SOME STUDIES ON TERTIARY HEXADECYL MERCAPTAN AS A

MODIFIER IN BUTADIENE-STYRENE COPOLYMERIZATIONS

A Thesis

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SOME STUDIES ON TERTIARY HEXADECYL MERCAPTAN AS A MODIFIER IN BUTADIENE-STYRENE COPOLYMERIZATIONS

Tertiary hexadecyl mercaptan was investigated as a modifier in the emulsion copolymerization of butadiene and styrene. This mercaptan disappeared slowly during the first 50-60 per cent of the polymerization but underwent a rapid increase in rate of disappearance thereafter.

This rapid rate of disappearance at high conversion cannot be accounted for on the basis of changing styrene content during polymerization or upon mercaptan addition to the polymer double bonds.

Changes in viscosity of the polymer during polymerization were studied. A decrease was observed in the same conversion range where the rate of the mercaptan disappearance increased.

Tertiary hexadecyl mercaptan was applied to the preparation of relatively homogeneous polymers of different composition and molecular size. On the basis of the modifier reaction theory polymers of various compositions but of the same molecular weight were prepared and studied. It was found that the viscosity decreased and the solubility increased with an increase in the styrene content of the polymer.

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GENERAL INTRODUCTION

The large scale manufacture of synthetic rubber on this continent was undertaken of necessity during the war years. Along with this industrial expansion came improvement in quality so that the synthetics now produced can compare favorably with the natural product.

Much of this success can be attributed to the discovery of useful chain transfer agents, usually designated as "modifiers". These modifiers control the polymerization by regulating the molecular size. They are, for the most part, sulfur-containing compounds of which the most useful are the aliphatic mercaptans. The effect of many such compounds, on the rate of polymerization and on the physical character of the polymer, has been extensively investigated.

One of the most interesting of these mercaptans from a research standpoint is tertiary hexadecyl mercaptan. This mercaptan undergoes a slow initial rate of disappearance which results in a homogeneous polymer of high molecular weight. Thus, by using only low conversion polymer, this mercaptan lends itself to a study of polymer properties. By suitable variation in the initial monomer ratios relatively homogeneous polymers of different composition could be studied. By variation in the mercaptan content polymers of the same composition but of different molecular weight could be evaluated. However, at high conversion tertiary hexadecyl mercaptan undergoes a sharp increase in its rate of disappearance. This gives rise to polymers of lower molecular weight and results eventually in a more heterogeneous product.

It was considered of interest to carry out a more intensive study of the behaviour of tertiary hexadecyl mercaptan along the following lines.

(1) Investigation of the possible causes for the increased rate of disappearance at high conversions:

- (a) effect of changing styrene content during polymerization,
- (b) effect of mercaptan-polymer interaction.
- (2) Utilization of hexadecyl mercaptan for:
 - (a) the evaluation of the changes of viscosity and solubility with composition,
 - (b) the preparation of relatively homogeneous polymer fractions of different composition over a wide viscosity range.

HISTORICAL INTRODUCTION

The two general methods of preparing polymeric materials are condensation polymerization and addition polymerization. Condensation polymerization occurs with di- or polyfunctional molecules chemically constituted in such a manner that the monomers can condense repeatedly and indefinitely with one another to build up a polymeric product. The reaction proceeds stepwise yielding material of successively increasing degree of polymerization throughout the course of the reaction. This is the type of process involved in the preparation of polyesters and poly-In contrast to condensation polymerization, the amides. molecules formed at any instant during addition polymerization are essentially the same as those formed at any other period throughout the course of the reaction. Thus the polymer does not grow gradually but rapidly attains a certain size This behaviour, as well as the and then stabilizes itself. susceptibility of these reactions to catalysis and inhibition, points to a chain reaction mechanism for their formation.

The mechanism generally accepted today for addition polymerization involves three stages: (1) initiation, the starting of the chain by activation of the monomer, (2) propagation, the growth of the polymer chain by successive addition of monomer molecules to the active intermediate, (3) termination of the chain by deactivation of the polymer

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intermediate. These steps may be represented as follows:

- 1. Initiation $M \longrightarrow M^*$
- 2. Propagation M*+ M \longrightarrow M^{*}₂ \xrightarrow{M} \xrightarrow{M} M^{*}_n
- 3. Termination $M_n^* \longrightarrow M_n$

In the above "M" represents a monomer molecule and "*" an activated state. It has also been postfulated that under certain conditions this activation may be passed on to some other molecule, monomer or solvent, in a process known as chain transfer (1). Thus:

$$\mathbb{M}_{n}^{*} + \mathbb{X} \mathbb{Y} \longrightarrow \mathbb{M}_{n} \mathbb{X} + \mathbb{Y}^{*}$$

With respect to the activation step considered above it is now generally conceded that it may arise in a variety of ways depending upon the type of monomer, reaction conditions, catalyst, etc. However, three general theories have been advanced involving cationoid, anionoid and free radical activation.

Cationoid:

$$\begin{array}{c} x^{+} & \overset{H}{\underset{H}{}} : : : \overset{H}{\underset{H}{}} \to x \begin{bmatrix} \overset{H}{\underset{C:C}{}} : : : \\ \overset{H}{\underset{H}{}} & \overset{H}{\underset{H}{}} \end{bmatrix}^{+} \overset{H}{\underset{C:C}{}} : : : \\ \overset{H}{\underset{H}{}} & \overset{H}{\underset{H}{}} & \overset{H}{\underset{H}{}} \end{bmatrix}^{+} \overset{H}{\underset{C:C}{}} : : : \\ \overset{H}{\underset{H}{}} & \overset{H}{\underset{H}{}} \end{bmatrix}^{+} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \end{bmatrix}^{+} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{} \overset{H}{} \overset{H}{\underset{H}{}} \overset{H}{\underset{H}{} \overset{H}{}} \overset{H}{\underset{H}{} \overset{H}{} \overset{H}{$$

These mechanisms are postulated for those reactions catalyzed by strong mineral acids and metallic halides, such

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as borontrifluoride or aluminum chloride (2) (3).

Free Radical:

Staudinger (4) was one of the first to postulate that activation might involve the formation of a free radical.

 $\begin{array}{cccc} & & & & & & \\ R^{*}+ & CH_{2} & : & CH \longrightarrow R: CH_{2}: & CH^{*} & \xrightarrow{X} & R: CH_{2}: CH: CH: CH^{*} & \xrightarrow{X} & etc. \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ \end{array}$

The free radical mechanism has been supported by both chemical and kinetic methods.

Many workers in the field have shown that a large number of reactions which on the basis of entirely independent evidence are believed to generate active free radicals, initiate many addition polymerizations (5, 6, 7, 8, 9, 10). Furthermore, the detection of catalyst fragments in the polymer offers further support for the free radical mechanism. Such catalysts as 3,4,5-tribromobenzoyl, p-bromobenzoyl, p-anisoyl and chloroacetyl peroxides have been used. In every case fragments have been found in the polymer, and by correlating analytical and molecular weight data, it has been shown that there is very nearly one catalyst fragment per polymer molecule (11, 12, 13).

Other evidence favoring the free radical theory is offered by the action of retarders which deactivate the active centres in the chain growth process and reduce the overall rate as well as the molecular weight. In this class the aromatic nitro compounds are found. Price and Durham (14) polymerized styrene in the presence of nitrobenzene, 2,4-dinitrochlorobenzene and nitromethane. They postulated that the retarding effect of the aromatic nitro compounds was due to an activation of the aromatic nucleus by the nitro group and that it is this activated nucleus which then reacts with growing chains. This was proven by carrying out the reaction in the presence of nitromethane where polymerization proceeded at the normal rate to give polymer containing no detectable amount of nitrogen. They represent the reaction as follows:

$$\begin{array}{cccc} R: (CH:CH)_{n}^{\bullet} + & C_{6}H_{5}NO_{2} \longrightarrow & R: (CH:CH)_{n}^{+} & & & \\ & & X & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & &$$

Kinetic studies have also been used to support the free radical mechanism. Investigations of the peroxide catalysed polymerizations of styrene, (15) vinyl acetate (16) and many other vinyl compounds have indicated a rate dependent on monomer concentration as well as the square root of the catalyst concentration. On the basis of a first order decomposition of catalyst (17) this has been accepted as offering conclusive support for a second order cessation reaction with respect to active centres. This substantiates the free radical mechanism, since deactivation of a free radical can only occur by reaction with another free radical. On this basis the following rate relationships may be derived where the initiation of active centres is accomplished by a first order decomposition of peroxide, followed by a second order propagation reaction between active centres and monomers and a second order termination step by reaction of two active radicals.

Initiation.

 $(C_{6}H_{5}CO_{2})_{2} \xrightarrow{ka} \frac{C_{6}H_{5}CO_{2}^{*} + C_{6}H_{5}^{*}}{R^{*}} + CO_{2}$

Propagation

 $R' + M \xrightarrow{kb} RM' \xrightarrow{kb} \xrightarrow{kb} RM'_n$

Termination

- (a) $\operatorname{RM}_{n}^{\bullet} + \operatorname{RM}_{m}^{\bullet} \xrightarrow{\mathrm{kcl}} \operatorname{RM}_{n} + \operatorname{RM}_{m} \operatorname{or} \operatorname{RM}_{n} \operatorname{M}_{m} \mathbb{R}^{1}$
- (b) $RM_n^{\bullet} + R^{\bullet} \xrightarrow{kc_2} RM_nR$
- (c) $2C_6H_5CO_2^{\circ} \xrightarrow{kc_3} (C_6H_5CO_2)_2$

If the rate constants of the reactions of active free radicals k_b , k_c are large compared to the rate constant of their formation, k_a , then a steady state with respect to their formation and destruction will soon be reached.

$$\frac{d(RM_n^{\bullet}) - k_a(Cat) = -\frac{d(RM_n^{\bullet})}{dt} = k_c(RM_n^{\bullet})^2$$

Therefore $(RM_n^{\bullet}) = \sqrt{\frac{k_a}{k_c}(Cat)}$
The rate of monomer disappearance may be represented:

$$-\frac{\mathbf{d}\mathbf{M}}{\mathbf{d}\mathbf{t}} = \mathbf{k}_{\mathbf{b}}(\mathbf{R}\mathbf{M}_{n})(\mathbf{M})$$

and substituting the value for the concentration of the active intermediate in the above equation there is ob-

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_1(\mathrm{Cat})^{\frac{1}{2}}(M).$$

This agrees with the experimentally observed condition that the rate of reaction was dependent upon both the catalyst and monomer concentration.

Chain Transfer Mechanism

The concept of chain transfer was introduced by Flory (1) to explain the decrease in degree of polymerization with increasing dilution when such reactions were carried out Schulz and co-workers (18) and Suess in solvent medium. and co-workers (19) have supplied data on the rate and degree of polymerization of styrene in several solvents. Mayo (20) and Eyring (21) have used their data to evaluate the activities of various solvents as chain transfer agents. Breitenbach and Maschin (22) have demonstrated the presence of carbon tetrachloride residues in styrene polymerized in that Correlation of molecular weight and analytical solvent. data indicated that the ratio of carbon tetrachloride fragments per polymer molecule was nearly unity. Except for the above work on solvent medium, and a few references in the patent literature to compounds referred to as "modifiers" in styrene polymerization, little was accomplished in obtaining

useful chain transfer agents until the discovery by Semon (23) that certain organic sulfur compounds drastically changed the physical character of butadiene-styrene copolymers.

The most effective modifiers of the sulfur-containing compounds have been the aliphatic mercaptans which have been incorporated into the mutual formula for the preparation of GR-S. Since it was apparent that these modifiers reduced the amount of cross linking and branching to give soft, soluble, processable rubber, an extensive investigation was undertaken to evaluate various modifiers and to gain insight into their function.

Two theories were postulated to explain modifier action: (1) The modifier inhibited 1,2 addition or promoted 1.4 addition so that the polymer formed had essentially a linear structure. In the absence of modifier it was assumed that the polymer contained a large proportion of vinyl whose double bonds were supposedside chains, -CH2-CH- $CH = CH_2$, ly much more reactive than the double bonds contained in the chain itself and would be capable of participating in the polymerization process thus leading to branched and cross linked structures. (2) The modifier acted through a chain transfer mechanism in which a mercaptan molecule may react with a polymer radical to stop its growth but at the same time produce a new radical which may start a new polymer chain.

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The following reactions serve to illustrate the point:

(1) $Z(CH_2-CH)_n CH_2 CH' + R'SH \rightarrow Z(CH_2-CH)_n CH_2 CH_2 + R'S'$ R (2) $R'S' + CH_2 = CH \longrightarrow R SCH_2-CH' \xrightarrow{n} CH_2 = CHR$ $R'S(CH_2-CH)_n - CH_2 - CH'$ R (3) Chain transfer as in (1)

Thus as each chain is terminated a new one is initiated.

Snyder Wall et al. (24) furnished evidence for the chain transfer theory. By consideration of the two theories as well as the above equations they designed experiments to evaluate the true function of the modifier. If the modifier functions only to regulate the ratio of 1,2 to 1,4 addition then it should have no effect on styrene polymerizations, but if it acts through a chain transfer mechanism, then increasing initial concentrations of mercaptan should yield polystyrenes of decreasing molecular weight. The same general effect should be observed with polybutadiene and butadiene-styrene copolymers (GR-S). Furthermore, the RS group should appear in every polymer molecule except those initiated by catalyst fragments so that there should be very nearly one sulfur atom per polymer molecule.

Studies on the relationship between mercaptan concentration and the molecular weight in styrene polymerization were carried out in bulk and emulsion systems. It was found that the molecular weight varied inversely while the sulfur content varied directly with mercaptan concentration. It was also found by correlating molecular weight and sulfur content data that the number of sulfur atoms per polymer molecule was nearly unity. Similar relationships were found to hold for butadiene polymers and copolymers.

The presence of the lauryl residue (n-dodecyl mercaptan was used) in the polymer was proved in the case of polystyrene by hydrogenolysis over Raney nickel to yield n-dodecane, and in the case of polybutadiene by cleavage with chlorine and water to yield 1-dodecanesulfonyl chloride.

> $C_{12}H_{25}S$ - polymer + $3Cl_2 + 2 H_2O \longrightarrow C_{12}H_{25}SO_2Cl +$ polymer - Cl + 4HCl

It was also shown on the basis of ozonolysis studies with polybutadienes that the ratio of 1,2 to 1,4 addition remained constant regardless of mercaptan concentration.

On the basis of a chain transfer mechanism Ewart, Smith and Hulse (25) developed a kinetic relationship for the rate of mercaptan disappearance during polymerization. They developed a "regulating index" for any particular modifier or regulator on the following basis.

Let P = number of grams of polymer formed per gram of initial monomer, R = the regulator concentration expressed

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as mols of regulator per gram of initial monomer. They assumed that the relative rate of regulator disappearance to polymer formation was proportional to the regulator concentration as follows:

$$-\frac{dR}{dP} = rR \quad \text{or } r = -\frac{d\ln R}{dP} \qquad \dots \dots \dots (1)$$

where "r" = a constant known as the regulating index.

Actually their assumption is valid since it has been shown by many workers (26, 27) that the rate of polymerization is constant up to seventy per cent conversion and Kolthoff (26) has shown that the rate of mercaptan disappearance is first order with respect to modifier concentration. This may be expressed as follows:

$$\frac{dP}{dt} = k_1$$
 and $-\frac{dR}{dt} = k_2 R$

and combining the two

$$-\frac{\mathrm{dR}}{\mathrm{dP}} = \frac{\mathrm{k_2R}}{\mathrm{k_1}} = \mathrm{rR} \qquad \dots \dots \dots (\mathrm{II})$$

which is identical with the expression of Ewart et al.

Thus "r" is a rate constant relating the rate of mercaptan disappearance to polymer formation. A mercaptan with a large value of "r" would participate in a frequent chain transfer reaction yielding polymer of low molecular weight while the inverse would be true of a mercaptan with a small value of "r".

Mathematically this may be expressed as follows. Let M_R = number average molecular weight of polymer formed in time interval dt. Then:

or combining II and III

$$M_{\rm R} = \frac{1}{r R} \qquad \dots \dots \dots (IV)$$

MR is defined as the regulator theory molecular weight and is in effect the number average molecular weight in the absence of branching.

It should be pointed out that this relation will hold only in that part of the polymerization where the reaction rate is constant. At higher conversions where the reaction begins to slow down the concept of regulating index fails to hold.

Another expression relating the rate of mercaptan disappearance to polymer formation has been derived by Kolthoff (26). This is expressed as follows:

$$P = -K \log_{10} \frac{(R)}{(R_0)} - constant$$

where $P = \text{fraction of monomer converted to polymer}, \frac{(R)}{(R_0)}$ is the fraction of mercaptan remaining at a certain value of P, K is a constant comparable to the regulating index of Ewart, Smith and Hulse and indicates the true rate of disappearance during the reaction. The rate of disappearance of mercaptan or its modifying action becomes greater with decreasing value of K. This is the inverse of the "r" of Ewart, Smith and Hulse. The constant is known as the "waste factor". Its value is found graphically and from it the fraction of mercaptan lost by undesirable reactions at the beginning of the reaction can be calculated.

Carlin (28), in addition, proposed an expression as follows: $\frac{M}{M_0} = \left[\frac{(R)^K}{(R_0)}\right]^K$ where R_0 and M_0 are the initial concentration of R, mercaptan and M, monomer. This derivation was based on false premises and it has been found to be inconsistent with experimental results. Still another relation was proposed by research workers at the Phillip's Petroleum Company (29) which they express as follows:

 $\frac{dR}{dM} = K \frac{R^2}{M} \quad \text{where } R = \text{quantity of mercaptan present}, M = \text{quantity of monomer present} \text{ and } K \text{ is a constant}.$ This relation is also in error since it has been shown by Kolthoff (26) that the rate of mercaptan disappearance is first order with respect to concentration.

Mercaptans as Activators

Besides their role as modifiers in the emulsion polymerization of styrene and butadiene, the mercaptans have also been shown to act as activators in this system. Without mercaptans ten per cent reaction is attained in the same time that 75-80 per cent is attained in their presence (30). It has been shown in the case of 0.E.I. (a mixture of primary mercaptans ranging from C_{10} to C_{14}) that 0.005 per cent based on monomer is sufficient to give maximum activation. Above this value the rate is independent of mercaptan concentration (26, 31, 32), except at very high concentrations where the rate decreases (33). This has been explained as a dilution effect. Tertiary mercaptans have a higher critical activating concentration although 0.01 per cent has been found sufficient (34).

The dependency of the reaction rate on the molecular weight of the mercaptan has been extensively studied by Kolthoff (35). With primary mercaptans the rate of reaction reaches a maximum at twelve carbon atoms and then falls off slowly with increasing molecular weight. With tertiary mercaptans the rate reaches a maximum at ten carbon atoms and then levels off with increasing molecular weight of the mercaptan.

Mercaptan-Polymer Interaction

Another reaction which mercaptans have been found to undergo in the emulsion polymerization of butadiene and styrene is that of interaction with the double bonds of the polymer particles. This effect was first observed by Kolthoff and Harris (36). They found that mercaptan disappeared from latex on standing both in the presence and absence of a shortstop. In a later report from the University of Minnesota (37), the change in unsaturation of the polymer after reaction with mercaptan was studied. From this work it was established that one molecule of mercaptan may add to each polymer double bond.

Snyder, Allen and Stewart (38) were the first to study the effect of this mercaptan-polymer interaction on the physical character of the polymer. They noted that, when O.E.I. was added to an insoluble polymer, there was a marked increase in its solubility. This work was extended to study the effect of ether mercaptans. In every case it was observed that the mercaptan addition increased the solubility (39, 40, 41). Contradictory evidence was offered by Kolthoff (42), who found that presence of the mercaptan failed to break up the gel but merely dispersed it. Thus this increase in solubility was stated to be an "apparent" and not a true increase.

Snyder, Wall et al. (43) studied the effect of mercaptan polymer interaction in benzene solution. The most striking change was the great decrease in intrinsic viscosity while the change in osmotic pressure was slight. Hence they concluded that the mercaptan must bring about some kind of intra-molecular cross linking with the result that the molecules are rolled up into relatively small spheres.

Further work by Kolthoff and his group substantiated

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the observations of Synder and others that the mercaptanpolymer interaction resulted in an increase in solubility of partly soluble polymers and a decrease in the intrinsic viscosity of soluble polymers (44, 45, 46, 47, 48, 49). They noted, however, that this decrease in intrinsic viscosity occurs only in the absence of extra persulfate and in the presence of oxygen and a catalyst, composed of ferric iron and cobalt in the presence of excess oxalate. They postulated that the addition reaction is accompanied by a considerable breakdown of the polymer to lower molecular weight. No such depolymerization occurs when persulfate is used as a catalyst.

Because of the complexity of the emulsion system it is very difficult to determine the extent of this addition reaction during the course of the polymerization. However, Kolthoff (50) is of the opinion that this reaction occurs only to a very small extent if at all.

<u>Tertiary Hexadecyl Mercaptan as a</u> <u>Modifier in the GR-S recipe</u>

Tertiary hexadecyl mercaptan has been subjected only recently to intensive study as a modifier in the GR-S recipe, although references to its use have appeared from an early date in the Rubber Reserve Company reports. Hess and Borders (51) in an investigation of several Sharples' tertiary mercaptans, state that they found tertiary hexadecyl

an effective modifier and an efficient activator when used at a concentration of 0.5 per cent based on initial Kolthoff and Harris (35) determined the dismonomer. appearance curve of Sharples' tertiary hexadecyl mercaptan at a concentration of 0.38 per cent based on monomer. Thev found that gel was present at 76.7 per cent conversion when the mercaptan was used in that concentration. In the dehydrogenated rosin soap recipe Sharples' tertiary hexadecyl mercaptan was found a poor modifier by Kolthoff, Williams and Carr (52). Kolthoff and Harris found a very slow disappearance of mercaptan up to 50 per cent conversion followed by a rapid disappearance during the later stages of the reaction. This type of behaviour for Sharples' tertiary hexadecyl mercaptan was also noted by Morton and Nicholls (27), who found a value of the regulating index of 0.58. By comparison of the two sets of results it was found that the rate of disappearance as reported by Kolthoff and Harris was slower than that reported by Morton and Hence the regulating index of Kolthoff and Harris Nicholls. would be somewhat lower. Morton and Nicholls (27) offered and explanation for the increase in the rate of mercaptan disappearance at high conversions. They postulated that such an increase in regulating activity could possibly be due to the following effects.

1) Change in the locus of reaction,

2) Slow rate of solubilization of hexadecyl mercaptan

3) Change in butadiene-styrene ratio.

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Schulze and Crouch (53), while investigating the laboratory polymerization of various tertiary mercaptans of the Phillips Petroleum Company, found that in bottle polymerization, the rate of reaction of Phillips tertiary hexadecyl mercaptan was proportional to the rate of polymer formation throughout the course of the reaction. They found also when tertiary hexadecyl mercaptan was used in high concentrations, that the intrinsic viscosity was relatively high at low conversions and increased gradually with conversion. Morton and Nicholls (27) observed an increase in viscosity for Sharples' tertiary hexadecyl mercaptan when used at a concentration of 1.3 per cent, up to about 40 per cent conversion followed by a decrease with increasing conversion. They postulated that this phenomenon could be due to two possible mechanisms:

1) formation of lower molecular weight polymer during the later part of the polymerization reaction due to an increased rate of modifier disappearance,

2) formation of lower molecular weight polymer by interaction between the mercaptan and polymer already present, that is, by some mechanism of chain scission.

Further work on the Phillips tertiary hexadecyl mercaptan was carried out by Kolthoff (54, 55, 56). Disappearance curves were determined for several samples and various fractions of tertiary hexadecyl mercaptan supplied by the Phillips Petroleum Company. He stated that the Phillips

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product was a much better modifier (faster disappearance rate) than the Sharples' tertiary hexadecyl but was unable to obtain constant viscosity rubber as reported by Schulze and Crouch (53). The shape of the mercaptan disappearance curves for Phillips tertiary hexadecyl was markedly different from those determined for the Sharples' product. A reasonably constant disappearance was observed throughout the polymerization reaction instead of a slow initial rate, followed by a much faster disappearance in the later stages of the reaction.

Kolthoff (55) also investigated the effect on the disappearance rate of Phillips tertiary hexadecyl mercaptan when the polymerization was carried out with soap formed in situ instead of with preformed soap. A decreased rate of disappearance was observed with preformed soap. Troyan (57) found that agitation definitely affected the disappear-In both these respects tertiary hexadecyl merance rate. captan appears to behave somewhat like primary mercaptans which also show sensitivity to these two variables. The explanation offered is the slow rate of solubilization of Soap formed in situ provides a finely disthis mercaptan. persed emulsion which has a large oil-water interface. With increased interfacial area the rate of solubilization is The effect of increased agitation is self increased. evident.

Because of its slow disappearance rate during the

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early part of the polymerization tertiary hexadecyl mercaptan has been used in blends of other lower molecular weight mercaptans with higher regulating indices. Its function was to provide modification in the higher conversion ranges when the mercaptans of lower molecular weight had all reacted. Experiments of this nature have been reported in a number of papers(58, 59, 60). In every case the benzene solubility limit was shifted to a higher conversion.

Renewed interest was shown in tertiary hexadecyl mercaptan used in high concentrations when Wall demonstrated that the number average molecular weight of tertiary hexadecyl modified polymer underwent little change with conversion (61). In later reports it was shown that the experimental molecular weight and those calculated from mercaptan disappearance data were remarkably close (62, 63). Indications were that there was also little or no chain branching.

Recently Kolthoff and Meehan (47) determined the per cent polymerization, mercaptan disappearance and intrinsic viscosity of polymers modified with Sharples and Phillips tertiary hexadecyl mercaptan. The Sharples' product showed a slow initial disappearance followed by increased disappearance at higher conversions in contrast to the fairly regular disappearance of the Phillips' sample. The intrinsic viscosity increased regularly from 2.0 at 4 per cent conversion

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to 2.4 at 60 per cent conversion and then fell off slowly for the samples modified with Sharples mercaptan. With the Phillips mercaptan the viscosity increased regularly from 1.4 at 3 per cent to 2.29 at 78 per cent conversion. The precipitation curves (48) for the polymer modified with Sharples tertiary hexadecyl were determined on samples These were essen-79, 62, 44 and 23 per cent conversions. tially the same although the polymer of lowest conversion appeared to contain the greatest amount of high molecular weight material. These results differ somewhat from those of Morton and Nicholls (27), who found a large proportion of high molecular weight polymer at low conversion but a marked increase in heterogeneity with conversion.

The slow rate of mercaptan disappearance, which gives rise to a slow increase in viscosity with conversion as well as a sharp molecular weight distribution at low conversions, renders tertiary hexadecyl mercaptan a useful By using only low convertool for the research worker. sion polymer samples, it is possible to obtain, by changing the initial mercaptan concentration, polymers of relatively sharp molecular weight distribution over a wide range of Furthermore, by varying the monomer molecular weights. ratios, it is possible to produce polymer of different composition but of the same molecular weight. This approach offers a method of evaluating the effect of changing composition on polymer properties.

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Heterogeneity in Copolymers

The function of mercaptans in regulating the molecular size of polymer molecules has already been examined. It is of interest, however, to consider the various types of heterogeneity which may arise in a copolymer system and also some of the methods of evaluating this heterogeneity. In the copolymerization of two monomers such as butadiene and styrene there are the following variables:

- 1) cis-trans isomerism in the polymer chain,
- 2) relative amount of 1,2 vs 1,4 additions,
- 3) molecular size,
- 4) chain branching,
- 5) composition of chains (monomer ratios).

At present no data are available on the extent of isomerism in GR-S molecules or its variation during GR-S polymerization. As for 1,2 addition the best available evidence based on infra red spectroscopy and Ozonolysis, indicated that this variable is independent of conversion or modifier content, and occurs to the extent of 15-20 per cent of the butadiene present in the chain (64, 65, 66, 67).

Molecular Size of Polymers

Heterogeneity of molecular size results as a natural consequence from the complexity of the polymerization system. Its study has been the subject of countless investigations. Because of this heterogeneity any determination of the molecular weight of a polymer sample will result in an average value. Of the methods used for determining the molecular weights of polymer molecules the most widely used are osmotic pressure, sedimentation analysis by the use of ultracentrifuge, and the measurement of viscosity of dilute polymer solutions. In this investigation the latter method has been chosen to evaluate qualitatively the products obtained. However, no steps have been taken to calculate average molecular weights by this method.

Staudinger (4) postulated a relation on purely empirical grounds to relate the viscosity of dilute solutions to molecular weight. This relation is expressed as follows:

> $\eta sp = KcM$ $\eta sp/c = KM$

or

where γ sp is the specific viscosity and is expressed as $\gamma/\gamma \circ -1$, where $\gamma = viscosity$ of the solution, $\gamma \circ = vis$ cosity of the pur solvent, C is the concentration of the solution usually in grams per 100 ml., M is the molecular weight and K is a characteristic constant. By evaluating K by osmotic data it is possible to determine the molecular weight of a high polymer by viscosimetric methods.

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In order to avoid any non-ideality in the polymer solution the specific viscosity is usually extrapolated to zero concentration by plotting the function $\eta \operatorname{sp/c}$ against c thus obtaining what Kraemer (68) calls the intrinsic viscosity designated as $[\eta]$

$$\lim_{c \to 0} (\eta_{sp/c}) = [\eta] = KM$$

Actually it has been found that the Staudinger equation does not hold for a large number of different polymers. Instead a more general relation is applicable, thus:

$$[\eta] = KM^{a}$$

where K and "a" are characteristic constants for any polymer solvent system and "a" lies between zero and one. This relation is similar to one derived from purely theoretical premises, (69, 70, 71, 72) for randomly kinked molecules whose atoms are capable of free rotation about their interatomic bonds, thus providing flexible polymer chains.

In the case of molecularly heterogeneous polymer, viscosity measurements yield an average which Flory (73) has designated as a viscosity average molecular weight. This may be expressed as

$$\overline{\mathbf{M}}_{\mathbf{v}} = \begin{bmatrix} \underline{\mathbf{m}_{1}\mathbf{M}_{1}^{1+\mathbf{a}}} \\ \underline{\mathbf{m}_{1}\mathbf{M}_{1}} \end{bmatrix}^{\frac{1}{\mathbf{a}}}$$

where \overline{M}_{v} is the viscosity average molecular weight, n_i is the

number and M_i the molecular weight of molecules of the ith species.

This contrasts with the average obtained by osmotic pressure measurements which is the number average and may be expressed as:

$$\overline{M}_{n} = \underset{\leq \overline{n_{i}}}{\overset{\underline{n_{i}}M_{i}}{\underset{=}{\times}}}$$

where \overline{M}_n = number average molecular weight and M_i and n_i are the same as defined above.

Chain Branching

Wall undertook to evaluate the changes of polymer properties with conversion (62, 74, 75, 76). From a knowledge of the average properties at any conversion he obtained increment data by graphical methods. Osmotic pressure and intrinsic viscosity data were evaluated in this manner to show qualitatively the degree of chain branching and cross linking which occurred during the course of the reaction. He also showed that increasing the amount of butadiene in the initial charge caused this branching to occur at lower conversions. Apparently, however, he took no account of the effect of changing composition on the molecular weight of the polymer.

Compositional Heterogeneity of Copolymers

Baker (77) was one of the first to point out the

complications of compositional heterogeneity in molecular analysis, when the standard methods of evaluating polymeric systems were applied to copolymers. For instance, when GR-S was fractionated in order to obtain a distribution function it was tacitly assumed that fractions of decreasing solubility represented some smoothly increasing function of molecular weight. This assumption was entirely unfounded as he demonstrated by fractionation of an artificial mixture (78, 79). A blend of a high styrene (50 per cent), high molecular weight polymer and a low styrene (15 per cent), low molecular weight polymer, was carefully fractionated. Overlapping of composition and of size was The first fraction precipitated had a styrene revealed. content of only 45.8 per cent. This indicated the presence of species whose low styrene content caused relative insolubility in benzene-methanol mixtures compared to larger molecules having a higher styrene content.

Wall was one of the first to undertake a theoretical treatment of the mechanism of copolymerization (80). He developed the relation

$$\frac{dA}{dB} = \frac{k_A}{k_B} \quad \frac{(A)}{(B)} = \alpha \quad \frac{(A)}{(B)}$$

where (A) represented the concentration of one component, and (B) the concentration of the other component in the system at any time, kA is the rate constant for the reaction of a molecule of A with a growing chain, while kB

is the rate constant for the reaction of a molecule of B with the growing chain and $\alpha = \frac{k_A}{k_P}$ Only in the case where $\alpha = 1$ will a polymer be formed which has the same composition as the charging ratio. When q > 1 the first polymer formed will be richer in A than the original reaction mixture. As polymerization proceeds the polymer forming at any time will change continuously until the last polymer formed will consist of nearly pure B. This treatment was based on the assumption that **change** with changing concentrations of the two monomers. However this has been proven incorrect by the work of Logan (81) for the butadiene-styrene emulsion system and by Mayo and Lewis (82) for the styrene-methyl methacrylate system. Despite the false premises on which Wall's treatment was based it indicated that, in most copolymerizations, high conversion polymer would have a high degree of compositional heterogeneity.

Another theoretical approach to the copolymerization reaction has been offered by Mayo and Lewis (82) who studied the styrene-methyl methacrylate system. Their treatment differed from that of Wall in that they distinguished between the reaction of methyl methacrylate and, or styrene with a styrene-headed or a methacrylate-headed growing radical. They developed four rate equations to express the reactions in a binary system:

$$s' + s \xrightarrow{k_1} s'$$

$$s' + M \xrightarrow{k_2} M'$$

$$M' + M \xrightarrow{k_3} M'$$

$$M' + s \xrightarrow{k_4} s'$$

There are two types of radicals forming the growing ends of polymer molecules. These are designated S[•] and M[•] depending upon whether the active centre ends in a styrene or the methyl methacrylate unit. The reactions of these radicals are assumed to be independent of the number and kind of attached units.

From the above rate equations it is possible to obtain the following relation:

$$\frac{dS}{dM} = \frac{(S)}{(M)} \frac{\delta}{\mu} \frac{(S) + (M)}{(M) + (S)}$$
where Wall's α has now become $\frac{\delta(S) + (M)}{\mu(M) + (S)}$ and $\delta = \frac{k_1}{k_2}$
and $\mu = \frac{k_3}{k_4}$

The above equations describe the relative rate at which S and M react and enter a copolymer, in terms of two constants 6 and μ which are designated as monomer reactivity ratios of the types of radicals involved. 6 is the ratio of the rate constant for the reaction of a styrene type radical with styrene and the rate constant of a styrene type radical with methyl methacrylate and μ represents a similar relationship for the reaction of methacrylate type radicals with either styrene or methyl methacrylate.

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By use of an integrated form of the Mayo and Lewis equation one may obtain values of \boldsymbol{b} and $\boldsymbol{\mu}$ which are characteristic and constant for any system of two monomers. Upon obtaining these two constants, it is possible to calculate, for any monomer ratio, the average composition of the polymer at any conversion, by use of a rearranged form of the Mayo and Lewis equation presented by Logan and Nicholls (83). Once the average composition is obtained values of (S) and (M) may be calculated. Substituting (S) and (M) in the differential form of the Mayo and Lewis equation gives the increment composition at any conversion. Logan and Nicholls (83) have determined 6 and μ for the styrene-butadiene They found excellent agreement, over a emulsion system. wide conversion range, between the theoretical composition of the polymer and that experimentally determined by refractive index measurements.

Meehan (84) and Logan (81) have shown that the composition of the polymer in the GR-S system is independent of a large number of variables, e.g. kind and amount of mercaptan, catalyst, emulsifier and also the polymerization temperature. Their data indicated that the average polymer composition varied from 17.2 per cent styrene at zero conversion to 21.2 per cent styrene at 80 per cent conversion with a 25/75 charging ratio while the increment composition varied in the same range from 17.2 per cent to 29.5 per cent. Thus it is seen that ordinary GR-S as produced by the Mutual Recipe has a wide degree of compositional heterogeneity.

From the foregoing discussion it is evident that the conditions prevailing in a copolymer system are very complex. Besides the usual variables of molecular size and chain branching there is the added complication of compositional heterogeneity. Hence the classical methods of evaluating polymer properties are of limited use when applied to a copolymer unless methods are devised for distinguishing between these variables.

EXPERIMENTAL PROCEDURE

This investigation involved the following experimental methods:

- Emulsion polymerization using various monomer ratios
- 2) Determination of the rate of polymerization
- 3) Characterization of the polymer
 - (a) Coagulation and drying of the polymer
 - (b) Sol-gel separation
 - (c) Determination of the intrinsic viscosity of the polymer
 - (d) Determination of a precipitation distribution function for the polymers obtained
- Determination of the rate of mercaptan disappearance.
- 5) Determination of the extent of mercaptan-polymer interaction in stripped latices.

1. Polymerization

<u>Apparatus</u>: The polymerization was carried out in either one-ounce or four-ounce round-formed bottles with metal screw caps. The caps were fitted with Neoprene gaskets which were always extracted with hot acetone before use. The bottles were rotated end over end in a thermostated water bath kept at $50 \pm 0.1^{\circ}$ C. The speed of rotation was capable of variation.
<u>Materials</u>: In this investigation the Mutual Recipe was used with variations in the kind and amount of mercaptan used as well as the ratio of the monomer.

Mutual Recipe for GR-S

Water	180	parts	
Soap	6	tt	
Potassium Persulfate	0.	.3 "	
Styrene	25	11	
Butadiene	75	**	
Mercaptan	vai	riable	

For the greater part of this investigation Rubber Reserve Soap, obtained from Polymer Corporation Limited, was used, although some preliminary work was carried out with the household variety of Ivory Flakes.

The potassium persulfate was Merck's Analytical Reagent Grade.

The styrene was obtained from the **h**ow Chemical Company of Canada, Sarnia, Ontario. This styrene was inhibited with 10 p.p.m. of p-tertiary butyl catechol. It was used as received except in the determination of the rate of polymerization of styrene where the crude product was subjected to vacuum distillation under a nitrogen atmosphere. Kolthoff (85) and Morton (27) found that identical polymerization rates were obtained in GR-S polymerization whether the styrene was redistilled or used as received. Butadiene used was obtained from the Canadian Synthetic Rubber Limited, Sarnia, Ontario. A typical analysis of the butadiene as received from the supplier follows:

Butadiene Analysis

Purity	98.5%
Acetylenes	300 p.p.m.
Peroxides	0.001%
Aldeh y de s	Nil
Non-Volatile matter	0.04%
Inhibitor (p-tertiary butyl catechol)	300 p.p.m.

It was purified by bubbling through a 2 N sodium hydroxide solution to remove any inhibitor and then through a glass U-tube, packed with glass wool and kept at -5°C. This technique was recommended by Kolthoff (86) who found it resulted in better reproducibility of rates of polymerization. The purified butadiene was collected in a dryice-acetone trap from which it was apportioned to the required charges.

The mercaptans used were tertiary dodecyl, tertiary pentadecyl, tertiary hexadecyl and normal tetradecyl. The first three were obtained from Sharples' Chemicals Inc., Philadelphia, Pa., while the normal tetradecyl was received from the Connecticut Hard Rubber Company, New Haven, Conn.

Purification of these mercaptans was accomplished by

fractional distillation in every case except that of tertiary pentadecyl where no purification was undertaken. A Whitmore-Fenske column, packed with glass helices and having an efficiency of thirty theoretical plates was used for these fractionations. The physical constants of the fractionated samples as well as their mercaptan content are listed below.

Physical Constants of the Main Fractions of Sharples (3B) Tertiary Dodecyl Mercaptan and Cohardite Normal Tetradecyl Mercaptan

	t-C ₁₂	$n-C_{14}$
Boiling Point	112°C.(16 m.m.)	125-127°C.(1 m m.)
Refractive Index (n_D^{25})	1.4655	1.4612
Mercaptan Content	98.1% (as C ₁₂ H ₂₅ SH)	97.0% (as C14H29SH)

Sharples t-pentadecyl unfractionated, had a mercaptan content, based on C₁₅H₃₁SH, of 94 per cent.

On fractional distillation the sample of Sharples' t-hexadecyl mercaptan did not yield any sizeable fraction of constant boiling point. Instead a variation in boiling point and refractive index was noted. That portion which was collected in the boiling range $105-115^{\circ}$ C. (1 m m.), was selected. All samples collected in this interval had the same mercaptan content, namely 97 ± 0.5 per cent. The refractive index varied from 1.4749 to 1.4765. This anomalous behaviour was possibly due to a mixture of structural isomers. <u>Procedure</u>: The total charge used was 22.5 g. for oneounce bottles and 95.0 g. for four-ounce bottles except in those cases otherwise specified. The aqueous solution containing the scap and potassium persulfate was added to the tared bottle, whereupon the bottles were cooled until the scap solution gelled. Then the styrene, containing the required amount of mercaptan, was added, followed by the butadiene in slight excess. The cap was then placed loosely on the bottle and the excess butadiene allowed to evaporate until the bottle reached the desired weight. It was then capped tightly in order to prevent leaks.

Slight variations in this technique were required when preparing polystyrene or polybutadiene. For the styrene polymerization it was found necessary to remove oxygen from the free space in the bottle. This was accomplished by inserting a hypodermic needle through a butyl rubber gasket (butyl rubber was used instead of neoprene because of its self-sealing character) and sweeping out the air space with tank nitrogen. With the butadiene polymerization it was necessary to weigh the mercaptan directly into the polymerization bottle. This process was carried out after the soap solution had been placed in the bottle.

2. Determination of the Rate of Polymerization

At periodic intervals duplicate bottles were removed from the water bath and cooled in ice water. Care was taken to prevent gelling of the latex which occurs readily with samples of high styrene content. Each bottle was then opened and 0.1 per cent hydroquinone, based on initial weight, was added as an inhibitor of further polymerization. Conversions were determined for the one ounce bottles by coagulation of the whole bottle in 400 -500 ml. of n-butanol, followed by washing with another portion, 150 - 200 ml., of the same material. The samples were then filtered, transferred to a tared petri dish, and dried for 24 hours in a vacuum oven at 2 - 3 mm. and 40°C. Agreement between duplicate determinations was of the order of 10 parts per thousand.

For four ounce bottles the procedure differed. After addition of the hydroquinone the conversion was determined by the total solids method as described by Fisher and Day (87). Sempling of the latex for this determination was carried out by the stop cock method of Medalia (88)... Since this procedure had only a limited use in this investigation the details are omitted.

A limited investigation, of the effect of bottle charge in one ounce bottles, was undertaken. This is tabulated below and the figures obtained for a 95 gram charge in four ounce bottles are listed for comparison.

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	Bott siz	tle ze	Bottle Charge	2	Tim 4	e in H 6	ours 9	12
Conversion in %	1 0	DZ	15.0	11.0	23.6	37.4	58.0	76.0
Ħ	1	T	22.5	12.5	27.1	41.6	65.0	81.0
11	4	t f	95.0	13.0	24.4	36.4	54.0	71.5

Effect of Bottle Charge on Reaction Rate

From the above table it is observed that variation in bottle charge as well as variation in bottle size produced a change in reaction rate. An investigation of the cause of this phenomenon was not undertaken since it was considered outside the scope of this problem. The data have been presented to indicate, that, for the purpose of comparative work, some fixed loading charge must be used.

3. Characterization of Polymer

(a) <u>Coagulation and Drying</u>

The latex was coagulated and dried as described in the previous section. Introducing the latex in a fine stream into the vigorously stirred butanol was found to give a finer precipitate than dropwise addition. This was accomplished by attaching a capillary stop cock to the bottle to dispense the latex for low conversion samples. In the case of high conversion samples the latex was forced through a capillary jet by means of an aspirator. (b) Sol-gel Separation

Solutions of the polymer were prepared by placing the finely shredded sample in benzene, containing 0.02 grams per litre of phenyl- β - napthylamine, and allowing to stand for forty-eight hours in the dark. Polymer solutions were made up at various concentrations, depending upon their proposed use, but usually at 0.25 per cent. The solutions were gently swirled on the second day in order to promote mixing. After forty-eight hours, the solutions were examined for any visible gel, and then filtered through a layer of glass wool, supported on 100 mesh stainless steel wire screen. The amount of insoluble material was then determined indirectly, by determination of the concentration of the filtrate and comparison with the concentrating of the original solution. This was accomplished by evaporating 25 ml. of the solution to dryness in an oven at 70°C.

The above method usually gave a good separation of sol from gel since it was found that the resulting solution could be easily forced through a coarse pyrex frit. This test, according to Baker and Mullen (89) is very sensitive to dispersed gel, since as little as 0.5 mg. of highly swollen gel will clog the frit completely.

It might be noted here that a one per cent solution of GR-S, modified with 1.4 per cent n-tetradecyl mercaptan, showed indications of containing large quantities of gel when the determination was carried out according to

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the above method. A gel content determination was made with a Baker cell (90), which showed no traces of any insoluble material. The resulting solution in the Baker cell had a concentration of 0.4 per cent. Hence it was assumed, that the apparent insolubility of the polymer, as noted above for one per cent concentration, was probably due to the presence of extremely high molecular weight fragments. It seems desirable, therefore that solubility determinations on high molecular weight polymer should be carried out with solutions of 0.4 per cent concentration or less.

(c) <u>Determination of Intrinsic Viscosity</u>

The viscosities of the polymer solutions were determined by means of an Ostwald type viscometer, which had the approximate specifications as outlined by the Committee on Standardized Methods and Apparatus for Molecular Weight Determinations of GR-S Polymers (91). The viscometer had an outflow time of about 130 seconds for pure benzene. The kinetic energy correction was determined by measuring the outflow times of four liquids of known viscosity, viz. water, benzene, n-heptane and chloroform. The constants were then evaluated by applying the method of Bingham (92). The viscosity of a polymer solution was then determined by use of the following equation.

$$\gamma = K \rho t - \frac{A \rho}{t}$$

where η is the viscosity of the solution, K and A are in-

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strument constants, ρ is the density of the pure solvent and t is the outflow time.

The temperature used was 25° C which was maintained in a water bath kept within $\pm 0.01^{\circ}$ C. The concentration of the polymer solutions was 0.2 to 0.4 grams per 100 ml. of benzene. This concentration was determined for each polymer sample by evaporation of a 25 ml. or 50 ml. sample to dryness in an oven at 70°C. In addition to this solution, two others were obtained from it by aliquot dilution with benzene, using dilution ratios of 1:1 and 1:3 respectively. The viscosity of each solution was then determined from the equation above and from this the specific viscosity was calculated. These were plotted against concentration and extrapolated to zero concentration for the determination of the intrinsic viscosity.

When a large number of determinations were to be carried out at any one time, it was found necessary to rinse the viscometer thoroughly with benzene after each solution. This was in addition to the usual rinsings with the next solution. This procedure was adopted, when an increase in the outflow time of the pure solvent was noted after a number of solutions had been run through. Even with this innovation a slight increase in outflow time has been observed when a large number of determinations was made. Allowing the viscometer to soak overnight in benzene reverted the outflow time of the solvent to its ori-

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ginal value. This indicated that the increase was very likely due to polymer deposition on the capillary wall.

The following variables in viscosity measurement were also investigated: determination of polymer content of solutions by oven drying; polymer sampling technique; ageing of polymer; reproducibility of viscosity measurements, and effects of stirring on intrinsic viscosity.

In regard to the first variable listed it was found that prolonged drying of the evaporated solution in the 70°C. oven resulted in a gradual increase in weight. This was observed both in the presence and absence of phenyl- β -napthylamine, an antioxidant. This weight increase may be due to oxidation of the polymer at the elevated temperature used. Two to three hours drying has been found adequate.

When high molecular weight material was analysed it was found necessary to make up polymer solutions of 0.2 to 0.3 per cent. At higher concentration linearity of the plot of specific viscosity against concentration was not attained. Preparing solutions of low concentration required the use of small amounts of polymer. Hence it was considered necessary to determine if the polymer sample was homogeneous. Four portions were selected from a polymer sample, two from the surface and two others from the interior. The two surface samples showed intrinsic viscosities of 3.42 and 3.37 while the interior samples showed a wider variation of 3.37 and 3.52, a deviation of \pm 2 per cent from the mean value. The samples above were taken from a polymer which had been standing for two weeks in the dark in a closed container. The original viscosity was 3.44. Thus it would seem that sampling errors and ageing effects, for short periods at least, are relatively unimportant.

In an investigation of this nature it was important to determine the reproducibility of viscosity measurements when duplicate samples of polymer were prepared in different bottles. Three samples of GR-S, N3, N4 and N5 prepared in one ounce bottles at the same mercaptan concentration were examined. Values of 2.81, 2.79 and 2.72 were obtained where the deviation from the mean is ± 1.5 per cent.

The effect of the rate of stirring on the polymer obtained, using the same concentration of tertiary hexadecyl mercaptan was investigated for three samples. The results are tabulated below.

Rate of Stirring (R.P.M.)604530Intrinsic Viscosity2.102.342.75

At 60 R.P.M. the rate of stirring is so fast that

the actual agitation is not as great as the figure would seem to indicate. This would account for the smaller change between 45 R.P.M. and 60 R.P.M. than that between 30 R.P.M. and 45 R.P.M. A discussion of this stirring effect will be presented in a later portion of this report. The data was included here to show that in any investigation of viscosity changes, whether they are changes with conversion or changes with mercaptan concentration, strict attention must be paid to the rate of stirring.

(d) Determination of a Precipitation Distribution Function

Some measure of the heterogeneity of the polymer fractions prepared in this investigation seemed desirable. A simple method of fractional precipitation was used for this purpose, as outlined by Wall et. al (93). Twelve to fifteen fractions of 15 ml. each of 0.4 per cent polymer solution were used. There was added to each of these, with vigorous stirring, 10 ml. of a mixture of varying propor-The ratio of benzene to tions of benzene and methanol. methanol was such that the final volume per cent methanol in the final solution ranged from 16.7 to 35.0 per cent. Care was taken to add the precipitating solution drop by drop The fracafter precipitation of the polymer had begun. tion of polymer remaining in solution (f) was then plotted against the volume per cent methanol in the solution, (Φ) and a solubility curve obtained. By differentiating this solubility function and plotting the negative slope, $-\frac{df}{d\delta}$

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against the volume per cent methanol, (Φ) , a precipitation distribution curve was obtained. According to Wall (94) such a precipitation curve has been found to agree fairly closely with the molecular weight distribution existing in the polymer sample.

4. Determination of the Rate of Mercaptan Disappearance

The method used for mercaptan analysis was the amperometric titration with silver nitrate, as described by Kolthoff and Harris (86, 95). The strength of the silver nitrate solution used was 0.005 N. When this investigation was undertaken the procedure, as outlined by Morton and Nicholls (27) for sampling of the latex was This involved the use of four ounce bottles, samused. pling the short stopped latex by the capillary stop-cock method, venting this sample to constant weight on a steam cone and then coagulating 5 ml. of this vented sample in 100 ml. of vigorously stirred ethanol. The results obtained for a series of bottles using one per cent tertiary hexadecyl mercaptan are listed in Table I. Conversions were determined by the total solids method.

Several other runs were carried out in an effort to obtain more consistent results, and although a little better agreement was found for conversion figures the mercaptan results remained extremely variable. It was assumed therefore that errors were involved either in sampling or in venting of the latex. These variables were

TABLE I

SHARPLES TERTIARY HEXADECYL MERCAPTAN

INITIAL CONCENTRATION = 1.0%

Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %	
2	10.5	63.0	
4	24.0, 16.0	66.0, 84.0	
6	31.6, 36.8	82.5, 72.0	
9	46.5, 46.5	68.0, 69.5	
12	74.7, 63.5	55.6, 50.3	
18	84.0, 86.5	31.1, 26.3	

.

were thoroughly checked.

The effect of venting temperature was investigated using Sharples tertiary dodecyl mercaptan at 0.5 per cent, based on initial monomer. The sampling was carried out as above. Four bottles were prepared, and one conversion determination and duplicate mercaptan determinations were carried out on each bottle. The results are listed in Table II.

The 25°C. venting apparently yielded more consistent results although it may be observed that these figures are in no way conclusive.

The next variable investigated was the shortstopping agent. Instead of hydroquinone β -napthol was used. 0.5 ml. of 2 per cent β -napthol in 0.15 N sodium hydroxide solution was added to each bottle before sampling by the stop cock method. The effect of temperature was also investigated. The results are tabulated in Table III.

Better reproducibility of mercaptan analysis was obtained with β -napthol as shortstop. Agreement between duplicate determinations was relatively good. However this shortstopping agent failed to function effectively as an inhibitor of the reaction. Hence a method was still required which would give both mercaptan and conversion data.

The next approach to be investigated was sampling

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TABLE II

THE EFFECT OF VENTING TEMPERATURE ON MERCAPIAN ANALYSIS SHARPLES TERTIARY DODECYL MERCAPIAN

Initial Concentration - 0.5%

Bottle Time Number		Venting Temperature	Conversion %	Unreacted Mercaptan %		
1	3	40°C.	22.8	56.0, 66.5		
2	3	40°C.	16.8	63.5, 69.0		
З	3	25°C.	19.9	66.7, 68.0		
4	3	25 °C .	22.6	60.5, 61.7		

TABLE III

MERCAPTAN ANALYSIS IN THE PRESENCE OF & - NAPTHOL

SHARPLES TERTIARY DODECYL MERCAPTAN

Initial Concentration-0.5%

Polymerization Time - hrs	Venting Temperature °C.	Conversion %	Unreacted Mercaptan %
2.5	40	23.8	70.7, 70.5
2.5	40	21.7	52.0, 60.0
2.5	25	25.0	74.0, 76.5
2.5	25	24.1	64.0, 68.0
2.5	25	23.6	66.3, 63.5
2.5	25	24.2	56.0, 59.5
1.5	25	18.3	79.5, 79.2
1.5	25	18.7	74.0, 73.8

without preliminary addition of short stop. The determination of residual mercaptan was undertaken on the nonshortstopped, vented sample, while the conversion was determined by use of the total solids method after adding hydroquinone to the vented sample. The results of this investigation are listed below:

Sample No.	Time (hrs)	Conversion	Unreacted Mercaptan %
1	3.5	22.0	68.5, 69.3
2	3.5	21.3	66.0, 65.7
3	3.5	22.7	66.6, 67.0

The agreement was good both within and between bottles. Thus it was assumed that sampling errors had been eliminated. With this modified procedure polymerization runs were carried out using the following modifiers: Sharples tertiary pentadecyl mercaptan at 1.1 per cent concentration, Cohardite normal tetradecyl mercaptan at 1.4 per cent, Sharples tertiary hexadecyl mercaptan at 1.1 per cent. The results of these runs appear in Tables IV, V and VI.

As observed from these tables satisfactory results were obtained only in the case of Sharples tertiary pentadecyl mercaptan. However, it will be noted that discrepancies occur in Tables V and VI only with low conversion samples. It would seem therefore, that the nature of the mercaptan has an effect on the sampling procedure to be adopted.

TABLE IV

SHARPLES TERTIARY PENTADECYL MERCAPTAN

Initial	Concentration -	1.1%

Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
2	13.6, 19.5	95.0, 98.0, 95.0, 93.5
4	24.7	85.5, 87.0
6	36.4, 36.5	80.5, 80.5, 76,0, 82.5
9	54.6, 53.0	71.5, 69.5
12	71.2, 71.5	51.8, 51.0
18	88.3, 88.3	17.3, 14.9

TABLE V

COHARDITE NORMAL TETRADECYL MERCAPTAN

Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
2	9.8, 10.5	99.0, 102.0, 95.0, 93.0
4	21.7, 22.4	87.5, 92.3, 87.0, 92.8
6	34.9, 35.8	88.0, 91.5, 81.5, 84.3
9	53.5, 54.5	80.3, 79.5
12	65.5, 67.8	72.5, 70.5
18	82.0, 80.0	72.0, 76.0

Initial Concentration-1.4%

TABLE VI

SHARPLES TERTIARY HEXADECYL MERCAPTAN

Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %	
2	15.0, 13.0	78.0, 88.0, 81.0,	91.0
4	24.0, 24.0	73.0, 85.0, 85.0,	86.0
6	33.0, 32.0	84.0, 82.0, 74.0,	67.0
9	52.0, 54.0	80.0, 81.0	
12	69.0, 68.5	64.0, 68.0	
18	82.0, 83.0	51.0, 48.0	

Initial Concentration - 1.1%

It is seen from Table VI that greater discrepancies can be noted for tertiary hexadecyl mercaptan than for any of the others investigated. It seems obvious, therefore, that although this analytical method is applicable to mercaptans such as Sharples tertiary dodecyl, it shows increasingly greater discrepancies for mercaptans of higher molecular weight. It was possible that solubility could be a factor since tertiary hexadecyl mercaptan is known to be much less soluble in ethanol than tertiary dodecyl mercaptan. However, precipitation of the later in various mixtures of butanol and ethanol did not show any improvement. Various methods of coagulation were next investigated. It was thought that the mercaptan might be occluded within the rubber when precipitation was carried out dropwise. Hence a modification was used whereby the unvented latex was sampled directly from the bottle by means of a fine capillary This procedure caused the latex to enter the coagulajet. ting medium in a fine stream under pressure. Although the mercaptan figures did not improve, this method of coagulation was adopted in future work because of its rapidity, simplicity and the finer precipitated curd obtained in this manner.

Other modifications attempted with the four ounze bottles included venting of the complete sample by pouring into a one litre beaker. This, however, proved slow and troublesome, in that it was difficult to prevent freezing of the latex with subsequent coagulation of the rubber.

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This condition rendered sampling extremely difficult. Finally, the Kolthoff technique of venting under vacuum was tried. This method, as well as being slow and laborious, proved difficult to control. Freezing of the latex was its main disadvantage.

The above results show that no satisfactory method was found for sampling low-conversion latices from 4 ounce bottles in the case of tertiary hexadecyl mercaptan. It was therefore considered that the use of one ounce bottles would yield improved results, since no sampling would be required.

Preliminary experiments were designed to investigate the following variables: reaction rate, mercaptan diaappearance rate, bottle charge, venting of latex and coagulating medium.

It was found that unvented latex could be coagulated without interfering with the mercaptan titration. Low conversion latices were sampled, without shortstopping, through a fine capillary jet. This method delivered the latex into the coagulating medium in a fine stream which resulted in the formation of a fine curdy precipitate. With respect to coagulating medium it was found that absolute ethanol was entirely satisfactory.

The three other factors, bottle charge, mercaptan disappearance rate and reaction rate were found to be

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interrelated. The mercaptan disappearance rate increased while the reaction rate decreased, for a decrease in the bottle charge. Observation of Table VII will illustrate this point.

Due to the increased volume of the latex sample it was found necessary to use two 200-ml. portions of absolute ethanol for the coagulation of each sample. Finally the bottle was rinsed with another 10-ml. portion of ethanol and this was added to the main sample before titration. Following this procedure agreement of the order of \pm 0.75 per cent was obtained for duplicate determinations.

At this time no adequate explanation can be offered to account for the change in polymerization rate with changing bottle charge although it may possibly be due to surface effects. Since it was considered that an investigation of this variable was outside the scope of this work no further experiments of this nature were undertaken.

The change in the rate of mercaptan disappearance with bottle charge can be accounted for on the basis of increased agitation with decreased bottle charge. Troyan (57) has already shown the dependency of Phillip's tertiary hexadecyl mercaptan on agitation. Reynolds (96) has undertaken an extensive investigation of the solubility and rate of solubilization of mercaptans in aqueous soap solutions. He has found that tertiary hexadecyl mercaptan, besides being

TABLE VII

EFFECT OF BOTTLE CHARGE ON THE REACTION RATE AND MERCAPTAN DISAPPEARANCE RATE WITH POLYMERIZATION IN ONE OUNCE BOTTLES

Tertiary Hexadecyl Mercaptan

Initial Concentration - 0.3%

Bottle Charge Grams	Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
15	2	11.0	93.8
t t	4	23.6	88.0
11	6	37.4	80.8
īt	9	58.0	60.0
Ħ	12	76.0	32.0
22.5	2	12.5	94.0
TT	4	27.1	90.0
Ħ	6	41.6	88.0
11	9	65.0	74.0
Ħ	12	81.0	54.0

less soluble has a much smaller rate of solubilization into the aqueous phase than mercaptans of lower moleculer weight. Since the polymerization is postulated to occur in the aqueous phase, any factor which will tend to aid this diffusion of mercaptan into the reaction locus will consequently give rise to a faster disappearance rate.

Solubilization and solubility phenomena may also be used to explain the anomalous results obtained with tertiary hexadecyl mercaptan when sampled by the stop-cock method from four ounce bottles. Because of its low solubility in the aqueous phase the mercaptan would tend to concentrate in the organic layer during cooling of the latex. Upon shaking, before sampling, a homogeneous dispersion was apparently not attained. The fact that discordant results were only noted in low conversion samples tends to substantiate this assumption. At high conversions, above six hours a relatively stable emulsion was formed and did not break on cooling, so that sampling errors were avoided.

The procedure adopted for subsequent work involved the use of one ounce bottles with a total charge of 22.5 grams. For mercaptan analysis, the whole bottle was coagulated in two 200 ml. portions of absolute ethanol. The bottle was then rinsed with another 10-ml. portion of absolute ethanol and this was added to the main sample before titration. Duplicate determinations were always made and the average of these results has been reported. The

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conversion was obtained by drying of the polymer coagulated for mercaptan titration. When samples for viscosity measurements were required these were prepared separately.

5. Determination of the Extent of Mercaptan-Polymer Interaction

In order to obtain soluble polymer it is necessary to use tertiary hexadecyl mercaptan in high initial concentrations. This high initial concentration coupled with the slow rate of disappearance results in relatively high concentrations of residual mercaptan in 50-70 per cent conversion latex. Hence it is possible to study the disappearance of this residual mercaptan in a stripped latex. Former workers always added mercaptan in bulk or in solution to the latex. With tertiary hexadecyl mercaptan no supplementary addition is required so that it is possible to approximate the polymerization conditions more closely.

Work along this line was carried out with stripped polybutadiene and polystyrene latices. Since the techniques involved are dissimilar it is convenient to treat them separately.

Polybutadiene Latex

Polymerizations were carried out in four ounce bottles as previously described. Latices of various conversions were obtained by removing the bottles from the polymerization bath at appropriate times. Venting of the latices was accomplished by pouring the latex with a 1-1 suction flask and stripping the butadiene under reduced pressure. In order to remove the last traces of monomer the latex was heated to 50°C under 200 mm. pressure for one-half hour. This is the procedure recommended by Kolthoff (97) Twenty-millilitre samples of the vented latex were then transferred to one ounce bottles and rotated at 50±0.1°C. in a water bath. Samples were removed at various time intervals and analysed for mercaptan. A sample for viscosity measurement was also taken.

Polystyrene Latex

Attempts to prepare a stripped polystyrene latex proved unsuccessful. Long periods of heating under reduced pressure were required to lower appreciably the residual monomer content. During the stripping procedure nearly all the mercaptan was lost either by distillation or oxidation. Along with this complication it was also difficult to prevent coagulation of the latex at the temperature $(50^{\circ}C)$ and pressure (200 mm.) required to remove the styrene.

An alternative procedure was developed. The styrene was polymerized for twenty-four hours or more in order to approximate 100 per cent conversion. By using a high initial mercaptan concentration enough residual mercaptan was present to follow further changes in mercaptan disappearance. Small traces of monomer remaining in the latex should not polymerize further when oxygen is present in the system since Price and Adams (98) state that air is an efficient shortstop of styrene polymerization.

Mercaptan-polymer interaction was studied both in the presence of air and nitrogen. A nitrogen atmosphere was obtained by inserting a hypodermic needle through the loose fitting metal screw cap lined with a butyl rubber gasket and then sweeping out the free space for two to three minutes with tank nitrogen. The cap was then tightened and the needle removed.

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RESULTS AND DISCUSSION

In this investigation tertiary hexadecyl mercaptan has been used as a modifier in the butadiene-styrene emulsion system for the following purposes:

1) To study the changes in rate of polymerization and rate of mercaptan disappearance using various monomer ratios.

2) To determine the extent of mercaptan-polymer interaction in polybutadiene and polystyrene latices.

3) To evaluate the changes in viscosity during polymerization using various monomer ratios.

4) To evaluate the changes in viscosity and precipitation distribution function of relatively homogeneous polymers of the same molecular weight but of different composition.

5) To prepare relatively homogeneous polymers of the same composition over a wide viscosity range.

1. Polymerization and Mercaptan Disappearance Rates for Varying Butadiene-Styrene Ratios

Data on the rates of polymerization and mercaptan disappearance for the five runs are contained in Tables VIII, IX, X, XI and XII. It can be seen that the rate of polymerization increases with increasing percentage of styrene in the initial charge. This is shown graphically in Figure 1 where the per cent conversion is plotted against time for all five monomer charges, and in Figure 2 where the reaction rate per hour is plotted against the initial weight per cent of styrene. The reaction rate per hour was determined from the linear portion of the rate curve.

In every case it is noted that a relatively constant rate of reaction is maintained up to approximately seventy per cent conversion, after which the rate falls off rapidly. These figures are in agreement with those obtained for bottle polymerization by other workers in the field (99, 100, 101) although the rates reported here are somewhat faster because of the use of one ounce bottles. An induction period is shown in Figure 1 for every rate curve but this is not necessarily true because no measurements were made at lower conversions. It is more likely that an S-shaped curve would be obtained since this has been noted in other investigations.

The mercaptan disappearance curves are shown in Figures 3 and 4. It is noted that the linear portion of the curve passes through the origin in every case except for polystyrene. This anomaly is very likely due to oxidated effects since undistilled styrene was used for this run and the air space was not swept with nitrogen.

It was originally thought that the changing styrene content in the charge might have had some effect on the increased rate of mercaptan disappearance at high conversions. How far this postulate was untrue may be seen

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from Figure 5 where the regulating indices of the various mercaptans are plotted against the weight per cent of styrene in the initial charge. A value of the regulating index is obtained which shows a continual decrease with increasing styrene content. This is in agreement with the work of Kolthoff who measured the regulating index of GR-S and polystyrene (48).

The regulating index of a modifier is based upon the weight of the polymer formed. However, to get a true evaluation of its chain transfer activity, it would be more plausible to consider it on a molar basis. If this were done, and keeping in mind that styrene has twice the molecular weight of butadiene, it would be seen that the changes in regulating index with changes in initial monomer charge were not so great. However, tertiary hexadecyl mercaptan would still be a more active chain breaker in butadiene than in styrene polymerization. Thus, if the nature of the disappearance curve was dependent on the change in butadienestyrene ratio with conversion, there would be obtained a curve, which would be the inverse of those shown in Figures Instead of an increase in the rate of disappear-3 and 4. ance at high conversions, a decrease would be noted.

It is of interest to examine the several mercaptan disappearance curves. However it must be remembered that a change in the shape of the curve is expected at seventy per cent conversion where the rate of polymerization begins to

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TABLE VIII

BUTADI ENE

Sample No.	Polymerization 	Conversion %	Unreacted Mercaptan %
D-1	4	16.6	92.0
D-3	8	34.0	88.3
D-5	12	54.8	72.1
D-7	16	70.9	52.6
D-9	21	86.6	26.4
D-11	27	92.5	8.4
	Regulating Ind	lex, $r = 0.52$	12

Reaction Rate per hour = 4.5%

TABLE IX

BUTADIENE/STYRENE = 75/25

Sample No.	Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
A-1	2.0	12.5	94.0
A-3	4.0	27.2	89.5
A-5	6.0	41.6	87.0
A-7	9.0	65 .0	74.0
A- 9	12.0	81.3	54.0
A-11	16.5	91.0	19.4
	Regulating Ind	lex, $r = 0.3$	70
	Reaction Rate	per hour =	7.6%

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TABLE X

BUTADI ENE/STYRENE = 50/50

Sample No.	Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
K-l	1.5	11.7	95.5
K-3	3.0	28.7	91.5
K-5	4.5	47.0	87.5
K - 7	6.0	61.7	80.5
K-9	8.0	79.2	57.8
K-11	10.0	87.5	34.1
			7.0

Regulating Index, r = 0.272

Reaction Rate per hour = 12.9%

TABLE XI

BUTADIENE/STYRENE=25/75

Sample No.	Polymerization Time - hrs	Conversion %	Unreacted Mercaptan %
H-1	0.75	6.3	99.3
H-3	1.5	18.7	97.4
H -5	2.25	35.1	94.7
H -7	3.0	51.0	88.0
H -9	4.0	62.5	85.7
H -11	5.0	82.0	60.6
	Regulating Ind	dex, $r = 0.13$	85
	Reaction Rate	per hour =1	9.4%

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TABLE XII

STYRENE

Sample No.	Polymerization Time - Minutes	Conversion %	Unreacted Mercaptan %
L-1	60 *	37.2	83.3
L-2	6 0*	24.0	85.1
L-3	90*	74.6	79.5
L-4	90*	55.7	80.0
L-5	120*	82.0	74.5
L-6	120*	85.1	74.0
L-7	180*	85.3	66.6
L-8	180*	87.5	65.3
L-9	15	6.7	-
L-10	25	12.5	-
L-11	30	27.2	-
L-12	40	39.4	-
L-13	60	66.0	-
L-14	90	78.0	-
L-15	120	84.7	-
L-16	180	89.5	-
	Regulating Ir	ndex, $r = 0.1$	181
	Reaction Rate	e per hour = 7	74.5%
* These de	terminations were	made with und	listilled styrem





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FIGURE 1



Effect of styrene content on rate of polymerization





Rate of disappearance of tertiary hexadecyl mercaptan


Rate of disappearance of tertiary hexadecyl mercaptan



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slow down. At this point the regulating index fails to hold since it was derived on the basis of a constant reaction rate. Observation of Figures 3 and 4 indicates a rapid increase in rate of mercaptan disappearance after seventy per cent conversion. A deviation from linearity of these curves before seventy per cent conversion is also noted.

An explanation of the rapid rate of disappearance after seventy per cent conversion is offered on the basis of the slow rate of solubilization of tertiary hexadecyl mercaptan into the aqueous phase or reaction locus. If the rate of diffusion of mercaptan into the reaction locus is the rate-determining step, then, with a decrease in reaction rate, the mercaptan concentration in the reaction locus would build up. From purely kinetic considerations this would result in an increased rate of mercaptan disappearance. This effect would be more noticeable in the butadiene system where the rate of polymerization is least.

Another mechanism is offered on the basis of a change in reaction locus. Harkins (102) has obtained evidence that such a change occurs of about fifty per cent conversion in the GR-S system with consequent changes in the solubility relationships between the mercaptan and the polymerization system. An increased amount of mercaptan reaching the reaction locus would result in an increased rate of disappearance. This mechanism should help to account for

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the deviation from linearity of the mercaptan disappearance curves.

Another factor which might play some part in these changes is mercaptan-polymer interaction. A discussion of this effect is presented in the following section.

2. <u>Polymer-Mercaptan Interaction in Polybutadiene and Poly-</u> styrene Latices

Data on the extent of mercaptan disappearance in stripped polybutadiene latices are contained in Tables XIII and XIV for reaction in air and nitrogen media. In Figure 6 these data are shown graphically from which it can be seen that the reaction is initially much faster in the presence of air. In some respects these data are similar to those reported by Kolthoff (103) where tertiary dodecyl mercaptan and O.E.I. were reacted with stripped polybutadiene latex. He found a sharp initial disappearance of mercaptan followed by a slower reaction thereafter both in the presence of air and nitrogen. However the reaction in a nitrogen medium was much faster. This is opposite to the results obtained here. He postulated that the rapid initial reaction may be due to oxygen or to compounds formed with oxygen during venting, and probably does not occur in GR-S polymerizations, where oxygen is absent after polymerization has begun.

In order to gain further insight into this problem

TABLE XIII

MERCAPTAN DISAPPEARANCE IN VENTED POLYBUTADIENE

LATEX IN AIR MEDIUM

Initial Mercaptan Content of Latex-3.0 mg. per ml.

Reaction Hours	Time	Unreacted Mercaptan %
0		100
0.25		81.7
0.50		75.8
0.75		67.6
1.00		61.5
3.33		33.3
4.00		36.4
4.75		20.1
5.50		27.0
15.50		22.6
20.00		18.4
25.00		15.6

Conversion - 80% (approx.)

TABLE XIV

MERCAPTAN DISAPPEARANCE IN VENTED POLYBUTADIENE

LATEX IN AIR AND NITROGEN MEDIA

Initial Mercaptan Content of Latex - 2.6 mg. per ml.

Reaction Time Hours	Unrea Mercar	nreacted rcaptan %		
	air	nitrogen		
0	100	100		
0.66	75.0	-		
0.75	-	81.4		
1.50	-	72.0		
2.00	46.2	-		
2.25	-	63.9		
3.00	39.2	-		
3.25	-	62.1		
4.00	-	55.0		
5.00	33.7	52.5		
6.00	-	50.9		
7.00	30.0	48.4		
19.00	-	19.8		
30.00	10.0	11.8		
70.00	1.0	-		

Conversion - 80% (approx.)



Mercaptan disappearance in polybutadiene latex

it was considered desirable to follow the mercaptan charges in a polystyrene latex. Data on this investigation are tabulated in Table XV and are shown graphically in Figure 7. These results indicate that essentially the same type of mercaptan disappearance occurred with polystyrene as with polybutadiene. Since polystyrene cannot be considered to contain any active double bonds, then this reaction of mercaptan must arise by some other mechanism. By analogy the polybutadiene reaction very likely arises by some process other than mercaptan addition to the polymer double bonds.

It was considered that a study of the charges in polymer properties might help to clarify this problem. Data on solubility changes are recorded in Table XVI. It is observed from these results that the polymer gels much earlier in the air than in the nitrogen system. By correlating solubility changes and mercaptan disappearance data it is observed that the gel content begins to increase only when the residual mercaptan has reached a value of approximately 40 per cent. Hence it would seem that the mercaptan acts in some manner to prevent gel formation.

Further work of the same nature was carried out in a polybutadiene latex containing polymer of much lower viscosity. These results are listed in Table XVII for reaction in nitrogen and Table XVIII for reaction in air. In this case gelation failed to occur to any appriciable extent

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TABLE XV

MERCAPTAN DISAPPEARANCE IN POLYSTYRENE LATEX IN AIR AND_NITROGEN_MEDIA

Initial Mercaptan Content-1.0 mg. per ml. of Latex

Reaction Time Hours	Ui Mei	Unreacted Mercaptan %		
	air	nitrogen		
0.5	76.5	93.0		
1.0	68.2	87.2		
1.8	59.7	72.8		
3.0	49.4	72.0		
4.0	37.6	61.1		
5.5	30.4	56.0		
7.0	24.6	44.0		
10.5	15.4	31.9		
25.0	3.1	8.2		

Conversion - 100% (approx.)



Mercaptan disappearance in polystyrene latex

TABLE XVI

SOLUBILITY CHANGES IN A STRIPPED POLYBUTADIENE

LATEX IN AIR AND NITROGEN MEDIA AT 50°C.

Initial Mercaptan Content of Latex - 1.8 mg. per ml.

		Air Satu	Nitrogen Saturated			
Reaction Hours	Time M	Unreacted lercaptan %	Solubility %	Unreacted Mercaptan %	Solubility %	
0		100.0	96.5	100	96.5	
4		44.4	92.6	71.0	93.8	
8		35.0	64.0	59.5	92.4	
18		22.2	50.4	37.3	88.5	
28		13.1	37.3	20.5	66.3	
47		2.1	15.9	5.0	22.5	
72		-	-	-	8.6	
125		-	4.4	-	5.0	

Conversion — 80% (approx.) Initial Viscosity — 2.00

TABLE XVII

VISCOSITY CHANGES IN A STRIPPED POLYBUTADIENE LATEX

AT 50°C. IN NITROGEN MEDIUM

Initial Mercaptan Content of Latex -2.6 mg. per ml.

Viscositv

							•		
6			Solution I		Solution	II	Solution III		Intrinsic
No.	Hrs.	bility %	gm./100 ml.	ηsp/c	gm./100 ml.	<u>1sp/c</u>	gm./100 ml.	η sp/c	ln
R -0	0	97.0	0.3584	1.72	0.1792	1.54	0.0896	1.44	1.34
R-2	2	98.2	0.3464	1.79	0.1732	1.58	0.0866	1.46	1.34
R -7	4	98.2	0.3590	1.85	0.1795	1.61	0.0898	1.49	1.37
R -1	6	98.0	0.3376	1.90	0.1688	1.67	0.0844	1.54	1.41
R -4	8	97.8	0.3288	1.94	0.1644	1.69	0.0822	1.57	1.45
R -3	11.5	98.0	0.3260	2.00	0.1630	1.74	0.0815	1.61	1.48
R - 6	23.5	97.0	0.3396	2.38	0.1698	1.94	0.0849	1.73	1.52
R - 5	50	95.0	0.3286	2.27	0.1643	1.90	0.0822	1.73	1.56

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TABLE XVIII

VISCOSITY CHANGES IN A STRIPPED POLYBUTADIENE LATEX

AT 50°C. IN AIR MEDIUM

Initial Mercaptan Content of Latex - 2.6 mg. per ml.

<u>Viscosity</u>

Sample Time No. Hrs.	mt	Solu-	Solution I		Solution	II	Solution III		Intrinsic	
	bility %	gm./100 ml.	<u>nsp/c</u>	gm./100 ml.	<u>1sp/c</u>	gm./100 ml.	η <u>sp/c</u>	1150051 ty		
R-0	0	97.0	0.3584	1.72	0.1792	1.54	0.0896	1.44	1.34	
R -13	2	96.1	0.3666	1.80	0.1833	1.58	0.0917	1.47	1.36	
R-10	4	99.5	0.3526	1.74	0.1763	1.53	0.0881	1.44	1.35	
R-9	6	97.5	0.3396	1.85	0.1698	1.63	0.0849	1.52	1.41	
R -11	8	97.5	0.3254	1.84	0.1627	1.63	0.0813	1.53	1.43	
R-14	11.5	97.5	0.3432	1.92	0.1716	1.66	0.0858	1.54	1.42	
R-8	23.5	98.0	0.3294	2.01	0.1647	1.75	0.0824	1.63	1.51	

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although indications of its origin in later samples are evident. Differences between air and nitrogen samples are not evident in this case. However a gradual viscosity rise occurred.

In Tables XIX, XX and XXI viscosity data are recorded for polystyrene when treated in air or nitrogen. No significant changes can be observed.

From the foregoing data it is observed that:

1) Tertiary hexadecyl mercaptan disappears in polybutadiene and polystyrene latex at about the same rate.

2) In high viscosity polybutadiene latex the mercaptan appears to function in some manner to prevent gel formation.

3) In low viscosity polybutadiene latex the polymer fails to gel when treated in nitrogen or air media either in the presence or absence of mercaptan but undergoes a slow viscosity rise with time.

4) Polystyrene latex when treated in air or nitrogen with or without mercaptan does not undergo any change in viscosity or solubility.

Either of the following possibilities may help to explain these results.

1) The mercaptan may undergo an oxidative attack in the presence of polymer particles. This does not occur to any appreciable extent in the absence of polymer as

TABLE XIX

VISCOSITY CHANGES IN POLYSTYRENE LATEX

50°C. IN NITROGEN MEDIUM

Initial Mercaptan Content of Latex-1.25 mg. per ml.

<u>Viscosity</u>

G	Time Hrs.	Solution I		<u>Solution I</u>	I	<u>Solution I</u>	Intrinsic	
No.		gm./100 ml.	<u>ηsp/c</u>	gm./100 ml.	η <u>sp∕c</u>	gm./100 ml.	<u>nsp/c</u>	<u> [η]</u>
T-0	0	0.2706	1.20	0.1353	1.14	0.0676	1.10	1.07
T-3	2	0.2796	1.15	0.1393	1.10	0.0697	1.07	1.04
T-7	7	0.2836	1.15	0.1418	1.09	0.0709	1.05	1.01
T -5	23	0.2986	1.16	0.1483	1.10	0.0742	1.07	1.04
T-2	33	0.2796	1.15	0.1393	1.10	0.0697	1.07	1.04
T-6	46	0.2924	1.14	0.1462	1.09	0.0731	1.06	1.03
T-1	74	0.2990	1.20	0.1495	1.14	0.0747	1.11	1.08
T-9	101	0.2832	1.14	0.1416	1.07	0.0708	1.04	1.01

TABLE XX

VISCOSITY CHANGES IN POLYSTYRENE LATEX

AT 50°C. IN AIR MEDIUM

Initial Mercaptan Content of Latex-1.25 mg. per ml.

<u>Viscosity</u>

G	~.	Solution I		<u>Solution I</u>	Solution II		II	Intrinsic
No.	Hrs.	gm./100 ml.	<u>lab/c</u>	gm./100 ml.	¶sp/c	gn./100 ml.	<u>¶sp∕c</u>	
T-0	0	0.2706	1.20	0.1353	1.14	0.0676	1.10	1.07
T-13	2	0.2898	1.22	0.1449	1.17	0.0725	1.11	1.05
T-11	7	0.3018	1.16	0.1509	1.11	0.0754	1.09	1.07
T-15	11	0.2926	1.15	0.1463	1.09	0.0732	1.06	1.03
T-14	23	0.2992	1.16	0.1496	1.09	0.0748	1.06	1.03
T-12	33	0.3238	1.14	0.1619	1.08	0.0810	1.05	1.02
T-18	46	0.2942	1.11	0.1471	1.05	0.0735	1.02	0.99
T-19	74	0.3302	1.19	0.1651	1.14	0.0826	1.12	1.10

TABLE XXI

VISCOSITY CHANGES IN A POLYSTYRENE LATEX

AT 50°C. IN AIR MEDIUM

Initial Mercaptan Content of Latex - Zero

<u>Viscosity</u>

G	Time Days	Solution I		Solution	Solution II		II	Intrinsic	
No.		gm./100 ml.	<u>lsb/c</u>	gm./100 ml.	<u>ηsp/c</u>	gm./100 ml.	$\frac{\eta \text{sp/c}}{2}$	<u>_[η]</u>	
S- 0	0	0.2830	2.09	0.1415	1.94	0.0707	1.87	1.80	
S- 8	1	0.2448	2.02	0.1224	1.90	0.0612	1.83	1.76	
S- 5	2	0.2750	2.04	0.1375	1.91	0.0687	1.84	1.77	
S-7	3	0.2972	2.01	0.1486	1.85	0.0743	1.78	1.71	
S-3	4	0.2592	2.00	0.1296	1.87	0.0648	1.80	1.73	
S-1	5	0.2882	1.98	0.1441	1.85	0.0720	1.76	1.67	
S-2	7	0.2994	2.02	0.1497	1.88	0.0749	1.81	1.74	
S-6	9	0.3406	2.00	0.1703	1.84	0.0852	1.76	1.68	
S- 4	15	0.2782	1.94	0.1391	1.80	0.0696	1.74	1.68	

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indicated by a blank using benzene in place of monomer. Only a few per cent of the mercaptan had disappeared in twenty-four hours.

2) The polymer molecules may become activated thermally or by oxidative attack of the persulfate. The mercaptan would then be consumed by stabilizing these active centres. In the case of polybutadiene this results in changes of the characteristics of the polymer molecules such as gel formation or viscosity changes. With polystyrene no such attack on the polymer is evident.

It is of interest to obtain a qualitative estimate of the extent of this polymer-mercaptan interaction as it affects the rate of disappearance of mercaptan at high conversion. Such information can be obtained from the data in Tables VIII and XIV. Considering the disappearance of mercaptan between 21 and 27 hours in butadiene polymerization this amounts to 68 per cent of the residual mer-In Table XIV it is found that in a nitrogen atcaptan. mosphere in a six hour period 49 per cent of the mercaptan disappeared by non-modification reactions. If this condition prevailed in the polymerization system it would indicate that 19 per cent of the mercaptan has been consumed by modification. Further calculation will show that the polymer formed in this conversion range is still modified to a greater extent than the polymer formed during the

first 50 per cent of the reaction. This would indicate that polymer-mercaptan interaction alone does not account for the increased disappearance rate. Other factors such as solubility or diffusion as previously discussed very likely have some effect.

3. <u>The Change in Intrinsic Viscosity during Polymerization</u> with Changing Initial Monomer Content

The intrinsic viscosities of polymer obtained over a wide range of conversion was determined for polybutadiene, 75:25 butadiene-styrene, 50:50 butadiene-styrene and 25:75 butadiene-styrene. Data for these runs are contained in Tables XXII, XXIII, XXIV and XXV.

Some qualitative conclusions may be drawn from these results. First of all it is seen that the intrinsic viscosity begins to fall off between 50-60 per cent conver-This is the same point at which the mercaptan dission. appearance rate begins to increase. In the case of GR-S these results are similar to those reported by Nicholls and Morton (27) but differ from those of Kolthoff (47) who observed no drop until 80 per cent conversion and then only Furthermore, it is seen that the initial invery slight. crease in viscosity is greatest in the case of polybutadiene. Little or no change is observed with samples containing sty-They all show a small initial increase in viscosity rene. followed by a decrease at higher conversion. This is pro-

TABLE XXII

VISCOSITY OF POLYBUTADIENE MODIFIED BY TERTIARY HEXADECYL MERCAPTAN

Mercaptan Concentration -1.7%

Vi	scos	ity
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Sample No.	-	Solution I		Solution	Solution II		Solution III		
	Conv. %	gm./100 ml.	nsp/c	gm./100 ml.	<u>ŋsp/c</u>	gm./100 ml.	<u>nsp/c</u>	יוscosi נא ו <u>ק</u> ו	
D-13	16.8	0.2416	1.97	0.1208	1.82	0.0604	1.77	1.72	
D-14	34.8	0.2460	2.22	0.1230	2.10	0.0615	2.04	1.98	
D-15	54.0	0.2460	3.52	0.1230	3.05	0.0615	2.80	2.55	
D-16	76.0	0.2164	3.48	0.1082	2.88	0.0591	2.60	2.32	
D-17	87.0	0.2472	2.64	0.1236	2.28	0.0618	2.14	2.00	

TABLE XXIII

VISCOSITY OF 75/25 - BUTADIENE/STYRENE COPOLYMER MODIFIED

BY TERTIARY HEXADECYL MERCAPTAN

Mercaptan Concentration - 1.5%

<u>Viscosity</u>

Sample Conv.	0	Solution I		Solution	Solution II		II	Intrinsic Viscosity	
	%	gm./100 ml.	¶sp/c	gm./100 ml.	<u>1sp/c</u>	gm./100 ml.	<u>ηsp/c</u>	<u>(η)</u>	U
A- 13	12.5	0.3972	5.86	0.1986	4.36	0.0993	3.67	2.95	1
A-14	27.2	0.4080	6.94	0.2040	4.97	0.1020	4.00	3.05	
A-15	41.6	0.4076	6.43	0.2038	4.50	0.1019	3.80	3.10	
A-1 6	65.0	0.4312	4.61	0.2156	3.45	0.1078	2.90	2.35	
A-17	81.4	0.4204	4.69	0.2102	3.31	0.1051	2.73	2.08	

TABLE XXIV

VISCOSITY OF 50/50 - BUTADIENE/STYRENE COPOLYMER MODIFIED

BY TERTIARY HEXADECYL MERCAPTAN

Mercaptan Concentration - 1.7%

<u>Viscosity</u>

Comple	Conv.	Solution I		Solution	II	Solution III		Intrinsic Viscosity	
No.		gm./100 ml.	$\eta sp/c$	gm./100 ml.	<u>ηsp/c</u>	gm./100 ml	·ηsp/c	<u></u>	
K-13	10.1	0.2556	3.18	0.1278	2.73	0.0639	2.50	2.27	
K-14	26.6	0.2576	3.13	0.1288	2.71	0.0644	2.51	2.31	
K-15	41.2	0.2564	2.96	0.1282	2.64	0.0641	2.50	2.36	
K-16	56.5	0.2572	2.48	0.1286	2.23	0.0643	2.10	1.97	
K-17	74.4	0.2564	2.18	0.1282	1.89	0.0641	1.74	1.60	

1

TABLE XXV

VISCOSITY OF 25/75 - BUTADIENE/STYRENE COPOLYMER MODIFIED

BY TERTIARY HEXADECYL MERCAPTAN

Mercaptan Concentration - 1.7%

<u>Viscosity</u>

Sample No.	Conv.	Solution I		<u>Solution</u>	II	<u>Solution I</u>	Intrinsic	
		gm./100 ml.	ηsp/c	gm./100 ml.	<u>γsp/c</u>	gm./100 ml.	$J^{sp/c}$	
H-13	4	0.2424	2.81	0.1212	2.58	0.0606	2.45	2.32
H -14	18	0.2524	3.04	0.1262	2.78	0.0631	2.62	2.46
H-15	31	0.2472	2.97	0.1236	2.68	0.0618	2.51	2.34
H-16	57	0.2484	2.66	0.1242	2.52	0.0621	2.47	2.42
H -17	82	0.2492	2.20	0.1246	2.06	0.0623	1.98	1.90

bably indicative of decreased branching when styrene is included in the system. In any event these changes are of little use in evaluating molecular weight changes with conversion because of the variation in styrene content of the polymer formed during the course of the polynerization.

4. <u>Effect of Polymer Composition on Intrinsic Viscosities</u> and Precipitation Distribution Curves

A study was undertaken of the changes in intrinsic viscosity and precipitation distribution curves with changing polymer composition. The polymers evaluated were prepared using the following initial monomer charges: butadiene, 75:25, butadiene-styrene, 50:50, butadiene-styrene, 25:75, butadiene-styrene and styrene. Samples of the same molecular weight as well as samples of the same degree of polymerization were investigated. The preparation of these was accomplished by using varying initial concentrations of tertiary hexadecyl mercaptan and by stopping the reaction at 10 per cent conversion to avoid too great a compositional heterogeneity.

Wall (62, 63) has shown that the number average molecular weight of polymer, prepared with tertiary hexadecyl mercaptan, as determined by osmotic measurement is very similar to the molecular weight as calculated from the mercaptan disappearance curve. Since the mercaptan disappearance curves had been determined for all five monomer ratios it was a simple matter to calculate the amount of mercaptan required to give samples of the same molecular weight. The calculation may be readily carried out by use of the following equation:

$$M_{R} = \frac{Wt. of polymer formed}{mols. of regulator consumed}$$

where M_R = the regulator theory molecular weight and is equal to the number average molecular weight in the absence of branching.

In the case of butadiene, 1.4 per cent mercaptan concentration, based on initial monomer, was chosen for furnishing polymer safely within the limit of benzene solubility. The percentage of mercaptan consumed was determined from the disappearance curve and from this the number of mols of mercaptan was calculated. With these data it was possible to calculate M_R for polybutadiene prepared in the presence of 1.4 per cent tertiary hexadecyl mercaptan and at 10 per cent conversion. All the other polymers were prepared on the basis of 1.4 per cent mercaptan concentration for polybutadiene. The calculations are summarized The reaction time rein Table XXVI for all nine samples. quired for 10 per cent conversion was calculated from the reaction rate curves.

Data on the intrinsic viscosity of the polymers, prepared with the mercaptan concentrations and at the monomer ratios designated in Table XXVI are listed in Tables XXVII

and XXVIII. The results are shown graphically in Figure It can be noted that for polymers of the same molecu-8. lar weight the intrinsic viscosity decreases almost linearly with increasing styrene content until a minimum is reached between 70-80 per cent styrene content after which a small increase in the viscosity is noted up to polystyrene. A different type of curve is evident when the changes of viscosity with composition are plotted for polymer of the same degree of polymerization. However, a minimum in the curve is again noted. This minimum is observed at essentially the same position as before. Since viscosity of a polymeric solution is assumed to be primarily dependent on chain length, the decrease of viscosity with increasing styrene content of the polymer would be expected. However, the appearance of a minimum in the curve is entirely unexpected. A possible explanation of this behaviour is offered along the two following lines: 1) decreased branching with increasing styrene content, 2) increased linearity of the chain because of the bulkiness of styrene molecules. On this basis the primary effect of styrene in shortening the chain might be overcome at high styrene contents by these two effects.

Precipitation distribution curves of the polymers investigated are presented in Figures 9 and 10. The series of curves obtained for polymers of the same molecular weight is quite similar to that obtained for polymers of the same

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TABLE XXVI

CALCULATED RELATION BETWEEN MERCAPTAN CONCENTRATION AND MOLECULAR

WEIGHT OR D.P. OF POLYMER

	Butadiene	Butadiene/Styrene 75/25	Butadiene/Styrene	Butadiene/Styrene 25/75	Styrene	_
% RSH consumed at 10% conversion	5.0	3.6	2.7	1.82	1.79	
M _R % of Cl6H33 S H required to	36,900	36,900	36,900	36,9 00	36,900	<mark>۔</mark> 95
prepare polymer of 36,900 M.W.	1.4	1.94	2.59	3.84	3.91	t
* % styrene in polymer	0	16 .8	36.9	61.8	100.0	
Degree of Polymerization	685	590	509	435	355	
% of Cl6H33 S H required for D.P. of 685	1.4	1.67	1.93	2.44	2.03	

* Calculated from data on Wall's "or " value as supplied by K. R. Henery-Logan

TABLE XXVII

EFFECT OF POLYMER COMPOSITION ON INTRINSIC VISCOSITY-POLYMER OF THE

SAME DEGREE OF POLYMERIZATION

Viscosity

Sample	Initial	Charging	Conv.	Solution I		Solution II		Solution III		Intrinsic
NO.	Concentration %	% Styrene	% 	gm./100	. <u>¶sp/c</u>	gm./100	<u>,7sp/c</u>	gm./100	<u>nsp/c</u>	130051 ty
N-17	1.4	0	8.9	0.1948	3.54	0.0974	3.08	0.0487	2.88	2.68
N-5	1.67	25	9.2	0.2022	3.63	0.1011	3.18	0.0505	2.94	2.72
N-11	1.93	50	9.4	0.1902	3 .2 8	0.0951	2.96	0.0475	2.78	2.60
N-15	2.44	75	9.0	0.1980	2.44	0.0990	2.26	0.0495	2.16	2.06
N-21	2.03	100	11.0	0.2680	2.78	0.1340	2.52	0.0670	2.38	2.24

TABLE XXVIII

EFFECT OF POLYMER COMPOSITION ON INTRINSIC VISCOSITY_POLYMER OF THE

SAME MOLECULAR WEIGHT

<u>Viscosity</u>

G	T - 1 + 1 - 1		0	Solution I		Solution II		Solution III		Tutuluala	
No.	Mercaptan Concentration %	Ratio in % Styrene	%	gm./100 	ηs p/c	gm./100 nl	ηs p/c	gm./100 	η sp/c	Viscosity	1
N-17	1.4	0	8.9	0.1948	3.54	0.0974	3.08	0.0487	2.88	2.68	- 76
N-7	1.94	25	9.1	0.2008	2.9 8	0.1004	2.66	0.0502	2.49	2.32	
N-9	2.59	5 0	9.2	0.1834	2.24	0.0917	2.12	0.0458	2.03	1.94	
N-13	3.84	75	9.0	0.1970	1.37	0.0985	1.31	0.0492	1.29	1.27	
N-19	3.91	100	11.5	0.3010	1.69	0.1505	1.57	0.0752	1.50	1.43	



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Effect of styrene content on precipitation distribution curves Polymers of the same molecular weight



FIGURE 9

-99-

-100-





Effect of styrene content on precipitation distribution curves. Polymers of the same degree of polymerization

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Precipitation distribution curves of GR-S modified with 1.5% tertiary hexadecyl mercaptan

molecular weight is quite similar to that obtained for polymers of the same degree of polymerization. The sharpness of the distribution is about the same in all cases although polystyrene seems to show the greatest degree of homogeneity in this respect. The most striking feature of these results is the shift of the solubility curves to higher volume per cent methanol as the polymer composition changes from 100 per cent butadiene to 100 per cent styrene. As a consequence of this the peak of the precipitation distribution curve also shows a similar trend.

These results indicate that no true measure of molecular heterogeneity can be made in a system showing compositional heterogeneity unless due regard is taken of this factor. Thus, following changes in viscosity or precipitation distribution curves with conversion in a copolymer system is of doubtful value especially when these data are used to evaluate changes in molecular heterogeneity.

A series of precipitation distribution functions were determined for a GR-S run using an initial concentration of 1.5 per cent tertiary hexadecyl mercaptan. The solubility and precipitation distribution curves appear in Figure 11. It is observed that an increased heterogeneity is noted with increasing conversion. It has also been shown that over this same range of conversion the composition of the polymer changed markedly. The polymer forming initially had a styrene content of approximately 17 per cent while the polymer forming at 80 per cent conversion has a content of approximately 30 per cent. A change of this magnitude would definitely have a noticeable effect on the solubility of the polymer. Hence the net effect would be similar to superimposing any two of the solubility curves in Figures 9 or 10. A decrease in the maximum as well as a broadening of the distribution curve would be observed. Thus this factor would partially account for the observed change in the shape of the distribution curve attained with changing conversion.

It is nevertheless admitted that there are other contributing factors. The increase in mercaptan disappearance rate at high conversions would of course lead to polymer of lower molecular weight, and consequently of greater solubility. Furthermore, in high conversion samples there is very likely to be some highly branched polymer present of high molecular weight and low solubility. These two factors would also contribute to the flattening of the solubility curve and the decrease in the maximum and increase in the spread of the precipitation distribution curves.

5. <u>The Preparation of Relatively Homogeneous Polymers of</u> <u>Different Composition Over a Wide Viscosity Range</u>

The usefulness of tertiary hexadecyl mercaptan in preparing homogeneous polymer fractions has already been demonstrated. At the request of the Polymer Corporation Sarnia, Ont. a series of homogeneous polymers of different composition over a wide viscosity range have been prepared. In this way the effect of different styrene content could be studied separately from the effect of molecular size at any given styrene content. If prepared in sufficiently large quantities, reliable measurements of physical properties, i.e. both as to performance tests and processing characteristics could be carried out. Work of this nature using tertiary hexadecyl mercaptan has already been undertaken at Sarnia.

In this investigation the following monomer charges were studied:

65:35, Butadiene-Styrene 75:25, Butadiene-Styrene 85:15, Butadiene-Styrene

Data on the rates of polymerization and rate of mercaptan disappearance appear in Table XXIX. It is noted that these results agree with those presented in Section 1 of this discussion.

Polymer fractions were prepared using the following mercaptan concentrations based on initial monomer: 1.3, 1.7, 2.1 and 2.5 per cent. These results are presented in Tables XXX, XXXI and XXXII. As expected it was possible to control the viscosity of the polymer by the mercaptan concentration.
EABLE XXIX

RATES OF POLYMERIZATION AND MERCAPTAN DISAPPEARANCE

Polymerization Time - Hrs	Butadiene Ratio =	-Styrene 65/35	Butadiene Ratio =	-Styrene 75/25	Butadiene-Styrene Ratio=85/15	
	Conversion %	Unreacted Mercaptan %	Conversion %	Unreacted Mercaptan %	Conversion %	Unreacted Mercaptan %
2	15.3	96.0	12.5	94.0	9.5	93.0
4	30.9	92.0	27.2	89.5	21.9	89.0
6	51.5	88.0	41.6	87.0	32.5	87.0
9	75.0	67.0	65.0	74.0	50.9	80.0
12	88.7	47.0	81.3	54.0	65.0	70.0
16.5	96.5	12.5	91.0	19.4	-	-
18	-	-	-	-	82.6	29.0
Regulating Index	0.	28	0.3	570	0.46	0

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TABLE XXX

POLYMERS OF LOW COMPOSITIONAL AND MOLECULAR HETEROGENEITY

INITIAL BUTADIENE-STYRENE RATIO = 65/35

Initial = 1.665

Increment Styrene Content in Polymer at Zero Conversion (calc.) = 25.5%Increment Styrene Content in Polymer at 12% Conversion (calc.) = 26.5%Average Styrene Content in Polymer at 12% Conversion (calc.) = 26.0%

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<u>Viscosity</u>

Sample Mercaptan		Conv.	Solution I		Solution II		Solution III		Intrinsic
NO.	gm./100 g monomer	<i>%</i>	gm./100 ml.	η sp/c	gm./100 ml.	η sp/c	gm./100 ml	. n sp/c	<u>η η</u>
E 1	1.3	11.5	0.3232	4.97	0.1616	4.20	0.0803	3.82	3.44
E 4	1.7	11.5	0.3832	5.27	0.1916	4.19	0.0958	3.63	3.07
E 7	2.1	11.2	0.3860	3.57	0.1930	3.07	0.0965	2.79	2.51
E 10	2.5	11.2	0.4068	2.61	0.2034	2.30	0.1017	2.13	1.92

TABLE XXXI

POLYMERS OF LOW COMPOSITIONAL AND MOLECULAR HETEROGENEITY

INITIAL BUTADIENE-STYRENE RATIO = 75/25

Initial $\mathbf{C} = 1.640$

Increment Styrene Content in Polymer at Zero Conversion (calc.) = 17.0%Increment Styrene Content in Polymer at 12% Conversion (calc.) = 17.8%Average Styrene Content in Polymer at 12% Conversion (calc.) = 17.4%

Viscosity

Sample	Mercaptan	Conv.	<u>Solution</u>	I	<u>Solution</u>	II	Solution	<u>III</u>	Intrinsic
110.	gm./100 g monomer	70	gm./100 ml.	¶sp/c	gm./100 gml	.ηsp/c	gm./100 ml.	ηsp/c	<u> η </u>
E 13	1.3	11.9	0.4280	5.90	0.2140	4.45	0.1070	3.77	3.09
E 16	1.7	11.5	0.4128	4.00	0.2064	3.31	0.1032	3.03	2.75
E 19	2.1	11.3	0.4488	2.70	0.2244	2.31	0.1122	2.10	1.89
E 22	2.5	11.1	0.3980	2.16	0.1990	1.93	0.0995	1.82	1.71

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TABLE XXXII

POLYMERS OF LOW COMPOSITIONAL AND MOLECULAR HETEROGENEITY

INITIAL BUTADIENE-STYRENE RATIO - 85/15

Initial $\propto = 1.620$

Increment Styrene Content in Polymer at Zero Conversion (calc.) = 9.8%Increment Styrene Content in Polymer at 12% Conversion (calc.) = 10.2%

Average Styrene Content in Polymer at 12% Conversion (calc.) = 10.0%

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Sample No.	Mercaptan Conc ⁿ	Conv. %	<u>Solution 1</u>	<u> </u>	Solution	n <u>II</u>	Solution	<u>III</u>	Intrinsic Viscosity
	gm./100 g monomer		gm./100 ml.	ηsp∕c	gm./100 ml.	ηsp/c	gm./100 ml.	ηsp/c	171
E 25	1.3	12.1	0.4560	5.86	0.2280	4.32	0.1140	3.59	2.86
E 28	1.7	12.4	0.4140	4.53	0.2070	3.59	0.1035	3.09	2.59
E 31	2.1	12.1	0.4316	3.64	0.2258	2.88	0.1129	2.55	2.22
E 34	2.5	12.0	0.4628	2.31	0.2314	2.01	0.1157	1.85	1.69

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Precipitation distribution curves of polymers of low compositional heterogeneity. Butadiene-Styrene Ratio = 65:35

FIGURE 12



Precipitation distribution curves of polymers of low compositional heterogeneity. Sutadiene-Styrene Ratio = 75:25

IGURE 13

-110-

FIGURE 14



Precipitation distribution curves of polymers of low compositional heterogeneity. Butadiene-Styrene Ratio = 85:15

Precipitation curves and precipitation distribution curves for all these polymers are shown in Figures 12, It is obvious from these results that an in-13 and 14. crease in initial mercaptan content seems to result in a polymer of greater heterogeneity as shown by the greater spread in the distribution curve. It is quite probable that this spread may be only an apparent one, due to a decrease in sharpness of precipitation of the lower molecular weight species. From the view point of the modifier reaction theory, the molecular weight distribution should be statistically the same both in the higher and lower regions. The relative homogeneity of the polymer is well illustrated by the sharp curves obtained with the lower concentrations of mercaptan.

SUMMARY

1. A satisfactory method of determining residual mercaptan in emulsion systems was developed. This was accomplished by carrying out the polymerization in one ounce bottles with analysis of the total charge. For mecaptans of limited solubility in the aqueous phase, e.g. normal tetradecyl and tertiary hexadecyl representative samples could not be obtained when the reaction was carried out in larger containers. The presence of hydroquinone and the venting of latex at elevated temperatures both led to low results.

2. The effect of agitation on the mercaptan disappearance rate and intrinsic viscosity of polymer prepared with Sharples tertiary hexadecyl mercaptan was investigated. It was found that the mercaptan disappearance rate increased while the intrinsic viscosity of the polymer decreased with an increase in the rate of stirring.

3. The regulating index of tertiary hexadecyl mercaptan was determined for five initial monomer charges. The rate of polymerization was also investigated for the same monomer ratios. The following results were obtained:

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Initial Monomer Cha	arge	Regulating Index	Reaction Rate per Hour %
Butadiene		0.512	4.5
Butadiene/Styrene	75/25	0.370	7.6
Butadiene/Styrene	50/50	0.272	12.9
Butadiene/Styrene	25/75	0.185	19.4
Styrene		0.181	74.5

It is observed that with increasing styrene content the reaction rate per hour increased. The rate of mercaptan disappearance and consequently the regulating index of the mercaptan decreased.

From these results a decrease in the rate of mercaptan disappearance at high conversions would be indicated. Hence the changing styrene content of the charge during polymerization cannot account for the increased rate of mercaptan disappearance at high conversion in the GR-S system.

4. The extent of mercaptan-polymer interaction in stripped polybutadiene and polystyrene latices was studied. A rapid rate of mercaptan disappearance was noted in each case. Since polystyrene cannot be considered to contain any active double bonds some mechanism other than mercaptan addition to polymer double bonds must account for this reaction. Several were suggested.

5. The changes in intrinsic viscosity over a wide range of conversion were determined for the following monomer charges:

Butadiene 75:25, Butadiene-Styrene 50:50, Butadiene-Styrene 75:25, Butadiene-Styrene

The viscosities in every case indicated an initial increase in viscosity up to 50-60 per cent conversion followed by a rapid decrease with increasing conversion. The initial increase in viscosity was greatest in the case of polybutadiene. The decrease in viscosity at conversions of 50-60 per cent was expected from the nature of the mercaptan disappearance curve.

6. On the basis of the theory of modifier action polymer samples of the same molecular weight and of the same degree of polymerization but of different composition were prepared.

Intrinsic viscosity and precipitation distribution curves were obtained for all samples. It was found that the intrinsic viscosities decreased with increasing styrene content of the polymer sample. A maximum in the curve of intrinsic viscosity vs. styrene content was observed. A possible explanation of the phenomenon was offered. The precipitation distribution curves shifted toward higher volume per cent methanol with increasing styrene content of the sample. This investigation indicates that molecular analysis of a copolymer system by classical methods is of dubious value unless due regard is taken of the changing composition of the polymer with conversion.

7. A method is presented for the preparation of relatively homogeneous polymers of the same composition over a wide viscosity range. It was pointed out that this method could be readily adapted to plant studies. The effect of molecular weight separate from that of styrene content on the precipitation distribution function of the polymer was studied.

CLAIMS TO ORIGINAL RESEARCH AND CONTRIBUTIONS

TO KNOWLEDGE

It is claimed that the work presented in this thesis constitutes:

1. A review of the analytical method of Kolthoff and Harris for the determination of mercaptan in latex with special reference to higher mercaptans,

2. The first reported study of the relation between the initial styrene content of the monomer charge and the regulating index of tertiary hexadecyl mercaptan.

3. The first reported study of the interaction between polystyrene latex and tertiary hexadecyl mercaptan as compared to the same reaction with polybutadiene latex.

4. The first reported application of tertiary hexadecyl mercaptan for:

(a) the evaluation of the changes of polymer properties with composition

(b) the preparation of relatively homogeneous polymers of any desired composition or molecular size.

5. An original contribution to the mechanism of the disappearance of tertiary hexadecyl mercaptan during the later stages of the polymerization reaction.

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LITERATURE CITED

1.	Flory, P.J., J. Am. Chem. Soc. <u>59</u> , 241 (1937)
2.	Hunter, W.H., and Yohe, R.V., J. Am. Chem. Soc. <u>55</u> , 1248 (1933)
3.	Whitmore, F.C., Ind. Eng. Chem. <u>26</u> , 94 (1934)
4.	Staudinger, H., "Die Hochmolekularen organischen Verbindungen", Berlin, J. Springer (1932)
5.	Hey, M.H., and Waters, V.F., Chem. Rev. <u>21</u> , 169 (1937)
6.	Schulz, G.V. and Wittig, G., Naturwiss, 27, 387, 456 (1939)
7.	Schulz, G.V., ibid. <u>27</u> , 659 (1939)
8.	Melville, W.H., Trans. Inst. Rubber Ind. <u>15</u> , 209 (1939)
9.	Melville, W.H., Proc. Royal Soc. (London) A <u>163</u> , 511 (1937)
10.	Blomquist, A.T., Johnson, J.R., and Sykes, H.J., J. Am. Chem. Soc. <u>65</u> , 2446 (1943)
11.	Price, C.C. and Durham, D.A., ibid. <u>64</u> , 2508 (1942)
12.	Price, C.C., Kell, R.W. and Krebs, E., ibid. <u>64</u> , 1103 (1942)
13.	Price, C.C. and Tate, B.E., ibid. <u>65</u> , 517 (1943)
14.	Price, C.C. and Durham, D.A., ibid. <u>65</u> , 757 (1943)
15.	Schulz, G.V. and Husemann, E., Zeit. physikal Chem. B <u>39</u> , 246 (1938)
16.	Medrede v, S. and Kamenskaya, S., Acta. Physiochim. U.S.S.R. <u>13</u> , 565 (1940)
17.	McClure, J.H., Robertson, R.E. and Cuthbertson, A.D., Can. Jour. Res., <u>20</u> B, 103 (1942)
18.	Schulz, G.V. and Dingliner, A. and Husemann, E., Zeit. physikal. Chem. B <u>43</u> , 385 (1939)
19.	Suess, H. and Springer, A., ibid. A <u>181</u> , 81 (1937)
20.	Mayo, F.R., J. Am. Chem. Soc. <u>65</u> , 2324 (1943)

21. Hulburt, H.M., Harmon, R.A., Tobolsky, A.V. and Eyring, H. Ann. N.Y. Acad. Sci. 44, 371 (1943) 22. Breitenbach, J.W., and Maschin, H., Zeit. physikal Chem. A <u>187</u>, 175 (1940) 23. Semon, W.L., Chem. Eng. News, 21, 1617 (1943) 24. Snyder, H.R., Wall, F.T., Stewart, J.M., Allen, R.E., Sands, G.D. and Dearborn, R.J., Rubber Reserve Co. Report No. CR-310, April 14, 1944. 25. Ewart, R.H., Smith, W.V. and Hulse, G.E., Rubber Reserve Co., Report No. CR-73, June 16, 1943 26. Kolthoff, I.M., Rubber Reserve Co. Report No. CR-185, OCt. 15, 1943 27. Morton M. and Nicholls, R.V.V., National Research Council (Canada) Report No. OSR-25, Sept. 1, 1945. 28. Carlin, R.B., Rubber Reserve Co., Report No. CR-104, July 1, 1943 29. Phillips Petroleum Co., Research Department, Rubber Reserve Co. Report No. CR-229, Nov. 5, 1943 30. Kolthoff, I.M. Rubber Reserve Co. Report No. CR-323, April 20, 1944 31. Biggs, B.S. et al., Rubber Reserve Co. Report No. CR-100 May 27, 1943 32. Rubber Reserve Co., Report No. CPD-74, Haden, R.L., May 28, 1943 Eolkin, D. and Heller, W., Rubber Reserve Co. 33. Report No. CR-228, March 7, 1944 34. Kolthoff, I.M., Rubber Reserve Co. Report No. CR-326 May 13, 1944 Kolthoff, I.M. and Harris, W.E., 35. Rubber Reserve Co. Report

36. Kolthoff, I.M. and Harris, W.E., Rubber Reserve Co. Report No. CR-64, June 15, 1943

No. CR-355, June 13, 1944

37. Kolthoff, I.M., Wendland, R.T. and Carr, C.W., Rubber Reserve Co. Report No. CR-262, March 6, 1944

38. Snyder, H.R., Allen, R.E. and Stewart, J.M., Rubber Reserve Co. Report No. CR-204, Dec. 7, 1943 39. Rubber Reserve Co. Report No. CR-233, Marvel, C.S., Nov. 20, 1943 40. Marvel, C.S., Rubber Reserve Co. Report No. CR-240. Dec. 20, 1943 41. Marvel, C.S., Rubber Reserve Co. Report No. CR-298, Feb. 20, 1944 42. Kolthoff, I.M., Rubber Reserve Co. Report No. CR-300, March 22, 1944 43. Snyder, H.R., Wall, F.T., Allen, R.E., Beste, L.F. and Oppegard, Rubber Reserve Co. Report No. CR-430, Sept. 15, 1944 44. Kolthoff, I.M., Rubber Reserve Co. Report No. CR-609 Feb. 20, 1945 45. Kolthoff, I.M. and Stenberg, R.S., Rubber Reserve Co. Report No. CR-643, March 31, 1945 46. Kolthoff, I.M., Rubber Reserve Co. Report No. CR-750, June, 1945 47. Kolthoff, I.M. and Meehan, E.J., Rubber Reserve Co. Report No. CR-783, Aug. 9, 1945 48. Kolthoff, I.M. and Meehan, E.J., Rubber Reserve Co. Report No. CR-794, Aug., 1945 49. Kolthoff, I.M. and Stenberg, R.J., Rubber Reserve Co. Report No. CR-928, Dec. 11, 1945 50. Harris, W.E. and Kolthoff, I.M., Rubber Reserve Co. Report No. CR-626, March 22nd 1945 51. Hess, L.D. and Borders, A.M., Rubber Reserve Co. Report No. CR-214, Dec. 1, 1943 Rubber Kolthoff, I.M., Williams, D.E. and Carr, C.W., 52. Reserve Co. report No. CR-514, Dec. 21 1944Schulz, W.A. and Crouch, W.W., Rubber Reserve Co. Report 53. No. CR-534, Jan. 11, 1945 Rubber Reserve Co. Report No. CR-542 Kolthoff, I.M., 54. Dec. 20, 1944 Rubber Reserve Co. Report No. CR-636 55. Kolthoff, I.M.,

April 10, 1945

56.	Kolthoff, I.M. and Harris, W.E., Rubber Reserve Co. Report No. CR-644, April 6, 1945
57.	Troyan, J.E., Rubber Reserve Co. Report No. CR-320 Feb. 23, 1945
58.	Hycar Chemical Company, Rubber Reserve Report No. CR-642, April 11, 1945
59.	Kolthoff, I.M. and Harris, W.E., Rubber Reserve Co. Report No. CR-645, April 14, 1945
60.	Schulz, W.A., Rubber Reserve Co. Report No. CR-757 July 9, 1945
61.	Marvel, C.S., Rubber Reserve Co. Report No. CR-744 June 10, 1945
62.	Marvel, C.S., Rubber Reserve Co. Report No. CR-844 Sept. 10, 1945
63.	Wall, F.T. and Beste, L.F., Rubber Reserve Co. Report No. CR-862 Oct. 1, 1945
64.	Swaney, M.W. and White, J.V., Rubber Reserve Co. Report No. CR- 129, Aug. 27, 1943
65.	Lawson, J.K. and Rabjohn, N and Marvel, C.S., Rubber Reserve Co. Report CR-234, Dec. 15, 1943
66.	Snyder, H.R. and Inskeep, G.E., Rubber Reserve Co. Report No. CR-649, May 12, 1945
67.	Flory, P.J., Rubber Reserve Co. Report No. CR-660, April 20, 1945
68.	Kraemer, E.O., Ind. Eng. Chem. <u>30</u> , 1200 (1938)
69.	Kuhn, W., Z. physikal Chem. A <u>161</u> , 1 (1938)
70.	Huggins, M.L. Jour. Applied Phys. <u>10</u> , 700 (1939)
71.	Huggins, M.L. Jour. Phys. Chem. <u>42</u> , 911 (1938)
72.	Huggins, M.L. ibid. <u>43</u> , 439 (1939)
73.	Flory, P.S., J. Am. Chem. Soc. <u>65</u> , 372 (1943)
74.	Wall, F.T., Rubber Reserve Co. Report No. CR-429, Sept. 15, 1944
75.	Marvel, C.S., Rubber Reserve Co. Report No. CR-615 Feb. 10, 1945

76. Marvel, C.S., Rubber Reserve Co. Report No. CR-722 May 10, 1945 77. Baker, W.C. and Heiss, J.H. Rubber Reserve Report No. CR-198, Dec. 1, 1943 78. Baker, W.O., Heiss, J. H. and Walker, R.W., Rubber Reserve Co. Report No. CR-715, May, 1945 79. Baker, W.C., Heiss, J.H. and Walker, R.W., Rubber Reserve Co. Report No. CR-740, June, 1945 80. Wall, F.T., J. Am. Chem. Soc. 63, 1862 (1941) 81. Henery-Logan, K.R., Unpublished Data, McGill University, Montreal, Que. 82. Mayo, F.R. and Lewis, F.M. J. Am. Chem. Soc. 66, 1594 1944 Henery-Logan, K.R. and Nicholls, R.V.V., National Research 83. Council (Canada) Report No. OSR-28, Oct. 31, 1945 84. Rubber Reserve Co. Report No. CR-665 Meehan, E.J., April 16, 1945 85. Kolthoff, I.M. and Harris, W.E., Rubber Reserve Co. Report No. CR-136, Sept. 8, 1943 86. Kolthoff, I.M. and Harris, W.E., Rubber Reserve Co. Report No. CR-62, June 15, 1943 87. Fisher, W.V. and Day, J.H. Rubber Reserve Co. Report No. CR-65, Feb. 15, 1944 88. Medalia, A.I., Rubber Reserve Co. Report No. CR-318 April 20, 1944 89. Baker, W.O. and Mullen, J.W., Rubber Reserve Co. Report No. CR-70, June 24, 1943 90. Baker, W.O. and Mullen, J.W., Rubber Reserve Co. Report No. CR-148, Sept. 3, 1943 91. Flory, P.J. et.al., Rubber Reserve Co. Report No. CR-232 Dec. 22, 1943 92. "Fluidity and Plasticity", McGraw-Hill Bingham, E.O., Book Co., New York, 1922

93.	Wall, F.T., Sands, G.D., Beste, L.F. and Powers, R.W. Rubber Reserve Co. Report No. CR-345, June 13, 1944
94.	Wall, F.T., Rubber Reserve Co. Report No. CR-389, June 20, 1944
95.	Kolthoff, I.M. and Harris, W.E. Rubber Reserve Co. Report No. CR-136, Sept. 8, 1943
96.	Reynolds, W.B., Rubber Reserve Co. Report No. CR-600, January, 1945
97.	Meehan, E.J. and Kolthoff, I.M., Rubber Reserve Co. Report No. CR-113, July 31, 1943
98.	Price, C.C. and Adams, C.E., Rubber Reserve Co. Report No. CR-501, Nov. 10, 1944
99.	Kolthoff, I.M., Rubber Reserve Co. Report No. CR-387 July 19, 1944
100.	Davies, T.L. and Maher, E.D., National Research Council (Canada) Report No. SSR-18, 1945
101.	Wall, F.T., Powers, R.W., Sands, G.D. and Stent, G.S. Rubber Reserve Co. Report No. CR-734, June 4, 1945
102.	Harkins, W.D., Rubber Reserve Co. Report No. CR-672 April 20, 1945
103.	Kolthoff, I.M., Rubber Reserve Co. Report No. CR-400 Aug. 12, 1944