ethylene and butadiene derivatives by various substances and found in some cases that the chain ends are extremely sensitive to cessation while in others they are surprisingly resistant.

Melville (17) reported the formation of an insoluble polymer by the action of ultra-violet light on methyl methacrylate. This polymer continued to grow on the walls of the vessel for several days after the source of radiation was removed. Its rate of growth was practically unaffected by storage in vacuo for 43 hours or after treatment with oxygen. In addition to the polymer growth at the walls a rore rapid gas phase polymerization was initiated by hydrogen atoms producing soluble polymer. Melville concluded from this that the gas phase and the wall polymerization took place by different mechanisms. He postulated a free radical chain polymerization for the gas reaction and a polymerization proceeding by addition of monomer to the double bond at the end of the chain for the wall reaction. To deactivate these chains the unsaturated ends of two of them would have to react with each other. Such a reaction would involve the migration of a methyl group to an adjacent carbon; since this migration is very improbable the chains have a long life.

In all these studies the polymer which continued to grow had been precipitated on the walls of a glass tube as an insoluble mass or was formed in a very viscous system. Hence another possible explanation of this effect is that the probability of collisions between chains growing in the polymer is considerably hindered because of structural considerations.

## Copolymerization

Norrish and Brookman (42) were 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.

M≇	Ŧ	М —	<b>→</b>	Мŧ	Rat	e =	<sup>k</sup> p11	M <sup>A</sup> M
M	Ŧ	s —	<b>→</b>	S <sup>‡</sup> t		*	<sup>k</sup> p12	M <sup>≜</sup> S
s≇	+	M —		M <sup>♠</sup>		=	k <sup>p21</sup>	S <sup>⋬</sup> M
s≇	ŧ	s —	<b></b>	s≇		-	kp22	S <sup>‡</sup> S

M and S represent the two monomeramolecules,  $M^{\bigstar}$  and  $S^{\bigstar}$  the active centres.

Assuming that the polymerization is zero order with respect to monomer, then the rate of propagation is given by:

 $\frac{dp}{dt} = k_{p_{11}} M^{\bigstar}M + k_{p_{12}} M^{\bigstar}S + k_{p_{21}} S^{\bigstar}M + k_{p_{22}} S^{\bigstar}S - - - - (15)$ The rate of increase in the number of active centres  $M^{\bigstar}$  is

$$\frac{dM^{\ddagger}}{dt} = k_{p_{21}} S^{\ddagger}M - k_{p_{12}} M^{\ddagger}S$$
ists such that  $\frac{dM^{\ddagger}}{dt} = 0$ 

If a steady state exists such that  $\frac{dM^{-}}{dt} = 0$ 

$$k_{p21}$$
 S<sup>\*</sup>M =  $k_{p12}$  M<sup>\*</sup>S

and also, since  $M^{\bigstar} + S^{\bigstar} = \text{constant} = n$ , substituting for  $M^{\bigstar}$  and  $S^{\bigstar}$  in (15) and letting M = 100 - S gives:

$$\frac{dp}{dt} = n \left[ \frac{100 \ k_{p11} + 2S(k_{p12} - k_{p11}) + \frac{S^2}{100}(\frac{k_{p11}k_{p22}}{k_{p21}} - 2k_{p12} + k_{p11})}{1 + \frac{S}{100}(\frac{k_{p12}}{k_{p21}} - 1)} \right]$$

or 
$$\frac{dp}{dt} = n \left[\frac{a + bS + cS^2}{1 + dS}\right] = - - - - - - - - - - - - (16)$$

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

In calculating the values of a, b, c and d from their experimental data Norrish and Brookman assumed that the same concentration of peroxide in the different mixtures of monomers would give the same concentration of active centres. Mayo and Lewis (43) were able to show that this assumption was false and hence the empirical equation which Norrish and Brookman found for the styrene - methyl methacrylate system is of little value. There is nothing fundamentally wrong with their theoretical equation. However, it is necessary to be certain that each system has the same steady state concentration of active centres n.

Studies based upon the propagation reactions suggested by these authors have been made by a number of investigators (43-52). The equation relating the composition of the copolymer to initial concentrations of monomers and to the time was derived independently by Mayo and Lewis (43) and Alfrey and Goldfinger (44), as follows:

$$\frac{\mathrm{dM}}{\mathrm{dS}} = \frac{[\mathrm{M}]\boldsymbol{\sigma} \ [\mathrm{M}]}{[\mathrm{S}]} \left[\mathrm{M}] + \boldsymbol{\mu} \ [\mathrm{S}]\right]$$
(17)

where  $\sigma = \frac{k_{p_{11}}}{k_{p_{12}}}$  and  $\mu = \frac{k_{p_{22}}}{k_{p_{21}}}$ .

Wall (45) has published two papers on the same topic and, although his treatment is from a different viewpoint, his results are identical.

Equation (17) has been applied to many monomer pairs. Logan (46) found values of  $\sigma = 0.23 \pm 0.07$  and  $\mathcal{M} = 1.48 \pm 0.08$  for the bulk phase copolymerization of styrene and butadiene, where M above refers to styrene and S to butadiene. This indicates that butadiene will react faster

than styrene with either type of chain although it has been shown that reaction with  $M^{\ddagger}$  is faster than with  $S^{\ddagger}$ .

Alfrey and Goldfinger (44), as well as Branson and Simha (47), have developed equations applicable to two components for the overall rate of polymerization and the number average of the degree of polymerization. Branson and Simha (48) later extended their derivations to systems of any number of components. Recently Melville et al (49) published a general theory of copolymerization in which the rate expressions were derived for percentage polymerization against time and for initial rate against monomer concentration. Their initial rate expressions are of the general form:

$$-\frac{d[M+S]}{dt} = \frac{1+aM+bM^{2}}{(1+cM+dM^{2})} x (R_{m}+R_{s})^{x} - - - - (18)$$

where  $x = \frac{1}{2}$  or 1,  $R_m$  and  $R_s$  represent the rates of initiation of M and S respectively and a, b, c, d are constants which involve the values of  $\sigma$  and  $\mu$ .

## Molecular Weights of High Polymers

The methods used at present for the molecular weight determination are:

- (1) End group determination
- (2) Osmotic pressure
- (3) Light scattering by solutions
- (4) Sedimentation analysis by the ultracentrifuge
- (5) Viscosity of dilute solutions.

End group determination methods can only be applied to linear molecules having reactive end groups. The calculation of the molecular weight of an emulsion polymerization polymer from the consumption of modifier is essentially an end group method (52). Osmotic pressure determinations have been widely applied to solutions of various polymers. A membrane must be used which is truly semi-permeable to the polymer-solvent system. Methods involving light scattering by solutions of polymers are based on Rayleigh's Law and have been used by Debye (53). All these methods determine the number of molecules present in a given weight of polymer. Hence, for a polymer containing molecules of different weights the actual result is only a "number average molecular weight". This is expressed as follows:

$$\overline{M}_{n} = \frac{\sum n_{y} M_{y}}{\sum n_{y}} \qquad (19)$$

where  $M_n$  is the number average molecular weight and  $n_y$  is the number of molecules of the y<sup>th</sup> species, having a molecular weight of  $M_y$ .

The ultracentrifuge has been used to make sedimentation analyses of solutions of macromolecules by Svedberg (54) and others. In such an analysis, a distribution of the polymer is obtained according to the weight fractions of molecules of different molecular weights. Hence, a molecular weight distribution function is obtained. To obtain an average molecular weight, the function must be summed and divided by the total weight of polymer. Thus, a weight average molecular weight results:

$$\mathbf{M}_{\mathbf{w}} = \frac{\sum \mathbf{M}_{\mathbf{y}} \mathbf{w}_{\mathbf{y}}}{\sum \mathbf{w}_{\mathbf{y}}}$$

where  $w_y$  is the weight of the y<sup>th</sup> species, having a molecular weight of  $M_y$ . Now since  $w_y = n_y M_y$ then  $\overline{M}_w = \frac{\sum n_y M_y^2}{\sum n_y M_y} - - - - - - - (20)$ 

The most widely used method for molecular weight determination has been the dilute solution viscosity of polymers. Staudinger (55) first postulated hiw well-known relation, on purely empirical grounds, in 1932.

$$\gamma_{sp} = KcM$$
  
or  $\frac{\gamma_{sp}}{c} = KM$ 

where  $\frac{\mathcal{N}_{sp}}{c}$  is the specific viscosity and is expressed as

$$\chi_{\rm sp} = \frac{\chi}{\chi_{\rm o}} -1$$

where  $\chi$  is the viscosity of the solution;  $\chi$  is the viscosity of the solvent; c is the concentration of the solution in grams per 100 ml.; M is the molecular weight and K is a characteristic constant.

Staudinger's relation then made it possible to determine the molecular weight of a high polymer by viscometric methods, provided the characteristic constant had been evaluated by calibration against some absolute method, such as osmotic pressure. In using Staudinger's equation a weight average molecular weight would be obtained, thus:

$$\mathcal{H}_{spy} = Kc_{y}M_{y}$$

Hence, for the whole polymer

$$\chi_{sp} = \sum \chi_{spy} = K \sum c_y M_y$$

and

$$\frac{\chi_{sp}}{c} = \frac{K \sum c_y M_y}{\sum c_y} = \frac{K \sum n_y M_y^2}{\sum n_y M_y} = K \overline{M}_w$$
(21)

To avoid any non-ideality in the polymer solution, the specific viscosity is usually extrapolated to zero concentration, by plotting the function  $\frac{\varkappa_{sp}}{c}$  against c, thus obtaining the "intrinsic" viscosity, designated as  $[\varkappa]$ .

Kuhn (56) and later Huggins (58) derived a relation between viscosity and molecular weights on purely theoretical grounds, by a consideration of the effect on the flow of solution caused by long molecules lying across the velocity gradients. Their results may be expressed as follows: For rigid rod-like molecules

$$\gamma_{\rm sp} = K_{\rm Z} c M^2 = K_{\rm Z} n M^3$$

For rigid randomly kinked molecules

$$\gamma_{sp} = K_2 cM = K_2 nM^2$$

For non-rigid randomly kinked molecules

$$\chi_{sp} = K_1 c M^a = K_1 n M^{1+a}$$

where 1 > a < 0.

It can be seen that Staudinger's equation applies only to rigid randomly kinked molecules. In actual practice it has been found that the more general equation

holds for a large number of different polymers. The values of K and a are characteristic of a given solvent-solute pair, with a lying between zero and unity.

With molecularly heterogeneous polymers, equation (22) yields an average which is not necessarily a weight average but is called a "viscosity average". Thus the viscosity average molecular weight  $\overline{M_{\mathbf{v}}}$  may be derived as follows:

$$\chi_{spy} = Kc_y M_y^a$$

For the whole polymer

$$\gamma_{sp} = \gamma_{spy} = K \sum y^{M} y^{a}$$

Then

$$[\mathcal{M}] = (\frac{\mathcal{M}_{sp}}{c}) = \frac{K \sum c_y M_y^{a}}{\sum c_y} = \frac{K \sum n_y M_y^{1+a}}{\sum n_y M_y}$$

1

Substituting

$$[\mathcal{T}] = K \overline{M}_{v}^{a}$$

then

$$\overline{M}_{v} = \left[\frac{\sum_{n_{v}} M_{v}}{\sum_{n_{y}} M_{y}}\right]^{1/a}$$
(23)

The values of K and a are determined from measurements of osmotic pressure and viscosity on narrow fractions of relatively homogeneous polymer.

The divergence between the number average and the viscosity average molecular weights is a measure of the molecular heterogeneity of the polymer. This may be calculated if the sums in equations (19), (20) and (23) can be evaluated. A derivation for the distribution of molecular size is required for this and a procedure similar to that used by Schulz (59) is followed. The argument proceeds as follows:

Consider the growing molecules at a small increment of conversion. Let "p" represent the probability that a growing molecule adds an additional monomer unit. Then the probability of termination, which is equal to the ratio of the rates of termination and propagation, is 1-p. Since the formation of a terminated primary molecule of y structural units requires y-l propagation steps and one termination step, the number fraction  $n_y$  of y<sup>th</sup> species in the polymer formed is

$$n_y = p^{y-1}(1-p)$$

while the weight fraction (wy) is

$$\mathbf{w}_{y} = \frac{yn_{y}}{\sum_{y=1}^{\infty} yn_{y}} = yp^{y-1}(1-p)^{2}$$

The number average molecular weight is then

and the weight average value is

The heterogeneity index is

$$\frac{\overline{M}_{w}}{M_{n}} = 1 + p = 2$$

since p must be close to unity if a high polymer is to result.

Ncw

Hence the viscosity heterogeneity index is

For GR-S dissolved in benzene or toluene Harris (53) found a = 0.67 and hence

$$\overline{M}_{v} = 1.85 \overline{M}_{n}$$

This derivation holds only where branching does not occur; hence, will apply only for the initial stages of the reactions to be studied.

#### PART I

## POLYMERIZATION OF SYSTEMS CONTAINING BUTADIENE AND STYRENE IN THE RATIO OF 75:25

By the copolymerization of two monomers it has been found possible to create polymers, which apparently have the intermolecular relations, in respect of configuration and attractive forces, required for a rubberlike substance. Such a pair are butadiene and styrene which are copolymerized to yield a polymer known as GR-S. This polymer has been found to possess many desirable mechanical and chemical properties. However, two possible disadvantages, among others, may be mentioned:

(1) The GR-S polymers have a broad molecular weight distribution in contrast to a narrow distribution in natural rubber.

(2) Since the diene polymer still contains a double bond for each monomeric unit, these bonds act as a source of activity for cross linking reactions between the chain molecules, leading to the formation of molecular nets during the course of the polymerization. Such characteristics as solubility, plasticity, tensile strength, modulus and elongation at break are all apparently enhanced in polymers consisting essentially of straight chain macromolecules of reasonably high molecular weight.

It was thought that by incorporating the principle of fractionation by a precipitant into a polymerization reaction the homogeneity and the molecular weight of the polymer could be controlled within reasonable The solubility of polymers is known to decrease with increasing chain length and precipitation occurs at a given chain length. If the polymerization were to proceed in a suitable solvent or mixture of solvents, it might be expected that only those chains greater than a certain length should precipitate while all others remain in solution and continue to grow. This might lead to a material of greater homogeneity than is attainable in emulsion polymerization. In 1936 a process of this type was patented (59), in which vinyl chloride was polymerized with vinyl acetate in hexane as solvent and with benzoyl peroxide as catalyst.

Such an investigation could be made either in an emulsion system or in solution. The latter was chosen for this study, since it was considered to be the simpler system. However, before proceeding with any attempt to homogenize the polymer by fractionation simultaneously with polymerization it was obviously necessary to obtain information on the copolymerization of butadiene and styrene in homogeneous systems.

Two investigations have been made on the copolymerization of butadiene and styrene in the bulk phase.

Marvel et al (60) studied the bulk copolymerization of styrenebutadiene in the ratio of 75:25 (by weight), using sodium sand as catalyst. The copolymers found were soluble in benzene and had intrinsic viscosities similar to those of GR-S. The composition of the copolymer was constant throughout the reaction and the molecular weight distribution was very similar to that of natural rubber. The introduction of a diluent increased the time for polymerization manyfold, and the molecular weight was so reduced that the product became soft and tacky.

Koningsberger and Solomon (61) have recently published a series of papers on the preparation and properties of rubberlike substances in bulk and emulsion phase systems. By determining the solubility and swelling of the bulk copolymers of butadiene and styrene in different solvents they showed that a true copolymer was formed. A side reaction which proceeded at an appreciable rate when the polymerization proceeded in the bulk phase at 100°C was found. The products isolated indicated that this side reaction was a dimerization of butadiene and butadiene with styrene to form cyclic products.

Several authors have investigated the polymerization of various monomers in the presence of non-solvent. Norrish and Smith (62) showed that the rate of polymerization of methyl methacrylate and the chain length of the polymer were increased when the reaction occurred in the presence of a non-solvent for polymer. They ascribed their effects to interference with the chain termination reaction when precipitation of the polymer occurred; i.e. to a reduction in the value of  $k_t$  in:

Rate of destruction of active chains =  $k_t M_n^{\pm 2}$ 

This concept of a diffusion controlled termination reaction cannot be considered as a principle applicable to polymerization in general, since very different results and conclusions have been recorded by other workers in this field.

White and Haward (63), working with methyl vinyl ketone, found that the rates of polymerization were less in liquids which did not dissolve the polymer. The intrinsic viscosity of the polymer, although greater than for good solvent, was less than when pure monomer was polymerized by itself with the same concentration of catalyst. However, when using methyl isopropenyl ketone, Haward (64) found an increase in both rate and intrinsic viscosity in the range 40 to 80 percent of diluent.

Abere et al (65) found that methanol had little effect on rate and molecular weight for the polymerization of styrene at  $60^{\circ}$ C.

This section deals principally with polymerization in systems containing butadiene and styrene in the ratio 75:25 (by weight). Since no results were available when this investigation was started to indicate whether or not true copolymerization did occur in solution, the rates of polymerization have been determined for systems containing styrene, butadiene and different mole fractions of the two as a preliminary to the study of possible fractionation simultaneously with polymerization.

#### EXPERIMENTAL PROCEDURE

#### 1. Polymerization

Styrene from Dow Chemical Co., Sarnia, containing t-butyl catechol as inhibitor, was purified by vacuum distillation through a small column packed with glass beads, a slow stream of air being used to agitate the contents of the distilling flask. The purified material was stored in a refrigerator at 0°C for periods not exceeding 48 hours.

Butadiene, a commercial grade supplied by Polymer Corporation, Sarnia, was purified by bubbling the gas through an absorber containing a 2N solution of sodium hydroxide (to remove any traces of the inhibitor, n-butyl catechol), dried by passing through two tubes of activated alumina and condensed into the storage vessel with a dry ice acetone bath.

The benzoyl peroxide used was the Eastman Kodak product which was approximately 98.7 percent pure.

The diazo-amino-benzene was the Eastman Kodak reagent grade material.

The solvents used were C.P. grade except for the benzene which was thiophene free.

For the polymerization of styrene pyrex reaction tubes were used, which had a volume of approximately 12 ml. when sealed off. For copolymerization studies, the reaction tubes were made of thick walled combustion tubing (23 mm 0.D., 17 mm I.D.) and the volumes varied so that there was approximately 2 ml. dead space in all the vessels when sealed off. Since most polymerization reactions are very sensitive to traces of impurities, considerable care was taken in cleaning the reaction tubes. They were first filled with hot chromic acid, then rinsed several times with tap water, followed by distilled water, and finally dried in a vacuum oven at  $60^{\circ}$ C.

The benzoyl peroxide was weighed into a flask and dissolved in a measured volume of styrene. When this was not possible, as in the butadiene polymerizations, a known volume of a solution of benzoyl peroxide in benzene was added to the reaction vessel and the benzene evaporated under reduced pressure.

In the 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 that the specific volumes of the two components were additive.

For the polymerization of styrene the solution containing the correct concentration of solvent, monomer and catalyst was measured volumetrically into the reaction tubes which were then cooled, flushed with nitrogen, sealed and stored at  $-10^{\circ}$ C.

For the copolymerizations the solution consisting of solvent, styrene monomer and catalyst was measured into the capsules volumetrically. Condensed butadiene was then weighed into the tubes in slight excess and allowed to evaporate until the correct weight of material remained. This served also to flush out the air. The tubes were tightly stoppered, chilled in a dry ice acetone mixture and then sealed.

In general, five identical samples were prepared for each experiment. The tubes were placed in thermostats controlled to within  $\pm .1^{\circ}$ C and left for definite intervals of time. When removed from the bath the reaction was stopped by chilling in an ice-salt-water bath. Tubes which contained butadiene were placed in a dry ice-acetone mixture before opening.

The contents when chilled were poured into a tared beaker containing an excess of methanol and a little hydroquinone. When the polymer had coagulated and the supernatant liquid was clear, the liquid was decanted and the remaining polymer washed three times with methanol and then dried to constant weight (3-5 hours) in a vacuum oven at  $40^{\circ}$ C.

### 2. Characterization of Polymer

(a) Determination of styrene content

For polymers containing low percentages of bound styrene (around 25 percent) the refractive index method was used for determining the styrene content. This was calculated from the equation:

% Styrene = 22.94  $\div$  0.118(N<sub>D</sub><sup>25</sup> - 1.5339) X 10<sup>4</sup> - 2340(N<sub>D</sub><sup>25</sup> - 1.5339)<sup>2</sup> A correction of -0.60 was made since no mercaptan was present in the solutions.

For polymers of high styrene content the degree of unsaturation was determined by the halogen addition method of Galletly and Maher (66). A known weight (approximately 0.10 grams) of finely divided polymer was placed in a 500-ml. iodine flask with 50 grams of reagent-grade / -dichlorbenzene and the flask placed on a hot plate at 175-185°C to decompose the polymer. When the polymer was completely decomposed (20-180 minutes) the flask was allowed to cool and 50 ml. of chloroform added to liquefy the material before crystallization becomes complete. To the cooled solution 25 ml. of 0.2 N iodine monochloride in carbon tetrachloride was added. A thin film of 15 percent potassium iodide was placed on the stopper before closing and the flask was left for 1 hour in the dark at room temperature to complete the reaction, after which 25 ml. of 15 percent potassium iodide was added, followed by 50 ml. of distilled water. The excess iodine monochloride was immediately titrated with standard 0.1 N sodium thiosulfate with starch as the indicator. Occasionally it was necessary to add 25 ml. of ethanol toward the end of the titration to break the emulsion. A blank was similarly carried through all the steps of a determination. The iodine number was calculated as follows:

where B = titration for the blank

- T = titration for sample
- N = normality
- w = sample weight in grams

The percent bound styrene is then calculated from

% Styrene = 
$$(I.N. of polybutadiene-I.N. of sample) X 100I.N. of polybutadiene$$

where the iodine number of polybutadiene = 458.

(b) Determination of molecular weight

Ubbelohde viscometers were used for the determination of intrinsic viscosities. The outflow times for the two viscosimeters used in this part of the work were 197.6 and 226.1 seconds for pure benzene, so that the kinetic energy correction was very small. This correction was determined by calibrating the viscometer by means of three different liquids, viz. benzene, water and carbon tetrachloride, and applying the standard viscosity equation which has the form

$$V = At - \frac{B}{t}$$

where  $\boldsymbol{v}$  is the kinematic absolute viscosity

A is the instrument constant B is the kinetic energy constant t is the outflow time

Hence, by using any two liquids whose kinematic viscosity is accurately known, the two constants may be evaluated. Unfortunately these data were lost in a laboratory fire and cannot be presented here. The procedure used was developed by Cragg (67) and allowed a one point determination of the intrinsic viscosity at concentrations such that  $t_r>1.2\langle1.4$ by use of the equation

$$\left[\mathcal{N}\right] = \frac{8(t_r^{1/8}-1)}{C}$$

where  $[\mathcal{X}]$  is the intrinsic viscosity

tr is the relative time of outflow

C is the concentration

This equation was found to give a horizontal straight line  $for[\mathcal{X}]$  plotted against C for several polymer samples taken at random from the samples on hand at the time. These data were also lost in the fire; however, in Part III data to illustrate the  $[\mathcal{X}]$  vs. C plot will be presented for the viscometers used in that portion of the work.

The intrinsic viscosities were converted to molecular weight by using the equation derived by Hulse et al (68)

$$\log M = 4.95 + 1.52 \log[7]$$

#### EXPERIMENTAL RESULTS

The first question to be answered in this work was whether true copolymerization did occur for the experimental conditions used. Experiments were, therefore, made using different mole fractions of butadiene and styrene in the presence of carbon tetrachloride as solvent, with benzoyl peroxide as catalyst. The total concentration of monomers in the solution was 3.85 moles per litre, the catalyst concentration 0.0415 moles per litre, and the temperature 75°C. The results are given in Table I. In Tables II and III data are given for the polymerization of butadiene and styrene alone in concentrations corresponding to those used in the copolymerizations.

If the two substances were reacting independently it would seem reasonable to expect that the styrene polymerization, which is the faster, would dominate the reaction to yield a curve which would be linear at least for that portion of the curve where the styrene concentrations are the larger. However, as may readily be seen from fig. 1, small amounts of butadiene greatly reduce the rate of polymerization. This may be explained if butadiene copolymerizes with styrene since the rate of copolymerization should be remarkedly reduced by the less easily polymerizable substance which, having entered the chain, would retard its growth.

The polymers varied from a hard, clear, brittle form at high styrene content to a polymer which was quite viscous at high butadiene content.
### TABLE I

### FORMATION OF STYRENE-BUTADIENE COPOLYMER IN CARBON TETRACHLORIDE

Total monomer concentration = 3.85 moles/litre Benzoyl peroxide concentration = 0.0413 moles/litre Temperature = 75°C

Styrene Concentration		Conversion %		Styrene in Polymer	
Mole %	Moles/litre	Wt. %	6 hr.	12 hr.	after 12 hrs.
1.0	3.85	100	58.5	74.0	
0.9	3.47	94.6	34•5	57.2	94.1
0.8	3.08	88.4	26.8	45.1	83.2
0.7	2.70	81.5	21.5	36.2	76.9
0.6	2.31	74.1	17.2	32.6	65.9
0.5	1.93	65.8	13.6	27.1	
0.4	1.54	56.2	12.4	25.0	50.5
0.3	1.16	45.1	12.2	23.5	
0.2	0.770	32.7	11.7	22.9	29.1
0.1	0.385	17.6	11.5	21.0	
0.0	0.000	0	11.2	20.7	

#### TABLE II

# FORMATION OF POLYSTYRENE IN CARBON TETRACHLORIDE

Benzoyl peroxide concentration = 0.0413 moles/litre Temperature = 75°C

Styrene Concentration (moles/litre)	Conversi 6 hr.	on % 12 hr.
3.85	59.6	74.0
3.08	47.7	65.9
2.31	40.8	60.7
1.54	33.0	50.1
0.770	20.2	25.9

#### TABLE III

FORMATION OF POLYBUTADIENE IN CARBON TETRACHLORIDE

Benzoyl peroxide concentration = 0.0413 moles/litre Temperature = 75°C

Butadiene Concentration	Converstion %		
(moles/litre)	6 hr.	12 hr.	
3.85	10.8	21.9	
3.08	10.6	19.2	
2.31	10.1	18.5	
1.54	9.8	16.2	
0.77	6.93	13.3	



Figure 1 - Polymerization of butadiene, styrene and copolymerization of 25% by weight of styrene and 75% of butadiene in a 3.85 molar solution of carbon tetrachloride with a catalyst concentration of 0.0413 moles per litre. Temperature = 75 C.

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Analysis for styrene content (Table I) showed that more butadiene was present in the polymer than in the initial mixture, i.e. that butadiene reacted faster than styrene. This can only be explained if copolymerization occurred.

Having shown that true copolymerization did occur in homogeneous solution polymerization, butadiene and styrene in the ratio of 75:25 (by weight) were then polymerized in systems containing different concentrations of carbon tetrachloride. The polymers formed in these experiments were all of low molecular weight. This was believed to be the result of using carbon tetrachloride as the solvent since there is direct evidence that it may function as a chain transfer agent (69).

These experiments were then repeated using benzene as the diluent. The results of the polymerization for a 3.85 molar solution of monomer in benzene are given in Table IV. Again, the polymers were of low molecular weight even after 90 hours polymerization when the reaction was approximately 50 percent completed. The low molecular weights might have resulted from dilution by solvent, either by chain transfer or a straight concentration effect.

If the effect is one caused purely by dilution, then it is to be expected that the molecular weight of material formed at high monomer concentrations should be high but decrease progressively with dilution. A survey of the literature showed that no information was available on this aspect of copolymerization.

Since it was desirable to obtain a product with molecular weight in the range generally associated with synthetic rubbers at an adequate rate, it seemed advisable to determine the effect of catalyst concentration and

### TABLE IV

FORMATION OF POLYMER IN BENZENE AT 75°C FOR A BUTADIENE-STYRENE RATIO OF 75-25

Concentration of monomers = 3.85 moles/litre Benzoyl peroxide concentration = 0.0413 moles/litre

Time hr.	Conversion %	Styrene in Polymer %	Mol.Wt. (X10 <sup>-3</sup> )
5.0	9.20	20.1	
10.6	12.5		
18.0	25.8	20.1	4.57
24.0	32.2		
48.0	45.0	20.3	
66.5	49.9		6.92
90.0	53•5	20.5	11.9

temperature, as well as solvent, on the copolymerization of 75 percent butadiene and 25 percent styrene.

Benzoyl peroxide as catalyst:

1. Effect of catalyst concentration -

The catalyst concentration was varied from 0.055 gm. to 0.500 gm. per 12 gm. of monomers. The results for a temperature of  $75^{\circ}$ C are given in Table V.

Unlike the polymerization of styrene alone the average molecular weight of the polymers formed increased with reaction time; hence the molecular weights were compared at the same percentage conversions to determine the effect of the catalyst concentration. The comparison must be made at conversions of twenty percent or less. Above this point the catalyst is no longer the controlling factor and cross-linking or branching comes to the fore, especially for low catalyst concentrations.

In fig. 2 the molecular weights are plotted against percent conversion for various catalyst concentrations. In fig. 3 the molecular weights are plotted against the inverse of the square root of the catalyst concentration for 20 percent conversion. The points all fall on a straight line except for a catalyst concentration of 0.055 gm. per 12 gm. of monomers.

These experiments were repeated at  $100^{\circ}$ C to test the validity of the above relation. The results are given in Table VI and plotted in fig. 4. The molecular weights are plotted against the inverse of the square root of the catalyst concentration for 20 percent conversion in fig. 3. Here again the points for high catalyst concentrations fall on a straight line while those for 0.055 and 0.022 gm. are higher than expected, probably as a result of branching.

# TABLE V

### THE EFFECT OF CATALYST CONCENTRATION ON MOLECULAR WEIGHT AND RATE

wt. of butadiene = 9.0 gm..
wt. of styrene = 3.0 gm..
Temperature = 75°C

### Catalyst Concentration in gm. per 12 gm. of monomers

Time (hr)	Con <b>v.</b> (%)	Mol.Wt. (X10-4)	Conv. (%)	Mol.Wt. (X10-4)	Con <b>v.</b> (%)	Mol.Wt. (x10-4)	Con <b>v.</b> (%)	Mol.Wt. $(x10^{-4})$
	0.0	55	0.0	80	0.1	.15	0.	.150
5.1 10.5 18.0 24.0 60.1 108.0 154.7	3.60 6.90 11.05 13.4 22.8 29.1 33.3	1.21 1.58 1.85 3.24 6.31	4.72 8.94 13.5 17.1 28.4 36.6 42.8	1.15 1.29 1.44 2.59 6.61 9.08	6.49 11.15 16.9 20.9 36.1 45.7 54.3	0.617 0.832 0.981 1.40 2.40 7.50 12.1	6.64 12.7 19.8 23.8 40.8 53.6 60.9	0.631 0.851 1.09 1.16 2.37 9.23 10.1
Rate (%	/hr) .705		.926		1.05		1.30	
	0.2	250	0.1	100	0.5	500		
5.0 5.4 10.3 11.1 15.7 16.5 20.9 22.7 30.7 44.8	8.04 13.2 22.7 28.1 37.3 46.1	0.679 0.811 0.944 1.24 1.73	10.8 21.4 29.6 37.9	0.530 0.641 0.720 0.900	11.6 23.6 33.6 42.9	0.450 0.492 0.645 0.825		
Rate (%	/hr) 1.60		1.95		2.10	)		

# TABLE VI

THE EFFECT OF CATALYST CONCENTRATION ON RATE AND MOLECULAR WEIGHT

wt.	of	butadiene	=	9.0	gm.
wt.	of	styrene	=	3.0	gm.
Temp	pera	ature	=	1000	0°

Catalyst Concentration in gm. per 12 gm. of monomers

Time (hr)	Conv. (%)	Mol. Wt (X10-4)	•	Time (hr)	Con <b>v.</b> (%)	Mol. Wt. (X10-4)
	.022				.055	
0.75 1.50 2.00 4.91 9.00	3.00 5.00 6.11 9.25 10.8	1.11 1.60 3.52		0.50 1.00 1.50 2.00 6.90	3.24 6.21 8.28 9.13 14.0	0.596 1.83
14.1 26.0	12.2 15.7	4•91 8•07		17.1	17.0	3.43
Rate (%	%/hr) 3.75				6.21	
Time (hr)	Conv. (%)	Mol.Wt. (X10-4)	Con <b>v</b> . (%)	Mol.vt. (X10 <sup>-l</sup> +)	Conv. (%)	Mol.Wt. (X10-4)
	.08	0	0.	115	0.	160
0.33 0.50 0.75	2.75		5.88		6.91 9.98	
1.00 2.00 4.50 6.00	7.65 11.6 15.7 17.1	0.775 1.37 2.12	9.52 14.1 19.0 20.5	0.690 1.19 1.68	16.9 22.2 23.9	0.625 1.04 1.57
16.0 23.8	20.6 21.2	4.95	24.7 27.1	3.90 5.30	29.0 31.0	5.05 
Rate (%	(hr) 8.2	5	10	•2	13.	1
	0.2	00	0.300		0.	400
0.25 0.50 0.75 1.00 3.00 6.00 15.9 24.0	4.10 6.90 11.0 12.7 22.1 26.6 31.2 33.9	0.430 0.760 1.23 2.82 4.25	4.58 10.6 14.5 16.2 28.9 32.3 37.3 38.6	0.345 0.609 1.10 2.59 2.84	5.91 10.4 16.5 18.3 33.7 38.4 45.4 46.3	 0.330 0.830 0.920 2.26 3.18
Rate (%	hr) 14.0	D	18.	5	22.	U

Cutalyst Concin. gm./12 gm. Mon. 0 0022 0 0 0 055 9 0.080 0 0 0.115 0.150 0 0.250 8 0.400 Θ 0.500 0 0 7 0 C Molecular Weight ( x10-4 0 C 0 C C O 2 1 0 20 30 Percent Conversion 40 50 10 0

Figure 2 - Effect of Catalyst Concentration on Molecular weight at 75 C.

\*







Figure 4 - Effect of Catalyst Concentration on Molecular Weight at 100 C.

Initial rates of polymerization, obtained from the results in Tables V, VI and VII, and plotted in figs. 5, 6 and 7, for the experiments at  $50^{\circ}$ ,  $75^{\circ}$  and  $100^{\circ}$ C, gave the linear relation shown in fig. 8 when plotted against the square root of the catalyst concentration.

2. Effect of temperature -

In Table VIII the data for experiments at  $143^{\circ}$ C and catalyst concentrations of 0.022 and 0.055 gm. per 12 gm. of monomers are given. It is to be noted that the curves level off at approximately 40 percent conversion (fig. 9). This is believed to be the result of a Diels-Alder side reaction to yield cyclic dimers of butadiene and styrene, similar to that found by Koningsberger and Solomon (61) for the bulk copolymerization at 100°C.

A comparison of the results of Tables V, VI, VII and VIII, as in fig. 10, indicates that there is no definite relation between temperature and molecular weight below 25 percent conversion, while above this value an increase in temperature corresponds to an increase in molecular weight of the product. This may be readily accounted for by an increase in the extent of branching with increased temperature, above 25 percent conversion.

When the logarithm of the initial rate is plotted against the inverse of the absolute temperature a broken curve is obtained. The points for  $50^{\circ}$ , 75° and 100°C fall on a straight line giving an activation energy of approximately 24 kcal. for a catalyst concentration of 0.055 gm. (fig. 11). However, the point for 143°C is much lower than would be expected for the catalyzed polymerization. This may be the result of thermal activation playing a more important role than catalytic. Experiments made at 143°C in systems which were free of oxygen indicate that the reaction is mainly

### TABLE VII

# THE EFFECT OF CATALYST CONCENTRATION ON RATE AND MOLECULAR WEIGHT

Wt. of butadiene = 9.0 gm.Wt. of styrene = 3.0 gm.Temperature =  $50^{\circ}C$ 

Catalyst Concentration in gm. per 12 gm. of monomers

Time (br)	Conv.	Mol.Wt.	Conv.	Mol. Mt.
(111)	(%)	(X10 4)	(%)	(X10-4)
	0.0	)22 gm.	0.05	55 gm.
5.25	0.24	مور من من		
12.0	0.47		0.63	1.50
36.0	1.31		1.93	1.64
91.0	3.09	4.37	4.51	2.42
216.6	6.55	6.09	9.50	
431.0	12.5	9.05	18.9	6.00
Rate (%/hr)	.036		.051	
	0.0	80 gm.	0.11	.5 gm.
46.0	2.40	•• = •• •*	2.89	
61.7	3.47		3.96	
95•7	5•53		6.30	
Rate (%/hr)	.061		.069	
	0.1	50 gm.	0.20	00 gm.
46.0	3.30		3.80	
61.7	4.77		5.60	
95.7	7•53		8.81	
Rate (%/hr)	.083		.096	an a
	0.3	00 gm.	0.40	0 gm.
1:6.0	4.70		5.60	
61.7	6.96		7.78	
95.7	10.8		12.55	
Rate (%/hr)	.118		.134	

### TABLE VIII

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### EFFECT OF CATALYST CONCENTRATION ON RATE AND MOLECULAR WEIGHT AT 143°C

Wt. of butadiene = 9.0 gm. Wt. of styrene = 3.0 gm.

Catalyst concentration in gm./12 gm. monomers

	0.022		0.055	
Time	Conversion	Mol.wt	Conversion	Mol.Wt
(hr)	%	(x10-4)	%	(X10-4)
2.05	10.4	9.06	13.5	10.2
6.00	20.9	gel	23.4	gel
9.75	27.7	gel	28.9	gel
16.0	32.3	gel	34.4	gel
22.0	35.5	gel	40.5	gel
49•1 69•3	41.4	gel	43.3	gel









Figure 8 - Initial rate of polymerization vs C<sup>2</sup> (where C=the catalyst concentration in gm.) for various temperatures.







thermal (Table IX, fig. 9). This is to be expected at such a high temperature where the half-life of benzoyl peroxide is undoubtedly very short. The dimerization reaction also becomes very important at this temperature (61).

Gel appears in the polymer at 143°C after approximately 15 percent conversion. Since gel formation results from cross linking of high molecular weight polymers the average molecular weights of the soluble portions of polymer will be too low and have little meaning.

To obtain material of as large molecular weight as possible without gel formation, the addition of hexadecyl mercaptan to the reaction was studied. Some results are given in Table X and those for 0.01 gm. of mercaptan are plotted in fig. 9. These show that the addition of hexadecyl mercaptan has very little effect on the rate but decreases the molecular weight considerably.

3. Dilution with benzene -

For the study of the effect of dilution with a given solvent the catalyst concentration must be kept constant. There are two possible methods of doing this -

(1) Keeping the catalyst concentration constant on the basis of monomer present or

(2) Keeping the catalyst concentration constant on the basis of total solution (i.e. moles per litre).

Method (1) seemed to be the better for determining whether the effect of the solvent is that of a diluent only. Hence the first experiments were made with catalyst concentrations of 0.055 gm. and 0.115 gm. per 12 gm. of monomers. The results are given in Tables XI and XII.

### TABLE IX

### THERMAL POLYMERIZATION OF BUTADIENE AND STYRENE AT 143°C

(Tubes prepared under nitrogen)

Time (hr)	Conversion %
2.2 4.9	. 9.05 15.2
12.0	25.6
19.5	30.5
24.8	33.8

### TABLE X

# EFFECT OF HEXADECYL MERCAPTAN ON RATE AND MOLECULAR WEIGHT AT 143°C

# Cat. conc. = 0.055 gm. per 12.0 gm. monomers

Mercaptan	Time	Conversion	Mol. 77t.
(gm)	(hr)		(X10-4)
0.050	2.00	10.7	1.67
	5.25	18.3	2.54
	9.50	27.9	2.72
	16.3	32.9	3.17
	23.0	36.6	3.52
	47.0	39.6	3.99
	71.7	41.9	5.27
0.010	1.91 4.00 9.90 12.7 18.1 23.7 36.0	12.6 18.0 29.0 30.5 35.0 37.7 41.8	4.06 5.07 8.65 14.3 19.6 gel
0.005	5.山	22.0	gel
	10.8	31.3	gel

### TABLE XI

DILUTION WITH BENZENE AT 100°C

### Peroxide Concentration = 0.055 gm. per 12 gm. of monomers

#### Mole Percent of Solvent

٦

Time (hr)	Conversion (%)	Mol. Wt. (X10-4)	Time (hr)	Conversion (%)	Mol. Wt. (X10-4)
	10.0		1	25.0	
1.0 2.0 3.0 7.5 17.0 24.0	6.11 9.50 11.5 15.0 17.4 20.8 24.7	0.740 0.955 1.23 4.45	1.0 2.0 3.0 7.5 17.0 24.0	5.98 8.33 11.1 14.6 17.8 18.9 23.7	0.720 0.970 1.30 1.95 4.15 4.73 9.30
Rate (%	/hr) <b>±</b> 2.00	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		1.95	
35.0				43•5	
1.5 3.0 5.0 7.5 19.9 46.3 91.3	8.16 11.3 13.2 14.4 18.1 23.7 30.0	0.810 1.17 1.62 3.61 4.66 6.30 14.0	1.5 3.0 5.0 18.5 38.8 63.2 85.2	7:53 11.0 12.8 17.3 22.5 26.2 28.1	0.78 1.10 1.55 4.31 6.60 10.4 12.8
Rate (%,	/hr)# 1.92			1.86	
	69.0			80.0	
4.1 7.5 19.0 42.3 66.5 89.4 138.5	9.85 11.9 16.7 21.2 23.6 25.2 27.9	1.10 2.78 3.10 5.50 7.37 8.46 9.00	7.5 14.0 19.0 47.8 63.5 138.5 186.5	9.62 12.0 13.4 18.0 22.1 23.9 26.7	1.28 2.60 2.82 6.06 8.60 9.70
Rate $(\%/hr)^{\pm}$ 1.58 1.28					

\* Rate calculated from percent polymerized at 7.5 hours.

### TABLE XII

# DILUTION WITH BENZENE AT 100°C

# Peroxide Concentration = 0.115 gm/12 gm. of monomers

Time (hr)	Conversion (%)	Mol.Wt. (X10-4)	Conversion (%)	Mol.Wt. (X10-4)	Conversion (%)	Mol.Wt. (X10-4)
0.0		20.0		35.0		
9.6 17.6 34.8 82.1 130.0 177.7	24.1 30.9 42.1 49.9 54.9	3.68 8.30 26.2` gel gel	21.4 24.2 29.6 39.0 44.2 47.2	1.17 3.00 5.95 13.4 30.0 gel	20.5 23.5 28.1 35.4 39.4 42.5	1.76 2.84 5.08 10.2 16.6 19.4
Rate (%/hr)* 1:37			1.37		1.33	
	43.5		52•3		69.0	
9.6 17.6 34.8 82.1 130.0 177.7	19.8 22.5 26.6 33.3 34.9 37.9	1.73 2.75 5.20 8.52 11.7 15.4	18.6 21.9 26.1 31.1 35.2 36.9	1.62 2.50 4.47 7.60 9.50 11.9	16.7 19.1 23.1 28.1 30.7 33.3	1.34 2.49 3.55 5.21 7.70 9.00
Rate (%/hr) <sup>±</sup> 1.28			1.24		1.08	

Mole Percent of Benzene

\* Rate calculated from percent converted at 17.6 hours.

The rates given in the Tables are not initial rates; hence the apparent discrepancy. The rate of polymer formation decreased as the solvent concentration increased, but the change in molecular weight with change in solvent concentration is within experimental error (fig. 12). This would indicate that the chain transfer reaction in benzene as solvent is not of great importance. However, there may be two contesting influences here: chain transfer tending to decrease the molecular weight and decrease in catalyst concentration relative to total solution tending to increase molecular weight.

Although the molecular weight was maintained in these experiments the rate was considerably decreased for any appreciable degree of dilution. Therefore, studies were also made on the effect of dilution with benzene when the catalyst concentration was held constant on the basis of total solution.

Results for a catalyst concentration of 0.0267 moles per litre are given in Table XIII and fig. 13. Here the rates show a tendency to increase as dilution increases. The molecular weight is approximately proportional to the monomer concentration; the true dependence is probably  $M^{a}$  where a lies between 0.5 and 1 and is closer to 1 than 0.5. The rate is maintained under these conditions but the molecular weight rapidly decreases with increasing dilution.

The results in the previous sections show that as rate increases the general tendency is for the molecular weight to decrease. To obtain a product with molecular weight in the range generally associated with synthetic rubbers, consistent with an adequate rate of producing such product, it appeared necessary to obtain a new catalyst or possibly a



Figure 12 - Influence of Benzene Concentration on the Molecular weight of the polymer when the catalyst concentration is held constant relative to monomer concentration (ie. catalyst concentration = 0.115 gm. per 12 gm. of monomer) at a temperature of 100 C.

### TABLE XIII

## DILUTION WITH BENZENE AT 100°C

# Peroxide Concentration = 0.0267 moles per litre

#### Mole Percent of Benzene

Time (hr)	Conversion (%)	Mol.Wt. (X10 <sup>-4</sup> )	Time (hr)	Conversion (%)	Mol.Wt. (X10 <sup>-4</sup> )
	0.0			20.0	
6.0 17.6	20.5 21.1	1.68	6.1 16 h	21.8	2.00
34.8	30.9	8.30	30.0	30.3	4.80
130.0 161.3	42•1 49•9 54•9	26.2 gel gel	56.9 113.2 163.0	57•9 44•7 47•4	9.50 18.5 gel
Rate (%/hr)1	<b>t</b> 3.45		*****	3.58	9
	35.0		in an	43.5	
6.1 16.4 30.0 66.9 113.2	22.9 26.6 30.5 34.9 40.1	1.48 2.40 3.82 7.01 11.2	6.1 16.4 30.0 66.9 113.2	24.0 27.8 30.2 35.6 39.8	0.91 1.92 2.95 5.48 8.20
163.0	43.4		163.0	43.0	9.35
Rate (%/hr)	3.76			3.94	
	52.3			69.0	
6.1 16.4 30.0 66.9 113.2 163.0	24.5 28.5 32.4 37.8 39.7 43.0	0.62 1.62 2.65 4.41 6.25 7.67	6.1 16.4 30.0 66.9 113.2 163.0	25.6 29.1 32.8 38.2 39.0 39.0	0.46 1.53 3.30 3.80 3.85
Rate (%/hr)	4.02			4.20	

\* Rate calculated from percent polymerized after 6.1 hours.



Figure 13 - Influence of benzene concentration on Molecular weight when the catalyst concentration is held constant on basis of total solution (ie. catalyst concentration = 0.0267 moles per litre) at a temperature of 100 C.

\*

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different solvent for the reaction. Of the two possible approaches, it was expedient to study first the effect of different solvents.

4. Effect of various solvents -

In Table XIV are recorded the results for experiments made at 100°C with a catalyst concentration of 0.0267 moles per litre in the solvents methyl ethyl ketone, methyl amyl ketone, chlorobenzene, carbon tetrachloride, dioxane and benzene. The same volume of each solvent was used. Nitromethane was also used, but after a few hours the solution separated into three layers so the reaction was discontinued. In the other solvents the reaction mixture remained homogeneous throughout the period studied.

From fig. 14 it is obvious that the polymerization proceeded at the fastest rate in dioxane. A comparison of figs. 14 and 15 shows that in general an increase in rate resulted in a decrease in molecular weight. However, with carbon tetrachloride, the reaction proceeded at a rate comparable to that with benzene but the molecular weights of the products were very low in comparison with the other solvents, probably owing to the fact that carbon tetrachloride is an efficient chain transfer agent.

The same general trend in rate is found when the rates of polymerization in the various solvents are compared with the rates of peroxide decomposition determined by Bartlett (70) and Cass (71) in these solvents.

It appears from the results that a change of solvent offers no real solution to the problem of high rate and high molecular weight, since an increase in rate of polymerization results from an increase in the rate of peroxide decomposition, the greater initial concentration of free radicals thus formed resulting in a product of lower molecular weight. For this reason a change of catalyst was then tried.

### TABLE XIV

EFFECT OF VARIOUS SOLVENTS ON THE REACTION RATE AND MOLECULAR WEIGHT

-----

	Cat. Conc. Vol. of So Wt. of Sty Wt. of But Temperatur	re		
Solvent	Time (hr)	Conversion (%)	Mol. Weight (X10-4) 1.32 3.25 4.32 5.35 6.20	
Methyl-ethyl ketone	12.5 38.8 68.0 109.0 159.0	23.0 28.5 30.1 32.0 33.1		
Methyl-amyl ketone	12.5 38.8 68.0 109.0 159.0	28.4 38.1 41.1 43.0 48.5	1.98 4.05 6.00 7.58 10.2	
Chlorobenzene	12.5 38.8 68.0 109.0 159.0 204.0	30.4 35.3 41.3 44.6 46.4 49.3	1.92 4.80 6.77 9.50 8.30 15.6	
Carbon Tetrachloride	12.5 38.8 68.0 109.0 159.0	28.0 33.3 37.8 40.3 43.0	0.670 0.772 0.930 1.10	
Dioxane	12.5 38.8 68.0 159.0	28.3 41.7 46.5 51.7	1.70 3.57 3.85 7.60	
Benzene	6.1 16.4 30.0 66.9 113.2 163.0	24.0 27.8 30.2 35.6 39.8 43.0	0.91 1.92 2.95 5.48 8.20 9.35	





Figure 15 - Influence of various solvents on molecular weight of polymer at 100 C with a Catalyst concentration of 0.267 m/l.

Several catalysts of the ionic type (such as AlCl3) were tried but were found to be quite insoluble in styrene and butadiene mixtures. Although it was realized that another catalyst of the free radical type would probably not show any marked improvement with regard to rate and molecular weight, it was decided to try diazo-amino benzene. Since the decomposition takes place more slowly than that of benzoyl peroxide (72), the rate of reaction is maintained over longer periods of time. The quantitative relations of rate and molecular weight with catalyst concentration, temperature and solvent concentration were, therefore, checked with this catalyst since it was felt that at least more reproducible results, both for yields and physical properties, might be obtained. Diazo-amino benzene as catalyst:

1. Effect of catalyst concentration -

The catalyst (D.A.B.) concentration was varied from 0.0652 gm. to 0.3255 gm. per 12 gm. of monomers (equivalent to 0.08 to 0.40 gm. of benzoyl peroxide on a molar basis). The results for a temperature of  $100^{\circ}$ C are given in Table XV. The percent conversion-time results are plotted in fig. 16 while the viscometric molecular weights are plotted against percent conversion in fig. 17.

In fig. 16(b) the initial rates of polymerization are plotted against the square root of the catalyst concentration. All the points are found to lie on a straight line.

Since the molecular weight of the polymers increased with reaction time, comparison of the molecular weights of the products formed with different catalyst concentrations is made at the same percentage conversion. The results for 20.0 percent conversion are plotted against the inverse of

### TABLE XV

# EFFECT OF D.A.B. CONCENTRATION ON RATE AND MOLECULAR WEIGHT

Wt. of styrene = 3.0 gm. Wt. of butadiene = 9.0 gm. Temperature = 100°C

Catalyst Concentration in gm. per 12 gm. of monomers

Time (hr)	Conv. (%)	Mol.Wt. (X10 <sup>-4</sup> )	Conv. (%)	Mol.Wt. (X10-4)	Conv. (%)	Mol. Nt. (X10-4)
	0.0652		0.0938			
6.75	3.62	5.15	3.83	4.58		
17.1	9.02	6.80	10.63	5.88		
23.8	12.7	7.40	13.9	6.40		
40.5	20.0	9.00	24.4	8.35		
63.0	30.9	14.9	30.1	11.2		
112.0			36.6	16.5		
Rate (%	/hr) 0.	532	0.	590		
	0.1221		0.2038		0.3255	
5.75	3.55	4.26	4.34	3.41	4.90	2.98
17.6	11.2	5.50	13.2	4.52	14.6	3.22
23.4	15.1	5.78	17.0	4.95	20.2	3.95
48.3	27.4	7.88	34.1	6.63	39.8	5•77
68.8	38.8	12.5	46.8	11.5	53 <b>•3</b>	12.0
68.8			46.3	10.5	54•4	12.0
Rate (%/	ate (%/hr) 0.646		0.72	23	0.8	62




Figure 17 - Effect of DAB concentration on the molecular weight of polymer formed at 100 C.

the square root of the catalyst concentration in fig. 17(b). A linear relation is found.

2. Effect of temperature -

In Table XVI the data for experiments at  $60^{\circ}$  and  $75^{\circ}$ C with catalyst concentrations of 0.0652 and 0.0938 gm. per 12 gm. of monomers are given. The molecular weight data for 0.0652 gm. of catalyst at the two temperatures have been plotted in fig. 18. An increase in temperature corresponds to a decrease in molecular weight. A plot of the logarithm of the molecular weight against the inverse of the absolute temperature gives a straight line (fig. 18(b)). This is the usual relation found for polymerizations with free radical catalysts since, with the same initial concentration of catalyst, an increase in temperature means an increase in the number of free radicals formed per unit time; hence a decrease in the molecular weight of the polymer formed.

The initial rates of polymerization for a catalyst concentration of 0.0652 gm. at  $60^{\circ}$ ,  $75^{\circ}$  and  $100^{\circ}$ C are respectively 0.0180, 0.0570 and 0.532%/hr. From these results an activation energy of approximately 21 kcal. was calculated.

3. Dilution with benzene -

Experiments were made at a temperature of 100°C with a D.A.B. concentration of 0.0267 moles per litre at various dilutions with benzene.

As may readily be seen from the results in Table XVII the rate of polymerization is independent of monomer concentration but the molecular weight of the product decreases with increasing dilution. In fig. 19 the molecular weights are plotted against percent conversion for the various concentrations of solvent. A linear relation is found to exist

## TABLE XVI

# POLYMERIZATION WITH D.A.B. AS CATALYST

Wt. of styrene = 3.0 gm. Wt. of butadiene = 9.0 gm.

# Catalyst Concentration in gm. per 12 gm. of monomers

Temp. oC	Time (hr)	Conversion (%)	onversion Mol.Wt. (%) (X10-4)		Mol.Wt. (X10 <sup>-4</sup> )	
		0.06	52	0.0938		
60	63.1	1.00	7•35	1.07	8.30	
	136.2	2.54	10.0	3.23	9.70	
	230.6	4.10	12.4	4.80	10.8	
	329.6	6.22	13.4	6.36	13.3	
	454.0	8.62	gel	8.27	gel	
	717.0	717.0 9.58 gel		9•75	gel	
Rate (%/nr)		.0180		•0230		
		0.065	2	0.0938		
75	40.8	2.28	7.72	2.03	7.98	
	112.4	6.66	11.5	6.97	11.3	
	190.5	10.8	14.9	11.1	13.4	
	260.9	12.6	19.8	13.4	17.8	
	310.7	17.3	17.3 20.5		19.6	
	380.7	17.3	25.6	19.1 22.8		
Rate (%/hr)		.0570		.0620	C	



Figure 18 - Effect of Temperature on Molecular Weight of Polymer formed with DAB as catalyst.

### TABLE XVII

### EFFECT OF MONOMER CONCENTRATION ON RATE AND MOLECULAR WEIGHT

## Temperature = 100°C Conc. of D.A.B. = 0.0267 moles/litre

Mole % Monomer	Time (hrs)	Percent Conversion	Mol. Wt. (X10-4)	$k_1(hr^{-1})$ <u>x 10<sup>3</sup></u>
100	6.75 17.1 23.8 41.75 63.0 112.0	3.83 10.36 13.9 24.4 30.1 36.4	4.58 5.88 6.40 8.35 11.2 16.5	6.06 6.43 6.32 6.66
80	6.0 17.3 23.3 41.6 69.6 89.0	3.66 10.30 13.95 22.15 33.25 41.35	4.05 5.17 5.61 6.62 8.70 10.8	6.52 6.16 6.30 6.04
65	6.0 17.3 23.3 41.6 69.6 89.0	3.37 10.25 12.75 22.25 33.0 40.6	3.45 5.18 5.40 5.70 6.80 7.88	5.74 6.34 5.88 6.10
55	6.0 17.3 23.3 11.6 69.6 89.0	3.17 10.35 13.9 21.8 32.5 39.8	3.49 4.42 4.21 5.39 5.60 6.42	6.34 6.42 5.92
1 <sub>t</sub> o	5.7 18.1 23.8 46.0 65.5 89.4	3.00 10.2 14.4 23.7 31.9 39.7	2.92 3.45 3.33 3.58 3.69 5.65	5.91 6.50 5.85
25	5.7 18.1 23.8 46.0 65.5 89.4	3.35 9.70 14.3 24.4 31.9 40.0	1.82 2.08 2.41 2.40 2.35	6.04 6.50 6.07





between molecular weight and monomer concentration (fig. 19(b)).

A comparison of the results for the polymerizations with benzoyl peroxide and D.A.B. as catalysts will be made later.

It seems an inescapable conclusion from the above experimental results that attaining a reasonably fast rate of polymerization and a high molecular weight polymer is impossible in homogeneous solution systems which are catalyzed by free radicals, since an increase in catalyst concentration or temperature decreases the molecular weight while increasing the rate of polymerization. Increasing the solvent concentration has little effect on the rate but decreases the molecular weight. Hence the original problem of fractionating during polymerization would seem to have academic interest only. The following work was done, however, to determine whether the presence of a non-solvent in the system was effective to any extent in narrowing the molecular weight distribution. The data presented are for benzoyl peroxide catalyzed polymerizations. A few experiments were made with D.A.B. as the catalyst and similar results obtained.

## Dilution with Isobutyl Alcohol - a non-solvent:

Work in this laboratory by Downes (73) has shown that in ethyl alcohol there is an induction period in the decomposition of benzoyl peroxide at 75°C followed by a period in which most of the peroxide decomposes, followed in turn by a very slow decomposition of the remaining peroxide. The other solvents studied, benzene, pyridine, carbon tetrachloride and isobutyl alcohol, give first-order decompositions. For this reason isobutyl alcohol, a precipitant for the copolymer, was chosen instead of

ethanol or methanol for these experiments.

For purposes of comparison it was decided that volume percent rather than mole percent of solvent should be compared. For example a 20 mole percent solution of benzene, such as 2.5 gm. of styrene, 7.5 gm. of butadiene and 3.9 gm. (3.63 ml.) of benzene should be compared with a solution containing the same amounts of butadiene and styrene with 3.63 ml. of isobutyl alcohol. In Table XVIII are recorded data for the polymerization of these two monomers at  $75^{\circ}$ C in the presence of benzene as solvent, which may be compared with the data in Table XIX, illustrating the effect of the non-solvent, isobutyl alcohol. It is clear that the polymer did not behave in the simple manner expected. Although precipitation, as a coacervate, was evident in experiments A-3, 4 and 5 (Table XIX), the average molecular weights are higher than for polymer formed in the comparable benzene solutions. This cannot be explained by differences in rates of conversion since these are within experimental error.

A series of experiments at  $50^{\circ}$ ,  $60^{\circ}$ ,  $75^{\circ}$  and  $100^{\circ}$ C, in which 5 tubes (40 mole percent of monomers) with solvents varying in composition from 100% benzene to 100% isobutyl alcohol were heated for a given period of time, showed the same results. The percent conversions were the same within 5 percent but the molecular weights of the polymers varied from low in benzene to high in isobutyl alcohol. At 100°C the coacervate was an insoluble gel. Typical results for  $60^{\circ}$ C are given in Table XX.

The only explanation seemed to be that further polymerization was taking place in the coacervate. The molecular weights in Tablex XIX and XX are the average molecular weights of all the polymer formed, i.e. both coacervate and soluble polymer. To determine whether the molecular

### TABLE XVIII

# EFFECT OF BENZENE ON RATE AND MOLECULAR WEIGHT

		Catalyst o Temperatur	conc. = re =	0.0267 mo] 75°C	les/litre	
Solvent Mole %		Time (hrs)		% Convers	sion	Molecular Weight (x 10 <sup>-4</sup> )
0	3 gm of st	cyrene and 19.3 43.3 67.3 91.2 115.3 170.2	9.0 gr	n of butadie 18.3 26.9 37.0 41.2 47.4 51.9	ene ,	1.16 2.89 3.20 5.76 9.00
20	2.5 gm of	styrene, 19.3 43.3 67.3 91.2 115.3 170.2 211.8	7•5 gm	butadiene, 17.4 32.3 37.9 - 47.7 49.0 49.3	3.63 ml of	benzene 0.875 1.65 3.02 - 4.83 6.92 9.80
35	2.0 gm of	styrene, 19.3 43.3 67.3 91.2 115.3	6.0 gm	butadiene, 20.7 31.8 38.4 41.5 45.5	5.75 ml of	benzene 0.965 1.37 1.75 2.49 2.910
45	2.0 gm of	styrene, 18.7 42.7 66.7 90.7 145.6 187.2	6.0 gm	butadiene, 21.9 34.4 39.7 43.9 49.6 50.8	8.70 ml be	nzene 0.810 1.28 1.70 1.78 2.58 4.25
60	1.5 gm of	styrene, 1 18.7 42.7 66.7 90.7 145.6 187.2	4.5 gm	butadiene, 23.4 35.0 41.5 45.6 48.5 50.8	12.7 ml be	nzene 0.632 0.692 1.02 1.23 1.58 1.77
75	1.0 gm of	styrene, 18.7 42.7 66.7 90.7 145.6 187.2	3.0 gm	butadiene, 25.0 35.1 42.9 48.2 49.2 50.8	17.1 ml be	nzene 0.420 0.565 0.583 - 0.870 0.990

### TABLE XIX

EFFECT OF ISOBUTYL ALCOHOL ON RATE AND MOLECULAR WEIGHT

Catalyst Conc. = 0.02675 moles/litre Temperature = 75°C

Series	No.	Time (hrs)				% Conversion			Molecular Weight (X 10 <sup>-4</sup> )		
A-l	2.5	gm	of	styrene + 18.6 42.5 64.2 88.2 135.2 183.2	7.5	gm	butadiene	+ 3.63 20.3 30.6 36.7 40.3 43.5 48.4	ml	of	isobutyl alcohol 1.025 1.53 2.26 2.97 4.25 5.73
A-2	2.0	£m.	of	styrene + 18.6 42.5 64.2 88.2 135.2 183.2	6.0	gm	butadiene	+ 5.75 22.1 33.6 39.6 41.1 46.9 50.9	ml	of	isobutyl alcohol 0.94 1.41 - 2.55 3.39 4.50
A-3	2.0	gm	of	styrene 4 18.6 42.5 64.2 88.2 135.2 183.2	6.0	gm	butadiene	+ 8.70 22.4 34.7 - 45.1 47.1 48.2	ml	of	isobutyl alcohol 0.880 1.275 1.74 2.45 3.34 3.35
A-4	1.5	gm	of	styrene + 18.6 12.5 61.2 88.2 135.2 183.2	4•5	gm	butadiene	+ 12.7 24.5 38.7 44.9 49.7 - 51.8	ml	of	isobutyl alcohol 0.700 1.07 1.55 2.20 2.89 3.34
A <b>-</b> 5	1.0	gm	of	styrene 18.6 42.5 64.2 88.2 135.2 183.2	• 3.0	e gm	butadiene	+ 17.1 21.3 40.5 44.1 51.6 52.6 51.4	ml	of	isobutyl alcohol 0.453 0.748 0.935 1.06 1.30 1.27

### TABLE XX

### EFFECT OF NON-SOLVENT ON MOLECULAR WEIGHT

Temperature = 60°C Wt. of styrene = 1.5 gm Wt. of butadiene = 4.5 gm Vol. of solvent = 12.7 ml

Volume % of isobutyl alcohol		Mol. Wt. (X 10 <sup>-4</sup> )				
Catalyst 0 25 50 75 100	conc.	= 0.2000	gms per 39.9 38.6 38.5 40.0 41.2	12 gms	of monomers	1.27 1.125 1.21 2.82 1.63 ± 4.45 ±±
Catalyst 0 25 50 75 100	conc.	= 0.4000	gms per 54.9 53.3 52.8 54.3 58.3	12 gms	of monomers	0.810 0.635 0.875 1.00 2.22

☆ Soluble polymer **#** Coacervate

weight of the polymer in the coacervate increased with increasing reaction time, a small tube was sealed on the end of the main tube. The coacervate was collected in this tube as it formed to permit its separation from the supernatant liquid.

The results in Table XXI show that the molecular weight of the coacervate does increase as reaction proceeds.

This increase in molecular weight is similar to that found by other investigators (62,64). Norrish and Smith ascribed their effects to an interference with the chain reaction when precipitation of the polymer occurred. This concept assumes that precipitation of the polymer does not cause deactivation. The fact that very different results have been recorded by different workers investigating this effect indicates that this assumption is not valid in all cases. However, the monomers, methyl methacrylate and isoprenyl ketone, which show pronounced increases in molecular weight of the polymer, belong to Melville's class of monomers which form polymers having a long life (17). It is interesting to note here that Medvedev (36) has also detected free radicals with a long life in a copolymer of butadiene and vinyl cyanide.

This increase in molecular weight relative to that formed in benzene could also be the result of an interaction between monomer and polymer or polymer and polymer in the presence of the catalyst in the coacervate to give rise to branching and cross linking.

The results show that, at the temperatures used in this study, reaction in the coacervate may seriously complicate any attempt to use a non-solvent to narrow the molecular weight distribution of a polymer during its formation. A method for continuously removing the polymer

### TABLE XXI

### MOLECULAR WEIGHT OF COACERVATE

Temperature	= 74.5°C
Wt. of styrene	= 1.5 gm
Wt. of butadiene	= 4.5 gm
Vol. of isobutyl alcohol	= 12.7 ml
Catalyst conc.	= 0.02675 moles/litre
-	

Time (hrs)	Mol. Wt. (X 10-4)
23.6	1.06
46.8	1.42
71.4	2.07
94.1	2.02
117.6	4.18
169.5	4.64

from the reaction as it is formed might give satisfactory results since this would allow "freezing-out" any reaction in the coacervate. However, it would not seem easy to obtain a satisfactory, yet reasonably simple, way of removing the coacervate without disturbing the reaction system.

A catalyst which would cause the polymerization in solution to proceed rapidly at room temperature may also prove effective; for example, a catalyst of the ionic type. The value of this suggestion is doubtful since the polymers which have a long life are believed to be formed by an ionic (or polarized bond) mechanism.

At this point two main paths for this investigation to follow were open: the original problem could be retained and addition of solvent-nonsolvent to the emulsion phase system investigated or the kinetics of the copolymerization in homogeneous solution could be further studied. It was felt that the time available could be used to greatest advantage if the second path were followed, particularly in view of the fact that the addition of non-solvent to the emulsion system was also being considered for investigation by Polymer Corporation. An investigation of the kinetics of copolymerization in homogeneous solution should prove useful for comparison with emulsion phase data.

#### DISCUSSION

A consideration of the apparent mechanism for the copolymerization of butadiene and styrene in the ratio 75:25 is of interest in relation to any extension of the studies into other types of systems.

A linear relation was found between the initial rate of copolymerization and the square root of the catalyst concentration for both catalysts (figs. 8 and 16(b)), a relation which holds for a free radical mechanism in which the radicals are formed by a first-order decomposition of catalyst and are removed by a second-order termination of the radical chains.

If it is assumed that this is the true mechanism, an analysis identical with that proposed by Price (30) for d-s-butyl- $\alpha$ -chlorocrylate will apply.

The free radicals are formed by the first-order decomposition of the catalyst,

$$\frac{dR}{dt} = k_1 C \tag{1}$$

built into chains by the normal propagation process,

$$\frac{dM}{dt} = k_p [R]M$$
(2)

and destroyed by collision of two activated molecules

$$-\frac{\mathrm{dR}}{\mathrm{dt}} = k_{\mathrm{t}}[\mathrm{R}]^2 \tag{3}$$

The value of [R], the concentration of free radicals, is determined by the initiation and termination steps on the assumption that a steady state

concentration of free radicals is rapidly reached and remains constant as long as there is enough monomer left to maintain it. By equating equations (1) and (3) the value of [R] is determined.

$$[R] = \sqrt{\frac{k_1 C}{k_t}}$$
(4)

The rate of polymerization is then obtained by substituting (4) in (2)

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_{\mathrm{p}} \left(\frac{\mathrm{k}_{\mathrm{l}}}{\mathrm{k}_{\mathrm{t}}}\right)^{\frac{1}{2}} \mathrm{MC}^{\frac{1}{2}}$$
(5)

The rate of the entire reaction is obviously obtained by multiplying the rate of activation,  $\frac{dR}{dt}$ , by the average number of monomers bound per chain; i.e. by the average degree of polymerization  $F_{a}$ .

$$\frac{dM}{dt} = \frac{dR}{dt} P_n \tag{6}$$

Hence the number average degree of polymerization is given by

$$\overline{P}_{\eta} = \frac{dM/dt}{dR/dt} = \frac{k_{p}}{\sqrt{k_{1}k_{t}}} \qquad \frac{M}{C^{\frac{1}{2}}}$$
(7)

As pointed out above the linear relation between dM/dt and  $C^{\frac{1}{2}}$  holds for both catalysts. It is realized that the average molecular weights calculated from viscosity measurements give only a rough approximation to the weight average molecular weight (which is twice the number average molecular weight). However, the fact that the molecular weights determined here for both catalysts are inversely related to the square root of the catalyst concentration may be taken as qualitative support for the relation in equation (7).

From equation (5) the disappearance of monomer is predicted to be first order for a given catalyst concentration. It is evident from Table XVII that satisfactory first-order constants are obtained for different monomer concentrations when D.A.B. is the catalyst. When benzoyl peroxide is used an increase in the rate of polymerization occurs on dilution, as is evident from data in Tables XIII and XVIII.

A direct proportionality exists between monomer concentration and molecular weight for D.A.B. (fig. 19(b)) while this is not true for benzoyl peroxide.

It is well known that the rate of benzoyl peroxide decomposition varies greatly in different solvents (70,71,73). This might be the explanation of the apparent divergence in the above results for the two catalysts and might also explain the difference in reaction kinetics for different monomers when polymerized in peroxide solutions.

Since the rate of free radical production from a catalyst such as benzoyl peroxide is dependent upon the solvent used, it is apparent that the kinetics of copolymerization of butadiene and styrene in a solvent might be highly dependent upon variations in composition of the reaction medium; i.e. upon relative proportions of the two monomers and solvent. This possibility made it appear necessary to study the rate of decomposition of benzoyl peroxide dissolved in butadiene, in styrene and in mixtures of the two at different dilutions with solvent. From such information it should be possible to establish conditions for constant rate of initiation of polymerization under different conditions to permit a sound comparison of rate data obtained.

Therefore, an investigation into the decomposition of benzoyl peroxide under conditions of different catalyst concentrations in solutions of different compositions and at different temperatures was undertaken as a preliminary to the study of the polymerization of styrene, butadiene and the copolymerization of mixtures of the two. These results with those for the polymerizations are discussed in the next section.

#### PART II

#### COPOLYMERIZATION IN HOMOGENEOUS SOLUTION AT CONSTANT FREE RADICAL CONCENTRATION

The only published kinetic investigation of copolymerization was made using the same initial concentration of catalyst, benzoyl peroxide (42). As pointed out in the discussion of the first section, the rate of free radical production from benzoyl peroxide is dependent upon the solvent used and, therefore, the kinetics of copolymerization, under conditions of constant initial catalyst concentration, may be expected to be dependent upon variations in the composition of the reaction medium. For a sound comparison of rate data obtained across the entire concentration range of monomers the rate of initiation of polymerization should be constant. To attain this end, rates of polymerization in the present investigation were compared at catalyst concentrations such that the initial rates of decomposition of the catalyst, benzoyl peroxide, were the same; i.e. the initial concentrations of free radicals were the same. The rate of initiation would be constant under these conditions only if all the free radicals from the catalyst, or at least the same fraction of radicals, were available for initiating polymerization. The presence of side reactions involving the catalyst radicals might introduce complications.

#### Introduction:

The fact that benzoyl peroxide generally reacts with organic solvents under the influence of moderate heating was first reported by Gelissen and Hermans in 1924 (74). To describe the reactions these authors presented a

scheme which involved the removal of a hydrogen atom from the solvent molecule. At the same time a careful analysis of the products of the reaction in boiling benzene was made and diphenyl, triphenyl, quaterphenyl, benzoic acid, phenyl benzoate and a mixture of other esters of benzoic acid were identified.

During the next few years it was amply demonstrated by various investigators that the solvent participated in the reaction. This was done by examining the products when benzoyl peroxide was decomposed by heating with toluene (75), chlorobenzene, nitrobenzene, ethyl benzoate (76,77) and pyridine, and further by a consideration of the products of decomposition of substituted benzoyl peroxides (78).

In their discussion of the benzoyl peroxide decomposition Gelissen and Hermans (79,80) had noted the correspondence between this compound and the diazonium compounds, and they suggested that an addition product was formed between peroxide and solvent, which then decomposed with liberation of carbon dioxide. This mechanism was discussed at length by Hey and Waters (81) who concluded that the evidence indicated the thermal decomposition of benzoyl peroxide both alone and in various solvents to involve an initial break up of the molecule into free radicals. These authors proposed as the initial step

 $(C_{6H_5CO_2})_2 \longrightarrow C_{6H_5COO} + C_{6H_5} + CO_2$  (3)

and showed that further plausible reactions among these radicals and solvent molecules could account for all the products which had been observed. These views have been generally accepted by subsequent investigators.

A kinetic study of the decomposition of benzoyl peroxide in benzene at

80°C was made by Brown (82) who found that the rate of decomposition depended on the concentration. A reaction order of 1.33 was deduced. Brown suggested that parallel monomolecular and bimolecular reactions occurred, viz. the monomolecular thermal decomposition of benzoate radicals into phenyl radicals and carbon dioxide, and the bimolecular oxidation of benzene by benzoate radicals forming benzoate ions.

The dependence of the rate of decomposition of benzoyl peroxide on concentration was confirmed by Bartlett and Altschul (83).

Kamenskaja and Medvedev (31) appear to have made the first measurement of the activation energy of benzoyl peroxide decomposition, finding a value of 29600 cals. per mole for the reaction in benzene. A slightly higher value of 31000 cals. per mole was found by McClure, Robertson and Cuthbertson (84).

An extensive study of the decomposition of benzoyl peroxide in various solvents at  $79.8^{\circ}$ C was made by Nozaki and Bartlett (70). These authors recognized that the reaction which appeared to be first order in individual experiments, but in which the rate depended on the initial concentration, probably involved a complexe mechanism. They suggested that the decomposition of peroxide might be induced by the presence of free radicals normally present in a solution of decomposing benzoyl peroxide. No actual reaction between such radicals appears to be assumed, the chain reaction being written:

 $C_{6H_5}COO + (C_{6H_5}CO_2)_2 \longrightarrow CO_2 + C_{6H_5}COOC_{6H_5} + C_{6H_5}COO \cdot$ In support of this mechanism it was shown that the decomposition was accelerated by the presence of such free radicals as triphenyl methyl and slowed down by such inhibitors as oxygen, hydroquinone and picric acid. The rates of decomposition in a large number of solvents were obtained, and it was shown

mathematically that the data were explicable on the basis of a spontaneous first-order decomposition with simultaneous three-halves order chain decomposition, or spontaneous first-order decomposition with simultaneous second-order chain decomposition.

The behaviour of benzoyl peroxide in a variety of solvents at 50°C has been studied by Cass (71). He found that the reaction orders varied from first to third according to the solvent used and that when the solvent was an ether only small amounts of carbon dioxide were evolved. Cass accepted the chain mechanism suggested by Nozaki and Bartlett but modified it to account for the reduced amount of carbon dioxide found with some solvents.

Similar results have also been published by Barnett and Vaughan (85).

The rate of benzoyl peroxide decomposition and the yield of carbon dioxide therefrom have been studied by Downes (73) at temperatures of  $79.8^{\circ}$ C and  $75^{\circ}$ C. The rate of decomposition was found to vary from solvent to solvent and as the rate of decomposition increased the yield of carbon dioxide decreased. A simple explanation of the behaviour was suggested on the assumption that the rate of decomposition of benzoyl peroxide in a given solvent is controlled by the rate of removal from the system of the benzoate radicals, which exist in equilibrium with the peroxide.

In benzene the benzoate radicals are assumed to be removed from the system mainly through thermal decomposition according to the equations

$$(c_{6H_{5}COO})_{2} \xrightarrow{k_{1}} 2c_{6H_{5}COO}$$
 (1)

$$c_{6H_{5}coo}$$
,  $k_{3}$ ,  $c_{6H_{5}}$ ,  $c_{02}$ . (2)

while in solvents which give rapid rates of peroxide decomposition it is assumed that the benzoate radicals are removed both by thermal decomposition

and by chemical reaction with the solvent molecules resulting in a shift to the right in equation (1).

The assumption of an equilibrium between benzoate radicals and benzoyl peroxide has also been used by Matheson (86) to derive an equation for the rate of polymerization of vinyl derivatives such as styrene and methyl methacrylate. As pointed out in the general introduction, the rate of polymerization of styrene was found to be directly proportional to the square root of the catalyst concentration and to the three-halves power of the monomer concentration (15b). This indicated that an initiation reaction must occur which is first order in both monomer and catalyst. Other authors (15,87), however, have found that, in general, the dependence of the rate of polymerization on the monomer concentration is much more complicated than predicted by the elementary theory, which considers the following three elementary steps:

Activation 
$$\frac{dM^{H}}{dt} = k_{i}mC$$
 (1)

Propagation 
$$-\frac{dM}{dt} = k_p M [M^{k}]$$
 (2)

Termination 
$$\frac{-dM^{\pm}}{dt} = k_t [M^{\pm}]^2$$
 (3)

where C is the catalyst concentration, M the monomer concentration and  $[M^{\pm}]$  the concentration of active centres.

Using the steady state assumption these yield the following expression for the rate of polymerization:

$$\frac{-dM}{dt} = k_p \int \frac{k_i}{k_t} C_{ZM}^2 \frac{1}{2}$$
(4)

from which

$$\frac{M^3}{(dM/dt)^2} = \frac{k_t}{k_i k_p^{2C}}$$

This indicates that a graph of  $M^3/(dM/dt)^2$  against M should be a horizontal straight line but such is not found. To explain this Josefowitz (87) postulated that an active centre is not formed as an immediate consequence of the collision between monomer and catalyst but that they first form a molecular compound (Cm) which is held together by comparatively weak secondary valencies which can undergo one of two possible transformations:

(a) It can decompose into unactivated monomer and catalyst

$$(Cm) \longrightarrow C + m$$

(b) It can undergo some internal rearrangement and be transformed into an active centre

(Cm) 
$$\longrightarrow$$
 Cm <sup>$\pm$</sup>  or m <sup>$\pm$</sup> 

Hence the rate of active centre formation is

$$\frac{d\mathbf{M}^{\pm}}{dt} = k_{1}(Cm)$$
 (5)

The concentration of (Cm) is computed by the use of the law of mass action, and the fact that (Cm) is always small in comparison with m. This yields

$$(Cm) = \frac{KmC}{1 + Km}$$
(6)

where K is the equilibrium constant which controls the concentration of (Cm). Introducing (6) in (5) and using this in place of (1) we find that

$$-\frac{dM}{dt} = k_p \sqrt{\frac{k_i}{k_t}} K \frac{m^{3/2} C^{\frac{1}{2}}}{\sqrt{1 + Km}}$$
(7)

This will give  $m^3/R^2$  as a linear function of m which was found to fit experimental results. The values of K obtained showed the complex to be more stable at higher temperatures which is unlikely.

Matheson derived equation (7) by applying the considerations used by Franck and Rabinowitch (88) to photolysis in solution. The essential idea is that two fragments from a dissociated molecule find themselves held in a cage of solvent molecules and, therefore, the radical pair collide many times with each other and the surrounding molecules before they can diffuse apart.

It is expected that, if two radicals or a radical plus a molecule are in contact with each other in solution and may react with a very low activation energy, then in general reaction will occur before the components can separate. The rate of activation is derived by consideration of the three equations:

$$\begin{pmatrix} (C_{6}H_{5}COO)_{2} & \frac{k_{1}}{k_{2}} & 2C_{6}H_{5}COO \cdot \\ 2C_{6}H_{5}COO \cdot & \frac{k_{2}}{k_{2}} & (C_{6}H_{5}COO)_{2} \\ C_{6}H_{5}COO \cdot & M & \frac{k_{3}}{k_{2}} & M^{\pm} \\ \frac{dM^{\pm}}{dt} &= k_{1}C - k_{2} \left[ C_{6}H_{5}COO \cdot \right] &= k_{3} \left[ C_{6}H_{5}COO \cdot \right] M \\ \left[ C_{6}H_{5}COO \cdot \right] &= \frac{k_{1}C}{k_{2} + k_{3}M} \\ \frac{dM^{\pm}}{dt} &= \frac{k_{3}k_{1}C}{k_{2} + k_{3}M} \cdot M$$

$$(8)$$

Substituting (8) for (1) yields

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = \sqrt{\frac{\mathrm{k}}{\mathrm{k}_{t}}} M C^{\frac{1}{2}} \left( \frac{\mathrm{k}_{1}\mathrm{k}_{3}/\mathrm{k}_{2}}{1 + \frac{\mathrm{k}_{3}}{\mathrm{k}_{2}}} M \right)^{\frac{1}{2}}$$
(9)

where  $k_3/k_2$  is analogous to K in (7). It is reasonable that  $k_3/k_2$  should increase with temperature. This explanation of styrene polymerization kinetics fits in very well with the Downes mechanism for benzoyl peroxide decomposition. It would, therefore, appear that, if the overall rate of benzoyl peroxide decomposition  $(k_1C - k_2 [C_{6H_5}COO \cdot])$  were held constant as the monomer concentration was varied, a very simple kinetic pixture would result. In 1945 Cohen (89) determined the effect of temperature on the rate of decomposition of peroxide in 3.85 molar solution of styrene in benzene. When using the same initial concentration of free radicals at the three temperatures he found an increase in temperature resulted in an increase in the rate of polymerization and the molecular weight of the polymer formed. Activation energies for the propagation and chain transfer reactions were calculated using equation (4).

The peroxide-catalyzed polymerization of butadiene in bulk phase has received little attention. The only known study was done by Graham (90) incidental to studies on butadiene popcorn growth. The usual dependence of rate on the square root of the catalyst concentration was found. The effect of adding a diluent to the system was not studied.

The development of the formal kinetics of copolymerization has received considerable attention in the past few years. However, the experimental data for homogeneous solution systems lags far behind, the only published work directly concerning the rate of copolymerization being that of Norrish and Brookman (42) for styrene and methyl methacrylate.

Because of the lack of experimental data on the bulk copolymerization of butadiene and styrene and because of the value of such data for comparison with that of emulsion phase polymerization this work was undertaken.

The investigation embraced a study of the polymerization of butadiene, styrene and copolymerization of the two in the liquid state with a view to determining the effect of catalyst concentration, solvent concentration and temperature on the initial rate of polymerization and on the molecular weight of the product. All comparisons were made at the same initial concentration of free radicals. The data for the rate of decomposition of

benzoyl peroxide in the different reaction media and under various conditions from which the required peroxide concentrations were calculated are also presented and discussed in this section.

#### EXPERIMENTAL AND RESULTS

### 1. Decomposition of Benzoyl Peroxide

#### (a) Experimental Procedure:

In the present work the disappearance of benzoyl peroxide was followed in each of the monomers and in mixtures of them as the catalyst concentration, solvent concentration and temperature were varied.

Benzoyl peroxide was estimated by the iodometric method of Gelissen and Hermans (91). Potassium iodide was added to the solution of benzoyl peroxide in acetone with about 5 ml. of water. After waiting a few seconds for the reaction to complete itself, 0.05N thiosulfate solution was run in until the iodine colour was nearly discharged, when about 50 ml. of water and a little starch solution were added and the titration completed. The reaction between benzoyl peroxide and potassium iodide may be represented thus:

(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub> + 2KI → 2KCOOC<sub>6</sub>H<sub>5</sub> + I<sub>2</sub>

To determine the rate of benzoyl peroxide decomposition in the various solutions, a solution of the peroxide of desired concentration was made at room temperature and the reaction tubes filled as described in part I. The tubes were placed in a thermostat at the desired temperature and withdrawn at definite intervals. The reaction was "frozen out" by placing the tubes in a dry ice-acetone bath.

With solutions containing polymer, the polymer solution was dropped slowly into an excess of alcohol which was being rapidly stirred. In this way almost complete separation of peroxide from polymer was obtained. If

the solution contained 5 percent or more of polymer two precipitations were made to ensure complete removal of peroxide from the polymer. After standing for a few hours the supernatant liquid became clear and was decanted into an Erlenmeyer flask. The polymer was washed 3 times with ethanol and the washings added to the peroxide solution.

The sample solution was evaporated almost to dryness at room temperature either in a vacuum oven or by a stream of air. Benzene solutions of the catalyst were also evaporated almost to dryness. This procedure gives very sharp end points and is preferable in this respect to the procedure outlined by Siggia (92), although it is more time consuming. Acetone (5 ml.) was added to the residue and the analysis completed as described.

- (b) Experimental Results:
- (i) The rate of benzoyl peroxide decomposition in benzene at various concentrations and temperatures -

It has been shown that the rate of decomposition of benzoyl peroxide in benzene depends upon the initial concentration (73). The work which had been done on the copolymerization prior to this study had been at the same weight percent of catalyst for different monomer concentrations. This results in a variation in catalyst concentration of 0.0301 to 0.0245 moles per litre. The decomposition in benzene was studied over this range. The data are given in Table XXII. The concentrations of benzoyl peroxide at the times shown are given in terms of the amounts of thiosulfate solution required to complete the titration of a sample of constant size (10 ml.).

For calculation of the activation energy experiments were made at  $60^{\circ}$  and at  $87.5^{\circ}$ C with a catalyst concentration of 0.0476 moles per litre. These

results are also given in Table XXII. All the data are plotted in fig. 20. Straight lines are found in each case, from which it is evident that the individual experiments were first order.

A plot of the logarithm of the rate of decomposition against the inverse of the absolute temperature gave a straight line (fig. 26). From this curve an activation energy of 30.300 kcal. per mole was calculated. This is in good agreement with the values of 31.0 and 29.6 kcal. per mole found by other workers (31,84).

(ii) The decomposition of benzoyl peroxide in systems containing styrene -The concentration of benzoyl peroxide in pure styrene was varied from
0.05 gms. to 0.115 gms. per 12 gms. of styrene at 75°C and from 0.115 gms.
to 0.250 gms. at 60°C. The data presented in Table XXIII (and plotted in
fig. 21) are for a sample of constant weight (12 gms. of styrene or 13.2
ml.). There is no appreciable change in the rate of decomposition at a
given temperature over the range of concentrations studied.

In Table XXIII the data for the decomposition at 87.5°C of .115 gms. of peroxide in 12 gms. of monomer are also presented. An Arrhenius plot of the rates of decomposition at the different temperatures using the data for 0.115 gms. of benzoyl peroxide in 12 gms. of styrene yielded a straight line from which an activation energy of 26.5 kcal. per mole was calculated.

The rate of benzoyl peroxide decomposition in styrene is much faster than that in benzene (0.0966 hr<sup>-1</sup> compared with 0.0621 hr<sup>-1</sup> for 0.0361 m/1 of peroxide in benzene). It is to be expected, therefore, that the introduction of benzene into the reaction mixture will tend to decrease the rate of peroxide decomposition and hence the number of free radicals initially present in the solution. To determine the magnitude of this effect experi-

Temp. oc	Cat.Conc. (m/1)	Time (hr)	Mls. of Thios.	Log <sub>10</sub> T	$\frac{\text{Rate}}{(\text{hr}^{-1})}$
75	0.0476	0.00 0.83 2.75 3.50 4.50	19.50 18.47 16.35 15.65 14.60	1.2900 1.2665 1.2135 1.1945 1.1644 Аve.	- 0.0650 0.0639 0.0628 0.0640
	0.0361	0.00 0.75 1.50 2.17 2.83 4.00	14.75 14.15 13:30 12.90 12.40 11.52	1.1688 1.1507 1.1239 1.1106 1.0934 1.0614 Ave	- 0.0555 0.0688 0.0618 0.0618 - 0.0618
	0.0317	0.00 0.83 2.00 2.75 3.50 4.50	12.95 12.60 11.45 10.97 10.45 9.85	1.1123 1.1003 1.0588 1.0402 1.0191 0.9934 Ave	- 0.0615 0.0602 0.0612 0.0608 .= 0.0609
	0.0245	0.00 1.50 2.17 2.83 4.00	10.02 9.22 8.88 8.46 7.98	1.0009 0.9639 0.9484 0.9274 0.9020 Ave	0.0567 0.0557 0.0598 0.0568 .= 0.0567
	0.0238	0.00 0.83 2.00 3.50 4.50	9.75 9.32 8.69 7.91 7.54	0.9890 0.9694 0.9390 0.8981 0.8774 Ave	- 0.0545 0.0575 0.0596 0.0570 -= 0.0569
60	0.0476	0.00 1.00 2.08 3.00 4.00 5.20	19.50 19.32 19.00 18.80 18.70 18.37	1.2900 1.2860 1.2788 1.2742 1.2718 1.2641 Ave	- 0.0092 0.0124 0.0121 0.0105 0.0115 
87.5	0.0476	0 mins. 21 40 65 93 113	19.50 17.35 15.70 13.80 11.70 10.12	1.2900 1.2393 1.1959 1.1399 1.0682 1.0052 Ave	- 0.333 0.325 0.319 0.329 0.347 0.347

### TABLE XXII

### DECOMPOSITION OF BENZOYL PEROXIDE IN BEHZENE



### TABLE XXIII

## DECOMPOSITION OF BENZOYL PEROXIDE IN STYRENE

Peroxide Concentration in gm. per 12 gm. of monomer

Temp. oc	Time (hr)	Thios. (ml)	log <sub>lO</sub> T	Thios. (ml)	log <sub>10</sub> T	Thios. (ml)	$\log_{10}T$		
		0.05	0gm.	0.	080 gm.	0.115 gm.			
75	0.0 1.0 2.1 3.3 4.9	8.90 8.00 7.45 6.45 5.45	0.9494 0.9031 0.8722 0.8096 0.7364	13.60 12.35 10.85 9.87 8.95	1.1335 1.0917 1.0354 0.9943 0.9496	19.50 17.50 15.90 14.32 11.95	1.2900 1.2430 1.2014 1.1560 1.0774		
Rate (1	nr <sup>-1</sup> )	0.09	70	0.	0966	0.0	0.0971		
		0.11	5 gm.	0.	150 gm.	0.2	0.250 gm.		
60 Rate (1	0.00 0.95 1.45 1.87 2.00 2.40 3.20 4.10 6.10 7.70	14.75 <sup>*</sup> 14.42 14.15 14.30 - 14.15 13.75 - -	1.1688 1.1590 1.1501 1.1553 - 1.1501 1.1360 - - -	25.50 - - 25.07 - 23.80 22.55 21.80	1.4065 - - 1.3891 - 1.3766 1.3531 1.3385 0202	42.50 - - 40.70 - 39.00 37.55 36.25 0.0	1.6284 - - 1.6095 - 1.5911 1.5742 1.5593 207		
	(mins)	0.11	5 gm.		n yn Eine fan de stêl yn de sefter dê stêl en de sefter stêl				
87.5°	0. 20. 21. 30. 40. 40. 50. 60. 65.	14.75 <sup>±</sup> 12.82 12.65 11.97 10.95 11.12 10.10 9.27 9.15	1.1688 1.1079 1.1021 1.0781 1.0394 1.0461 1.0043 0.9671 0.9614						
Rate (h	n <b>r</b> -⊥)	0.4	<i>55</i>						

# 10 cc. sample used.



Figure 21 - Effect of Temperature and Peroxide Concentration on the Decomposition of Benzoyl Peroxide in Styrene.

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ments were made at 75°C, varying the benzene concentration from 0 to 78.4 mole percent while holding the catalyst concentration at 0.0361 m/l (equivalent to 0.115 gms. per 12 gms. of styrene). The data are tabulated in Table XXIV. The rate of decomposition decreases with increasing benzene concentration.

From these data the catalyst concentration required to give the same initial concentration of free radicals at different solvent concentrations and temperatures may be calculated. These values will be presented later.

(iii) The decomposition of benzoyl peroxide in systems containing styrene and butadiene in the ratio 75:25 -

Data for the effect of concentration of peroxide on its rate of decomposition at 75°C and 60°C, in a solvent comprised of 75 percent by weight of styrene and 25 percent of butadiene, are given in Table XXV and plotted in fig. 22. The variation in rate at a given temperature is within experimental error in the range of concentrations studied. An average value of 0.0726 hr<sup>-1</sup> at 75°C and 0.0138 hr<sup>-1</sup> at 60°C may be taken.

Combining the results for the decomposition of 0.115 gms. of peroxide  $\cdot$  in 12 gms. of the monomer mixture at 87.5°C (Table XXV) with those at 75°C and 60°C for the same peroxide concentration, an activation energy of 27.7 kcal. per mole was calculated.

When the monomer mixture was diluted with benzene while the peroxide concentration was held constant at 0.0323 moles per litre (equivalent to 0.115 gms. per 12 gms. of monomers) the rate of decomposition was found to decrease with increasing benzene concentration. The results for a temperature of  $75^{\circ}$ C are presented in Table XXVI.

### TABLE XXIV

### EFFECT OF BENZENE ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN STYRENE AT 75°C

B.P. conc. = 0.0361 mol/1

Monomer concentration in mole %

Time Thios. (hr) (mls)	log <sub>l0</sub> T	Rate (hr <sup>-1</sup> )	Thios. (mls)	log <sub>10</sub> T	Rate (hr <sup>-1</sup> )	Thios. (mls)	log <sub>lO</sub> T	Rate (hr-1)
	70.0%			43.6%	, )		20.6%	
$\begin{array}{c} 0.00 & 14.75^{\pm} \\ 0.68 & 13.95 \\ 1.00 & - \\ 1.43 & 12.95 \\ 2.00 & 12.30 \\ 2.10 & 12.50 \\ 3.00 & - \\ 3.10 & 11.25 \\ 3.85 & 10.73 \\ 1.00 \end{array}$	1.1688 1.1455 - 1.1117 1.0899 1.0969 - 1.0512 1.0306	.0790 .0918 .0906 .0829 .0875 .0920	14.75 <sup>★</sup> 13.70 	1.1688 1.1362 - 1.0927 1.0523 1.0362	- .0750 - .0834 .0816 .0888 .0794 .0802	14.75 <sup>*</sup> 13.95 13.93 13.30 12.97 12.58 11.90 - 11.15 11.00	1.1688 1.1455 1.1439 1.1238 1.1131 1.0992 1.0755 - 1.0473 1.0414	- .0574 .0724 .0642 .0763 .0715 - .0725 .0725
4.00 -	- Ave.	<b>=</b> .0870	10.10	Ave.	=.0805		Ave.	<b></b> 0725

★ 10 cc. sample used.
## TABLE XXV

## PEROXIDE DECOMPOSITION IN 75 STYRENE-25 BUTADIENE

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Time (hr)	Thios. (mls)	log <sub>10</sub> T	Time (hr)	Thios. (mls)	log <sub>lO</sub> T
75°C		0.08 gm.	0.115 gm.			0.150 gm.		
0.00 1.00 2.00 3.30 5.00	13.60 12.77 11.97 10.72 9.57	1.1335 1.1060 1.0781 1.0302 0.9803	0.00 1.00 2.00 3.17 4.33 5.33	19.50 18.10 16.77 15.65 13.70 13.10	1.2900 1.2577 1.2245 1.1945 1.1367 1.1156	0.00 1.00 2.10 3.33 4.90	25.50 23.87 21.85 20.32 17.92	1.4065 1.3778 1.3394 1.3079 1.2533
Rate	(hr-1)	0.0705		0.0756	>		0.072	6
60°C		0.150 gm.		0.250 (			о.400 g	m.
0.00 1.87 3.33 4.60 5.87	25.50 25.07 24.35 24.12 23.80	1.4065 1.3991 1.3865 1.3824 1.3766	0.00 1.87 3.33 4.60 5.87	42.50 41.45 40.57 40.20 38.85	1.6284 1.6175 1.6082 1.6042 1.5888	0.00 1.41 2.67 3.55 5.67	60.20 59.30 58.10 58.50 55.70	1.7796 1.7731 1.7642 1.7672 1.7459
Rate (	(hr <sup>-1</sup> )	0.0134		0.0138	}	,	0.013	8
87.59	рС С	0.115 gm.						
0 mir 10.0 20.0 30.3 41.7 54.2	ns.19.50 18.45 17.10 16.32 15.60 14.37	0 1.2900 5 1.2660 9 1.2330 2 1.2127 1.1931 1.1575						

# Peroxide conc. in gm/12 gm of monomers



on the decomposition of benzoyl peroxide in 75 styrene-25 butadiene.

### TABLE XXVI

#### EFFECT OF SOLVENT ON THE DECOMPOSITION OF PEROXIDE IN 75 STYRENE-25 BUTADIENE at 75°C

Peroxide conc. = 0.03225 moles per litre

Monomer concentration in mole percent

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Rate (hr <sup>-1</sup> )	Thios. (mls)	log <sub>10</sub> T	Rate (hr <sup>-1</sup> )	Thios. (mls)	log <sub>lO</sub> T	Rate (hr-1)
•	ن, ،	72.2			46.1			22.2	
0.00 0.78 1.47 2.30 3.20 4.00	19.50 18.42 17.80 16.72 15.55 15.10	1.2900 1.2653 1.2504 1.2233 1.1917 1.1789	.0700 .0620 .0667 .0706 .0640	19.50 18.65 17.87 16.90 16.10 15.30	1.2900 1.2707 1.2521 1.2278 1.2068 1.1846	- 570 - 593 - 622 - 597 - 605	19.50 18.60 17.87 17.05 16.10 15.60	1.2900 1.2695 1.2521 1.2317 1.2068 1.1931	.605 .593 .583 .597 .557
		Ave.=	•.0650		Ave.	=.598		Ave	•=•583

(iv) The decomposition of benzoyl peroxide systems containing styrene and butadiene in the ratio 50:50 -

The results here are similar to those in the above sections (Table XXVII, fig. 23). No appreciable change in rate occurs as the peroxide concentration is varied. The data at  $60^{\circ}$ C for 0.115 gms. of peroxide are not as accurate as those for 0.150 and 0.250 gms. and for this reason were not considered in the average. An average value of 0.0568 hr<sup>-1</sup> was taken for 75°C and 0.0118 at  $60^{\circ}$ C.

The activation energy was calculated from the rates at  $60^{\circ}$ C and  $87.5^{\circ}$ C. A value of 28.7 kcal. per mole was found.

When various proportions of benzene were added to the monomer mixture, the peroxide concentration being held constant at 0.0292 moles per litre, very little change in rate was found (Table XXVIII). This was expected since the rates of decomposition of the peroxide in benzene and in the monomer mixture were almost the same at this peroxide concentration (0.0590  $hr^{-1}$  for benzene and 0.0568  $hr^{-1}$  for the monomer mixture).

(v) The decomposition of benzoyl peroxide in systems containing styrene and butadiene in the ratio 25:75 -

The data in Table XXIX (plotted in fig. 24) show that the peroxide concentration still has no effect on the rate of decomposition over the range studied.

The activation energy calculated from the rate data at the three temperatures is 30.3 kcal.

Dilution with benzene was found to have no effect on the rate of decomposition of the peroxide at a concentration of 0.0266 moles per litre in this system (Table XXX, fig. 24). However, a short inhibition period seemed to occur since the values did not extrapolate to the true value at zero time.

## TABLE XXVII

# PEROXIDE DECOMPOSITION IN 50 STYRENE-50 BUTADIENE

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	
75°c	0.	080 gm.	0.115 gm.		0.1	50 gm.	
0.00 1.00 2.00 2.40 2.75 3.00 3.50 4.00	13.60 12.80 12.42 12.10 11.90 11.62 11.60	1.1335 1.1089 1.0941 1.0828 1.0754 1.0652 1.0644	19.50 17.75 17.00 16.55 15.70	1.2900 1.2492 1.2304 1.2175 1.1954	25.50 23.90 22.80 21.80 20.95	1.4068 1.3784 1.3580 1.3385 1.3212	
Rate (hr	·-1) 0	.0564	0.	0574	0.0	0564	
60°C	0.	115 gm.	0.	150 gm.	0.2	50 gm.	
0.00 2.00 4.00 5.50 6.75	19.50 18.87 18.35 17.95 18.05	1.2900 1.2780 1.2636 1.2540 1.2565	25.50 24.75 24.60 23.92 23.48	1.4068 1.3936 1.3909 1.3787 1.3707	42.50 41.45 40.65 40.20 39.40	1.6284 1.6175 1.6091 1.6042 1.5955	
Rate (hr	·-1) 0	.0138	0.	0122	0.0	0115	
87.5°0	; 0.	1 <b>1</b> 5 gm.					
0 mins. 10 20 30.3 41.7	19.50 18.12 17.75 16.35 15.85	1.2900 1.2580 1.2493 1.2135 1.200					
nave (III	, 0	• /+					

Peroxide concentration in gm/12 gm of monomers



Figure 23 - Effect of peroxide concentration and temperature on the decomposition of benzoyl peroxide in 50% Styrene - 50% Butadiene.

### TABLE XXVIII

## EFFECT OF SOLVENT ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN 50 STYRENE-50 BUTADIENE AT 75°C

`

Peroxide conc. = 0.0292 m/l

Time (hr)	Thios. (mls)	log <sub>lO</sub> T	Thios. (mls)	log <sub>lO</sub> T	Thios. (mls)	log <sub>10</sub> T
	73	• 5%	4	7 - 9,0	2	3•5%
0.00 1.17 2.25 3.17 4.17 5.17	19.50 18.10 17.20 16.35 - 14.25	1.2900 1.2577 1.2355 1.2135 - 1.1548	19.50 18.30 17.20 16.12 15.32 14.38	1.2900 1.2625 1.2355 1.2074 1.1855 1.1575	19.50 18.25 17.25 16.22 15.32 14.58	1.2900 1.2613 1.2355 1.2100 1.1855 1.1635
Rate (hr	<sup>-1</sup> ) 0.	0592	0.0	592	0	.0592

Monomer concentration in mole percent

## TABLE XXIX

# PEROXIDE DECOMPOSITION IN 25 STYRENE-75 BUTADIENE

Peroxide concentration in gm/12 gm of monomers

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	
	0.0	80 gm.	0.	115 gm.	0.1	150 gm.	
0.00 1.00 2.00 2.20 2.75 3.00 3.50 4.00	13.60 12.70 - 11.72 - 11.15	1.335 1.1038 - 1.0689 1.0473	19.50 18.55 17.37 17.20 16.75 16.45 16.25 15.40	1.2900 1.2683 1.2373 1.2355 1.2240 1.2162 1.2108 1.1875	25.50 24.15 22.82 21.80 - 20.40	1.4068 1.3829 1.3583 - 1.3385 - 1.3096	
Rate (1	nr <sup>-1</sup> ) 0.	0562	0.	0564	0.0	0557	
60°C	0.1	50 gm.	0.	250 gm.	n an an an an an Anna an an Anna Anna A		
0.00 2.00 4.00 5.50 6.75	25.50 24.85 24.30 24.00	1.4068 1.3953 - 1.3856 1.3800	42.50 41.65 40.95 40.30 39.95	1.6284 1.6196 1.6123 1.6051 1.6015			
Rate (1	$(nr^{-1}) 0.0$	0092	0.0	00935			
87.5°C	<b>c</b> 0.1	15 gm.					
0. mir 10.0 20.0 30.3 41.7 54.2	ns.19.5 18.45 17.70 16.55 15.27 15.10	1.2900 1.2660 1.2479 1.2188 1.1838 1.1789					
Rate (h	r - j = 0	• 500					





Figure 24 - Effect of Peroxide Concentration Temperature and benzene concentration on the Decomposition of benzoyl peroxide in 25% Styrene - 75% Butadiene.

### TABLE XXX

#### EFFECT OF SOLVENT ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN 25 STYRENE-75 BUTADIENE AT 75°C

Peroxide conc. = 0.0266 m/l

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>lO</sub> T	
	74	•6	49	•4	24	•5	
0.00 1.00 2.20 3.00 4.00 5.09	19.50 18.45 17.25 16.50 15.60 14.72	1.2900 1.2660 1.2368 1.2175 1.1931 1.1679	19.50 19.10 17.60 16.67 - 14.85	1.2900 1.2810 1.2455 1.2219 - 1.1717	19.50 19.00 17.47 16.95 15.97 15.00	1.2900 1.2782 1.2423 1.2292 1.2033 1.1761	
Rate (h	r-1) 0.	0564	0.0	564	0.0	564	

### Monomer concentration in mole percent

(vi) The decomposition of peroxide in systems containing butadiene -

The rates of decomposition were measured at peroxide concentrations of 0.08, 0.115 and 0.150 gms. per 12 gms. of butadiene at 75°C (Table XXXI, fig. 25). There appears to be a small increase in rate as the concentration increases, but it is less than four percent for an approximate two-fold increase in catalyst concentration.

An activation energy of 31.2 kcal. was found using the rate data of Table XXXI. A value of .0076 hr<sup>-1</sup> was taken as the rate of decomposition of a 0.115 gm. solution at  $60^{\circ}$ C. If the observed increase in rate with increased catalyst concentration is real and not to be attributed to experimental error, this value will be slightly high.

Dilution with benzene is again found to have no effect on the decomposition rate as may be seen from the data in Table XXXII and fig. 25 for a peroxide concentration of 0.0245 m/l (equivalent to 0.115 gms. of peroxide per 12 gms. of monomer). A short inhibition period occurs when benzene is added, the length of this period increasing with increasing solvent concentration.

As noted earlier, all these studies on the decomposition of benzoyl peroxide were undertaken so that peroxide concentrations could be calculated which would give a constant rate of initiation of polymerization under different conditions, on the assumption that the rates of initiation of polymerization would be constant when the initial rates of peroxide decomposition were held constant. A summary of the data obtained for the decomposition of benzoyl peroxide under the various conditions is given in Tables XXXIII - XXXV.

In Table XXXIII are presented the catalyst concentrations required

## TABLE XXXI

## PEROXIDE DECOMPOSITION IN BUTADIENE

Concentration of peroxide in gms/l2 gms of monomer

Time (hrs)	Thios. (mls)	$\log_{10}^{\mathrm{T}}$	Time (hrs)	Thios. (mls)	log <sub>10</sub> T	Time (hrs)	Thios. (mls)	log <sub>10</sub> T
75 <sup>0</sup> C	0.	08 gm.		0.115	gn •		0.150 gm	•
0.00 0.78 1.06 2.00 3.00 3.33 4.00	13.60 13.07 12.87 12.20 11.70 11.27 11.10	1.335 1.1163 1.1096 1.0864 1.0691 1.0519 1.0453	0.00 0.95 2.03 2.51 4.15 5.10	19.50 18.45 17.45 16.95 15.50 14.65	1.2900 1.2660 1.2418 1.2292 1.1903 1.1658	0.00 1.25 2.03 3.05 4.08	25.50 23.75 22.90 21.50 20.42	1.4065 1.3756 1.3598 1.3324 1.3103
Rate (hr	·1) 0.0	539		0.0552			0.0557	
60°C	0.	150 gm.		0.250	gm .			
0.00 1.38 3.00 3.50 5.86 6.10 7.35	25.50 25.20 24.95 24.70 24.35 24.45 24.15	1.4065 1.4014 1.3970 1.3927 1.3865 1.3883 1.3827	0.00 2.37 3.50 5.10 6.10	42.5 41.65 41.25 40.90 40.30	1.6284 1.6196 1.6154 1.6117 1.6053			
Rate (hr	·1) 0.	00 <b>7</b> 6		0.0080				
87.5°C	0.	115 gm.						
0.0 mins. 20. 30.3 41.7 54.2 Rate (hr <sup>-</sup>	19.50 17.72 17.05 16.12 15.30	1.2900 1.2485 1.2317 1.2074 1.1847 269						



Figure 25 - Effect of peroxide concentration, benzene concent and temperature on the decomposition of benzoyl peroxide in concentration butadiene. T · · ·



Figure 26 - Influence of Temperature on the Decomposition of benzoyl peroxide in various mixtures of butadiene and styrene.

### TABLE XXXII

#### EFFECT OF SOLVENT ON THE DECOMPOSITION OF BENZCYL PEROXIDE IN BUTADIENE AT 75°C

Peroxide conc. = 0.0245 m/l

Time (hr)	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T	Thios. (mls)	log <sub>10</sub> T
	7	5•4	50	•4	25	•4
0.00 1.15 2.03 3.17 4.15 5.10	19.50 18.20 17.55 16.55 15.40 14.60	1.2900 1.2600 1.2443 1.2183 1.1875 1.1644	19.50 18.42 17.78 16.70 15.50 14.65	1.2900 1.2653 1.2499 1.2227 1.1917 1.1658	19.50 18.70 17.72 16.70 15.85 15.05	1.2900 1.2718 1.2497 1.2227 1.2000 1.1775
Rate (h	r <sup>-1</sup> ) 0.	0552	0.0	552	0.05	52

Monomer concnetration in mole percent

## TABLE XXXIII

## CATALYST CONCENTRATIONS FOR COPOLYMERIZATION AT 75°C

Weight P Styrene	Percent of Butadiene	k (hr <sup>-1</sup> )	Peroxid gm/12 gm	e Conc. $m/1$	0 hr.	k <sub>C</sub> 1 hr.	ave.
100	0	0.0977	0.0600	0.01880	1.838	1.665	1.754
75	25	0.0726	0.0903	0.0253	1.838	1.705	1.77
50	50	0.0568	0.1285	0.0323	1.838	1.730	1.78
25	75	0.0562	0.1410	0.0327	1.838	1.735	1.785
0	100	0.0552	0.1550	0.0333	1.838	1.750	1.785

#### TABLE XXXIV

.

#### CATALYST CONCENTRATIONS FOR EFFECT OF TEMPERATURE

Weight Percent of Styrene Butadiene		60°C		Temperature 75°C		87.5°C	
		$k(hr^{-1})$	C(m/1)	k(hr <sup>-1</sup> )	C(m/1)	$k(hr^{-1})$	C(m/1)
100	0	0.0207	0.1170	0.0977	0.0248	0.433	0.0056
75	25	0.0138	0.1180	0.0726	0.0224	0.338	0.0048
50	50	0.0118	0.1000	0.0577	0.0203	0.324	0.0036
25	75	0.0093	0.112	0.0562	0.0185	0.306	0.0034
0	100	0.0080	0.114	0.0539	0.0170	0.269	0.0034

### TABLE XXXV

## CATALYST CONCENTRATIONS FOR SOLVENT EFFECT

	Styrene	)	75 Styrene-25 Butadiene				
Mole % Monomer	(hr <sup>-1</sup> )	Peroxide Conc. (m/1)	Mole % Monomer	(hr <sup>-1</sup> )	Peroxide Conc. (m/1)		
100 70.0 43.6 20.6	0.0977 0.0870 0.0815 0.0715	0.0360 0.0404 0.0431 0.0491	100 72.2 46.1 22.2	0.0726 0.0650 0.0622 0.0587	0.0322 0.0359 0.0375 0.0397		

to give the same rate of chain initiation for the bulk polymerizations of styrene, butadiene and copolymerization of mixtures of these two at 75°C, while from Table XXXIV values are obtained which give the same rate of chain initiation for a given system, styrene, butadiene or a mixture of the two, at  $60^{\circ}$ C,  $75^{\circ}$ C and  $87.5^{\circ}$ C. The concentrations of peroxide which result in the same initial concentration of free radicals when the systems containing styrene and 75 styrene-25 butadiene are diluted with benzene are given in Table XXXV, dilution with benzene having little effect on the other systems. These values were calculated assuming that the rates of decomposition of the peroxide were independent of the peroxide concentration. This. of course, will be true for pure monomer and concentrated monomer solutions, but Cohen (89) found a slight variation in the rate of decomposition of the peroxide with concentration for a 3.85 molar solution of styrene in benzene. The variation was less than four percent for a two-fold increase in peroxide The increase in concentration is much less than two-fold here, concentration. so it may be assumed that the error in the calculation of the required peroxide concentrations will be well within experimental error.

The results presented above will be discussed later, since some of the rate expressions to be derived are required for interpretation of the kinetics of polymerization in the analogous systems.

# 2. Polymerization in Systems containing Butadiene, Styrene and Mixtures of the Two

- (a) Experimental Procedure:
- (i) Polymerization -

The procedure used in this section was exactly the same as that described in Section 1.

## (ii) Determination of molecular weight -

Ubbelohde viscometers were used for the determination of intrinsic viscosities. The outflow times for the two viscometers used in this part of the work were 107.1 and 115.4 secs. for pure benzene at 25°C, so that a kinetic energy correction was required. This correction was determined by calibrating the viscometer with three different liquids, viz. benzene, water and toluene, and applying the standard viscosity equation which has the form

$$V = At - \frac{B}{t}$$

Hence, by using any two liquids whose kinematic viscosity is accurately known, the two constants may be evaluated. The data and values of the constants are given below:

		Viscometer	Constants			
Viscometer	Liquid	Flow Time	Abs. Visc.	Density (gm/cc)	A	В
		(sec)	<u>(cp)</u>	and the second se		
R <sub>11</sub>	Water Toluene Benzene	137.7 99.8 107.1	0.894 0.553 0.608	0.997 0.862 0.874	0.00659 .00659	1.614 1.535
R <sub>12</sub>	Water Toluene Benzene	148.2 107.1 115.4	0.894 0.553 0.608	0.997 0.862 0.874	.00611 .00609	1.399 1.000

A graph of actual flow time against true relative time (calculated on the assumption that the change in density of the polymer solutions over the concentrations studied is negligible) was used to determine the correct value of  $\eta_r$ .

Cragg's method for the one point determination of intrinsic viscosities at a concentration of 0.2 to 0.6 grams of polymer per 100 ml. of solvent was used. The equation

$$[\eta] = \frac{8(t_r^{1/8}-1)}{C}$$

where [n] is the intrinsic viscosity,

tr is the relative time of flow,

C is the concentration,

was found to give a horizontal straight line for  $[\eta]$  plotted against C for several polymer samples, all compositions of monomers (except pure butadiene) represented, taken at random from the polymer samples. This may readily be seen from fig. 27. The samples A, B, C and D refer to 100%, 75%, 50% and 25% of styrene.

The molecular weight of polystyrene was calculated using the equation found by Alfrey, Bartovics and Mark (93)

 $\log M = 1.43 \log [n] + 5.54$ 

while that for GR-S type polymer (75% butadiene, 25% styrene) was calculated from the equation derived by Hulse et al (68)

(b) Experimental Results:

In the present work the rates of polymerization and the molecular weights of the products were determined for the same initial concentration of free radicals in each of the monomers and in mixtures of them as the solvent concentration and temperature were varied. The effect of catalyst concentration was also determined in each of the systems.

(i) Polymerization in systems containing styrene -

The effect of catalyst concentration on the rate of the polymerization was determined at a temperature of  $75^{\circ}$ C. The catalyst was varied from 0.050 gms. per 12 gms. of monomer to 0.400 gms. The data are tabulated in Table



11



Figure 27

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XXXVI. Since the time curves were all linear, they have not been plotted here. The plot of rate against the square root of the catalyst concentration is linear (fig. 34). The molecular weight data were lost in the laboratory fire and the experiments were not repeated because it was felt that the relation between molecular weight and catalyst concentration (M.N.  $1/\sqrt{\text{cat}}$ ) had been soundly established by other investigators (87).

All the data in the literature on the effect of a diluent on the rate of polymerization and molecular weight were obtained using the same initial concentration of catalyst on the basis of moles per litre. As shown above, the addition of a diluent greatly decreases the rate at which the peroxide decomposes, resulting in a greater initial concentration of free radicals in pure styrene than in the diluted systems. To determine the true effect of an inert diluent on the reaction kinetics the experiments were made with the same initial concentration of free radicals. The values of C in moles per litre were taken from Table XXXV. The values of C for 56.5 and 31.7 mole percent were found by interpolation. The data for a temperature of 75°C are given in Table XXXVII and plotted in fig. 38. In fig. 36 the rate of polymerization is plotted against the square root of the monomer concentration and a linear relation is found. In fig. 37 the average molecular weights of the polymers are plotted against the three-halves power of the monomer concentration and a direct proportionality exists.

The effect of temperature on the rate of polymerization has previously always been measured using a constant concentration of benzoyl peroxide. It is obvious that under these conditions the concentration of free radicals will be greater at the higher temperature and the true effect of temperature on the polymers formed is not found. The peroxide concentrations necessary

## TABLE XXXVI

## EFFECT OF CATALYST CONCENTRATION ON THE POLYMERIZATION OF STYRENE AT 75°C

Time (hr)	Percent Conversion	Time (hr)	Percent Conversion	Time (hr)	Percent Conversion
0	.05 gms.	0	.08 gms.	0.3	115 gms.
1.00 1.75 2.50 3.25	7.17 12.8 18.1 23.5	1.00 1.75 2.50 3.25 4.00	9.45 16.6 23.3 29.8 35.9	0.41 0.75 1.03 1.50	5.31 9.41 13.2 18.6
Rate (	%/hr) 7.2		9.3		12.4
(	0.250 gms.	(	0.400 gms.		
0.75 1.50 2.25 3.00 3.75	14.5 28.9 39.1 53.9 66.3	0.75 1.50 2.25 3.00	15.5 33.5 49.8 70.6		
Rate (	%/hr) 18.5		22.5		

Peroxide concentration in gm. per 12 gm. of monomer

## TABLE XXXVII

# EFFECT OF SOLVENT CONCENTRATION ON THE POLYMERIZATION OF STYRENE AT 75°C

Tim (mi:	e Percen n) Convers	t Mol.Wt. ion $(X10^{-4})$	Percent Conversion	Mol.wt. (X10 <sup>-4</sup> )	Percent Conversion	Mol.Wt. (X10-4)
		100%	70.	0%	56.5	5%
25 45 62 90 120	5.31 9.41 13.2 18.6	8.80 8.00 - - - Ave.= <u>8.4</u> 0	5.82 9.27 12.6 16.8 23.4 Av	- 5.25 5.80 4.95 - e.= <u>5.35</u>	5.02 9.15 12.3 17.7 23.2 Ave	- 4.40 4.30 4.10 - -
Rate	(%/hr)	12.4	11.	7	11.7	7
		43.6%	31.	7%	20.6	5%
25 45 62 90 120	4.71 8.50 11.75 16.2 22.2	2.98 - 3.40 - Ave.= <u>3.20</u>	4.44 8.35 11.0 16.0 21.5 Av	2.45 - 2.27 e.=2.35	4.34 7.83 10.8 15.6 20.3 Av	1.50 - 1.47 - re=1.50
Rate	(%/hr)	11.05	10	•65	10.2	20

## Monomer concentration in mole percent

to yield the same initial concentration of free radicals at the three temperatures 60, 75 and 87.5°C were taken from Table XXXIV. The concentration at  $75^{\circ}$ C - 0.0248 m/l is equivalent to 0.08 gm. per 12 gm. of monomers. Results for the effect of temperature on the rate of polymerization of styrene in the bulk phase at constant free radical concentration are given in Table XXXVIII and plotted in fig. 28. It is devious that an increase in temperature not only increases the rate but also increases the molecular weight of the polymer. The molecular weight of the polymer at 87.5°C is found to increase with time because the half-life of the catalyst is very short at this temperature so that a steady state concentration of free radicals exists only for a short time. An activation energy of 8.3 kcal. was calculated from the slope of the Arhennius line in fig. 38.

(ii) Polymerization in systems containing styrene and butadiene in the ratio 75:25 -

The rates of polymerization at 75°C were determined for catalyst concentrations of 0.08, 0.115, 0.115, 0.150, 0.250 and 0.400 gms. per 12 gms. of monomers. The results are tabulated in Table XXXIX. The time curves were linear and are not reproduced here. A linear relation is again found between the initial rate of polymerization and the square root of the catalyst concentration (fig. 34). As no equation is known to exist which relates the intrinsic viscosity to molecular weight for this particular system (and also that of 50-50 Sty.-But.) the relations for molecular weight were determined by plotting  $[n]^{1/a}$  against the independent variable. The value taken for 1/a is 1.48 which is the average of the values for pure styrene - 1.43 and GR-S - 1.52. Since many polymers have values of 1/a within this range, it was felt the error would be well within the experimental error. A plot of  $[n]^{1/a}$  against the inverse of the square root of the catalyst concentra-

## TABLE XXXVIII

## EFFECT OF TELPERATURE ON THE RATE OF STYRENE POLYMERIZATION

Temp. oC	Time (hr)	Percent Conversion	Rate (%/hr)	Mol.Wt. (X10-4)
60	2.10 3.00 4.67 5.90 6.90	11.0 16.2 25.5 31.1 35.4	5.40 Ат	$6.75 \\ 6.75 \\ 6.00 \\ 6.00 \\ 6.30 \\ 7e. = 6.35$
75	1.00 1.75 2.50 3.25 4.00	9.45 16.6 23.3 29.8 35.9	9.30	10.0
87.5	0.65 1.25 1.93 2.47 3.17	8.84 16.3 23.1 28.3 34.0	13.6	11.1 12.0 12.8 17.4



Figure 28 - Effect of solvent and temperature on rate of styrene polymerization at constant initial rate of peroxide decomposition.

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### TABLE XXXIX

## EFFECT OF CATALYST CONCENTRATION ON THE POLYMERIZATION OF 75 STYRENE-25 BUTADIENE AT 75°C

Time (hr)	Percent Conversion	<b>n</b> <sup>1</sup> .48	Percent Conversion	n <b>n<sup>1.1</sup></b> <sup>18</sup>	Percent Conversion	1.48 <b>n</b>
	0.08	30 gms.	0.	.115 gms.	0.150	) gms.
1.00 2.00 2.75 3.50 5.00	1.94 4.19 6.04 7.52 10.2	0.182 0.164 0.164 0.164 0.174	2.51 5.07 6.93 9.36 13.7	- .150 .1140 .157 .192	2.78 5.45 7.83 - 14.53	.107 .120 .120 -
Rate (%	Ave	••=0 <u>•164</u>	Av 2.	re.=.145	Av 2.78	e.=.120
	0.250 gms.			400 gms.		an a
1.00 2.00 3.00 4.50 6.00 7.50	3.80 7.68 11.58 15.98 22.14 - Ave	0.081 0.090 0.089 0.096 0.125 - .=0.090	5.10 10.2 15.1 22.6 30.4 38.2 Ave	0.072 0.073 - 0.096 - 0.107 .=0.072		
Rate (%/hr) 3.80 5.09						

Catalyst concentration in gm. per 12 gm. of monomers

tion yields a straight line (fig. 35).

The effect on the kinetics of the reaction of a diluent was determined using catalyst concentrations such that kC was held constant (Table XXXV). These results are given in Table XL. The initial rate of polymerization was found to be independent of the monomer concentration while the molecular weight of the polymer is approximately proportional to the monomer concentration (fig. 37).

Peroxide concentrations necessary to yield the same initial concentration of free radicals at the temperatures 60, 75 and 87.5°C were obtained from Table XXXV. The data for rates of polymerization at these temperatures, given in Table XLI and plotted in fig. 29, were obtained using these catalyst concentrations. An increase in temperature results in an increase in rate and molecular weight. From the Arhennius line in fig. 38 an activation energy of 8.7 kcal. was calculated.

(iii) Polymerization in systems containing styrene and butadiene in the ratio 50:50 -

Again the initial rate of polymerization was found to be proportional to the square root of the catalyst concentration (fig. 34). The data are presented in Table XLII. Since the molecular weight is proportional to  $[n]^{1/a}$  (1/a is taken as 1.48) the relation between molecular weight and catalyst concentration was found by plotting  $[n]^{1/a}$  as the dependent variable. The usual relation was found, viz.  $[n]^{1/a}$  was inversely proportional to the square root of the catalyst concentration (fig. 35).

The addition of a diluent to the 50-50 styrene butadiene system was found to have very little effect on the rate of benzoyl peroxide decomposition, so for determining the role of diluent in the kinetics, a catalyst concentration of 0.0292 m/l was used. These results are given in Table

## TABLE XL

## EFFECT OF SOLVENT CONCENTRATION ON THE POLYMERIZATION OF 75 STYRENE-25 BUTADIENE AT 75°C

Time (hr)	Percent Conversio	n <b>n<sup>1.48</sup></b>	Percent Conversion	n <sup>1.48</sup>
	1	00%	<b>72.</b> 2	51 10
1.23 1.89 3.05 4.83 5.95	3.23 5.24 8.04 12.2 15.8	0.120 0.137 0.150 0.160 0.185	3.30 5.19 8.16 12.5 15.5	0.090 0.098 0.107 0.112 0.120
Rate (%	/hr)	2.58	2.5	8
		46.1%	22.2	%
1.23 1.89 3.05 4.83 5.95	3.38 5.23 8.16 12.5 15.1	0.066 0.065 0.070 0.069 -	3.33 4.82 7.81 12.1 14.7	- 0.031 0.0315 0.031 0.031
Rate (%	/hr)	2.58	2.52	

## Monomer concentration in mole percent

## TABLE XLI

## EFFECT OF TEMPERATURE ON THE POLYMERIZATION OF 75 STYRENE-25 BUTADIENE

Temp. oC	Time (hr)	Percent Conversion	Rate (%/hr)	<b>n</b> 1.48
60	2.10 3.00 4.67 5.90 6.90	2.60 3.66 5.74 7.04 8.31	1.20	.113 .105 .106 .117
75	1.23 1.89 3.05 4.83 5.95	2.57 4.23 6.48 10.75 13.2	2.17	.155 .156 .174 .192 .202
87.5	0.65 0.75 1.62 2.03 2.52	2.09 2.52 5.12 6.54 7.50	3.25	- 220 245 223 225



Figure 29 - Effect of solvent and temperature on the rate of polymerization of 75% styrene and 25% butadiene at constant initial rate of peroxide decomposition.

## TABLE XLII

## EFFECT OF CATALYST CONCENTRATION ON THE POLYMERIZATION OF 50-50 STYRENE-BUTADIENE

Time (hr)	Percent Conversio	<b>n n</b> <sup>1.48</sup>	Percent Conversion	<b>n<sup>1</sup>.</b> 48	Percent Conversion	<b>n<sup>1</sup>.</b> 48
		0.080 gm.	0.	115 gm.	0.15	0gm.
1.00 2.00 2.75 3.50 5.00	1.17 2.44 3.30 4.20 5.90	.107 .120 .120 .135 .150	1.47 3.04 4.00 5.13 7.29	.102 .110 .118 - .129	1.59 3.35 4.62 5.50	.093 .096
Rate	(%/hr)	1.15	1.4	.6	1.65	
		0.250 gm.	0	.400 gm.		
1.00 2.00 3.00 4.50 6.00 7.50	2.27 4.03 6.50 9.27 12.4 15.7	.081 .090 .089 .096 .124 .128	2.86 5.45 8.09 12.1 16.2 19.7	- •073 •073 - •096 •108		
Rate	(%/hr)	2.10	2.	70		

Catalyst concentration in gm. per 12 gm. of monomers

XLIII and plotted in fig. 30. A short inhibition period occurs in the systems containing 35.7 and 23.5% of monomer. The initial rate of polymerization was found to increase as the monomer concentration decreased and was directly proportional to the square root of the monomer concentration, fig. 36. The molecular weight of the polymer is proportional to the three-halves power of the monomer concentration (fig. 37).

In Table XLIV data are given for the rates of polymerization at three temperatures 60, 75 and 87.5°C, the catalyst concentrations being taken from Table XXXIV, i.e. kC was held constant. Again, an increase in temperature results in an increase in initial rate and molecular weight. An activation energy of 8.7 was calculated from the slope of the Arhennius line in fig. 38.

(iv) Polymerization in systems containing styrene and butadiene in the ratio 25:75 -

The relations between catalyst concentration, rate and molecular weight were determined in Section 1. There was the usual dependence of rate on the square root of the catalyst concentration and of molecular weight on  $1/C^{\frac{1}{2}}$ .

The experiments with the solvent, benzene, were made using a catalyst concentration of 0.0266 m/l since the solvent was previously found to have no effect on the rate of catalyst decomposition. The data are given in Table XLV and plotted in fig. 31. The rate was found to increase as monomer concentration decreased and was approximately proportional to the monomer concentration (fig. 36). The molecular weight is also approximately proportional to the monomer concentration (fig. 37).

An increase in temperature results in the usual increase in rate and molecular weight when the initial concentration of free radicals is held constant. The data are tabulated in Table XLVI and plotted in fig. 31. An activation energy of 7.5 kcal. was found (fig. 38).

### TABLE XLIII

## EFFECT OF SOLVENT CONCENTRATION ON THE POLYMERIZATION OF 50 STYRENE-50 BUTADIENE AT 75°C

Time (hr)	Percent Conversion	n <b>n<sup>1</sup>.</b> 48	Percent Conversion	<b>n<sup>1.48</sup></b>	Percent Conversion	<b>n</b> <sup>1.48</sup>
·····		100%	73	3•5%	60.75	10
1.00 2.03 3.00 4.08 5.25	1.57 2.88 4.44 5.90 7.56	0.081 0.083 0.105 0.113 0.109	1.69 3.21 4.74 6.40 8.15	0.054 0.087 0.087 0.080 0.090	1.73 3.33 4.96 6.78 8.40	0.055 0.055 0.071 0.073 0.085
Rate (7	%/hr)	1.46	1.	57	1.65	
		47.9%	35	5.7% <sup>±</sup>	23.5%	7, <del>a</del>
1.00 2.03 3.00 4.08 5.25	1.79 3.51 5.15 6.96 8.85	0.031 0.048 0.053 0.052 0.063	1.77 2.82 5.36 7.23 9.65	0.028 0.039 0.039 0.043 0.043	1.71 3.30 5.20 7.38 9.31	0.021 - 0.031 0.028 0.034
Rate (%	%/hr)	1.72	1.	85	1.90	)

## Monomer concentration in mole percent

**t** Inhibition period.



Figure 30 - Effect of solvent and temperature on rate of polymerization of 50% styrene - 50% butadiene at constant initial rate of peroxide decomposition.

## TABLE XLIV

EFFECT	$\mathbf{OF}$	TEMPERA	TURE	ON	THE	POLYMERIZATION
	OF	50-50	STYR	ENE-	-BUT/	ADIENE
and the state of the second state of the secon		and a state of the				

Temp. °C	Time (hr)	Percent Conversion	Rate (%/hr)	<b>n</b> <sup>1</sup> .48
60	2.10 4.67 5.90 6.90	1.40 3.14 3.90 4.56	0.66	0.079 0.074 0.082 0.082
75	1.00 2.03 3.00 4.09 5.25	1.18 2.38 3.50 4.75 6.03	1.15	0.113 0.127 0.118 0.127 0.125
87.5	0.65 0.75 1.25 1.62 2.03 2.52 3.00	1.18 1.43 2.36 2.91 3.68 4.60 5.85	1.82	0.148 0.198 0.185 0.210 0.193
## TABLE XLV

# EFFECT OF SOLVENT ON THE POLYMERIZATION OF 25 STYRENE-75 BUTADIENE AT 75°C

Time (hr)	Percent	Mol.Wt.	Percent	Mol.Wt.
(111 )	100	74.6	( <u>X10</u> 4)	
1.50 3.20 4.20 5.13 6.60	1.56 3.16 4.14 4.57 6.52	•750 •789 •790 - •880	1.70 3.18 4.53 5.89 7.53	• 530 • 480 • 560 • 670 • 700
Rate (	$\frac{\pi}{hr}$ 0.	99	1.1	5
	49.	4%	24.5	%
1.50 3.20 4.20 5.13 6.60	2.04 4.37 5.70 6.85 8.84	.428 .500 .490 .480 .530	2.04 4.65 6.41 7.38	- .255 .290 -
Rate (9	%/hr) 1.	35	1.	50

# Monomer concentration in mole percent



Figure 31 - Effect of Solvent and Temperature on rate of polymerization of 25% styrene - 75% butadiene at constant initial free radical concentration.

#### TABLE XLVI

#### EFFECT OF TEMPERATURE ON THE POLYMERIZATION OF 25-75 STYRENE-BUTADIENE

Temp. oc	Time (hr)	Percent Conversion	Rate (%/hr)	Mol.Wt. (X10-4)
60	2.10 3.00 4.67 5.90 6.90	1.08 1.58 2.45 3.16 3.73	0.52	0.420 0.445 - 0.590 0.480
75	1.50 3.20 4.20 5.13 6.60	1.34 2.58 3.37 4.34 5.49	0.85	0.742 0.860 0.810 0.925 0.900
87-5	0.65 0.75 1.25 1.62 1.93 2.03 2.47 2.52 3.00	0.77 0.90 1.50 1.96 2.34 2.46 2.93 2.99 3.52	1.22	- 1.38 - 1.33 - 1.55 1.65

(v) Polymerization in systems containing butadiene -

The data in Table XLVII, which are plotted in fig. 31, show that the usual dependence of rate on catalyst concentration was found. No viscosity data were obtained on the polymer samples, since the polymer was all of very low molecular weight, being quite liquid, and it was felt that the viscosity data would not be sufficiently accurate to allow comparison of the polymers under the different experimental conditions, especially at the low conversions adopted for this work.

The change of rate with solvent concentration was determined using 0.0245 m/l of catalyst. Again the rate is found to increase as the monomer concentration decreases and is directly proportional to the monomer concentration (Table XLVIII, figs. 33 and 36).

The rate data for 60, 75 and  $87.5^{\circ}$ C are given in Table XLIX and plotted in figs. 32 and 33. The catalyst concentrations were taken from Table XXXIV. An activation energy of 7.2 kcal. was calculated from the Arhennius line in fig. 38.

#### TABLE XLVII

### EFFECT OF CATALYST CONCENTRATION ON THE POLYMERIZATION OF BUTADIENE AT 75°C

## Catalyst concentration in gm. per 12 gm. of monomer

Time (hr)	Percent Conversion	Percent Conversion	Percent Conversion	Percent Conversion	Percent Conversion
	0.08 gm.	0.115 gm.	0.150 gm.	0.250 gm.	0.400 gm.
2.0	-	1.54	-	2.28	3.05
2.7	1.75	1.95	2.55	-	-
3.7	2.30	2.97	3.40	4.22	5.51
7.7	5.00	5.98	6.99	8.60	11.7
12.6	7.29	8.74	9.92	12.4	12.6
22.6	12.00	14.4	16.5	19.1	22.6
Rate	(%/hr) 0.65	0.75	0.90	1.15	1.50

## TABLE XLVIII

## EFFECT OF SOLVENT ON THE POLYMERIZATION OF BUTADIENE AT 75°C

Time (hr)	Percent Conversion	Percent Conversion	Percent Conversion
	100	75.4	62.8
1.60		1.52	1.61
3.25	2.42	3.03	3.46
4.27	3.26	4.07	4.56
5.31	4.02	5.04	5.62
6.30	4.70	6.00	-
Rate (%/	hr) 0.76	0.96	1.08
	50.4	37.9	25.4
1.60	1.74	1.89	2.02
3.25	4.03	4.16	4.54
Ĺ.27	5.03	5.50	5 <b>.92</b>
5.31	6.13	-	7.35
6.30	7.43	8.26	8.87
Rate (%/	/hr) 1.19	1.35	1.45

## Monomer concentration in mole percent

#### TABLE XLIX

EFFECT	OF	TEMPERATURE	ON	THE	POLYMERIZATION
		OF BUTADI	ENE		

		Tempe	rature <sup>o</sup> C		
60°		75°		87.5°	
Time	Percent	Time (hr)	Percent Conversion	Time (hr)	Percent Conversion
2.10 3.00 4.67 5.90	0.78 1.32 2.03 2.26	2.7 3.7 7.7 12.6 22.6	1.75 2.30 5.00 7.29 12.00	0.65 1.25 1.93 2.47 3.18	0.64 1.23 1.77 2.15 2.72
Rate (%)	/hr) 0.42		0.65	(	0.95



Figure 32 - Effect of catalyst concentration on rate of butadiene polymerization at 75 C.

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Figure 33 - Effect of Solvent and Temperature on Rate of Butadiene Polymerization.











Figure 38 - Influence of Temperature on the Rate of Polymerication

#### DISCUSSION OF RESULTS

Since some of the expressions derived from a kinetic analysis of the decomposition of the catalyst, benzoyl peroxide, are required to discuss the polymerization reactions the catalyst decomposition will be considered first.

The rate of benzoyl peroxide decomposition was found to decrease as the styrene content of the reaction medium was decreased by dilution with butadiene or benzene. Each individual experiment was found to conform to first-order behaviour but in butadiene and benzene the rate was not truly first order, since it depended to some extent on the peroxide concentration. This behaviour has been observed by many authors and has been explained by Downes (73) on the basis of the following assumptions:

- 1. The dissociation of benzoyl peroxide into benzoate radicals is a reversible process.
- 2. The removal of benzoate radicals from the reaction medium, rather than rupture of the peroxide bond, is the rate controlling step.

If the solvent does not react with benzoate radicals (e.g. benzene) the rate of peroxide decomposition, assumed to be determined by the rate of thermal decomposition of benzoate radicals, is minimal. If, on the other hand, the solvent is subject to attack by benzoate radicals, an increased rate of benzoyl peroxide decomposition is observed, the amount of the increase depending on the susceptibility of the solvent to attack.

Before deriving the rate equations, an expression must be found

relating the concentration of benzoyl peroxide to the concentration of benzoate radicals, since the benzoate radical is assumed to be the true reactant. This expression may be obtained by using the "primary recombination theory" of Franck and Rabinowitsch (88).

This theory is based on the assumption that two fragments from a dissociated molecule are held in a cage of solvent molecules so that the radical pair collide many times with each other before they diffuse apart. If, then, a reaction between such radicals and solvent is possible, either such reaction takes place or the radical pair recombines. Since only those radicals from the same molecule recombine, the recombination is considered to be first order.

Applying these ideas to the benzoyl peroxide decomposition it is clear that two benzoate radicals arising from the peroxide decomposition may be regarded as a modified form of the peroxide. Therefore, the relation between the concentration of benzoate radicals and benzoyl peroxide may be written:

$$\frac{[0.655000.]}{(0.655002)2} = K$$
(1)

or

where C is the peroxide concentration at any time.

 $[C_{6H_5}COO \cdot] = K C$ 

For benzene, a solvent which is assumed to be subject to no attack by benzoate radicals, the equations to be considered are:

$$(c_{6}H_{5}c_{2})_{2} \xrightarrow{k_{1}} 2c_{6}H_{5}c_{00}$$
 (1)

$$C_{6}H_{5}COO \cdot \xrightarrow{k_{3}} C_{6}H_{5} \cdot + CO_{2}$$
 (2)

$$C_{6H_5COO} + C_{6H_5} - \frac{k_{14}}{M}$$
 (3)

(II)

$$^{C}6^{H}5^{\bullet} + ^{C}6^{H}6 \xrightarrow{lc_{\mathcal{T}}} ^{M} + ^{H}$$
 (4)

$$c_{6H_5} + c_{6H_6} \xrightarrow{M} + c_{6H_5}$$
 (5)

$$C_{6}H_{5}COO \cdot + H \cdot \frac{k_{7}}{M}$$
 (6)

$$C_{\mathcal{S}^{H_{5}}} + H \cdot \underbrace{\kappa_{8}}_{K_{8}} M$$
 (7)

where M represents a neutral molecule.

The reactions

$$^{C}6^{H}5^{\bullet} + ^{C}6^{H}5^{\bullet} \longrightarrow ^{C}6^{H}5 - ^{C}6^{H}5$$
 (8)

$$2H \cdot \longrightarrow H_2$$
 (9)

have not been included as of major significance. This is not entirely an arbitrary choice since Wieland, Popper and Seefried (94) found no appreciable amount of biphenyl in their studies and Cuthbertson et al (84) found no trace of hydrogen.

The following kinetic equation may be obtained assuming solvent concentration constant and treating the recombination of benzoate radicals as first order:

$$- \frac{d}{dt} [(C_{6H_{5}CO_{2}})_{2}] = k_{1}C - k_{2}B$$
  
=  $k_{3}B + k_{L}BPh + k_{7}BH$  (III)

where B is the concentration of benzoate radicals, Ph of phenyl radicals and H of hydrogen radicals. Since the concentration of B is directly proportional to C, the concentration of benzoyl peroxide, (equation II) it is readily seen that the rate of decomposition in benzene is the sum of a first-order reaction and two second-order reactions. Only at high dilution will the last two terms of (III) approach zero and a true first-order rate be found.

Benzene and butadiene appear to behave in a similar manner when used as solvents for benzoyl peroxide decomposition; i.e., the rate of peroxide decomposition is approximately the same for a 0.0245 moles/litre solution and the activation energies for the decomposition, 30.3 and 31.0 kcal. respectively, are within experimental error. However, the variation with concentration in the rate of decomposition of the peroxide is very slight; in fact, the variation may merely be experimental error, a change of less than four percent being found for a two-fold increase in peroxide concentration.

Dilute solutions of styrene in benzene were found by Cohen (89) to give first-order rate constants for the decomposition which varied with concentration. This was not found for dilute solutions of styrene in butadiene.

The addition of benzene to styrene decreased the rate of peroxide decomposition in a uniform manner, from a large rate in styrene to a small rate in benzene. When only fifty percent by weight of butadiene was added, instead of benzene, the rate of decomposition dropped to approximately that in pure butadiene. This behaviour is to be expected since benzene merely acted as an inert diluent while butadiene not only diluted the styrene but also took part in the chemical reaction.

The fact that the decomposition is approximately first order in butadiene, although butadiene apparently does not rapidly remove benzoate radicals, may be explained by considering equations 1,2,3 as well as

$$C_{6H_5} \cdot + C_{4H_6} \xrightarrow{k_6} C_{6H_5} C_{4H_6} \cdot (10)$$

The reactions

are considered as negligible in comparison with the others.

Kinetic analysis yields the equation

$$\frac{d}{dt} [(C_{6}H_{5}CO_{2})_{2}] = k_{1}C - k_{2}B$$

$$= k_{3}B + k_{4}BPh \qquad (IV)$$

Assuming a steady state concentration of free radicals

$$\frac{dPh}{dt} = k_3 B - k_4 BPh - k_9 PhBu = 0$$
or  $k_4 BPh = k_3 B - k_9 PhBu$  (V)

where Bu is the concentration of butadiene. Considering the concentration of butadiene to be constant over the course of the decomposition, the reaction between phenyl radicals and butadiene will actually be pseudounimolecular, the magnitude of k9 Ph Bu then depending only on the phenyl radical concentration.

Since

$$\frac{d \left[ (\mathbf{c}_{6^{\mathrm{H}}5^{\mathrm{CO}}2)_{2}} \right]}{dt} = 2k_{3^{\mathrm{B}}} - k_{9^{\mathrm{PhBu}}}$$
(VI)

the rate of decomposition of peroxide in butadiene should be first order, any deviation from a first-order relation occurring as a result of neglecting reaction 11.

Butadiene and benzene belong to the group of solvents which is not subject to attack by benzoate radicals while styrene appears to belong to 'the group which is attacked, thus yielding a faster rate of peroxide decomposition. In styrene the decomposition is truly first order, no change in rate being observed when the concentration of peroxide is changed. The kinetic analysis is essentially similar to that for butadiene. Equations 1, 2 and 3 hold as well as

$$C_{6H_5}C_{00} + S \xrightarrow{k_{10}} C_{6H_5}C_{00}S.$$
 (12)

$$C_{6H_5}$$
 + S  $\xrightarrow{K_{11}}$   $C_{6H_5S}$  (13)

where S represents styrene.

Hence,

$$\frac{d}{dt} \left[ (c_{6}H_{5}COO)_{2} \right] = k_{3}B + k_{4}BPh + k_{10}BS$$
(VII)

Again assuming a steady state concentration of free radicals

$$\frac{dPh}{dt} = k_{3}B - k_{4}BPh - k_{11}PhS = 0$$

$$k_{4}BPh = k_{3}B - k_{11}PhS \qquad (VIII)$$

Since the concentration of styrene remains approximately constant the terms kloBS and kllPhS will be first order and substituting for  $k_{\perp}BPh$  the rate of decomposition of peroxide is given by

$$\frac{d}{dt} \left[ (c_{6}H_{5}coc)_{2} \right] = 2k_{3}B - k_{11}PhS + k_{10}BS \qquad (IX)$$

which is a first-order rate equation, in agreement with experimental data.

From the above, it is evident that the mechanism assumed by Downes for the decomposition of peroxide (i.e. that the removal of benzoate radicals, assumed to be in equilibrium with peroxide, is the rate controlling step) may be subjected to kinetic analysis to yield equations which are in agreement with the experimental results.

The fact that the "activation energy" of the decomposition varied from a low value of 26.5 kcal. in styrene to a high of 31 kcal. in butadiene would also indicate that the proposed mechanism is correct since it is to be expected that the activation energy would be lower in a medium which rapidly removes benzoate radicals.

Another interesting point which should be mentioned is that butadiene polymerization must apparently be activated by phenyl rather than benzoate free radicals if the proposed mechanism is correct since butadiene closely resembles benzene in which, it is assumed, attack is made on the solvent only by phenyl radicals and not by benzoate radicals. Medvedev (41) has shown by saponifying polyisoprene, formed in a benzoyl peroxide catalyzed polymerization, that no benzoate groups are attached to the polymer, while when polystyrene was treated similarly the results showed benzoate groups were present. Since isoprene closely resembles butadiene, it would indicate that the polymerization is activated by phenyl radicals and hence that the proposed mechanism for peroxide decomposition is correct.

The investigation of peroxide decomposition was undertaken solely to provide data from which peroxide concentrations could be calculated which would yield constant rates of initiation of polymerization under any desired conditions. It was assumed when this investigation was started that a constant rate of initiation would be obtained if the initial rate of peroxide decomposition ( $kC = k_1C - k_2B$ ) were held constant, the initial concentration of free radicals formed being the same. From the kinetic analysis given above for butadiene and styrene it became apparent that side reactions involving free radicals such as that given by equation (3) might introduce complications. Only a complete analysis of products could give any estimate of the relative importance of such a reaction in the different systems. Lacking such information it was assumed for the investigation that, for monomers such as styrene and butadiene, the benzoate and/or phenyl radicals were rapidly consumed in initiating polymerization so that reactions such as (3) might be neglected and the rate of initiation of polymerization might be written equal to the rate of decomposition of peroxide, i.e.

$$\frac{d}{dt} \left[ (C_6H_5CO_2)_2 \right] = kC = K[R]M = \frac{dM^{4}}{dt}$$
(X)

where [R] is the total concentration of catalyst free radicals, benzoate and/or pheny], and M is the monomer concentration.

The polymerizations which are to be discussed below are to be compared on the basis of kC constant.

In every polymerization system a linear relation between rate of polymer formation and the square root of the peroxide concentration was found. This indicates that the polymerizations all proceeded by a free radical mechanism in which the radicals were generated by a first-order decomposition of benzoyl peroxide and were destroyed by a second-order termination of the radical chains.

No general dependence of rate on monomer concentration was found under conditions of constant free radical concentration. With styrene, the rate was found to decrease as the monomer concentration decreased (proportional to  $M\overline{z}$ ); the rate remained constant for 75-25 styrene-butadiene, increased for 50-50 styrene-butadiene (proportional to  $M\overline{z}$ ), increased for 25-75 styrene-butadiene (approximately proportional to M) and increased in a manner directly proportional to M for butadiene. This uniform change in rate would indicate that a discussion of the kinetics of the two limiting cases, the pure styrene and pure butadiene systems, should be undertaken first, the kinetics of the copolymerizations being related to these.

### 1. Styrene Polymerization

In the present work the rates of polymerization for various monomer concentrations were determined when the initial rate of decomposition of peroxide, i.e. kC, was held constant. It was assumed that the rate of activation would then be constant, i.e. equation X holds

$$\frac{dl^{t}}{dt} = kC = constant \qquad (X)$$

where C is the initial catalyst concentration and k the measured rate constant for the peroxide decomposition. The usual kinetic analysis

yields the following expressions for the initial rate of polymerization and average degree of polymerization:

$$\frac{dP}{dt} = k_p \left(\frac{kC}{k_t}\right)^{\frac{1}{2}} M$$
 (XI)

and

$$\overline{P_n} = \frac{V_{\text{prop.}}}{V_{\text{term.}}} = k_p \left( \frac{M}{(k_t 2 k C) \overline{z}} \right)$$
(XII)

If the assumption of constant rate of activation is correct, no change in rate should occur as the monomer concentration changes, the polymerization being truly first order in monomer. Actually this was not found experimentally, the rate decreasing by approximately twenty percent over the concentration range studied and being proportional to the square root of the monomer concentration. It is apparent then that the assumption made here is not valid; i.e. when the initial rate of decomposition of the catalyst is held constant the rate of initiation is not constant.

As noted above this assumption is correct only if no side reactions, such as that represented in equation (3), do occur. It is probable that such reactions are of minor importance in pure styrene but become more prominent as dilution increases so that only a fraction of the free radicals formed from the peroxide decomposition are available to initiate polymerization. Thus, the rate of initiation of polymerization is not exactly equal to the rate of decomposition of peroxide given by equation (X) but is only proportional to it, kC actually being equal to the rate of initiation, KRM, plus a term involving free radical reactions.

The fact that the rate of polymerization is proportional to the square root of the monomer concentration is probably purely fortuitous. The degree of polymerization (which is directly proportional to the viscometric molecular weight) is also found to be approximately proportional to the threehalves power of the monomer concentration as would be expected from the dependence of rate on the square root of the monomer concentration. However, considering that the change in rate for a five-fold change in monomer concentration was only twenty percent, it is highly probable that under conditions of constant initial free radical concentration the polymerization of styrene would be found to be first order, the rate constant independent of monomer concentration and the degree of polymerization proportional to monomer concentration.

When the temperature was varied while kC, the initial rate of peroxide decomposition, was held constant, the molecular weight of the polystyrene formed increased with temperature. At present chain transfer is considered to play a major role in determining the molecular weight of the polymer formed in catalyzed polymerizations. If this is so, then it is to be expected that under conditions of constant initial free radical concentration the molecular weight of the product should decrease with increasing temperature since chain transfer has a higher activation energy than chain propagation (4) and the degree of polymerization, considering chain transfer, is given by equation (10) developed in the general introduction, i.e.

$$\overline{P}_{n} = \frac{k_{p} [R] M}{k_{t} [R]^{2} + k_{GT} [R] M + k_{ST} S[R]}$$

where k<sub>CT</sub> is the rate constant transfer to monomer

kgT is the rate constant transfer to solvent

[R] is the free radical concentration

The fact that the molecular weight increases with temperature when [R] is held constant both in pure styrene and in solutions of styrene in benzene (89) indicates that chain transfer plays only a minor role, if any, in

determining the molecular weight of polymer in the catalyzed polymerizations. The apparently erroneous idea of chain transfer governing the value of  $\overline{Pn}$  (4,8) has probably arisen from neglect of the fact that the rate of decomposition of peroxide varies as solvent is added to the polymerization systems and hence [R] varies under conditions of constant initial peroxide concentration. In a few solvents such as carbon tetrachloride the polymer active centres, apparently, actually attack the solvent and add a CCl<sub>3</sub>. group while releasing a Cl free radical which is available to initiate a chain (69) and chain transfer does become important. However, it is probably true that the apparent effect of most solvents on the molecular weight of polymers formed in catalyzed polymerizations is actually the result of a change in free radical concentration.

Chain transfer should be of major importance in determining the molecular weight of the product from a purely thermal polymerization where, in the absence of peroxides, there is a low concentration of free radicals so that the mutual termination term  $k_t[R]^2$  will be small and of the same order of magnitude as the chain transfer terms. The relative rates at the three temperatures used in this study (Table XXXVII) are 1, 1.72, 2.52 while the relative values of the molecular weights are 1, 1.58 and 1.89. If there were no chain transfer reaction and if equal numbers of chains were started at the three temperatures, the molecular weight would have to rise in the same proportion as the rate to account for the observed increase in rate. If chain transfer is assumed to be of little significance in the systems investigated, it would appear that free radicals initiate chains with greater efficiency at the higher temperatures.

Before discussing the polymerization of butadiene the activation energy

should be mentioned. It has been assumed that the rate of chain initiation is constant under the present experimental conditions, so that the rate of polymerization is given by the equation

$$\frac{\mathrm{dP}}{\mathrm{dt}} = \frac{\mathrm{k}_{\mathrm{p}_{1}}}{\mathrm{k}_{\mathrm{t}} \overline{\mathrm{z}}} \left( \mathrm{V}_{\mathrm{init.}} \right)^{\frac{1}{\mathrm{z}}} \mathrm{M}$$

Hence the activation energy (8.3 kcal.) calculated for the polymerization is actually the difference between  $E_p$ , the activation energy of propagation, and  $\frac{1}{2}E_t$ ,  $E_t$  being the activation energy of termination.

If the above assumption is incorrect and the catalyst is used with more efficiency at the higher temperature, the actual value of  $E_p - \frac{1}{2}E_t$ will be somewhat lower than that reported here. However, the value calculated is consistent with data available from thermal polymerizations. The apparent activation energy is 22-24 kcal. (38),  $\frac{1}{2}E_a$ , the energy of initiation, is 14 kcal. (95) and, therefore,  $E - \frac{1}{2}E_a = E_p - \frac{1}{2}E_t = 8-10$ kcal. per mole.

#### 2. Butadiene Polymerization

If a steady state concentration of free radicals is assumed to be rapidly reached in the bulk polymerization of butadiene, which appears to proceed by a free radical mechanism in which the free radicals are generated by a first-order decomposition of peroxide and terminated by a reaction second order in free radicals, equation (XI) should hold, i.e.

$$\frac{dP}{dt} = \frac{k_{p_1}}{k_t z} (kC)^{\frac{1}{2}} M$$
 (XI)

Substituting  $C = C_0 e^{-kt}$  and integrating

$$\frac{-\log(1-P)}{dt} = \frac{k_{p_1}}{k_t z} \frac{2C_{\frac{1}{z}}}{k_z^{\frac{1}{z}}} (1-e_{\frac{1}{z}})$$

where P is the fraction of monomer converted to polymer.

This equation was applied to the data in Table XLVIII and a value of 0.0795 calculated for  $\frac{k_{p_1}}{k_{t_2}}$ . In fig. 39 the actual and theoretical curves are plotted for catalyst concentrations of 0.667, 0.960 and 1.25 weight percent. In general the values of P determined experimentally are higher than the calculated values.

From equation (XI) it is apparent that the rate of polymerization in butadiene should be first order; i.e. the rate should be independent of the monomer concentration, but it does in fact increase as the monomer concentration decreases.

It appears, therefore, that the rate of initiation of chains may be greater than expected and increase with dilution despite the constant rate of peroxide decomposition.

Some other reaction may be responsible for free radical formation. Such a reaction might involve the opening of a double bond in a growing polymer chain similar to the reaction proposed by Medvedev (41) for chloroprene, and by Devins and Winkler(96) for butadiene-styrene "popcorn" growth. The energy released by monomer addition to the growing chain distributes itself along the chain, as vibrational and rotational energy, and occasionally sufficient energy concentrates in a double bond 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 be started. Such a reaction would result in a greater concentration of free radicals at any time.

The mechanism must, however, also account for the increase in the initial rate of polymerization as the solvent concentration is increased. It is to be expected that the rate of branching should decrease under such con-



ditions since, as the solvent concentration increases, the probability that a monomer molecule would collide with the "activated" double bond in the growing polymer decreases. It is possible that this branching reaction may become important later in the reaction, the radicals necessary for a given amount of polymer formation being formed in the initial stages by the peroxide decomposition, while later the radicals might be produced principally by the branching reaction so that polymerization would continue after all the catalyst was decomposed. Such a reaction would eventually lead to the insoluble gel usually found for polybutadiene.

A second initiation reaction, such as branching, does not appear to explain the experimental results. It may be possible, therefore, that the concentration of free radicals is actually greater than expected from the rate of decomposition of peroxide and increases with dilution despite the fact that the rate of peroxide decomposition is held constant.

Three explanations of the increase in free radical concentration with dilution appear possible.

- 1. There are a greater number of catalyst free radicals available to initiate polymerization in dilute butadiene solutions than in concentrated solutions.
- 2. Phenyl radicals may attack benzene to give appreciable quantities of hydrogen radicals which might react faster with butadiene than do phenyl.
- 3. The butadiene free radicals may have a long life so that the actual concentration at any time is greater than that calculated by assuming a steady state. It appears probable that, if only partial deactivation were to occur, corresponding to relatively long-lived radicals, it would decrease as the monomer concentration decreased

so that the actual concentration of active polymer at any time would be greatest in the most dilute butadiene solution.

If a greater number of catalyst free radicals are available to initiate polymerization in dilute butadiene solutions than in pure butadiene, when the initial rate of decomposition of peroxide is held constant, it would have to mean that phenyl radicals attack benzene more readily than they attack butadiene so that a smaller number of free radicals are lost in side reactions such as the combination of a phenyl and benzoate free radical in benzene than in pure butadiene. If this is correct, then the variation of rate of peroxide decomposition with concentration in pure butadiene should be greater than that in benzene, the second-order terms involving free radicals being more important for butadiene than for benzene. Actually just the reverse was found experimentally. Hence, if the concentration of catalyst free radicals available for polymerization does change on dilution, it probably decreases rather than increases.

If phenyl radicals did attack benzene to any appreciable extent to form biphenyl and a hydrogen free radical, the rate of polymerization might increase on dilution, the number of hydrogen free radicals, which might react faster with butadiene than phenyl radicals, increasing as the concentration of benzene increases. However, as noted earlier, only small amounts of biphenyl have been isolated in the products from the decomposition of peroxide in benzene (93) so the number of hydrogen free radicals must be low and could hardly be the cause of the two-fold increase in rate of polymerization with dilution.

If, on the other hand, the original assumption that a steady state con-

centration of free radicals is rapidly attained, is incorrect, i.e. the growing polymer has a long half-life, the number of active centres present in the system would continue to increase for some time after the start of the reaction. This would more than counterbalance the decrease in monomer concentration so that the overall rate, which is the product of these two factors, would increase. If partial deactivation occurs, it would have the effect of decreasing he fraction polymerized before maximum velocity is attained. However, as the solvent concentration is increased, it would seem probable that the relative extent of deactivation by mutual termination would decrease corresponding to an increased rate of polymerization with dilution.

The free radicals would be produced by the first-order decomposition of the catalyst, i.e.

$$\frac{\mathrm{d}\mathbf{R}\mathbf{I}}{\mathrm{d}\mathbf{t}} = \mathbf{k}\mathbf{C}.$$

Propagation would proceed by the reaction of an active centre with the monomer, i.e.

$$\frac{\mathrm{d}P}{\mathrm{d}t} = k_p \left( \mathbf{R} \right) \mathbf{M}.$$

Free radicals would be deactivated by mutual termination, i.e.

$$\frac{-dR}{dt} = k_t (R)^2$$

Since a steady state concentration of free radicals is no longer assumed valid, the concentration of free radicals at any time, t, must be calculated from the equation for the rate of change of free radicals with time, viz.

$$\frac{d\mathbf{R}}{dt} - \mathbf{kC} - \mathbf{k}_t [\mathbf{R}]^2 \qquad (XIII)$$

where  $C = C_0 e^{-kt}$  and [R] is the concentration of free radicals at time, t.

The term  $k_t [R]^2$  decreases as the monomer concentration decreases so that the rate of build up of free radicals is greatest in the most dilute monomer solution.

Integration of equation (XIII) is not possible. However, some idea of how the concentration of free radicals changes with time may be obtained by plotting  $\frac{dP}{dt}/M$  against time. This actually is a plot of kp [R] against time. From fig. 40 the concentration of free radicals is seen to increase in a manner linear with time over the range studied. The intercepts and the slopes are found to increase as the solvent concentration increases. The curve for the bulk polymerization shows that the concentration of free radicals passes through a maximum. This occurs when the rate of formation of free radicals becomes equal to the rate of termination. Beyond this point more free radicals will be terminated per unit time than are formed so that the concentration of free radicals decreases and the rate of polymerization decreases.

An S-shaped curve would be expected for the polymerizations if no deactivation occurred. The polymerization curves here are approximately linear over the time range studied, although the first points on the curves for the more dilute solutions of butadiene (fig. 32) are low. Whether this is merely the result of experimental error or an inhibition period rather than build up of free radicals is difficult to say. The course of the polymerization in dilute butadiene solutions, where deactivation is assumed to be a minimum, should be studied over a longer time range to determine whether S-shaped curves are found.

The assumption of a long-lived butadiene radical could be subjected to experimental test by studying the effect of catalyst concentration on the rate of polymerization of butadiene as the solutions are increasingly di-



luted. In pure butadiene, where deactivation is assumed to be at a maximum, the rate of polymerization should be approximately proportional to the square root of the catalyst concentration (equation XI) as actually found. In dilute butadiene solutions, where the rate of deactivation should be much reduced, the rate should be more nearly proportional to the catalyst concentration than to the square root of the catalyst concentration. Thus, if no deactivation occurs, equation (XIII), for the rate of change of free radical concentration with time, becomes .

$$\frac{\mathrm{dR}}{\mathrm{dt}} = \mathrm{kC} - \mathrm{kC}_{\mathrm{o}}\mathrm{e}^{-\mathrm{kt}}$$

Integrating

$$[R] = \int_{0}^{t} kC_{0}e^{-kt} = C_{0}(1-e^{-kt})$$

Substituting this value of [2] in the equation for the rate of propagation

$$\frac{dP}{dt} = k_p [R] M = k_p C_o (1 - e^{-kt}) M \qquad (XIV)$$

Hence, when no deactivation occurs, the rate of polymerization should be proportional to the catalyst concentration.

If the butadiene free radicals do have a long life then it is to be expected that the active polymer centres would continue to grow without interruption so that the molecular weight of the polymer at any time would be proportional to the fraction of material polymerized. If, on the other hand, deactivation is important so that a steady state concentration of free radicals is rapidly set up, the polymer chains should grow to a constant average length. Styrene obviously belongs to the latter class while pure butadiene and mixtures of butadiene and styrene should belong to the former group. No viscosity data are available for pure butadiene polymerization in the present investigation since over the short time interval the

polymerization was studied polymer of very low molecular weight was obtained. However, for the mixture 75 percent by weight of butadiene and 25 percent by weight of styrene, the molecular weight of the polymer was found to increase with reaction time; in fact this tendency for the molecular weight to increase with reaction time was found for all systems containing butadiene in appreciable quantities. This would indicate that butadiene free radicals are actually resistant to termination and have a long life. The shape of curves obtained by plotting the molecular weight against percent conversion (figs. 2,4), showing a slow increase in molecular weight during the initial stages of the reaction with a much more rapid increase in the later stages, may readily be explained on the assumption that a steady state concentration of free radicals is not present in butadiene polymerizations. It is evident that, if a steady state condition is not rapidly attained, the concentrations of free radicals must increase during the initial stages of the reaction so that the rate of increase in the concentration of active centres and time are competing and the average degree of polymerization does not increase rapidly. After the maximum concentration of free radicals is reached this will not be true and the increase in the average degree of polymerization should be almost proportional to the amount of monomer polymerizing. The presence of side reactions such as crosslinking may also become important in the later stages, making the average degree of polymerization increase much faster than would be expected from the amount of monomer polymerizing.

If the assumption of a long life for the butadiene free radicals is correct then it is to be expected that polymerization of butadiene monomer should continue even after all catalyst has been decomposed. From the

results for the rate of peroxide decomposition in butadiene the peroxide is found to have a half-life of approximately 12 hours. In the present investigation only the first few hours of the polymerization have been studied. However, the work done by Graham (90) shows that even after 10 days some growth is observed in polymerizations of pure butadiene at  $75^{\circ}$ C. This growth obviously cannot be the result of catalysis and may perhaps be attributed to long-lived butadiene radicals. Graham also found that his experimental results for the growth of polybutadiene popcorn in butadiene could only be explained on the basis of a long-lived butadiene free radical.

It is also interesting to note that Medvedev (36) has actually found free radicals in a polymer of butadiene and vinyl cyanide.

There is one piece of experimental data which might at first seem to invalidate the assumption of a long-lived free radical; i.e. the rate of polymerization of butadiene in carbon tetrachloride actually decreased with increasing solvent concentration (Table III). However, it is well known that carbon tetrachloride is an excellent chain transfer agent; the active polymer could then attack the solvent, adding on a CCl<sub>3</sub><sup>o</sup> group and freeing a Cl free radical which could then react with the catalyst free radicals and so prevent an increase in build up of free radical concentration.

Most of the experimental results would seem to indicate, therefore, that the assumption of a steady state concentration of free radicals in polymerization systems involving butadiene is not valid, butadiene free radicals actually having a relatively long lifetime.

#### 3. Copolymerization

In this study the monomers chosen were such that for one styrene, the half-life of the active polymer is short so that the steady state method may be employed to calculate the concentration of active polymer while for the other, butadiene, it would appear that the polymer half-life is long so that the concentration of active polymers increases with time.

It is obvious then that an empirical rate expression relating initial rates of polymerization in these two systems and in mixtures of the two monomers similar to that developed by Norrish and Brookman (42) would have little value. Even when the peroxide decomposes at the same initial rate in the different systems the initial concentration of active centres cannot be assumed to be constant because of the differences in the activation energies of the termination reaction, the concentration of active polymer centres being determined not only by the rate of peroxide decomposition (assumed equal to the rate of initiation) but also by the rate of mutual termination. If it can be assumed that each free radical formed by the decomposition initiates a chain then the concentration of free radicals varies inversely with the velocity of termination; the faster termination the lower the concentration of free radicals. Hence the concentration of free radicals in butadiene at any time may be expected to be greater than that in styrene for the same initial rate of peroxide decomposition.

An exact study of the rate expression for copolymerization clearly requires a different technique. The photochemical method developed by Melville (97) should be satisfactory. The rate of initiation can be controlled by the number of quanta entering the system and the termination can be inferred from the dependence on the light intensity. Melville et al (49) have
recently developed methods which will allow determination of the rate constants of all the individual steps of the copolymerization.

Although the data obtained in the present study will not give a quantitative expression for the dependence of rate on monomer concentration a qualitative picture may be obtained.

In fig. 41 the initial rates of polymerization for the same initial rate of decomposition of peroxide are plotted against the concentration of butadiene in mole percent. If the assumption is correct that the same initial rate of decomposition of peroxide results in the same initial concentration of active centres then the curve should fall more rapidly than it does in fig. 41, the initial concentration of free radicals in butadiene being greater than that in styrene as explained above.

There appear to be three possible explanations to account for the rate of polymerization falling off so rapidly as the concentration of butadiene increases:

- (1) Although the same initial concentration of catalyst free radicals is present in the various systems the rate of initiation is much greater in styrene than in butadiene so that the actual concentration of growing polymer at any time is much greater in styrene than in butadiene.
- (2) The rate of chain propagation in styrene is much greater than that in butadiene.
- (3) The rate of termination in pure butadiene is much faster than that in pure styrene so that very little monomer is consumed before the chains are deactivated.



Figure 41 - Copolymerization of butadiene and styrene in bulk phase at constant initial rate of peroxide decomposition at 75 C.

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The third explanation is not consistent with the idea of a long halflife for the growing butadiene polymer which appeared to be consistent with the data for the butadiene polymerization.

If the first postulate were correct, viz. that the rate of initiation of styrene is faster than that for butadiene, the rate of polymerization should be determined by the more readily activated monomer, the two monomers entering indiscriminately into the growing polymer. However, the rate is drastically decreased when butadiene is added. It might also be pointed out that all reactions involving a free radical and olefin that have been investigated have activation energies of approximately 5 kcal. (98). It would, therefore, seem probable that very little difference in activation energy for the reaction of free radicals with styrene and butadiene exists.

It would appear, therefore, that the rate of chain propagation in styrene must be much greater than that in butadiene. It has been shown in GR-S polymerizations that butadiene will react faster than styrene with either a butadiene or styrene active centre. This, however, is not contradictory since when styrene is present in the growing chain the electronic picture must be different from that in pure butadiene and must influence the relative rates at which the two monomers enter the chain. The idea of a long-lived butadiene free radical is also consistent with a high activation energy for growth of the active polymer, the free radicals being quite stable.

The "activation energies" determined for the different systems are 8.3, 8.6, 8.8, 7.5 and 7.2 kcal. for 100 percent styrene to 100 percent butadiene. These might appear at first to be inconsistent with the idea of a higher activation energy for growth in butadiene than in styrene, since they actually measure the difference in activation energy between the

propagation and termination reactions under the experimental conditions. However, the energy for termination in butadiene must also be greater than that in styrene so that the overall change actually results in a lower activation energy for butadiene.

One other interesting point in these polymerizations should be emphasized. The molecular weights of the polymers formed at the three different temperatures increase with an increase in temperature in all cases when the initial rates of peroxide decomposition are equal. In practice, it should then be more efficient to polymerize polymerizations at the upper limit of the temperature range of the catalyst. The initial catalyst concentration should be low and increment additions of catalyst made.

It would appear then that the original problem of trying to form a polymer with a molecular weight comparable to that formed in emulsion polymerization and a narrow molecular weight distribution might be solved by using a flow system in which the catalyst concentration is maintained at a low but constant value, the temperature maintained as high as possible and the polymer, which is precipitated from the monomer-solvent-non-solvent system, is removed continuously and shortstopped with hydroquinone to prevent further growth. To find a suitable non-solvent at temperatures around 90°C may introduce serious difficulty since it was found that non-solvent property changes rapidly with temperature.

## SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

## PART I

The kinetics of the copolymerization of 75 weight percent of butadiene and 25 percent of styrene in homogeneous solution have been studied in the hope that conditions could be established under which polymerization would proceed to yield a polymer sample with a molecular weight and homogeneity which could be controlled within reasonable limits. This was to be accomplished by incorporating the principle of fractionation by precipitation into the polymerization reaction.

The solution polymerization has been shown to yield a true copolymer. However, the polymers obtained in the initial polymerizations, with benzoyl peroxide as the catalyst, were of low molecular weight. This was believed to be the result of a dilution effect; hence a study of the bulk polymerization of 75-25 weight percent butadiene-styrene has been made. The effect of temperature, catalyst concentration and solvent on the rate of polymerization has been investigated.

The reaction has been found to have an activation energy of 24.1 kcal. for the range  $50^{\circ}$ C to  $100^{\circ}$ C but above  $100^{\circ}$ C a reaction of higher activation energy preponderated. No quantitative relation has been found between molecular weight and temperature, but above 25 percent conversion an increase in temperature increased the molecular weight, probably as the result of cross-linking.

The initial rate of polymerization has been found to be proportional

to the square root of the catalyst concentration while the viscosity average molecular weight varied inversely as the square root of the catalyst concentration. These relations hold as a general rule for reactions activated by free radicals.

The copolymerization has also been studied in various solvents. Benzene has been used to study the effect of solvent concentration on initial rate and molecular weight. When the catalyst concentration was held constant on the basis of moles per litre the initial rate showed a tendency to increase with increasing dilution while the molecular weight was approximately proportional to the monomer concentration. When the catalyst concentration was held constant on the basis of weight percent of monomer the rate of polymerization decreased with dilution but the molecular weight remained the same.

When different solvents were compared at the same volume percent the rates were found to agree qualitatively with results reported in the literature for the rates of decomposition of benzoyl peroxide. In general the molecular weights of the polymers were found to decrease as the rate of polymerization increased. Carbon tetrachloride was the exception to the rule, the molecular weights of the polymers being much lower than that for other solvents in which the rates were comparable. This would indicate that carbon tetrachloride acted as an efficient chain transfer agent.

The quantitative relations found for the polymerizations with benzoyl peroxide catalyst were checked with diazo-amino benzene catalyst. The latter decomposes more slowly than benzoyl peroxide so that the rate of the reaction is maintained over longer periods of time and it was felt that more reproducible results both for yields and physical properties of the

polymers might be obtained.

The usual dependence of rate and molecular weight on catalyst concentration has been found; i.e. rate was proportional to the square root of the D.A.B. concentration while the molecular weight was inversely proportional to the square root of the catalyst concentration.

Dilution with benzene when the D.A.B. concentration was held constant on the basis of moles per litre resulted in no change in rate while the molecular weight decreased proportional to the monomer concentration.

The molecular weight has been found to vary inversely with the temperature and an activation energy of 20.8 kcal. has been found for the reaction.

Although all the results indicated that attaining a polymer of molecular weight of the *mange* generally associated with synthetic rubbers consistent with an appreciable rate of polymerization was impossible under the experimental conditions, a study has been made of the addition of a precipitant merely to determine whether addition of precipitant would be effective to any extent.

Isobutyl alcohol has been used as the precipitant. The polymer precipitated as a coacervate was of very low molecular weight although greater than the molecular weight of the polymer formed in analogous benzene solutions. The polymer in the coacervate has been shown to polymerize. This could occur only if the growing polymer molecules were not deactivated when precipitated or if interaction between inactive polymer molecules occurred in the presence of catalyst; i.e. cross-linking occurred.

It was evident that the system used was unsuitable for investigating the effect of non-solvent.

The copolymerization with D.A.B. as catalyst has been shown to proceed by a mechanism similar to that postulated for the polymerization of other dienes and vinyl compounds. The main steps in the reaction are firstorder decomposition of the catalyst to yield free radicals, successive addition of monomer to the radicals and termination of radical chains by bimolecular reaction. Mathematical analysis of this mechanism predicted that the rate of polymerization should be first order in monomerand hence independent of monomer concentration, and that the degree of polymerization of the polymer should be directly proportional to the monomer concentration as found for the copolymerization with D.A.B. as catalyst. When benzoyl peroxide was used the rate of polymerization was found to increase as the monomer concentration decreased. This difference in behaviour between the two catalysts was believed to be the result of a variation in the rate of decomposition of benzoyl peroxide on the addition of inert solvent, benzene, and led to the study in part II.

## PART II

The influence of peroxide concentration, benzene concentration and temperature on the rate of decomposition of benzoyl peroxide has been studied in systems containing butadiene, styrene and mixtures of the two. Also the polymerization of butadiene, styrene and copolymerization of the two have been studied under various conditions at constant initial rate of benzoyl peroxide decomposition, which was assumed to be equivalent to constant rate of initiation of polymerization.

The rate of decomposition of benzoyl peroxide has been found to decrease as the styrene content of the reaction medium decreased by dilution

with either butadiene or benzene. Each individual experiment has been found to conform to first-order behaviour but in butadiene and benzene the rate has been found to depend to some extent on the concentration of peroxide. The "activation energy" for the decomposition of benzoyl peroxide varied from 26.5 kcal. in styrene to 31 kcal. in butadiene.

The mechanism assumed by Downes for the decomposition of benzoyl peroxide (viz. that the removal of benzoate radicals, assumed to be in equilibrium with peroxide, is the rate controlling step) has been subjected to kinetic analysis and yielded equations which were in agreement with the experimental results.

In every polymerization system a linear relation between rate of polymer formation and the square root of the peroxide concentration has been found while the molecular weight varied inversely as the square root of the peroxide concentration. This indicated that the polymerizations all proceeded by a free radical mechanism in which the radicals were generated by a first-order decomposition of benzoyl peroxide and were destroyed by a second-order termination of the radical chains.

No general dependence of rate on monomer concentration has been found under conditions of constant free radical concentration. With styrene the rate has been found to decrease as the monomer concentration decreased (proportional to the square root of the monomer concentration), increased for 25-75 styrene-butadiene (approximately proportional to monomer concentration) and increased in a manner directly proportional to the monomer concentration for butadiene.

In every polymerization an increase in temperature corresponded not

only to an increase in rate but also an increase in molecular weight. Activation energies have been calculated for each system: styrene -8.3 kcal., 75-25 styrene-butadiene - 8.6 kcal., 50-50 styrene-butadiene - 8.8 kcal., 25-75 styrene-butadiene - 7.5 kcal., and butadiene - 7.2 kcal.

Using the assumption of a constant rate of initiation of polymerization when the initial rate of benzoyl peroxide decomposition was held constant, a mechanism for styrene polymerization similar to that proposed in Part I for the copolymerization has been discussed. Such a mechanism predicts that the rate of polymerization of styrene should be first order in monomer and hence independent of the monomer concentration. Such has not been found experimentally. However, since the variation in rate was only twenty percent over the entire concentration range the deviation from the theoretical equation has been credited to an error in the original assumption that all free radicals produced from the catalyst were available to initiate polymerization.

Chain transfer has been shown to play only a minor role, if any, in determining the molecular weight of the polystyrene formed in peroxide catalyzed polymerizations either in pure styrene or styrene diluted with solvents such as benzene. The effects ascribed in previous work to chain transfer appear actually to be caused by the variation in the rate of benzoyl peroxide decomposition.

The equation derived for the rate of polymerization of styrene has been applied to the data for the rate of polymerization of butadiene in bulk phase at various catalyst concentrations. The theoretical curves have been found to be lower than the experimental in each case. This

fact coupled with the fact that the rate of polymerization of butadiene has been found to <u>increase</u> when the monomer concentration <u>decreased</u> for constant initial rate of decomposition of benzoyl peroxide indicated that the rate of initiation of chains must be greater han expected and increase with dilution.

Several possible mechanisms have been proposed. The assumption that butadiene free radicals have a relatively long life so that the steady state assumption is not valid was shown to conform best to all the experimental evidence.

Only a qualitative discussion of copolymerization has been possible because of the differences in behaviour of the two monomers. The shape of the copolymerization curve has been shown to depend mainly on the rate ´ of chain propagation rather than rate of chain initiation or termination.

A possible procedure for attacking the original problem has been suggested.

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