I. ASYMMETRIC POLYMERIZATION.
II. PURIFICATION OF BUTADIENE; NEW MODIFIERS FOR BUTADIENE-STYRENE COPOLYMERS.

BY

STEVENS STEWART DRAKE

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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
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BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

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I. ASYMMETRIC POLYMERIZATION

INTRODUCTION

It was the purpose of this investigation to prepare an optically active polymer, one which owed its optical activity to an active center inherent in the polymer chain. The approach that was to be used employed an optically active monomer. The polymerization of such a monomer, by the principle of asymmetric induction, should produce a polymer which is richer in one optically active form than in the other. Removal of the center which initially produced the ''asymmetric polymerization,'' to coin a new phrase, would then result in the desired product.

HISTORICAL AND THEORETICAL

The polymers derived from the esters of acrylic and α-methacrylic acids have been known for some time and have gained considerable commercial importance. The fact that halogens substituted in unsaturated compounds accelerate their rate of reactions led Marvel and Cowan[1] to investigate the α-haloacrylates. This work led to an important structural discovery. Contrary to the other types of vinyl polymers, their evidence indicated that α-haloacrylates gave rise to a ''head to head, tail to tail'' mode of polymerization. In this respect, they resembled the polysulfones,[2] but their behavior was unique in the vinyl series.

During the course of this investigation Marvel, Dec, and Cooke[3] prepared the optically active ester, d-sec-butyl α-chloroacrylate, and found that the polymer obtained gave a rotation that was materially different from the monomer. This was a revelation, and was immediately used as a new and improved means of studying the rate of polymerization--with the added implication that a new insight into the mode of polymerization and the structure of the polymers would be gained, that the ''head to head, tail to tail'' mechanism could be established as being one hundred per cent complete, or only a result of a random addition.

This insight has never been attained although optically active monomers have been used in several investigations[4,5] to study rate of polymerization.

It was felt that a different chemical approach to the problem might prove more satisfactory--that involving the principle of ''asymmetric induction.'' It has been known since about the beginning of this century that an asymmetric center within a molecule tends to influence the course of reaction. Kortum[6] defines this asymmetric induction

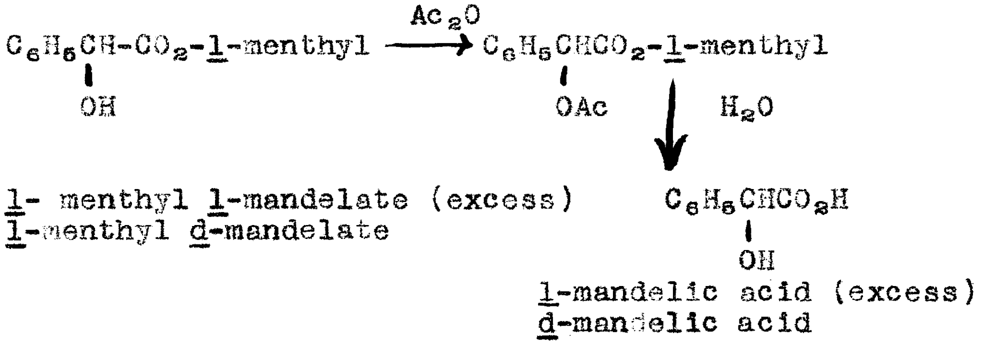
> ''as the action of a force, arising in an optically active molecule, which influences adjacent symmetrical molecules in such a way that they become asymmetric.''

There then results an ''asymmetric synthesis'', a phenomenon that was first observed in 1894 by Emil Fischer[7], and later defined by Marckwald[8] as those

> ''processes which produce optically active compounds from symmetrically substituted molecules by the intermediate use of an optically active reagent, but without the use of any of the methods of resolution.''

Although many examples are known, the contributions of McKenzie[9] are noteworthy, and the following illustration was taken from his work:

$$C_6H_5COCO_2H \rightarrow C_6H_5COCO_2\text{-}\underline{\text{l}}\text{-menthyl} \xrightarrow{(2H)}$$

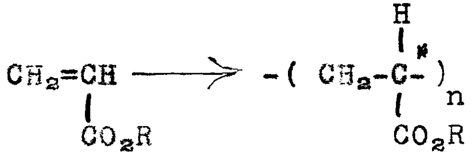


$$\underset{OH}{C_6H_5CH}-CO_2\text{-}l\text{-menthyl} \xrightarrow{Ac_2O} \underset{OAc}{C_6H_5CH}CO_2\text{-}l\text{-menthyl} \xrightarrow{H_2O} \underset{OH}{C_6H_5CH}CO_2H$$

l- menthyl l-mandelate (excess)
l-menthyl d-mandelate

l-mandelic acid (excess)
d-mandelic acid

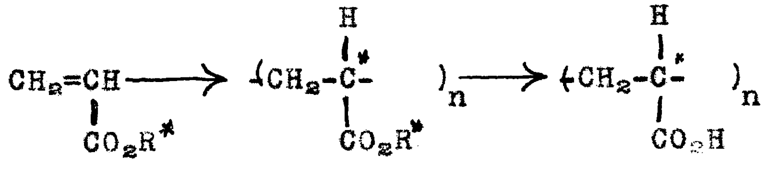
It will be noted that during the polymerization of an acrylate an asymmetric center is formed:



$$\underset{CO_2R}{CH_2=CH} \longrightarrow -(\,CH_2-\overset{H}{\underset{CO_2R}{C^*}}-\,)_n$$

If this compound were an optically active monomer, then under the influence of this active center, an asymmetric polymerization would take place, and the resultant polymer would be richer in one optically active form than in the other. Removal of the initial center would then leave a polymer which was active in its own right, that is, one which possessed optical activity inherent in the polymeric chain.

The formulation of our problem may then be summarized by the following series of equations:



$$\underset{CO_2R^*}{CH_2=CH} \longrightarrow (CH_2-\overset{H}{\underset{CO_2R^*}{C^*}}-\,)_n \longrightarrow (CH_2-\overset{H}{\underset{CO_2H}{C^*}}-\,)_n$$

Such a polymer, by the analogy of a pure active compound to its racemate, might be expected to have properties quite different from that of its diasteroisomers, properties such as hardness, higher point of fusion, etc. Marvel, Frank, and Prill[10] hoped to accomplish this by using an optically active peroxide as a catalyst. Frank[11] also prepared the brucine salt of acrylic acid, but was unable to polymerize it successfully.

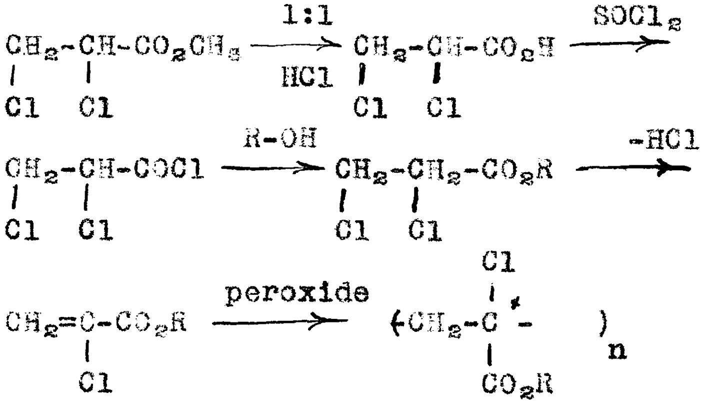
In seeking a suitable compound for study, l-menthyl α-chloroacrylate presented itself as a desirable possibility. The reasons for this were several: an alpha haloester would polymerize more rapidly than an ordinary acrylate, and the resultant polymer would also be an α-haloester with a much more reactive carbonyl group. It was for this latter reason that an ester of α-methacrylate was not chosen. Such a polymer would possess a carbonyl group attached to a tertiary carbon atom and would therefore be very unreactive. The use of l-menthol seemed appropriate because of its high rotatory power, and also because of its availability. The size of the l-menthyl group might also introduce a steric effect to promote the desired reaction.

After having once obtained the polymer, there are several means at ones disposal for degradating the polymer. Levesque,[12] using liquid ammonia, was able to convert polyesters into polyamides. This technique, however, would not be suitable for use on a polymer derived from a haloacrylate inasmuchas it would cause elimination of the halogen and probably racemization of any centers in the chain. Staudinger and Urech[13] successfully cleaved polyesters by an oxidative cleavage using concentrated nitric acid followed by dialysis in a pyroxylin sac. Probably the most obvious method of cleavage would be that involving alkaline hydrolysis, however this method would be open to question because of the possibility of racemization.

It is the author's intention to try both the oxidative cleavage and the hydrolytic approach, and if these fail, to devise another--possibly one based on an ester interchange.

DISCUSSION

The preparation of l-menthyl α-chloroacrylate proved to be much more difficult than was anticipated. Following the standard means as developed by Marvel and coworkers[14] the preparation of the following series of compounds was attempted:



$$\underset{Cl\quad Cl}{CH_2\text{-}CH\text{-}CO_2CH_3} \xrightarrow[HCl]{1:1} \underset{Cl\quad Cl}{CH_2\text{-}CH\text{-}CO_2H} \xrightarrow{SOCl_2}$$

$$\underset{Cl\quad Cl}{CH_2\text{-}CH\text{-}COCl} \xrightarrow{R\text{-}OH} \underset{Cl\quad Cl}{CH_2\text{-}CH_2\text{-}CO_2R} \xrightarrow{-HCl}$$

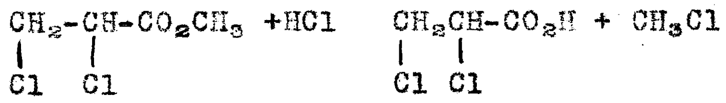
$$\underset{Cl}{CH_2=C\text{-}CO_2R} \xrightarrow{peroxide} \left(CH_2\text{-}\overset{Cl}{\underset{CO_2R}{C^{*}}}\text{-} \right)_n$$

l-Menthyl α, β -dichloropropionate was prepared as a new compound, but dehydrohalogenation could not be accomplished successfully. Both quinoline and pyridine were used to eliminate the hydrogen chloride from l-menthyl α, β -dichloropropionate while the conditions of the reaction were varied from gentle heating to refluxing, and from atmospheric conditions to a nitrogen atmosphere. In some cases slightly lower boiling fractions were obtained, but inasmuchas these failed to decolorize a solution of bromine in carbon tetrachloride, the variance was thought to be due to a difference in vacuum pressure and distillation conditions. This assumption later proved to be incorrect, because bromine in carbon tetrachloride is not decolorized by either l-menthyl α-chloro- or α-bromo-acrylates immediately, but only after standing overnight. The most successful preparation of a compound resembling the later prepared l-menthyl α-chloroacrylate was that using quinoline and heating the mixture at 150° in an oil bath for 30 minutes. Refluxing l-menthyl α, β -dichloropropionate with pyridine for one hour also seemed to give a product resembling the known compound, however a fifteen minute treatment only regenerated the starting material.

Under very strenuous conditions, that is refluxing a mixture of l-menthyl α, β -dichloropropionate and freshly distilled quinoline in a nitrogen atmosphere for 20 minutes, a chloroform soluble polymer was formed. It was also soluble in ether and dioxane, and could be precipitated as a light tan powder by adding any of the above solutions dropwise and with stirring to alcohol. The solutions of the polymer, however were brown in color and could neither be decolorized nor a polariscope reading taken to determine any optical rotation. A halogen determination, however showed 12.97% chlorine compared to the theoretical of 14.51% calculated for poly-l-menthyl α -chloroacrylate.

Because of the failure of the above attempts at dehydrohalogenation, and because of the vigorous experimental conditions necessary, other methods of eliminating hydrogen halide were tried on methyl α, β -dichloropropionate. Alcoholic potassium hydroxide gave an immediate precipitate with methyl α, β -dichloropropionate, the weight of which indicated complete removal of the propionate from solution. The nature of the reaction was not determined, however, potassium chloride had been formed. This was indicated by an X-Ray pattern. Since methyl α-chloroacrylate had not been formed, the reaction was not investigated further. Likewise, with morpholine in ether solution, a precipitate formed which was filtered off but upon working up the ether solution only a small amount, if any, of methyl α-chloroacrylate had been formed.

Before discussing the successful preparation of l-menthyl α-chloroacrylate, it might be well to by-pass at this point and discuss an interesting phenomenon observed in the preparation of α, β -dichloropropionic acid. This preparation invariably led to low yields, and all of the starting material could not be accounted for. In trying to locate this loss, it was found that an inert gas was being emitted from the top of the condenser during the hydrolysis process. This gas was insoluble in 5% sodium hydroxide; it failed to decolorize bromine in carbon tetrachloride; it was very soluble in cold ether and alcohol; and upon condensing some in a dry-ice acetone trap, was found to boil at about -18° as estimated on an ordinary thermometer. From this information it was concluded that the gas could either be methyl chloride, boiling point of -23°; or dimethyl ether, boiling point of -25°. An attempt to burn some as it issued from the condenser, hoping then to test for hydrogen chloride, proved unsuccessful. The liquid does burn, however, with a luminous flame. Another approach met with better success. This consisted of scrubbing the gas with a 10% solution of sodium hydroxide, then dissolving it in cold alcohol, and treating the solution with silver nitrate. Within five minutes a turbidity, which proved to be silver chloride, had formed. This certainly confirms the presence of methyl chloride, although the possibility of some dimothyl ether has not completely been eliminated. In view of the fact that methyl alcohol was tested and found not to give any such gas under similar experimental conditions, it was felt that either methyl chloride had been formed during the hydrolysis according to equation I:

I. 

$$\underset{Cl}{CH_2}-\underset{Cl}{CH}-CO_2CH_3 + HCl \quad \underset{Cl}{CH_2}\underset{Cl}{CH}-CO_2H + CH_3Cl$$

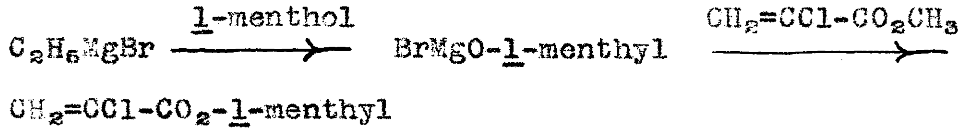
or else had been eliminated from the ester itself. (After chloroform extraction, the solution always has a very pleasant odor, perhaps due to a lactone). Since this was not the main interest, however, the reaction was not studied further.

It should be noted that the yields of α, β-dichloropropionic acid were successfully increased from 65% as reported by Marvel, Dec, Cooke, and Cowan[14] to 80%. This was accomplished by increasing the time of refluxing and by doubling the number of chloroform extractions. It is felt that the lower yields were due largely to an unfavorable equilibrium distribution set up between the chloroform and water layers.

The successful preparation of *l*-menthyl α-chloroacrylate and other related compounds listed as follows:

sec-butyl α-chloroacrylate
sec-butyl α-bromoacrylate
cyclohexyl α-chloroacrylate
cyclohexyl α-bromoacrylate
l-menthyl α-bromoacrylate

was accomplished through a unique method used in this laboratory by the action of an alkoxymagnesium halide on the appropriate methyl α-haloacrylate, thus:



$$C_2H_5MgBr \xrightarrow{\textit{l}\text{-menthol}} BrMgO\text{-}\textit{l}\text{-menthyl} \xrightarrow{CH_2{=}CCl\text{-}CO_2CH_3} CH_2{=}CCl\text{-}CO_2\text{-}\textit{l}\text{-menthyl}$$

Four of these compounds are listed in the literature.[14] The physical constants were found to check satisfactorily.

Poly-*l*-menthyl α-chloro- and α-bromo-acrylates were successfully prepared in dioxane solution using benzoyl peroxide as the catalyst. Poly-*l*-menthyl α-bromoacrylate displayed the unusual property of precipitating out of solution. It was so insoluble that an optical rotation could not be obtained even though a 0.1 gram sample in 50 ml. of dioxane was heated at 65° for 24 hours in an attempt to put it into solution.

Although the work was interrupted before a thorough investigation could be conducted, it should be pointed out that the chemical properties of the polymers derived from α-haloacrylates are not all that could be desired. In the brief work on oxidative cleavage with nitric acid, it was found that elimination of hydrogen halide occurred. Analysis of the resultant polymers showed that they still contained halogen, of the order of 9%; they were insoluble in water, but soluble in 5% sodium hydroxide. The imcomplete removal of halogen is suggestive of the work of Marvel and Cowan[1] and though it must represent some fundamental relationship, the results have not yet been interpreted.

Another disadvantage is the insolubility of poly-l-menthyl α-haloacrylates. The α-chloro compound is soluble in dioxane only to the extent of 1.6%, and the α-bromo compound is even less soluble.

In conclusion, then, the poly-l-menthyl α-haloacrylates seem to offer no promising characteristics.

EXPERIMENTAL

PREPARATION OF α, β -DICHLOROPROPIONIC ACID

To 212 grams (1.35 moles) of methyl α, β -dichloropropionate was added 400 ml. of 20% hydrochloric acid (1:1) and the mixture refluxed for nine hours. After cooling, the small amount of solid which invariably formed was removed by filtration, and the filtrate extracted seven times with 70 ml. portions of chloroform. This chloroform solution was dried over calcium chloride, then the solvent removed by distillation (b.p. 58-73°). The weight of the residue, α, β -dichloropropionic acid, was 154 grams (80%) and was used as such in its conversion to the acid chloride.

ISOLATION OF THE INERT GAS

To 245 grams (1.56 moles) of methyl α, β -dichloropropionate was added 250 ml. of concentrated hydrochloric acid and 200 ml. of water, and the mixture refluxed for eleven hours. During the process, the gas which escaped through the top of the condenser was collected in a dry ice-acetone trap, and found to weigh 28 grams (0.56 mole if methyl chloride, 34%). The approximate boiling point asestimated on an ordinary thermometer was -18°, which checks qualitatively with that of methyl chloride, -23°, or dimethyl ether, -25°.

The gas was tested and found to be insoluble in 5% sodium hydroxide solution, failed to decolorize a solution of bromine in carbon tetrachloride, and was appreciably soluble in cold ether, and alcohol. A cold alcohol solution was treated with 10% silver nitrate. No precipitate formed immediately, however within five minutes the solution became turbid. It was stoppered and placed in the ice box overnight. The slight precipitate was then filtered off, dissolved from the paper with dilute ammonium hydroxide, and this solution acidified with halogen free nitric acid. A curdy white precipitate formed in a sufficient quantity to be considered a good and positive test for methyl chloride.

The α, β -dichloropropionic acid obtained by working up hydrochloric acid solution as in the above experiment was 170.5 grams, (76.3%).

PREPARATION OF α, β -DICHLOROPROPIONYL CHLORIDE

To 70.5 grams (0.49 mole) of crude α, β -dichloropropionic acid was added 117 grams (0.98 mole) of thionyl chloride. The mixture was allowed to stand overnight, and then refluxed for one hour. The thionyl chloride was removed by distillation to a temperature of 79°, then the α, β -dichloropropionyl chloride collected by vacuum distillation. The yield of acid chloride boiling at 61-65° (20 mm.) was 56 grams (70.4%).

PREPARATION OF l-MENTHYL α, β -DICHLOROPROPIONATE

To 46.0 grams (0.269 mole) of l-menthol was added

46.5 grams (0.295 mole) of α, β-dichloropropionyl chloride. An exothermic reaction occurred with the concurrent evolution of hydrogen chloride gas. The reaction mixture was heated to very gently refluxing for thirty minutes, then cooled, dissolved in 100 ml. of chloroform, extracted with 5% sulfuric acid, washed with water, and dried over calcium chloride. Removal of the chloroform and vacuum distillation gave 67 grams (97% of 1-menthyl α, β-dichloropropionate).

The physical constants are as follows: b.p.= 117-120°/2 mm; $n_D^{20} = 1.4707$; $d_{20}^{20} = 1.0908$; $(\alpha)_D^{20}$ -50.2 (1.002 g. in 25 ml. carbon tetrachloride solution, a = -4.03°).

Anal. Calcd. for $C_{13}H_{22}O_2Cl_2$: Cl, 25.27. Found: Cl, 23.3.

ATTEMPTED PREPARATION OF 1-MENTHYL α-CHLOROACRYLATE

A. Quinoline Treatment.

To 60 grams (0.213 mole) of 1-menthyl α, β-dichloropropionate was added 35 grams (0.443 mole) of freshly distilled quinoline. The mixture was heated in an oil bath at 150° for 30 minutes. At the end of this time, the flask was partially cooled, water was added, then 200 ml. of ether. The layers were separated; the ether one being retained, washed several times with 5% sulfuric acid, water, and dried over calcium chloride.

Removal of the ether and subsequent vacuum distillation gave a product weighing 50 grams and boiling over a considerable range, 98-122°/2 mm.; $d_{20}^{20} = 1.067^{5}$;

$(\alpha)_D^{20}$ = -61.4 (2.122 g. in 25 ml. carbon tetrachloride solution, a = -10.43°).

B. Quinoline Treatment

To 50 grams (0.178 mole) of l-menthyl α, β-dichloropropionate was added 50 grams (0.380 mole) of quinoline, and the mixture refluxed for 30 minutes. In cooling, water was added as soon as it was expedient in order to prevent the formation of a solid cake. When cold, 200 ml. of ether was added and a separation effected. The ether layer was washed repeatedly with a 5% solution of sulfuric acid, then water, and finally dried over calcium chloride.

Removal of the ether and vacuum distillation gave only 7 grams of a product boiling at 94-100°/5 mm. The residue, 32 grams, was black and tarry in nature. The following constants on the liquid were taken: n_D^{20} = 1.4746; d_{20}^{20} = 0.9414; $(\alpha)_D^{20}$ = -61.8 (5.54 g. in 50 ml. carbon tetrachloride solution, a = -6.85).

To a 5.54 gram sample in 50 ml. of carbon tetrachloride was added 0.263 grams of benzoyl peroxide. At the end of eight days, no precipitate formed when the solution was poured into alcohol.

C. Quinoline Treatment in a Nitrogen Atmosphere

To 34 grams (0.430 mole) of freshly distilled quinoline was added 65 grams (0.23 mole) of l-menthyl α, β-dichloropropionate. The mixture was heated in a nitrogen atmosphere at the boiling point for 20 minutes, then cooled, taken up in chloroform, washed with a 10% sulfuric acid solution, water, dried over calcium chloride, and distilled under vacuum. There was no distillate. The residue in the flask, however, was found to be soluble in chloroform, dioxane, and ether. It could be precipitated as a light tan powder-like material by adding a dioxane solution dropwise to alcohol. It dissolved in each of the solvents to give a brown solution which did not lend themselves to polaroscope reading, and could not be decolorized by Darco carbon.

Anal. Calcd. for $C_{12}H_{21}O_2Cl$: Cl, 14.51. Found: Cl, 12.97.

D. Pyridine Treatment

To 26 grams (0.093 mole) of l-menthyl α, β -dichloropropionate was added 16 grams (0.20 mole) of pyridine. A cloudy suspension resulted which was refluxed for 15 minutes. Upon cooling, the mixture was dissolved in 100 ml. of chloroform, washed with a 5% sulfuric acid solution, water, and dried over calcium chloride.

Removal of the chloroform and vacuum distillation regenerated 16.5 grams of l-menthyl α, β -dichloropropionate, b.p. = 115-123°/3 mm.

E. Pyridine Treatment.

To 31.5 grams (0.112 mole) of l-menthyl α, β -dichloropropionate was added 19 grams (0.241 mole) of pyridine and the mixture refluxed for one hour. Upon cooling, the residue was dissolved in 100 ml. of chloroform, washed with a 5% sulfuric acid solution, water and dried over calcium chloride.

Removal of the chloroform and vacuum distillation gave 15 grams of product boiling at 100-110°/3 mm. A test with bromine in carbon tetrachloride solution gave a negative result. It was therefore thought that the desired compound had not been formed. This might be questioned now that the compound has been prepared and found to boil at 96-98°/3 mm.

ALCOHOLIC POTASSIUM HYDROXIDE AND METHYL α, β-DICHLOROPROPIONATE

To 20 grams (0.5 mole) of potassium hydroxide dissolved in 100 ml. of 90% ethyl alcohol was added 63 grams (0.4 mole) of methyl α, β-dichloropropionate. After refluxing for 15 minutes, the white precipitate (40 grams) which had formed immediately, was filtered off and the alcohol worked up as follows. It was taken up in 200 ml. of chloroform, washed with solutions of 10% sulfuric acid and 5% sodium hydroxide, water, and dried over calcium chloride. Removal of the chloroform and vacuum distillation gave 7 grams of product boiling near the range of methyl α-chloroacrylate, 62-69°/40-28 mm.

This 7 grams was treated with benzoyl peroxide in 10 ml. of dioxane, and after several days gave 5 grams of white polymer by precipitation in alcohol.

The above work was repeated omitting the refluxing operation. The amount of precipitate was greater, and no methyl α-chloroacrylate was obtained.

MORPHOLINE AND METHYL α, β-DICHLOROPROPIONATE

To 42 grams of methyl α, β-dichloropropionate was added 75 ml. of ether, then 25 grams of morpholine dropwise with stirring for the reaction is exothermic. The precipitate which formed was filtered, washed with ether, and found to weigh 28 grams. The filtrate was washed with 5% sulfuric acid, then water, and the ether solution dried over calcium chloride. Removal of the ether and vacuum distillation gave only 7 grams of product boiling near the range of methyl α-chloroacrylate. There was a residue of 22 grams.

PREPARATION OF METHYL α-BROMOACRYLATE

To 46 grams (0.350 mole) of crude quinoline was added 80 grams (0.325 mole) of methyl α, β-dibromopropionate, and the mixture distilled from an oil bath according to: b.p. to 80°/20 mm. Redistillation gave 45 grams (84%) of methyl α-bromoacrylate, b.p. 51-53°/ 18 mm.

PREPARATION OF sec-BUTYL α-BROMOACRYLATE

Ethylmagnesium bromide was prepared from 12 grams (0.500 mole) of magnesium and 55 grams (0.501 mole) of ethyl bromide in 100 ml. of anhydrous ether. To this mixture in a 500 ml. three-necked round-bottomed flask was added dropwise and with stirring 25 grams (0.337 mole) of *sec*-butyl alcohol in 100 ml. of anhydrous ether, then

70 grams (0.424 mole) of methyl α-bromoacrylate. The contents were stirred at room temperature overnight.

At the end of this time a whitish precipitate had formed. The contents of the flask were poured into an ice-hydrochloric mixture and stirred until all precipitate had dissolved and two homogeneous, clear layers had formed. These were separated, the water layer extracted with ether, and the ether extracts combined and dried over calcium chloride.

After filtering and removing the ether, the residue was distilled giving 54 grams (59% of ester). The physical constants were as follows: b.p.= 78-81°/24 mm; n_D^{20} = 1.4587; d_{20}^{20} = 1.3072.

PREPARATION OF CYCLOHEXYL α-BROMOACRYLATE

Ethylmagnesium bromide was prepared in a 500 ml. three-necked round-bottomed flask from 8 grams (0.333 mole) of magnesium, 37 grams (0.340 mole) of ethylbromide in 75 ml. of anhydrous ether.

To this solution was added dropwise and with stirring 32 grams (0.320 mole) of cyclohexanol in 15 ml. of anhydrous ether. A white precipitate formed which remained insoluble even when more anhydrous ether was added. Methyl α-bromoacrylate, 45 grams (0.273 mole), was now added and the mixture stirred overnight. At the end of this time it had acquired a milky appearance. It was poured into an ice-hydrochloric acid mixture and stirred until two homogeneous layers had formed. These were separated, the water layer extracted with ether, and the ether extracts combined and dried over calcium chloride.

After filtration and removal of the ether, the residue was distilled under vacuum giving 50 grams (79%) of colorless ester.

The physical constants were as follows: b.p. = 31-35°/3 mm; n_D^{20} = 1.4956; d_{20}^{20} = 1.3480.

PREPARATION OF 1-MENTHYL α-BROMOACRYLATE

Ethylmagnesium bromide was prepared in a 500 ml. three-necked round-bottomed flask from 8 grams (0.333 mole) of magnesium, 40 grams (0.367 mole) of ethyl bromide, and in 125 ml. of anhydrous ether. To this was added dropwise and with stirring a solution of 40 grams (0.254 mole) of l-menthol in 75 ml. of anhydrous ether.

Methyl α-bromoacrylate, 45 grams (0.273 mole), was now introduced and the mixture stirred for 24 hours. It was worked up by pouring into an ice-hydrochloric acid mixture and stirring until two homogeneous layers had formed. The layers were separated, the water layer extracted with ether, and the combined ether extracts dried over calcium chloride.

After filtration and removal of the ether, the residue was distilled under vacuum giving 47 grams (65%) of l-menthyl α-bromoacrylate as a very pale yellow-green, viscous liquid.

Its physical constants were as follows: b.p.= 100°/3 mm; n_D^{20}= 1.4859; d_{20}^{20} = 1.2007; $(\alpha)_D^{20}$ -74.1

(1.275 g. in 25 ml. carbon tetrachloride solution, a= -7.56°).

Dioxane could not be used in determining the optical rotation because the solution became turbid.

Anal. Calcd. for $C_{13}H_{21}O_2Br$: Br, 27.68; R, molecular refractivity, 69.1. Found: Br, 27.92; R, 69.1.

POLYMER OF l-MENTHYL α- BROMOACRYLATE

To 20 grams of l-menthyl α-bromoacrylate was added 100 ml. of dioxane, a pinch of benzoyl peroxide, and the mixture allowed to stand at room temperature. Within a few days, a white precipitate had formed; at the end of one month, this precipitate was removed by filtration, dried, and found to weigh 16.0 grams. An additional 3 grams was recovered from the filtrate by precipitation in excess alcohol. The total conversion was 95%.

Anal. Calcd. for $C_{13}H_{21}O_2Br$: Br, 27.68. Found: Br, 27.42.

An optical rotation could not be determined. A 0.111 gram sample heated in 50 ml. of dioxane at 65° for 24 hours gave only a cloudy suspension.

PREPARATION OF METHYL α-CHLOROACRYLATE

To 70 grams (0.445 mole) of methyl α, β -dichloropropionate was added 57 grams (0.442 mole) of purified quinoline and the mixture vacuum distilled using a fairly high pressure. Forty four grams of crude methyl α-chloroacrylate was collected boiling at 90-100°/100 mm.

This was redistilled before use and the fraction boiling at 43-57°/18 mm. taken: 32 grams (79%).

PREPARATION OF sec-BUTYL α-CHLOROACRYLATE

To 170 ml. of ethylmagnesium bromide solution (M= 1.5, 0.255 mole) in a 500 ml. three-necked round-bottomed flask was added dropwise and with stirring a solution of 19 grams (0.256 mole) of sec-butyl alcohol in 50 ml. of anhydrous ether. To this was added 30 grams (0.250 mole) of methyl α-chloroacrylate and the mixture stirred overnight.

The contents of the flask were now poured into an ice-hydrochloric acid mixture and stirred until the precipitate dissolved and two clear layers had formed. These were separated; the water layer extracted with ether, and the ether extracts combined and dried over calcium chloride. Filtration and removal of the ether followed by vacuum distillation gave 32 grams (79%) of sec-butyl α-chloroacrylate.

The physical constants were as follows: b.p.= 67-69°/18 mm; n_D^{20} = 1.4362; d_{20}^{20} = 1.0480.

POLYMER OF sec-BUTYL α-CHLOROACRYLATE

A 23 gram sample which had stood at room temperature for six months solidified to a clear, light amber solid. Upon dissolving this in dioxane and reprecipitating it by adding the dioxane solution dropwise to water, 22 grams (95%) of a stringy polymer was obtained.

OXIDATION OF POLY-sec-BUTYL α-CHLOROACRYLATE WITH NITRIC ACID

A. To 5.0 grams of poly-sec-butyl α-chloroacrylate was added 85 ml. of concentrated nitric acid, and the mixture refluxed for one hour. During this process, a copious evolution of nitric oxide gas occurred, and the polymer first fused together and then dissolved. The gases which emitted from the top of the condenser were tested with 10% silver nitrate solution and gave a positive halogen test.

Upon dilution of the nitric acid solution, a white precipitate formed which was removed by filtration, washed, dried at 80° for 3 hours, and found to weigh 2.2 grams. It was powdery in nature, insoluble in water, but soluble in 5% sodium hydroxide solution.

Anal. Calcd. for poly-sec-butyl α-chloroacrylate: Cl, 21.83. Calcd. for poly-α-chloroacrylic acid: Cl, 33.3. Found: Cl, 8.91.

B. To 3.0 grams of poly-sec-butyl α-chloroacrylate was added 50 ml. of concentrated nitric acid and the mixture refluxed for 3 hours. Upon dilution, a white precipitate formed which was removed by filtration, washed, dried for 3 hours at 80°, and found to weigh 1.5 grams. It was hard and brittle, insoluble in water, but soluble in 5% sodium hydroxide solution.

Anal. Calcd. for poly-sec-butyl α-chloroacrylate: Cl, 21.83. Calcd. for poly-α-chloroacrylic acid: Cl, 33.3. Found: Cl, 9.46.

PREPARATION OF CYCLOHEXYL α-CHLOROACRYLATE

To 200 ml. of ethylmagnesium bromide solution (1.5 M., 0.300 mole) in a 500 ml. three-necked round-bottomed flask was added dropwise and with stirring a solution of 27.6 grams (0.276 mole) of cyclohexanol in 75 ml. of anhydrous ether. Then 34 grams (0.282 mole) of methyl α-chloroacrylate was introduced and the mixture stirred overnight.

The contents were now added to an ice-hydrochloric acid mixture, stirred until the ether and water layers were clear, then the ether layer separated. The water layer was extracted again with ether and the extracts combined and dried over calcium chloride.

After filtration and removal of the ether, the residue was vacuum distilled. The yield was 38 grams (73%) of ester: b.p.= 111° (18 mm.); $n_D^{20} = 1.4751$; $d_{20}^{20} = 1.1144$.

PREPARATION OF 1-MENTHYL α-CHLOROACRYLATE

To 145 ml. of ethylmagnesium bromide solution (1.5 M., 0.217 mole) in a 500 ml. three-necked round-bottomed flask was added dropwise and with stirring a solution of 31 grams (0.199 mole) of _l_-menthol in 100 ml. of anhydrous ether. To this was added 29 grams (0.240 mole) of methyl α-chloroacrylate and the mixture stirred overnight. As the acrylate was added, the solution acquired a yellowish green color and some heat was evolved as indicated by an increase in reflux of the ether in the condenser.

After stirring overnight, the mixture had acquired a white precipitate. The total contents were poured into an ice-hydrochloric acid mixture and stirred until two homogeneous liquid layers resulted. The ether layer was separated, the water washed with ether, and the extracts combined and dried over calcium chloride. Filtration, removal of the ether, and vacuum distillation of the residue gave 40 grams (65.5%) of l-menthyl α-chloroacrylate.

The physical constants of this product were found to be: b.p.= 96-99°/3 mm.; n_D^{20} = 1.4712; d_{20}^{20} = 1.0326; $(\alpha)_D^{20}$ -80.72 (2.388 g. in 25 ml. dioxane solution, a= -15.42).

Anal. Calcd. for $C_{13}H_{21}O_2Cl$: Cl, 14.51; R, molecular refractivity, 66.2. Found: Cl, 14.30; R, 66.2.

POLYMER OF l-MENTHYL α-CHLOROACRYLATE

To 10 grams of l-menthyl α-chloroacrylate in 75 ml. of dioxane was added a pinch of benzoyl peroxide and the solution allowed to stand at room temperature for a month and a half. This solution was added dropwise to alcohol and the white precipitate which formed filtered off, dried, and found to weigh 6 grams (60%).

Anal. Calcd. for $C_{13}H_{21}O_2Cl$: Cl, 14.51. Found: Cl, 13.[illegible]7. $(\alpha)_D^{31}$ -73.7 (0.335 g. in 50 ml. dioxane solution, a= -0.99°).

A saturated solution of poly l-menthyl α-chloroacrylate gave a rotation of -2.41°. The calculated solubility is therefore 1.64%. Upon evaporating a 2 ml. portion to dryness and drying at 100°, a weight of 0.0319 gram was obtained. This corresponds to a solubility of 1.60%.

OXIDATION OF POLY l-MENTHYL α-CHLOROACRYLATE WITH NITRIC ACID.

To 0.5 grams of poly-*l*-menthyl α-chloroacrylate was added 10 ml. of concentrated nitric acid and 10 ml. of dioxane (for the purpose of wetting). Oxidation was incomplete at the end of two hours so an additional 10 ml. of concentrated nitric acid was added and the refluxing continued for another two hours. The precipitate which formed upon dilution was filtered, dried, and found to weigh 0.4 gram.

Anal. Calcd. for poly-*l*-menthyl α-chloroacrylate: Cl; 14.51. Calcd. for poly-α-chloroacrylic acid: Cl, 33.3. Found: Cl, 5.95.

The difference from poly-*sec*-butyl α-chloroacrylate might be explained by an incomplete hydrolysis of the ester grouping.

SUMMARY

The preparation of *l*-menthyl α, β -dichloropropionate as a new compound has been completed. An attempt to dehydrohalogenate it to the corresponding α-chloroacrylate using both quinoline and pyridine proved to be unsuccessful.

The reaction between an alkoxymagnesium bromide and an ester to form a new ester has been extended to the synthesis of the following compounds: *sec*-butyl α-bromoacrylate, *sec*-butyl α-chloroacrylate, cyclohexyl α-bromoacrylate, and cyclohexyl α-chloroacrylate. These are known compounds, and the physical constants have been found to check satisfactorily. In a like manner, the esters *l*-menthyl α-bromoacrylate and *l*-menthyl α-chloroacrylate have also been prepared as new compounds and characterized.

The polymers of α-chloroacrylates were found to be unsuited for chemical study in such reactions as oxidative cleavage of the ester grouping. Such reactions result in an elimination of hydrogen chloride as well as the cleavage.

The solubilities of *l*-menthyl α-chloro- and α-bromo-acrylates were found to be exceedingly low, too low to make the compounds of any practical value.

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II. PURIFICATION OF BUTADIENE; NEW MODIFIERS FOR BUTADIENE-STYRENE COPOLYMERS.

INTRODUCTION

The work of the W.P.B. Rubber Research group at the University of Illinois was concerned primarily with the determination of structure and the mechanism of polymerization of standard GR-S rubber. The author's particular problem followed along two lines: one, the preparation of very pure butadiene, and two, the preparation and study of new modifiers.[9]

A. Pure Butadiene

It has been known for some time that the presence of even traces of certain impurities will greatly alter the rubber formed in the standard GR-S recipe. It was therefore necessary to develop a means of purifying commercial butadiene in order to determine these impurities and their effect on the polymerization. This purification was to be accomplished through the preparation and subsequent thermal decomposition of butadiene cyclic sulfone, a method which at the present time was considered to give the most reliable results.

Having prepared the very pure butadiene, the effects of three known impurities, acetylene, vinylacetylene, and methylallene, were to be studied. The preparation of ethylacetylene was included in the present work.

Another problem which arose was a simple and quick analytical means of checking the purity of butadiene.

It was proposed that a gas interferometer be tried as a possible solution. It is reported to have an excellent accuracy and might possibly be useful in detecting traces of impurities without being able to identify them.

B. Modifiers

It had been observed that commercial dodecyl mercaptan (Naugatuck O.E.I.) was used up in the early stages of polymerization when it is not particularily needed and thus produced an over-modified product; it was therefore exhausted in the final stages where it was critically needed with the result that an under-modified, or benzene insoluble, rubber was formed. A program, designed to introduce the modifier gradually, was therefore proposed. Two methods suggested themselves: one, to introduce the modifier stepwise, and two, to generate the modifier in the polymerization system.

1. Derivatives of dodecyl mercaptan.

The latter approach of generating the modifier in the polymerization system, was undertaken. Several thiolesters of commercial n-dodecyl mercaptan (Naugatuck O.E.I.) were prepared and used as modifiers in the standard GR-S formula. It was hoped that these would hydrolyze in the alkaline soap solution and thus constitute an effective stepwise addition of the modifier. Organic acids of varying strengths were used because this factor might determine the rate of hydrolysis of the thiolester. Added alkali might also increase this rate and was therefore tried.

The solubility of the thiolesters in the water layer was thought to be an important factor. This solubility could be increased by introducing a solubilizing group. Several half thiolesters of dibasic organic acids, such as dodecyl acid thiolsuccinate, were prepared to be used as modifiers.

2. Other compounds.

Several other compounds which were not derivatives of dodecyl mercaptan were also of interest. Dimercaptans, according to the chain transfer mechanism of polymerization, should product long chain polymers which might or might not be insoluble, yet the effects of ethylene dimercaptan and decamethylene dimercaptan were sufficiently different to warrant the study of some intermediate compound. In this connection, hexamethylene dimercaptan was prepared and tested. Another point of interest was the comparison of tertiary and normal mercaptans. It had been pointed out that tertiary mercaptans were very effective modifiers. There was a particular interest in Esso S.O.D. which is a <u>tert</u>-octyl mercaptan. A comparison of this compound with <u>n</u>-octyl mercaptan was therefore included in the present work.

Other compounds such as melissyl mercaptan were prepared for usage by other members of the laboratory.

HISTORICAL AND THEORETICAL

A. Purification of Butadiene.

There are several methods listed in the literature for the purification of dienes. As early as 1910, Badische Anilin - und Soda Fabrik[1] obtained a patent for the purification of dienes through the use of sulfur dioxide. Harries,[2] and Hoffmann and Damm[3] likewise used sulfur dioxide in their purification of dienes. Staudinger[4] pointed out that the course of reaction could be entirely altered by the presence of peroxides. Thus in their presence, dienes polymerize with sulfur dioxide to produce a polysulfone. In the presence of such reagents as phenol, resorcinol, phloroglucinol, hydroquinone, pyrocatechol, and pyrogallol, liquids sulfur dioxide and butadiene react to form a cyclic sulfone, monomeric in nature. Pyrogallol was the best agent, however the same results could be obtained using slightly larger amounts of hydroquinone.

The monomeric sulfones are stable[4] in concentrated sulfuric and nitric acids, but are hydrolyzed by alkalis. Sulfones in general may be thermally decomposed at a temperature characteristic of their structure: monomeric cyclic sulfones are decomposed at temperatures between 100-150° whereas polymeric sulfones require a temperature anywhere from 200° to 300°. Staudinger[4] suggested a temperature of 120-130° for the decomposition of butadiene cyclic sulfone.

From a theoretical point of view, a thermal decomposition yielding a pure material might be questioned. Certainly the butadiene must separate from the butadiene cyclic sulfone as a free radical, and as such, would be capable of any number of rearrangements. The only argument in favor of this method is the fact that the temperature of decomposition is so low that any radical change in structure is unlikely, and anomolous results have not yet been observed.

B. Modifiers.

The subject of modifiers and modifier activity in the preparation of synthetic rubber is too recent to have any extensive historical background. The fact that sulfur compounds have long been used as accelerators in the vulcanization of natural rubber may have led to their investigation as modifiers for synthetic rubber. However, a surprisingly large number of compounds have now been studied and their results summarized in an official report.[8]

1. Derivatives of dodecyl mercaptan.

Until recently, there has only been a limited amount of work done on mercaptans and mercaptan derivatives. This limitation might be explained by the fact that one of the invariable starting materials, the mercaptan, is mildly toxic, may produce skin irritations similar to poison ivy, and at least the lower members have penetrating odors, characteristic and very unpleasant.

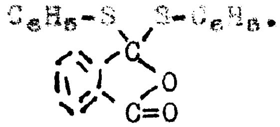
Gilman[6] lists several methods of preparing thiolesters. Among these are two which were of particular interest:

$$\text{I. } RCOCl + R'SH \rightarrow RCOSR' + HCl$$

$$\text{II. } RCOCl + R'SNa \rightarrow RCOSR' + NaCl.$$

Although the acid chlorides of aromatic compounds react with mercaptans in aqueous alkali according to equation II to give satisfactory results, Michler[7], and Jones and Tasker[8] have pointed out that aliphatic derivatives hydrolyze too rapidly for this method to be used. Oxalyl chloride[8], however, reacts violently with mercaptans, even in ether solution at 0°, according to equation I. Holmberg[10] and Ralston, Segebrecht, and Bauer[11] have pointed out that acylation proceeds much more smoothly and in accordance with equation I in the presence of tertiary amines such as pyridine or trimethylamine. It was this modification which was largely used in the following work.

The reaction between anhydrides and mercaptans apparently have never been studied. There were no directions in the literature for the preparation of half thiolesters of organic dibasic acids, and only a few references where anhydrides have been used for any acylations of mercaptans. Wertheim[12] proposed 3-nitrophthalic anhydride as a means for identification of mercaptans. Chakravarti and Saha[13] condensed thiophenol and phthalic anhydride and obtained two isomeric products: diphenyl dithiophthalate, and a compound whose structure was given as



These same products were obtained from phthalyl chloride and thiophenol. Hurd and Williams[14] used ketene, an internal anhydride, to prepare thiolacetates. Finally, maleic anhydride unique because of its double bond, was found to react[15] with thiolacetic acid to form an -thiosuccinic acid derivative. Even Beilstein lists no half thiolesters of either succinic, maleic, fumaric, phthalic, or oxalic acids.

The use of pyridine in conjunction with succinic anhydride to prepare these half thiolesters was new, however it does find some justification in the work of the sugar chemists in the preparation of oxyesters. It has since been found that Ruzicka, Goldberg, and Grob[16] used succinic anhydride and absolute pyridine to prepare the succinic acid half ester of dihydrotestosterone.

2. Other compounds.

From a theoretical point of view, dimercaptans, according to the chain transfer mechanism of polymerization should produce long chain polymers which may or may not be benzene soluble. The variance of ethylene and decamethylene mercaptans were sufficiently different to warrant the preparation and study of an intermediate such as hexamethylene dimercaptan. This compound had first been prepared, and characterized, by von Braun[17] from 1,6-diiodohexane and ammonium dithiocarbamate, however the action of thiourea on 1,6-dibromohexane was tried and found to be a good method of preparation.

Ethyl and octyl thioglycolates have been studied as modifiers, but were not found to be satisfactory. Cyclohexyl thioglycolate was studied to determine the effect of the cyclic structure. Its preparation was not given in the literature, however as a typical ester it was prepared in the standard way.

Melissyl mercaptan was also prepared but not studied as a modifier. The synthesis was interesting because it began with the saponification of carnauba wax to obtain the alcohol, then the bromide, and finally the mercaptan by means of thiourea. Haiduschka and Garies[18] used bromine and phosphorus on the alcohol to prepare the bromide, however, two methods given in Organic Syntheses for other alkyl bromides were tried and seemed very satisfactory. Melissyl mercaptan has not previously been prepared.

The other compounds studied were available from the laboratory's supply of chemicals.

DISCUSSION

A. Pure Butadiene.

1. Preparation

The directions for the preparation of butadiene cyclic sulfone were obtained from the du Pont Experimental Station, however, they required adaptation to the equipment in our laboratory. Whereas the instructions called for a 10-liter stainless steel autoclave, we had a 1-liter high pressure hydrogenation bomb; and where pyrogallol was used as an inhibitor to polysulfone formation, this same pyrogallol reacted with the iron of the bomb to form a blue black, ink-like, colored material which could not be successfully removed from the crystalline sulfone either chemically or by recrystallization. Although this color would probably have made little difference in the final production of pure butadiene, it hardly rendered the cyclic sulfone a useful looking material. The problem was successfully solved by substituting hydroquinone for pyrogallol. The cyclic sulfone came out white with yields equally as good as those using pyrogallol. It was found that the cyclic sulfone could be recrystallized more successfully from methanol than water; the loss was less and the color stability greater, that is, it did not change color upon standing. There was probably traces of hydroquinone still present, however, its presence was probably more beneficial than harmful because it would exclude any possibility of a transformation to the polysulfone.

Because of the large number of preparations of butadiene cyclic sulfone necessary, the experimental conditions could be carefully studied. It was found that considerable polysulfone was formed in the absence of the methanol solvent. Experiments conducted using recovered methanol from the recrystallization step showed that this procedure was not expedient. It was also found that shortening the heating period was not advisable.

The regeneration of pure butadiene was easily accomplished by thermal decomposition of the cyclic sulfone at 140-150° as given in the experimental part.

In each preparation of butadiene cyclic sulfone, there was invariably formed a small amount of methanol insoluble material. This could either be butadiene polysulfone, or a polysulfone formed from impurities present in the commercial butadiene. These were saved, although the amount in the preparation of two and one half kilos of butadiene cyclic sulfone corresponded to only a few grams, with the thought in mind of decomposing it and identifying these possible impurities. This decomposition was posponed pending the development of a successful infra-red spectral method of analysis. A small amount of butadiene polysulfone was prepared and compared with the above sample. It seemed to be identical, but exact comparisons were not easily carried out because of the insoluble character of the materials.

The residues from thermal decomposition of butadiene cyclic sulfone have also been saved with a similar thought in mind--to identify the impurities still present in the cyclic sulfone.

2. Study of Impurities

Ethylacetylene is one of the impurities known to be present in commercial butadiene. Its synthesis was accomplished by the method of Hurd and Williams[19] which consisted of condensing diethyl sulfate with sodium acetylide in liquid ammonia. Although the improved technique of adding the sodium and acetylene concurrently was used, the yields were no better than they reported. The crude ethylacetylene was purified by distillation through a modified Davis[20] column. A 1% residue of a liquid boiling somewhat above room temperature remained in the flask, and was thought to be diethylacetylene. Pending work on very pure starting materials, the effect of ethylacetylene on the GR-S polymerization has not yet been determined.

3. Use of the Gas Interferometer* for Testing Purity

The use of a gas interferometer was also tried as a method of testing for, without identifying, impurities in butadiene. It is said that such an interferometer will detect the carbon dioxide in air with an accuracy of 1/50

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* The author wishes to express his thanks to the Analytical Division of the University of Illinois for the use of their portable interferometer.

of 1%. Such precision should be useful in the above problem. When tried, butadiene and ethylacetylene showed a difference of some 2500 units. The author was unable to find a suitable standard, however although methyl bromide, ethylacetylene, and even butadiene itself were tried. The method was therefore abandoned.

B. Modifiers.

1. Derivatives of Dodecyl Mercaptan

The following derivatives of commercial dodecyl mercaptan (Naugatuck O.E.I.) were all prepared by the method of Holmberg[10] which consisted of condensing the mercaptan and acid chloride in the presence of pyridine: dodecyl thiolbenzoate, dodecyl p-nitrothiolbenzoate, dodecyl monochlorothiolacetate, and dodecyl thioloxalate. It is better to omit pyridine in the reaction mixture in the preparation of the monochlorothiolacetate. Its use necessitates a washing step which results in extensive hydrolysis of the thiolester and greatly reduces the yield.

Sulfur analyses on these compounds were invariably low. A mercaptan analysis[21] on the original O.E.I. showed its average molecular weight to be 243 as compared to 202 for dodecyl mercaptan. This value is in agreement with, and explains, the lower sulfur results on the thiolesters.

These compounds with the exception of p-nitrothiolbenzoate were also tried as modifiers in the standard

GR-S formula, but all gave unsatisfactory results. Dodecyl monochloroacetate was a promoter, but not a modifier. Dodecyl thioloxalate was a promotor, but gave lower yields than the standard and modified only in three equivalent concentrations. Dodecyl thiolbenzoate was an inhibitor.

The dodecyl thiolacetate was prepared from O.E.I., acetic anhydride, and pyridine. By itself, dodecyl thiolacetate was a promotor, but not a modifier. The presence of added alkali made little difference on the yield, but it did alter the product. As the concentration of alkali increased, the solubility of the corresponding rubbers also increased, particularily with the higher amounts of alkali. This can be explained by assuming the increase in alkali results in a more rapid rate of hydrolysis of the thiolacetate thus making the mercaptan available for modifying action.

Dodecyl trithiocarbonate was also used with alkali, but the results could not be interpreted. Alone, it acts as a promotor, but not a modifier.

2. Other Modifiers

Hexamethylene dimercaptan was prepared and identified by its dibenzoate. It was found to be a good promotor and behaved as a fair modifier in three molar equivalent concentration.

Cyclohexyl thioglycolate was prepared by a standard method using thioglycolic acid, cyclohexanol, and p-toluenesulfonic acid as the catalyst. It was a new compound and was therefore characterized and analyzed. Its behavior as a modifier was analogous to ethyl and octyl thioglycolates. In low concentrations, it behaved as a promoter, but in three equivalent concentrations, became a powerful inhibitor.

The comparison of tertiary and normal mercaptans gave rather unexpected results. n-Octyl mercaptan gave a rubber that was superior to the standard, but in lower yields, whereas tert-octyl mercaptan gave an inferior product, also in lower yields.

The B. F. Goodrich method of mercaptan analysis along with some typical results has been included as a source of reference.

EXPERIMENTAL

PREPARATION OF BUTADIENE CYCLIC SULFONE

A solution of 5.0 grams of hydroquinone in 50 ml. of methanol was placed in the glass liner of a liter-capacity high-pressure hydrogenation bomb and cooled in a dry ice-acetone bath. To this was added 121.5 grams (1.90 moles) of liquid sulfur dioxide, obtained from a commercial tank by condensation in a dry ice-acetone trap, and 10[illegible].3 grams (1.91 moles) of liquid butadiene, obtained in a similer way. The cold cylinder was immediately sealed in the bomb which was then heated for 24 hours in a water bath maintained at 80-90° by means of a steam cone. At the end of this time, the water in the bath was replaced by cold tap water, and the bomb allowed to cool before opening. The contents of the cylinder were poured into a 400 ml. beaker, heated to boiling, and filtered through a flutted filter paper. Upon cooling the methanol filtrate in an ice-salt bath, butadiene cyclic sulfone separated as a copious, yellowish precipitate which was filtered and washed to a white product with cold methanol. An additional quantity of butadiene cyclic sulfone was obtained by washing the interior of the bomb with hot water, filtering, and recrystallizing from an ice bath. The total yield of butadiene cyclic sulfone was 182.7 grams (81.4%).

The results of numerous preparations are listed in the following table:

TABLE I.

Butadiene Cyclic Sulfone.

Run	Methanol, ml.	Hydroquinone, gms.	SO_2, gms.	Butadiene, gms.	$C_4H_6SO_2$, gms.	% Yield
1.	40	0.8	77.5	48.0	68.3	65.2
2.	50	3.0	76.2	79.4	109.2	77.6
3.	50	4.0	102.1	90.7	136.8	70.7
4.	50	3.0	111.4	90.6	145.3	73.1
5.	50	4.0	132.4	110.8	191.1	78.9
6.	50	4.0	118.7	123.7	181.1	79.5
7.	50	4.0	105.1	190.6	157.6	81.4
8.	50	4.0	142.3	101.4	164.6	74.6
9.	50	4.0	159.1	132.5	155.1	55.5[1]
10.	50	5.0	177.5	115.3	215.0	86.4
11.	50	4.5	146.0	122.8	218.2	81.4
12.	50	4.5	130.4	108.5	176.5	74.3
13.	50	5.0	121.5	103.3	182.7	81.4
14[2]	-	9.5	195.1	166.8	241.5	68.4
15.	50	5.0	159.8	135.7	243.5	82.8[3]
16.	50	5.0	119.3	92.2	173.8	79.4
17.	50	5.0	130.8	115.3	192.9	80.0
18.	50	5.0	116.3	97.7	161.0	75.4
19[4]	50	5.0	134.5	115.4	159.5	65.0
20[4]	50	4.0	134.3	116.0	184.0	74.5
21[4]	50	4.0	122.3	105.7	186.0	82.0
22[4]	100	4.0	146.2	109.0	202.7	85.9
23[4]	100	3.0	120.7	103.1	135.8	61.0[5]
24[4]	100	4.0	158.6	102.8	201.0	89.5
25[4]	100	5.0	140.3	123.2	182.0	70.8
26[4]	100	5.5	143.7	121.5	193.7	73.3
27[4]	100	5.0	129.8	110.7	194.2	81.1
28[4]	100	10.0	156.1	106.2	179.2	77.1
29.	100	5.0	156.0	107.0	163.4	70.0
30.	100	10.0	119.7	98.0	163.5	75.0
31[4]	100	10.0	144.5	101.7	172.4	77.6
32[4]	50	10.0	143.7	90.7	170.8	86.2
33.	50	7.0	141.7	122.8	211.8	81.0
34[4]	50	10.0	133.0	106.0	201.2	86.7
35[4]	50	8.0	133.1	108.2	202.3	85.4
36.	50	8.0	130.2	105.8	184.8	79.8
37.	50	7.5	142.5	116.5	212.7	85.5
38.	50	8.0	134.0	102.5	197.0	87.0
39.	50	5.5	163.8	115.4	235.1	93.0
40.	50	6.2	144.0	109.0	211.1	88.5
41.	50	4.2	137.3	122.0	226.9	89.8

1. The heating period was reduced from twenty four hours to seven hours.
2. The solvent was omitted; 18 grams of insoluble polysulfone was formed.
3. When the $C_4H_6.SO_2$ ppt. was recrystallized once from

water, the yield dropped to 69.2%.
4. The methanol used in these syntheses consisted of the filtrate of the recrystallization of the butadiene cyclic sulfone from the preceding determination.
5. There was also obtained 31.8 grams of butadiene polysulfone (14.3%).

The effect of pyrogallol is indicated in the following: 46 grams of liquid sulfur dioxide and 28 grams of liquid butadiene in 30 ml. of methanol containing 0.5 grams of pyrogallol gave 48 grams (78%) of black colored butadiene cyclic sulfone. After three recrystallizations, the product was white and weighed 22 grams (36%).

RECRYSTALLIZATION OF BUTADIENE CYCLIC SULFONE

Two thousand six hundred and nineteen grams of crude butadiene cyclic sulfone of m.p. 61-63° was recrystallized from 2.5 liters of methanol by the process of warming, decolorization with carbon, filtering, and cooling in an ice-salt bath. The precipitate was then washed with an additional liter of cold methanol.

There was recovered 2410 grams of white product, or 92%. The melting point as recorded on a Fisher Melting Point apparatus was 62.5-63°.

PREPARATION OF BUTADIENE POLYSULFONE

To 5 ml. of methanol was added a pinch of Lucidol (benzoyl peroxide) and the solution placed in a 10 mm. Pyrex tube. To this was added 8.9 grams (0.139 mole) of liquid sulfur dioxide and 6.2 grams (0.115 mole) of liquid butadiene, and the tube sealed off.

The contents were heated at 50° for one day, at the end of which time, a white solid had formed. The tube was broken and the polysulfone removed.

The product was pure white in color and weighed 12.1 grams (91.1%).

It was found to be insoluble in such solvents as water, alcohol, ether, methanol, chloroform, dioxane, S-271, and acetone, and therefore could not be purified further by recrystallization. This behavior was checked with that of the polysulfone obtained in the preparation of butadiene cyclic sulfone and found to be the same.

PREPARATION OF BUTADIENE FROM BUTADIENE CYCLIC SULFONE

Twenty five grams of butadiene cyclic sulfone was placed in a 125 ml. distilling flask and thermally decomposed at 140-150° by heating the flask in an oil bath. The effluent gases were purified by passing them through a washing train consisting of 20% potassium hydroxide solution, solid calcium chloride, solid sodium hydroxide, and collecting the pure butadiene in a dry ice-acetone bath. The yield was 10 grams (80.5%).

PREPARATION OF ETHYLACETYLENE

Seven hundred and fifty milliliters of liquid ammonia in a one-liter three-necked flask cooled by a dry ice bath was saturated with commercial acetylene which had been purified by passing it through a train consisting of a tower of water and one of concentrated sulfuric acid. During this and the addition of the sodium, stirring was continuous and the outlet tube of the flask was connected to a water aspirator which removed any escaping ammonia gas. Forty three grams (1.87 moles) of sodium metal which had been scrapped clean and cut into small pieces was added. The formation of the undesirable blue color was avoided by the concurrent introduction of acetylene gas.

After all of the sodium had been added, the inlet tube was replaced by a dropping funnel with a pressure regulator; and the inlet tube, by a train consisting of a trap, scrubbing towers of water (a liter separatory funnel was used in which water could be introduced into the to and withdrawn from the bottom in a continuous fashion) and 10% sulfuric acid, a calcium chloride drying tube, and a dry ice-acetone condenser trap.

To this sodium acetylide was then added, dropwise and with stirring, 288 grams (1.87 moles) of diethyl sulfate. The bath temperature was allowed to rise to about -40°; dry ice was added only when the evolution of ammonia became too rapid.

Finally the flask was heated on a water bath to drive off all remaining ethylacetylene. A fluffy residue, water soluble, remained in the flask. The yield of crude product was 60.7 grams (60%).

The total time of synthesis was 2-1/2 hours. The purification of 83 grams of crude ethylacetylene by distillation through a Davis column left a residue of 1 gram whose boiling point was above room temperature.

ATTEMPTED INTERFEROMETRIC ANALYSIS OF BUTADIENE

A Zeiss portable interferometer was used. Readings for various substances are listed in the following:

Air	0.45, zero point
Air, free from CO_2 and H_2O	0.42
Nitrogen	-0.32
Oxygen	2.59
Butadiene	off scale.

The refractivity of butadiene is so different from air that the latter can not be used as a standard. Methyl bromide, ethyl acetylene, and butadiene itself were also tried as standards: Zero point for methyl bromide = -0.01; no reading for butadiene.

Zero point for ethylacetylene = -0.41; 27.47 ±0.5 for commercial butadiene. (Would be indistinguishable from pure butadiene).

Zero point for butadiene= -0.79; faded, and could not be reproduced.

PREPARATION OF DODECYL MERCAPTAN

To 235 grams (0.945 mole) of dodecyl bromide in a two-liter three-necked round-bottomed flask was added 470 ml. of 95% ethanol, and 71.7 grams (0.945 mole) of thiourea. This mixture was heated with stirring for three hours, at the end of which time a solution of 56.5 grams of sodium hydroxide in 565 ml. of water was added, and the heating continued for an additional two hours.

Upon cooling two layers formed which were separated. The water layer was acidified by a solution of 13.2 ml.

of concentrated sulfuric acid in 94 ml. of water and extracted once with 142 ml. of benzene. This was added to the crude mercaptan, the solution washed twice with 375 ml. portions of water and dried over 38 grams of anhydrous sodium sulfate.

Removal of the solvent and distillation in a nitrogen atmosphere at reduced pressure gave 164.3 grams (86%) of dodecyl mercaptan, b.p., 113-115°/3 mm; $n_D^{20} = 1.4578$.

The residue in the distilling flask, 14.9 grams, was recrystallized from the mixed solvent, absolute alcohol, and low boiling petroleum ether. It was found to have a melting point of 32°, and assumed to be the disulfide.

In the following polymerizations, the term ''standard GR-S formula'' is understood to mean the following proceedure: 35.0 grams of soap solution and 2.0 ml. of catalyst are admixed, and cooled in an ice-bath. The modifier, dissolved in 5.0 grams of styrene, is added to the soap solution, which is then cooled in an ice-salt bath. To this is added 15.0 grams of liquid butadiene, the polymerization bottle sealed and placed in a cage. After heating with rotatory agitation in a water bath maintained at 50° for 10 hours, the bottles are cooled to room temperature, opened and short-stopped with 5 grams of 10% Anax solution (Phenyl-β-naphthylamine). Coagulation is accomplished by titrating with a saturated and acidified solution of sodium chloride (2110 grams of sodium chloride, 75 ml. of concentrated sulfuric acid, and 6 liters of water). After washing the crude rubber with tap water, distilled water, and draining for two hours, it is broken into pea-sized pieces, placed on a tared watch glass, and dried for 8 hours at 70-80°. The % yield is obtained by subtracting 1.5 from the above weight of dried product and multiplying by 5.

The solubility is obtained by placing a 0.5000 gram sample in a 4 ounce bottle, adding 50.0 ml. of anhydrous benzene, and rotating in an air oven at 100°F (38°C) for 16 hours. A 10 ml. sample evaporated on a tared watch glass and dried for 2 hours at 70-80° gives the necessary data for calculating the solubility.

The intrinsic viscosity is obtained by diluting 1 ml. of the above solution with 10 ml. of benzene, and determining the viscosity on this solution:

$$n_t = \frac{\ln N_{rel}}{c}$$

c = grams /100 ml. solution.

POLYMERIZATION MODIFIED WITH DODECYL MERCAPTAN

The standard GR-S formula was used. The samples of dodecyl mercaptan were weighed out and to each was added 5.51 ml. of pure styrene. The results are listed in the following table:

TABLE II

Poly. No.	Sample, grams	Molar Equiv.	Weight, grams	% Yield	% Sol.[4] gm./100 cc. C_6H_6	η_t
1.	0.1022 DDM	1	16.2	73.5	99.2	1.87
2.	0.1020	1	16.7	76.0	98.9	2.22
3.	0.1074	1	17.2	78.5	100.0	1.82
4.	0.1137	1	17.7	81.0	97.7	2.02
5.	0.0917	1	17.7	78.5	103.5	2.21
6.	0.1057	1	16.6	75.5	98.0	2.31
7.	0.1091	1	17.2	78.5	98.0	1.96
8.	0.1129	1	16.7	76.2	100.3	1.97
9.	0.0994	1	18.2	82.5	98.5	2.14

The time of heating in the water bath was 10 hours; temperature, 50°.

PREPARATION OF HEXANE-1,6-DITHIOL (Hexamethylene Dimercaptan)

To 24.4 grams (0.10 mole) of hexamethylene dibromide was added 100 ml. of 95% ethanol, then 15.2 grams (0.20 mole) of thiourea. The mixture was heated with stirring for a period of five hours, at the end of which time, a solution of 6.0 grams of sodium hydroxide in 60 ml. of water was added. A color change of yellow, to orange, to reddish-brown resulted. The refluxing and stirring was then continued for an additional three hours.

The solution was then cooled in an ice bath. Two layers formed and were separated. The water layer was acidified by a solution of 15 ml. of concentrated sulfuric acid in 100 ml. of water and extracted with three twenty-five ml. portions of benzene. The benzene extracts were combined with the crude mercaptan, and dried over 4 grams of anhydrous sodium sulfate. A 67% yield of hexane-1,6-dithiol was obtained by vacuum distillation after decantation and removal of the solvent.

Its physical properties were as follows: b.p., 70°/2 mm. and 100°/5 mm; n_D^{20}, 1.5102; d_{20}^{20}, 0.991.

It was identified as the dibenzoate, m.p. 55-56°. The literature[17] gives a melting point of 57°, but no other physical constants.

PREPARATION OF HEXANE-1,6-DISULFONYL CHLORIDE

Two grams of hexane-1,6-dithiol was dissolved in 20 ml. of glacial acetic acid and 5 ml. of water. Chlorine gas was bubbled into this solution for 30 minutes. The precipitate which formed upon dilution with water was recrystallized from 95% ethanol. One and one half grams (40%) of a fluffy white product melting at 81-82° was obtained.

Anal. Calcd. for $C_6H_{12}O_4S_2Cl_2$: Cl, 25.15. Found: Cl, 25.52.

POLYMERIZATION MODIFIED WITH HEXANE-1,6-DITHIOL

The standard GR-S formula was used. The samples were made up volumetrically by dissolving an excess of hexane-1,6-dithiol in styrene and measuring out the proper volume by means of a burette. Sufficient pure styrene was then added to make the total volume of styrene 5.80 ml.

The results of a 10 hour run at 50° are given in the following table:

TABLE III

Poly. No.	Sample, grams	Molar Equiv.	Weight, grams	% Yield	% Sol. gm./10^4 cc. C_6H_6	η_r
58	0.0997 DDM	1	17.8	81.5	98.4	1.84
59	0.1000	1	18.0	82.5	98.8	1.81
60	0.1000	1	18.2	83.5	98.8	2.23
61	0.223 HD	3	16.8	76.5	98.6	1.80
62	0.223	3	16.4	74.5	98.3	1.98
63	0.223	3	17.5	75.0	99.1	2.03
64	0.0743	1	17.7	81.0	92.3	1.18
65	0.0743	1	17.5	80.0	80.5	1.30
66	0.0743	1	17.8	81.5	81.9	-
67	0.0186	1/4	16.7	76.0	44.3	-
68	0.0186	1/4	15.9	72.0	63.0	1.54
69	0.0186	1/4	14.7	66.0	80.8	1.87
70	0.0015	1/50	14.6	65.5	32.1	-
71	0.0015	1/50	11.3	49.0	48.3	-
72	0.0015	1/50	12.5	55.0	28.5	-

PREPARATION OF THIOGLYCOLIC ACID

To 94.5 grams (1.0 mole) of monochloroacetic acid was added 200 ml. of 95% ethanol, 76 grams (1.0 mole) of thiourea and 5 grams of hydroquinone. After refluxing for 2 hours, the white, crystalline solid was removed by filtration. It was placed in a 500 ml. round bottomed flask and treated with a solution of 80 grams of sodium hydroxide in 200 ml. of water. After refluxing for 1-1/2 hours, the solution was acidified with 200 ml. of concentrated hydrochloric acid, and extracted with two 150 ml. portions of ether. The combined ether extracts were dried over sodium sulfate; the ether distilled off and the residue taken over under reduced pressure in a nitrogen atmosphere. The weight of acid was 46.0 grams (50%), b.p., 109-111°/15 mm; d_{20}^{20}, 1.3169; n_D^{21}, 1.4990.

PREPARATION OF CYCLOHEXYL THIOGLYCOLATE $CH_2SHCO_2C_6H_{11}$

To 13.3 grams (0.145 mole) of thioglycolic acid was added 14.5 grams (0.145 mole) of cyclohexanol, a trace of p-toluenesulfonic acid, and 100 ml. of benzene. After refluxing in a water-removing apparatus for 3 hours, the benzene was distilled off, and the residue taken over under reduced pressure. The yield of ester was 15.4 grams (80%), b.p., 120-122°/15 mm.; n_D^{20}, 1.4898; d_{20}^{20}, 1.097.

It was insoluble in 5% sodium hydroxide solution.

Anal. Calcd. for $C_8H_{14}O_2S$: S, 18.40. Found: S, 18.31, 18.62.

POLYMERIZATION MODIFIED WITH CYCLOHEXYL THIOGLYCOLATE

The standard GR-S formula was used. Cyclohexyl thioglycolate was measured out volumetrically in styrene and sufficient pure styrene added to make the total volume 5.30 ml. The results of a 10 hour run at 50° are listed in the following table:

TABLE IV

Poly. No.	Sample, grams	Molar Equiv.	Weight grams	% Yield	% Sol. gm./10^4 cc. C_6H_6	η_+
10	0.258 CHTG	3	2.8[1]	6.5	Sol.	-
11	0.258	3	2.9[1]	7.0	"	-
12	0.258	3	2.8[1]	6.5	"	-
13	0.0861	1	9.9	42.0	99.5	2.12
14	0.0861	1	10.2	43.5	94.5	2.07
15	0.0861	1	11.9	52.0	98.3	1.70
16	0.0017	1/50	9.7	41.0	70.4	2.03
17	0.0017	1/50	9.1	38.0	89.9	1.74
18	0.0017	1/50	8.8	36.5	84.3	1.75
19	0.1000 DDM	1	17.3	79.0	97.7	2.19
20	0.1010	1	17.3	79.0	97.6	2.14
21	0.1010	1	17.3	79.0	97.6	2.28

1. Wet weight.

POLYMERIZATIONS MODIFIED WITH n-OCTYL AND tert-OCTYL (Esso S.O.D.) MERCAPTANS

The standard GR-S formula was used. Samples were measured out volumetrically in styrene and diluted with pure styrene to a total volume of 5.8 ml. The results of a 10 hour run at 51.5° are given in the following table:

TABLE V

Poly. No.	Sample, grams		Molar Equiv.	Weight, grams	% Yield	% Sol. gm./10^4 cc. C_6H_6	η_r
37	0.1000	DDM	1	18.7	86.0	99.3	2.01
38	0.1000		1	19.6	90.5	99.4	2.29
39	0.1000		1	18.5	85.0	98.6	1.94
40	0.217	SOD	3	16.0	72.5	98.1	0.67
41	0.217		3	16.5	75.0	98.8	0.74
42	0.217		3	(18.7)	(86.0)	99.0	0.76
43	0.0723		1	15.7	71.0	98.5	1.59
44	0.0723		1	15.8	71.5	99.1	1.82
45	0.0723		1	15.9	72.0	99.5	1.59
46	0.0014		1/50	8.6	35.5	68.8	-
47	0.0014		1/50	8.7	36.0	50.8	-
48	0.0014		1/50	8.2	33.5	60.9	-
49	0.217	OM	3	15.0	67.5	98.8	2.25
50	0.217		3	13.0	57.5	99.6	2.72
51	0.217		3	blew up			
52	0.0723		1	12.4	54.5	99.0	2.94
53	0.0723		1	12.9	57.0	99.3	2.91
54	0.0723		1	14.2	63.5	99.8	3.42
55	0.0014		1/50	9.4	39.5	80.6	2.06
56	0.0014		1/50	10.6	45.5	68.0	1.93
57	0.0014		1/50	8.3	34.0	90.5	2.28

PREPARATION OF MELISSYL ALCOHOL

To 124.3 grams of ground carnauba wax in a 1-liter round bottomed flask was added 374 ml. of 95% ethanol, and a solution of 47.4 grams of sodium hydroxide in 91 ml. of water. After refluxing for 35 hours, the resultant mush was poured into 3.75 liters of cold water with stirring. The content of the flask which failed to come out was dissolved in 95% alcohol and added to the water. This was then filtered by suction and the bulky precipitate set aside to dry. After several days, the dried product was ground to a fine powder, divided into four batches and each extracted with the same 250 ml. of hot benzene. The extraction was repeated with another 250 ml., which was combined with the first. Upon cooling in an ice bath, the melissyl alcohol precipitated as a pale yellow solid and was found to weigh 55 grams (44.4%), m.p. 87-89°. The residue insoluble in benzene weighed 62 grams.

Six and three tenths grams of the melissyl alcohol was placed in a 100 ml. Soxhlet extractor and extracted with 150 ml. of high boiling petroleum ether for 17 hours. Only a dark stain was left in the cup indicating complete extraction. The melissyl alcohol crystallized out upon cooling, and was filtered, and found to weigh 6.1 grams, m.p. = 87-88°.

PREPARATION OF MELISSYL BROMIDE

A. Gaseous hydrogen bromide

Twenty five grams (0.0554 mole) of melissyl alcohol in a 125 ml. distilling flask was placed in a metal bath maintained at 125°. Gaseous hydrogen bromide, generated by adding 33 grams (0.143 mole) of bromine to 26 grams (0.2 mole) of tetralin, was passed into this molten alcohol over a period of six hours. The color changed from a pale yellow to a dark brown.

The product was recrystallized from ether giving 23.1 grams (28.6%), m.p., 70-71°. The literature[18] gives 67°.

B. Concentrated sulfuric and hydrobromic acids

To 13 grams (0.0297 mole) of melissyl alcohol in a 250 ml. round bottomed flask was added a solution containing 70 grams of 48% hydrogen bromide and 22 grams of concentrated sulfuric acid, and the mixture refluxed for 10 hours during which time the color changed to a dark brown or black. This mixture was then poured into excess water, filtered, the precipitate washed with water, and dried. It was recrystallized from a 50% solution of benzene and methanol, and found to weigh 13.8 grams (93%), m.p., 70-71°.

PREPARATION OF MELISSYL MERCAPTAN

To 15.2 grams (0.0303 mole) of melissyl bromide was added 100 ml. of 95% ethanol and 2.3 grams (0.0303 mole) of thiourea, and the mixture refluxed for 15 hours. The two phases initially present gradually became one. A solution of 1.8 grams (0.045 mole) of sodium hydroxide in 50 ml. of water was now added and the refluxing continued for nine hours. The precipitate which formed during the addition of the sodium hydroxide solution was light and fluffy; during the refluxing, the color changed to a dark brown.

The hot mixture was poured into water; the precipitate removed by filtration and washed with alcohol. A lumpy product weighing 23.2 grams was obtained after drying overnight. This was recrystallized from a 50% benzene-absolute alcohol mixture by dissolving in benzene and adding the alcohol to the point of precipitation. The yield of melissyl mercaptan was 11.3 grams (79%), m.p. 77-84°. A good melting point was never obtained. One fraction from absolute alcohol melted at 71-74°.

<u>Anal.</u> Calcd. for $C_{31}H_{64}S$: S, 6.84; M.W., 478. Found: S, 6.24; M.W. 458 (0.191 gram sample in 5 ml. of chloroform elevated the boiling point 0.202°).

PREPARATION OF THE BENZOATE OF O.E.I.

A. Benzoyl chloride, Naugatuck O.E.I., and Pyridine

To 24.0 ml. (0.1 mole) of Naugatuck O.E.I. was added 14.0 grams (0.10 mole) of benzoyl chloride and 24 ml. of pyridine. A white precipitate formed and heat was generated. The contents were then heated at 65° for 24 hours, at the end of which time, they were poured into cold, diluted sulfuric acid and extracted with ether. The ether extract was washed with 10% sulfuric acid, 5% sodium carbonate, water, and dried over anhydrous sodium sulfate. Removal of the solvent, and distillation under reduced pressure gave 26.7 grams (87.3%) of the thiolester, b.p. 208-213°/1-2 mm; n_D^{28}, 1.5130; d_{20}^{20}, 0.963.

<u>Anal.</u> Calcd. for O.E.I. benzoate (M.W.*, 347): S, 922.

*The composition of O.E.I. varies, however, the average equivalent weight can be determined by a mercaptan analysis and this value used in the determination of the molecular weight.

Found; S, 8.95, 8.73.

The thiolester may be recrystallized from methanol solution as a crystalline white product, but melts considerably below room temperature.

B. Potassium Mercaptide and Benzoyl Chloride

To 24.0 ml. (20.2 grams, 0.1 mole) of Naugatuck O.E.I. was added 5.6 grams (0.10 mole) of potassium hydroxide in 6.0 ml. of water, and 50 ml. of benzene. After refluxing in a water removing apparatus for 2-1/2 hours, 14.0 grams (0.10 mole) of benzoyl chloride was added and the mixture refluxed for 3 hours. Upon cooling, washing with 5% sodium carbonate, water, and drying over anhydrous sodium sulfate, the benzene was distilled off and the residue distilled under reduced pressure.

A yield of thiolester was 23.8 grams (78%), b.p., 205-212°/1-2 mm.; n_D^{20}, 1.5141; d_{20}^{20}, 0.964.

The agreement with the product obtained in Part A is excellent.

POLYMERIZATION MODIFIED WITH THE BENZOATE OF O.E.I.

The standard formula was used. The one and three molar equivalent portions of thiolbenzoate were weighed out and dissolved in 5.80 ml. of pure styrene. The 1/50 molar equivalent was prepared volumetrically. The results of a ten-hour run at 48.0° are listed in the following table:

TABLE VI

Poly. No.	Sample, grams		Molar Equiv.	Weight, grams	% Yield	% Sol. gm./10^4 cc. C_6H_5	η_+
124	0.1518	DDTB	1	5.2	21.5	Sol.	a
125	0.1518		1	3.7	11.0	Sol.	a
126	0.1518		1	5.3	19.0	Sol.	a
127	0.4554		3	4.4	14.5	Sol.	a
128	0.4554		3	5.4	19.5	Sol.	a
129	0.4554		3	4.5	15.0	Sol.	a
130	0.0030		1/50	2.8	6.5	Sol.	a
131	0.0030		1/50	3.0	7.5	Sol.	a
132	0.0030		1/50	2.9	7.0	Sol.	a
133	0.1000	DDM	1	17.3	79.0	96.2	1.76
134	0.1000		1	17.3	79.0	97.6	2.13
135	0.1000		1	16.8	76.5	99.4	1.74
136	0.1000		1	17.0	77.5	98.3	1.81

a. The intrinsic viscosity was not determined because the yield was low.

PREPARATION OF THE p-NITROBENZOATE OF O.E.I.

Five and six tenths grams (0.03 mole) of p-nitrobenzoyl chloride, 6.6 ml. (6.0 grams, 0.03 mole) of Naugatuck O.E.I. and 12 ml. of pyridine were admixed and heated at 65° for 24 hours. Precipitation in cold diluted hydrochloric acid followed by filtration and recrystallization of the product from a 10% solution of acetone in methanol gave 7.1 grams (0.0244 mole) of a pale yellow solid, 78% yield; m.p. 53°.

The compound had decomposed before an analysis could be made.

A small scale determination indicated that the same results could be obtained by heating benzoyl chloride and Naugatuck O.E.I. together over an open flame.

PREPARATION OF THE MONOCHLOROACETATE OF O.E.I.

To 5.8 grams (0.051 mole) of monochloroacetyl chloride, prepared by the action of thionyl chloride on monochloroacetic acid, was added 13.9 ml. (8.4 grams, 0.06 mole) of Naugatuck O.E.I.. A copious evolution of hydrogen chloride resulted and heat was generated. The solution was heated at 65° for 24 hours, and then distilled giving 11.0 grams (77%) of the monochlorothiolacetate, b.p., 190-205°/20-25 mm.; n_D^{19}, 1.4743; d_{20}^{20}, 0.973.

Anal. Calcd. for O.E.I. monochloroacetate (M.W., 320) S, 10.01. Found: S, 10.06, 9.83.

POLYMERIZATION MODIFIED WITH THE MONOCHLOROACETATE OF O.E.I.

The standard GR-S formula was used. The one and three molar equivalents were weighed out and dissolved in 5.80 ml. of styrene. The 1/50 equivalent was prepared volumetrically. The results of a 10 hour run at 48° are given in the following table:

TABLE VII

Poly. No.	Sample, grams	Molar Equiv.	Weight grams	% Yield	% Sol. gm./10^4cc. C_6H_6	η_+
115	0.1379 DDCLAC	1	12.1	53.0	33.3	a
116	0.1379	1	12.1	53.0	33.6	a
117	0.1379	1	13.4	59.5	26.4	a
118	0.4137	3	14.8	66.5	28.8	a
119	0.4137	3	14.2	63.5	29.5	a
120	0.4137	3	14.4	64.5	62.1	a
121	0.0028	1/50	4.4	14.5	Sol.	a
122	0.0028	1/50	3.7	11.0	Sol.	a
123	0.0028	1/50	3.6	10.5	Sol.	a
133	0.1000 DDM	1	17.3	79.0	96.2	1.76
134	0.1000	1	17.3	79.0	97.6	2.13
135	0.1000	1	16.8	76.5	99.4	1.74
136	0.1000	1	17.0	77.5	98.3	1.81

a. The yields and solubility were so low that the intrinsic viscosity values were not determined, except to check standard.

ATTEMPTED PREPARATION OF THE TRICHLOROACETATE OF O.E.I.

To 32.8 grams (0.20 mole) of trichloroacetic acid was added 48.4 (0.40 mole) of dimethylanaline. Heat was evolved and solution effected. To this was added with cooling, 23.8 grams (0.20 mole) of thionyl chloride. A color change to amber, brown, then green resulted. The solution was taken up in 50 ml. of chloroform, 23.8 grams (0.12 mole) of Naugatuck O.E.I. added, and the mixture refluxed for 3 hours. Upon cooling it was washed with diluted hydrochloric acid, water, dried over calcium chloride, and the chloroform removed by distillation. A crude residue of 34.6 grams resulted which could not be crystallized upon cooling in an ice-bath, nor could it be distilled under reduced pressure maintained by a mercury vapor pump.

PREPARATION OF DODECYL THIOLOXALATE

To 3.0 grams (0.024 mole) of oxalyl chloride in 10 ml. of anhydrous ether was added 10 ml. of pyridine, 15.0 grams (0.074 mole) of pure dodecyl mercaptan, and the mixture heated at 65° overnight. The precipitate which formed upon acidification was removed by filtration, washed with water, and recrystallized from acetone. There was obtained 10.1 grams (74%) of white product, m.p., 60-61°.

Anal. Calcd. for $C_{26}H_{50}O_2S_2$: S, 13.67. Found: S, 13.60.

Dodecyl thioloxylate prepared from Naugatuck O.E.I.

in a similar way and recrystallized from acetone had a sharp melting point of 52°.

POLYMERIZATION MODIFIED WITH DODECYL THIOLOXALATE

The standard GR-S formula was used. Dodecyl thioloxalate was weighed out directly, and dissolved in 5.80 ml. of styrene. The results of a 10 hour run at a temperature of 51° are listed in the following table:

TABLE VIII

Poly. No.	Sample, grams		Molar Equiv.	Weight, grams	% Yield	% Sol. gm./10^4 cc. C_6H_6	η_t
22	0.2267	DDTO	1	16.8	76.5	58.2	
23	0.2267		1	16.6	75.5	36.6	
24	0.2267		1	17.2	78.5	36.2	
25	0.6801		3	17.8	81.5	99.4	1.53
26	0.6801		3	15.4	69.5	89.9	1.65
27	0.6801		3	15.1	68.0	100.1	2.09
28	0.0045		1/50	8.3	34.0	89.9	1.85
29	0.0045		1/50	foamed	over		
30	0.0045		1/50	10.9	47.0	37.4	1.36
31	0.1000	DDM	1	17.6	80.5	99.2	2.22
32	0.1000		1	18.4	84.5	99.2	2.68
33	0.1000		1	17.5	80.5	98.2	2.29
34	0.0567	DDTO	1/4	15.7	71.0	16.5	
35	0.0567		1/4	15.9	72.0	15.5	
36	0.0567		1/4	15.8	71.5	15.7	

In the one and three molar equivalent polymerization bottles, a residue floated on the top at the end of the reaction period. It was removed prior to coagulation, recrystallized from acetone, and found to melt at 59-60°. This corresponds to the original thioloxalate.

PREPARATION OF THE ACETATE OF O.E.I.

Twenty four milliliters (0.1 mole) of Naugatuck O.E.I., 10.2 grams (0.10 mole) of acetic anhydride, and 10 ml. of pyridine were admixed and heated at 65° for 24 hours. The solution was poured into cold, diluted sulfuric acid and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and the ether removed by evaporation. The residue, upon distillation under reduced pressure, gave 17.3 grams (62%) of thiolacetate, b.p., 130-145°/1-2 mm.; n_D^{20}, 1.4617; d_{20}^{20}, 0.8934.

Anal. Calcd. for O.E.I. acetate (M.W., 285) S, 11.12. Found: S, 11.8, 11.8.

POLYMERIZATION MODIFIED WITH THE ACETATE OF O.E.I. IN VARYING CONCENTRATIONS OF ALKALI

The standard GR-S formula was used. The samples of thiolacetate were weighed out directly and dissolved in 5.80 ml. of styrene. The catalyst concentration was doubled so that one instead of the usual two milliliters could be used; the sodium hydroxide was then added in one milliliter of solution. The results of a ten-hour run at 48° are summarized in the following table:

TABLE IX

Poly. No.	Sample, grams	NaOH, grams	Molar Equiv.	Weight, grams	% Yield	% Sol, g./10^4 cc. C_6H_5	η_t
103	0.1208	0.40	1	14.1	63.0	77.3	-
104	Of DDTAc.	0.40	1	13.6	60.5	65.1	-
105	"	0.40	1	13.5	60.0	61.0	-
106	"	0.06	1	13.1	58.0	38.6	-
107	"	0.06	1	10.7	46.0	30.6	-
108	"	0.06	1	13.2	58.5	28.2	-
109	"	0.02	1	16.9	(77.0)	20.3	-
110	"	0.02	1	14.6	65.5	25.8	-
111	"	0.02	1	13.6	60.5	23.7	-
112	"	none,	1	14.3	64.0	34.8	-
113	"	1 ml.	1	14.2	63.5	21.9	-
114	"	H_2O	1	12.2	53.5	29.6	-
133	0.1000 DDM	none,	1	17.3	79.0	96.2	1.76
134	0.1000	none,	1	17.3	79.0	97.6	2.13
135	0.1000	none,	1	16.8	76.5	99.4	1.74
136	0.1000	none,	1	17.0	77.5	98.3	1.81

In another run, the following were obtained:

Poly. No.	Sample, grams	NaOH, gram	Molar Equiv.	Weight, grams	% Yield	% Sol. g/10^4 cc. C_6H_5	η_r
100	0.1208	0.10	1	12.6	55.5	21.8	-
101	Of DDTAc.	0.01	1	12.0	52.5	23.3	-
102	"	1.00	1	12.4	54.5	87.9	2.71
97	0.1000 DDM	-	1	17.2	78.5	95.2	2.81
98	0.1000	-	1	16.8	76.5	95.7	2.46

POLYMERIZATION MODIFIED WITH DODECYL TRITHIOCARBONATE WITH AND WITHOUT ADDED ALKALI

The standard GR-S formula was used. The samples were weighed out and dissolved in 5.80 ml. of styrene. The results of two 10 hour runs at 50° are summarized in the following table:

TABLE X

Poly. No.	Sample, grams	DDM	NaOH, grams	Molar Equiv.	Weight, grams	% Yield	%Sol. g/10^4 cc. C_6H_5	η_r
75	0.1000	DDM	-	1	17.8	81.5	99.4	1.82
76	0.1000		-	1	18.0	82.5	99.8	2.26
77	0.1000		-	1	17.7	81.0	100.0	2.05
78	0.2208	DDTC	-	1	12.8	56.5	24.4	-
79	0.2208		-	1	13.6	60.5	25.7	-
80	0.2208		-	1	13.4	59.5	35.7	-
81	0.6624		-	3	10.9	47.0	25.5	-
82	0.6624		-	3	12.1	53.0	25.8	-
83	0.6624		-	3	13.5	60.0	(17.1)	-
84	0.0044		-	1/50	6.6	25.5	98.4	2.15
85	0.0044		-	1/50	3.6	10.5	98.4	1.30
86	0.0044		-	1/50	7.6	30.5	98.0	1.82
89[1]	0.6624		0.10	3	14.9	67.0	65.5	-
90[1]	0.6624		0.10	3	15.0	67.5	71.0	-
91	0.6624		0.10	3	10.4	44.5	29.4	-
92	0.2208		0.10	1	11.1	48.0	(51.0)	-
93[1]	0.2208		0.10	1	14.9	67.0	33.4	-
94[1]	0.2208		0.10	1	14.7	66.0	20.6	-
95[1]	0.2208		0.01	1	15.6	70.5	14.2	-
96[1]	0.2208		1.00	1	12.0	52.5	43.2	-
97	0.1000	DDM	-	1	17.2	78.5	95.2	2.81
98	0.1000		-	1	16.8	76.5	95.4	2.46
99	0.1000		-	1	16.7	76.0	94.1	-

[1] An older and apparently less pure material was used in

these runs.

2. The sodium hydroxide was added in 1 ml. of solution. In such cases, half the volume of doubled the concentration of catalyst was used.

In most of the polymerization bottles before coagulation, a yellow residue of unreacted modifier floated on top.

PREPARATION OF DODECYL ACID MONOTHIOLSUCCINATE (Pure and from O.E.I.)

To 5.4 grams (0.054 mole) of succinic anhydride was added 11.0 grams (0.054 mole) of pure dodecyl mercaptan, 11 ml. of pure pyridine, and the mixture heated at 65° for 24 hours. At the end of this time, the solution was poured into cold, diluted hydrochloric acid; the white precipitate which formed was filtered off, washed thoroughly with water, transfered to a beaker, washed with alcohol, filtered, dried, and found to weigh 13.7 grams. An additional 2.0 grams was recovered from the alcohol by pouring it into water. The total yield was 15.7 grams (96%), m.p., 74-75°.

Anal. Calcd. for $C_{16}H_{30}O_3S$: S, 10.62; neutral equivalent, 302. Found: S, 10.60; neutral equivalent, 304.

A sample of dodecyl acid monothiolsuccinate prepared from Naugatuck O.E.I. in a similar manner, was found to have a melting point of 61-63°. Samples were recrystallized from a dilute acetic acid solution and alcohol, however the product seemed sufficiently pure from the washing process to omit this step. The white precipitate feels waxy and retains water tenaciously.

ATTEMPTED PREPARATION OF DODECYL ACID THIOLPHTHALATE

To 3.7 grams (0.025 mole) of phthalic anhydride was added 5.0 grams (0.025 mole) of Naugatuck dodecyl mercaptan, 5 ml. of pyridine, and the mixture heated at 65° for 24 hours. After pouring into cold, dilute hydrochloric acid, an oil formed which was extracted with ether, and dried over anhydrous sodium sulfate. Filtration and removal of the ether gave 7.9 grams of a liquid which very slowly crystallized to a white solid, waxy in nature. It seemed heterogeneous, and could not be purified by recrystallization from any of the common organic solvents including methanol, which excluded the possibility of it being the disulfide.

MALEIC ANHYDRIDE AND NAUGATUCK O.E.I.

To 18.4 grams (0.091 mole) of Naugatuck O.E.I. was added 8.8 grams (0.091 mole) of pyridine. No reaction took place until the pyridine was introduced, then heat was evolved and the solution turned dark brown in color. After heating for one hour at 65°, the solution was precipitated in a cold, diluted solution of sulfuric acid and extracted with several 50 ml. portions of ether. (If precipitated by an ice-hydrochloric acid mixture, the product comes out as a solid and can be removed by filtration). The ether extracts were combined, dried over anhydrous sodium sulfate, and the ether removed by distillation. The residue of 21.5 grams was recrystallized from high boiling petroleum ether as a finely divided waxy material. Other organic solvents were unsatisfactory.

It was soluble in 5% sodium hydroxide.

<u>Anal.</u> Calcd. for dodecyl acid thiomaleate: neutral equivalent, 310. Calcd. for -dodecylthiomaleic acid: neutral equivalent, 159. Found: neutral equivalent, 175.

GOODRICH MERCAPTAN ANALYSIS

A 0.3-0.5 gram sample is weighed into 50 ml. of isopropanol. Ten ml. of pyridine and 10-15 ml. of 5% silver nitrate solution are added, and the mixture shaken thoroughly. At least 25-30 ml. of water are now added to aid coagulation, 4-5 drops of indicator introduced, and the suspension titrated with standard 0.1 N sodium hydroxide. The end point is a color change of yellow to pale green. The blank usually corresponds to 0.3 ml..

$$\% \text{ S} = \frac{3.2 \times \text{Vb} \times \text{Nb}}{\text{W sample}}$$

The indicator is prepared by mixing one part of 0.5% thymol blue in 50% ethanol and 3 parts of 0.5% phenolphthalein in 50% ethanol.

The results of a series of analyses are given in the following table:

TABLE XI

Mercaptan	Weight, grams	Vol. of Alkali in ml. (N=0.106)	Equiv. Weight found	theory
O.E.I. (1st. batch)	0.4052	18.0	212	202
''	0.4035	17.9	212	202
O.E.I.(2nd. batch)	0.3724	17.27	243	202
''	0.3465	14.79	242	202
S.O.D. (_t_-octyl)	0.3282	21.65	146	146
''	0.3143	20.67	145	146
''	0.3219	21.40	144	146
_n_-Octyl	0.3189	21.22	148	146
	0.3169	21.10	148	146
	0.3579	23.71	148	146
3B (t-dodecyl)	0.4104	19.00	204	202
	0.3965	18.55	202	202
	0.3226	15.03	202	202

Blank = 0.30 ml.

SUMMARY

A. Butadiene

The preparation of several kilos of butadiene cyclic sulfone to be used as the starting material for very pure butadiene has been completed, and a satisfactory method of preparation developed.

The possibility of using a gas interferometer as a means of checking the purity of butadiene was tried, but could not be made to give satisfactory results.

Ethylacetylene was prepared in order to study its effect as an impurity in commercial butadiene, but was not tried.

B. Modifiers

1. Derivatives of Dodecyl Mercaptan

The thiolesters of acetic, monochloroacetic, benzoic, p-nitrobenzoic, oxalic, and the half thiolester of succinic acids have been prepared from either pure or commercial dodecyl mercaptan. With the exception of the thiolsuccinate, they show no promise of being good modifiers. The thiolacetate, however, in the presence of added alkali, did show an increased modifying activity in a manner proportional to the amount of alkali used.

The investigation of dodecyl acid thiolsuccinate as a modifier was conducted by Mr. George Inskeep and by Mr. P. V. Smith who found it to give excellent results.

2. Miscellaneous Compounds

Hexane 1,6-dithiol was found to be a good promotor with some modifying activity in higher concentrations.

Cyclohexyl thiolglycolate was found to be a promotor in lower concentrations, but a powerful inhibitor in high concentrations.

A comparison of n-octyl mercaptan and tert-octyl mercaptan in the standard GR-S recipe indicated that n-octyl mercaptan gives a more uniform and better product. When compared to the standard, the yields were somewhat lower, but the intrinsic viscosity for equivalent concentrations was higher. tert-Octyl mercaptan is not as good a modifier.

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VITA

The author was born in Seattle, Washington, and at the age of five, moved to Chicago, Illinois. There he attended the public schools until his entrance to Northwestern University in 1935. In 1939 he was graduated as a Bachelor of Science With Honors, and continued there with an Assistantship in Chemistry. In 1941, he received his Master of Science Degree and moved to the University of Illinois. There he spent two years as an Assistant in Chemistry, and as a member of the W.P.B. Rubber Research group.

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