AN INVESTIGATION
OF THE
CONSTITUTION OF CAOUTCHOUC
WITH SPECIAL REFERENCE TO
THE MODE OF POLYMERIZATION

AN INVESTIGATION OF THE CONSTITUTION OF CAOUTCHOUC,WITH SPECIAL REFERENCE TO THE MODE OF POLYMERIZATION.

Thesis

by

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GENERAL INTRODUCTION

One of the outstanding problems of organic chemistry which has, as yet, received no satisfactory solution is that of the constitution of caoutchouc. Though many theories have been advanced from time to time, none have been able to answer all the requirements of a satisfactory formula.

Our knowledge too of polymerization processes, their mechanism, the effect of temperature, time of heating and catalysts on the amount and nature of the products, is in a still less advanced state and a more complete knowledge of this subject is particularly desirable on account of its very direct bearing upon the constitution of caoutchouc.

Accordingly it was decided to study **the polymerization of isoprene and dimethylbutadiene, (by dimethylbutadiene is meant** the 2-3-dimethylbutadiene-1-3) which are known to give polymers similar to caoutchouc, to see if any simple intermediate bodies, further polymerizeable, could be isolated. The determination of the constitution of any such compound would not only throw considerable light on the mechanism of polymerization but also on the constitution of caoutchouc.

B-myrcene, which is the only compound of this type mentioned in the literature, was isolated by **Ostromisslensky** from among the polymers of isoprene. However he did not prove its constitution. It was decided to repeat this work first, and then apply the same treatment to dimethylbutadiene in the hope of isolating from among its polymers a compound similar to B-myrcene.

At the same time it was decided to investigate the effect of temperature and duration of heating on the polymerization products of these and similar dienes.

II THE CONSTITUTION OF CAOUTCHOUC

The earliest work on the chemical properties and constitution of caoutchouc was done in connection with its destructive distillation. Although it had been noted by Gregory, Dalton, Himly and Barnard that such treatment gave rise to oily products, A. Bouchardat (1) in 1837 and G. Williams (2) in 1860 were the first to make a systematic study of these. Williams not only succeeded in isolating isoprene but also noticed that on standing it was transformed into a thick viscous fluid. On distilling the latter he found that, after the unchanged isoprene had passed over, the contents of the flask were transformed into a spongy elastic mass which on burning gave off the odor so characteristic of burning rubber. It is clear from the remarks made by him that he believed rubber to be a polymer of isoprene.

In 1875, C. Bouchardat (3) found that by heating isoprene in sealed tubes he got besides rubber-like substances, products similar to those which he obtained by the pyrogenic decomposition of rubber. This definitely connected the terpenes, represented by dipentene, with isoprene.

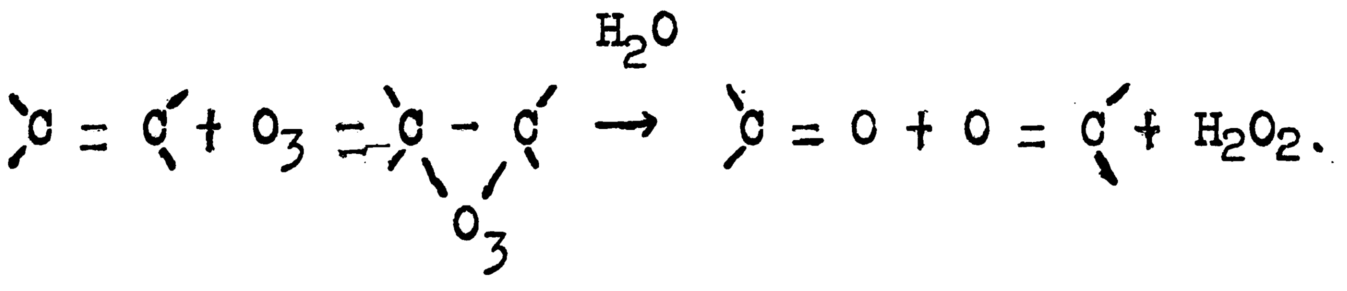
In 1879 (4), while attempting to prepare the hydrochloride of isoprene, he obtained a product which he said had the same physical and chemical properties and which gave the same pyrogenic decomposition products as rubber.

In 1882 Tilden (5) noted the conversion of isoprene to rubber-like substances on treatment with certain chemicals such as HCL or NOCL. In 1884 (6) he prepared isoprene by passing turpentine vapors through a red hot tube. This caused Tilden to believe that the synthesis of rubber might become a practical process. At the same time he proposed the formula for isoprene which was later verified by Euler (7) and by Ipatiew and Wittorf (8).

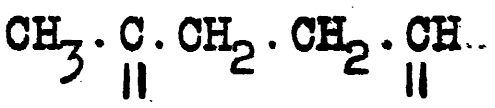
Since the constitution of isoprene was first determined many methods for its preparation have been found. Also many methods of polymerization have been found applicable not only to isoprene but also to its homologues and similar dienes.

Though numerous analyses had shown the empirical formula of purified rubber to be $(C_5H_8)_x$, and though it had been known for many years that it was a polymer of isoprene, whose constitution had been proved, the way in which the isoprene molecules were united in caoutchouc was a problem left untouched, except for the work of Gladstone and Hibbert (9), until the time of Harries. Though interesting, the study of the reactions between rubber and mineral acids (10) and the halogens (11) shed little light upon the structure of the rubber hydrocarbon. It proved certainly, however, that the hydrocarbon contained one double bond per (C_5H_8) unit. The work on the nitrosites revealed the relationship between caoutchouc and myrcene (12). Further studies of the destructive distillation of rubber yielded little more information than was already known. It was the investigation of the addition products of caoutchouc with oxygen and ozone, particularly the latter, and finally hydrogen that gave real insight into the structure of the hydrocarbon molecule.

Harries' classical work (12) on the action of ozone on caoutchouc may be considered the real commencement of modern rubber research. He obtained the ozonide by passing ozonized oxygen into dilute solutions of rubber and evaporating off the solvent under reduced pressure. After purification it was found to have the composition ($C_{10}H_{16}O_6)_x$, that is to say, two ozone residues were taken up for every ($C_{10}H_{16}$) group in the molecules -- further evidence of the presence of two double bonds per ($C_{10}H_{16}$) unit. On treatment with water the ozonide was hydrolyzed and yielded as the only recognizeable products laevulinic aldehyde, laevulinic acid, laevulinic aldehyde diperoxide and traces of hydrogen peroxide. He had shown previously (13) that ozone acted on an ethylenic linkage in the following manner:

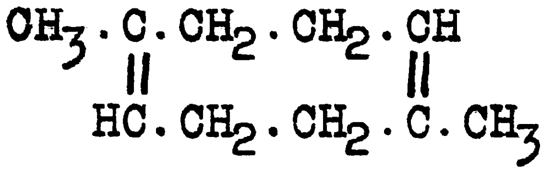


Hence he concluded that rubber contained the grouping:



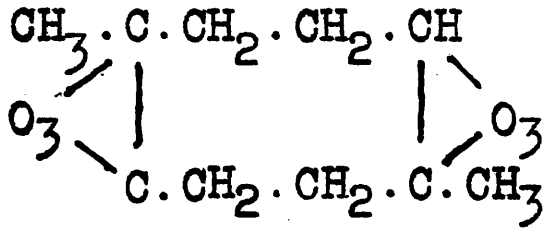
$$\mathrm{CH_3.\underset{\|}{C}.CH_2.CH_2.\underset{\|}{CH}}$$

Molecular weight determinations in acetic acid solution gave a value of 233 for the ozonide. This approximated that for a molecule containing ten carbon atoms. Harries concluded, then, that caoutchouc possessed the structure:

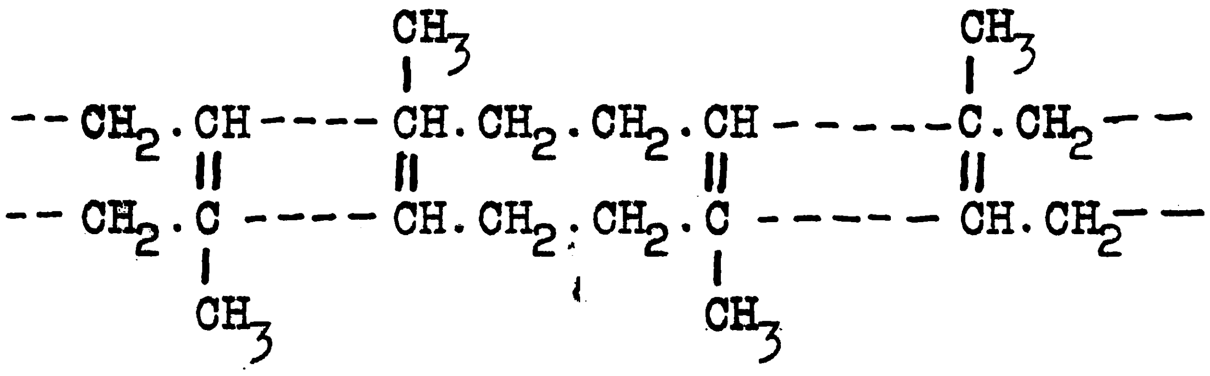


$$\begin{array}{cccccc} \mathrm{CH_3.} & \mathrm{C} & \mathrm{.CH_2.CH_2.} & \mathrm{CH} & & \\ & \| & & \| & & \\ & \mathrm{HC} & \mathrm{.CH_2.CH_2.} & \mathrm{C} & \mathrm{.CH_3} & \end{array}$$

and the ozonide

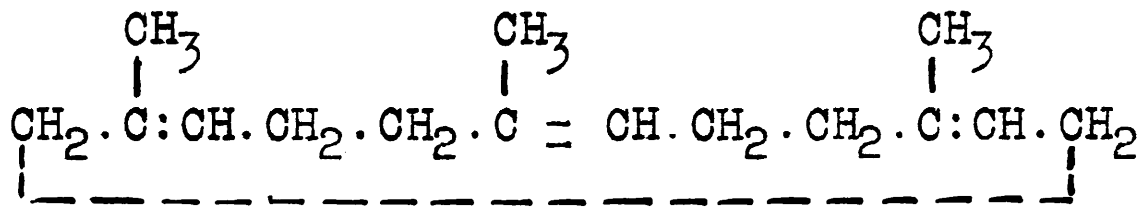


We can readily see how such a compound could give the products described by Harries. As the molecular weight of caoutchouc was known to be much higher than that of the ozonide, Harries assumed that the simple moles polymerized to a complex of very high molecular weight by means of their partial valences. i.e.



$$\begin{array}{ccccccccc} & & & \mathrm{CH_3} & & & & \mathrm{CH_3} & \\ & & & | & & & & | & \\ \mathrm{--CH_2.} & \mathrm{CH} & ---- & \mathrm{CH} & \mathrm{.CH_2.CH_2.} & \mathrm{CH} & ----- & \mathrm{C} & \mathrm{.CH_2--} \\ & \| & & \| & & \| & & \| & \\ \mathrm{--CH_2.} & \mathrm{C} & ---- & \mathrm{CH} & \mathrm{.CH_2.CH_2.} & \mathrm{C} & ----- & \mathrm{CH} & \mathrm{.CH_2--} \\ & | & & & & | & & & \\ & \mathrm{CH_3} & & & & \mathrm{CH_3} & & & \end{array}$$

He suggested that this loose combination would be easily depolymerized by ozone forming separate ($C_{10}H_{16}$) molecules, to which the ozone would be attached at the point of disruption. As was pointed out by Pickles (14), there was no reason why other reagents such as bromine, which was known to form a tetrabromide of the empirical formula $C_{10}H_{16}Br_4$, should not effect a similar depolymerization. As a matter of fact the tetrabromide exhibits a general behaviour which suggests a body of as complex a structure as caoutchouc itself. Pickles postulated the following structure:



$$CH_2.\overset{CH_3}{\overset{|}{C}}:CH.CH_2.CH_2.\overset{CH_3}{\overset{|}{C}}=CH.CH_2.CH_2.\overset{CH_3}{\overset{|}{C}}:CH.CH_2$$

That is to say, a closed chain of (C_5H_8) nuclei, indeterminate in number. In this case the union of the (C_5H_8) groups results from a rearrangement of the double bonds. Pickles suggests that in each molecule there is only one such ring. This avoids the necessity of assuming two steps in the polymerization of isoprene to caoutchouc. The scission products of the ozonide are accounted for quite as satisfactorily as by Harries' formula.

Harries (12) himself subsequently abandoned the C_8-ring formula as in further experiments, he isolated derivatives having a greater number of carbon atoms in the molecule. Starting with para rubber the addition product with hydrochloric acid was first prepared. This was then heated with pyridine to remove the elements of hydrogen chloride and so regenerate the caoutchouc. The ozonide prepared from this yielded on hydrolysis, laevulinic aldehyde, a heptane dione, undecanetrione, pentadecanetetrone, laevulinic acid, succinic acid, hydrochelidonic acid, oxalic acid, hydrogen peroxide and a number of unidentified products. The presence of the triketone and tetraketone is explicable only by assuming a ring larger than the octodiene. It was shown too that the molecular weight of the ozonide in benzene solution was 535, corresponding to $(C_5H_8O_3)_5$ the theoretical value of which is 580. Further, Harries found that the hydrochloride of caoutchouc $(C_{10}H_{16}2HCL)_x$ on being heated at 100° C. gradually gave off hydrogen chloride and analyses at the end of 5, 7, 14 and 20 days, respectively, were obtained which corresponded roughly to the compositions—

$$C_{25}H_{40}5HCL \longrightarrow C_{25}H_{40}4HCL \longrightarrow$$
$$C_{25}H_{40}3HCL \longrightarrow C_{25}H_{40}2HCL \longrightarrow C_{25}H_{40}HCL.$$

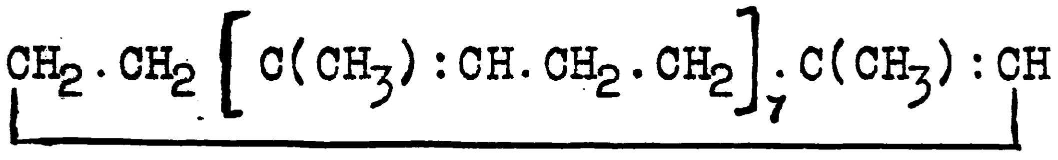
On these grounds it was assumed that the caoutchouc molecule was formed by the union of five (C_5H_8) nuclei thus giving a 20-carbon atom ring.

Olivier (15), however, has objected to some of the experimental work on which Harries conclusions are based. He has pointed out that the molecular weight of the ozonide cannot be taken as a criterion because considerable variations are found as the method for its preparation is changed. Olivier has also repeated Harries' work on the thermal decomposition of caoutchouc hydrochloride but states that his work was by no means as significant as that of Harries. The latter it may be noted has offered no evidence to show that his hydrochloride was homogeneous. The work of Boswell (16) too has cast doubt on the quantitative formation of the ozonide as postulated by Harries.

Later experiments have led Harries (17) to the conclusion that there are more than five isoprene nuclei present. He found that if the dihydrochloride is reduced by zinc dust, a hydrocaoutchouc, $C_{35}H_{62}$ or $C_{40}H_{70}$, is formed which may be distilled, in vacuo, unchanged. Its molecular weight, determined in bromoform, was 6067. The composition of the bromide and ozonide afford further evidence of thirty-five to forty carbon atoms in the molecule, pointing to at least seven or eight (C_5H_8) nuclei. Harries concludes then that caoutchouc is a polymer of a hydrocarbon containing seven or eight (C_5H_8) units joined into a large ring.

Olivier (15) has also objected to these conclusions. He argues that Harries has advanced no proof of the homogeneity of his hydrocaoutchouc. In fact the analyses of the hydrocaoutchouc itself and its ozonide indicate the very opposite.

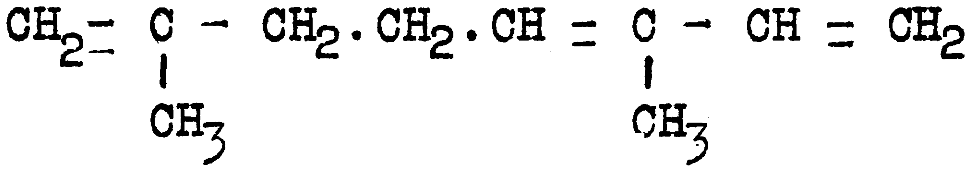
Previous to Harries' adoption of his final formula, Ostromisslensky (18), had proposed one very similar to this. From a comparison of the properties of the bromides of caoutchouc and of polymerized erythrene and of the polymer of vinyl bromide he decided that caoutchouc itself must be a polymer of the compound:



$$CH_2.CH_2\left[C(CH_3):CH.CH_2.CH_2\right]_7.C(CH_3):CH$$

Harries has objected strongly to the experimental results on which these conclusions are based (12a).

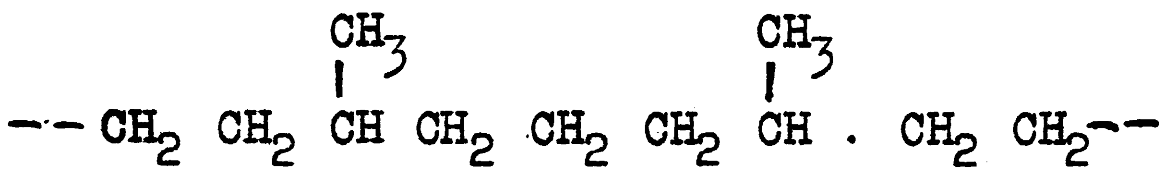
Ostromissleasky also proposes a mechanism for the polymerization of isoprene (19). This was based on the isolation, from among the polymers of isoprene, of a dimer, β-myrcene for which he advances tentitatively, the following formula (19a):



$$CH_2=\underset{CH_3}{C}-CH_2.CH_2.CH=\underset{CH_3}{C}-CH=CH_2$$

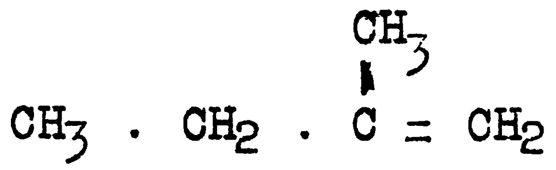
This product was polymerized by shaking at 60°-70° for five days in the presence of sodium and barium peroxide. It gave a product resembling caoutchouc more closely than isoprene under the same conditions. According to Ostromisslensky, then, the mechanism of the transformation of isoprene and B -myrcene into caoutchouc is as follows. First the isoprene breaks up into an atom of hydrogen and a radical which unite with another isoprene molecule to form a dimer, B -myrcene. This process repeats itself seven times and so forms an open chain octamer which then forms a ring and gives caoutchouc. The reason that barium peroxide and sodium on isoprene and B -myrcene do not give the same caoutchouc is that in the first case any one of the intermediate polymers may unite with the isoprene or with a lower polymer or with another molecule of itself. In the second case he supposes that B -myrcene forms a dimer and then a tetramer which on cyclation "gives" normal isoprene-caoutchouc". In the first case the different intermediate polymers cause a difference in the arrangement of the methyl groups and double bonds, so abnormal caoutchouc results. Of course under certain conditions cyclation of the dimer takes place and dipentene results. Ostromisslensky proposes a similar mechanism for the polymerization of other dienes, i.e. butadiene and ethylenic compounds, i.e. vinyl bromide. His caoutchouc is then a polymer of this 32-carbon atom ring compound.

Recent work by Staudinger and his co-workers (20) on the catalytic reduction of caoutchouc supports the idea of a large molecule for caoutchouc. The hydrogenation was carried out at a temperature of 270°-280° C. and under a pressure of 100 atmospheres of hydrogen, in the presence of platinum black. The product was a colorless non-elastic mass with the empirical formula $(C_5H_{10})_x$. It had the chemical properties of a saturated hydrocarbon and was not attacked by nitric acid or potassium permanganate and did not add on bromine. In its behaviour to solvents it resembled the original caoutchouc. On distillation in vacuo it decomposed completely at 350° C. giving a series of compounds of the composition $(C_5H_{10})_x$ ranging from methyl ethyl ethylene (C_5H_{10}), the simplest member of the series, to $C_{50}H_{100}$. Staudinger has suggested that hydrocaoutchouc bears the same relation to methyl ethyl ethylene as normal rubber does to isoprene (21a and b).



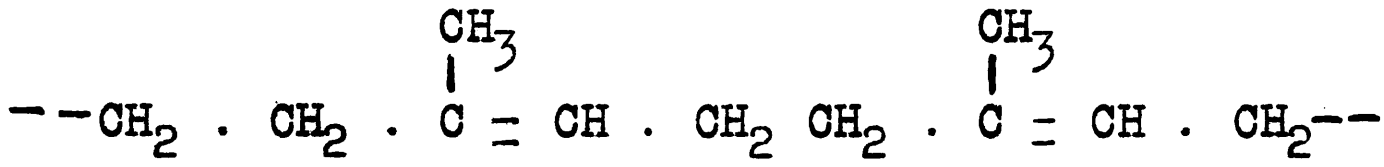
$$--CH_2\ CH_2\ \overset{CH_3}{\overset{|}{CH}}\ CH_2\ CH_2\ CH_2\ \overset{CH_3}{\overset{|}{CH}}\ .\ CH_2\ CH_2--$$

Hydrocaoutchouc.



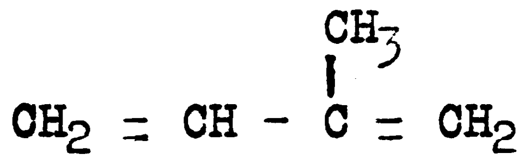
$$CH_3\ .\ CH_2\ .\ \overset{CH_3}{\overset{|}{C}} = CH_2$$

Methyl ethyl ethylene.



$$--CH_2\ .\ CH_2\ .\ \overset{CH_3}{\overset{|}{C}} = CH\ .\ CH_2\ CH_2\ .\ \overset{CH_3}{\overset{|}{C}} = CH\ .\ CH_2--$$

Normal caoutchouc.

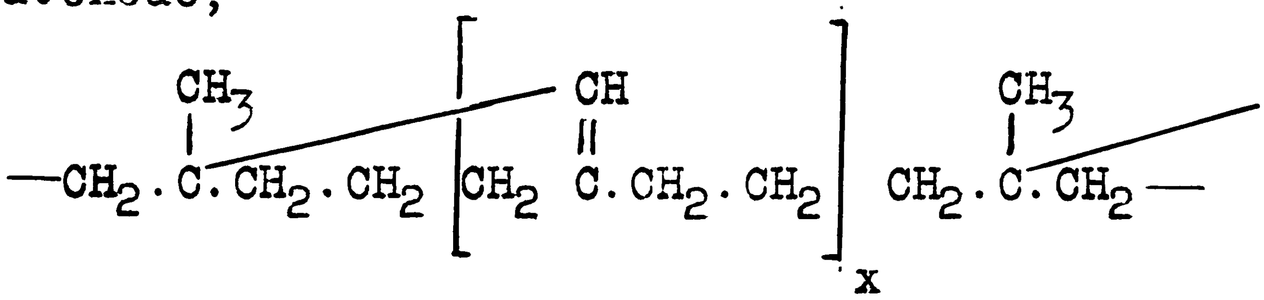


$$CH_2 = CH - \overset{CH_3}{\overset{|}{C}} = CH_2$$

Isoprene.

He obtained results similar to these with hydrogenated methyl rubber. Staudinger argues that caoutchouc cannot be a polymerized product such as suggested by Harries, for, if such were the case, the hydrocaoutchouc could not be colloidal in size. Then caoutchouc must be an ethylenic derivative of high molecular complexity, in which a large number, probably 100 or more molecules of isoprene are united together in a regular manner such as indicated above. He is not prepared to say definitely whether this molecule takes the form of a closed or open chain but is in favor of the latter idea.

Staudinger (22) also reduced caoutchouc using Harries method. From a study of the properties of the compound which he obtained he is convinced that Harries was dealing not with hydrocaoutchouc but with a cyclo-caoutchouc,



Harries had objected (23) that the temperature used by Staudinger in the reduction of caoutchouc was such that he was reducing its decomposition products rather than the caoutchouc itself. This objection was overcome by Pummerer and Burkard (24), and later by Staudinger (21). Pummerer and Burkard succeeded in hydrogenating purified rubber in dilute hexahydrotoluene solutions at 18°-20° C., in the presence of platinum black. They obtained by this means, a fully saturated hydrocarbon which was resistant to oxidation both by air and potassium permanganate. It possessed the empirical formula $(C_5H_{10})_x$. After prolonged heating at 200° C. and short heating at 300° C. it was found to have a molecular weight of about 1700. By careful vacuum distillation it yielded a compound whose analysis and molecular weight determinations indicated the formula $(C_5H_{10})_{10}$. They concluded then that the parent hydrocarbon had a molecular weight of 600-700. This however owing to its great tendency to associate gives rise to molecules of enormous molecular weight.

This idea seems to be quite contrary to that of Staudinger, unless the suggestion that he advances (21a), i.e. that the macromolecule can dissociate in solution, is accepted -- then these two ideas become practically the same. In favor of the association theory Pummerer, Nielsen and Gündel have shown that the molecular weight of caoutchouc does vary in solution (25). In camphor and menthol, using concentrations of 0.5 to 1%, they obtained for gel-rubber, sol-rubber and diffused rubber values as low as 520 to 600. With higher concentrations, 2%, they obtained values from 1200-1600. These determinations, then, indicated an extensive but limited dissociation. It is interesting too, to note these rubber samples which differ so much in solubility showed the same average molecular weight in camphor and menthol. It appears then that the essential difference between them must lie in their different powers of aggregation. Hydrocaoutchouc and cyclocaoutchouc were also investigated. These too gave values around 600. Pummerer concludes then that caoutchouc has a parent hydrocarbon, containing 8, 9 or 10 isoprene units, which through aggregation disaggregation association and disassociation accounts for the various phenomena. According to Pummerer it cannot be decided yet whether it has a ring or open chain structure but present evidence, obtained from a variety of sources points to a ring compound (26).

Other theories as to the constitution of caoutchouc are those of Barrows (27), Kirchhof (28), and Boswell (29). These however will not be dealt with here.

This concludes a brief summary of the most prominent theories of the constitution of caoutchouc.

III INTRODUCTION TO EXPERIMENTAL WORK

Since this research deals mainly with the examination of the products obtained by the polymerization of isoprene and dimethylbutadiene, a short summary will be given of the results obtained by other workers in this field.

Products of the Polymerization of Iosprene and Dimethylbutadiene other than High Polymers.

In regard to the polymerization of isoprene Kandakow (30) as early as 1900-1902 put forward an observation of very great interest: "that a transient stage in the polymerization of these hydrocarbons consists of dimeric, open chain isoprenes, containing several double bonds in the molecule". Only one case is mentioned in the literature however where a compound intermediate between isoprene and its caoutchouc-like polymer has been isolated. This the the B-myrcene of Ostromisslensky previously mentioned. Ostromisslensky prepared this compound by keeping isoprene at ordinary temperatures or by heating to a temperature not exceeding 120°C. in the presence of absence of catalysts. He gives no definite proof of its constitution but the properties mentioned by him indicate a formula of the type that he proposes.

Harries (12) isolated a dimer from the polymerization products of isoprene for which he proposes a formula the same as that given by Ostromisslensky to B-myrcene. Harries did not notice whether his compound would polymerize.

Though no other open chain dimers are mentioned as having been found among the polymerization products of isoprene, several cyclic dimers have been isolated. These of course are not intermediate between isoprene and its high polymer, but instead are by-products of the reaction. Among these is dipentene, which was recognized as far back as the time of Bouchardet and Tilden. Another, 1.3. dimethyl -3-ethenyl-6-cyclohexene, was isolated by Lebedeff (31). Lebedeff was unable to detect any trace of an open chain dimer from isoprene or any other of the divinyl compounds which he investigated.

More recently Aschan (32) has isolated a compound which he believes was 1-methyl-4-iropropenyl-2-cyclohexene. The latter too found no indication of an open chain dimer.

The polymerization of the other members of this series has been investigated by Harries (12), Lebedeff (31) and others but though dimeric compounds have been obtained none, would polymerize further.

The Effect of Temperature on the Polymerization of Isoprene and Dimethylbutadiene.

As in most reactions, an increase in temperature has a great effect on the rate of polymerization of isoprene and dimethylbutadiene. But not only does the temperature at which they polymerization is carried out influence the rate of reaction but also affects the amount and nature of the products obtained. As a result of a large number of experiments on isoprene and similar dienes Lebedeff (31) drew the following conclusions:

1. the higher the temperature used for polymerization, the higher would be the ratio of dimer to high polymer;
2. at a constant temperature the ratio remains the same.

The presence of a catalyst however may affect this. These conclusions have been investigated here in order to get some more quantitative data on the subject.

But not only do changes in temperature influence the amount of high polymers formed but also its properties. It has been shown by Staudinger (33) and by Whitby and his co-workers (34) that indene and styrene, when polymerized at elevated temperatures, always give polymers of lower molecular weights than when polymerized at lower temperatures. The temperature of formation of the polymer also influences its solubility in various solvents and the viscosity of the resulting solutions. So the effect of the temperature of formation and the time of heating upon the properties of the polymers of isoprene and dimethylbutadiene have also been investigated in this research.

IV EXPERIMENTAL WORK

The Preparation of Isoprene

The first step in the experimental work was the preparation of isoprene. The procedure followed was that of Harries and Gottlob (12). Figures I and 2 show the essential features of the apparatus used. In Figure I, A is a 3-liter Pyrex flask with a short neck and a side neck. The side neck is conveniently used for emptying and recharging.

B is the heating element shown in Figure 2.

C is a condenser through which water at 45-50° is circulated. The inner tube is of Pyrex glass. (The supply of warm water was conveniently obtained from the apparatus supplied with the Abbé refractometer).

D is a spiral condenser (with more coils than shown in the diagram), through the jacket of which cold water circulates.

E is a 300 cc. flask cooled to -10 C. or lower by an ice-salt mixture in the bath F.

G is placed in a Dewar flask H filled with ether cooled by solid CO_2. It serves to condense any isoprene which escapes E.

In Figure 2, the lower diagram shows an elevation of the heating element; the upper, a plan of the

Figure 1.

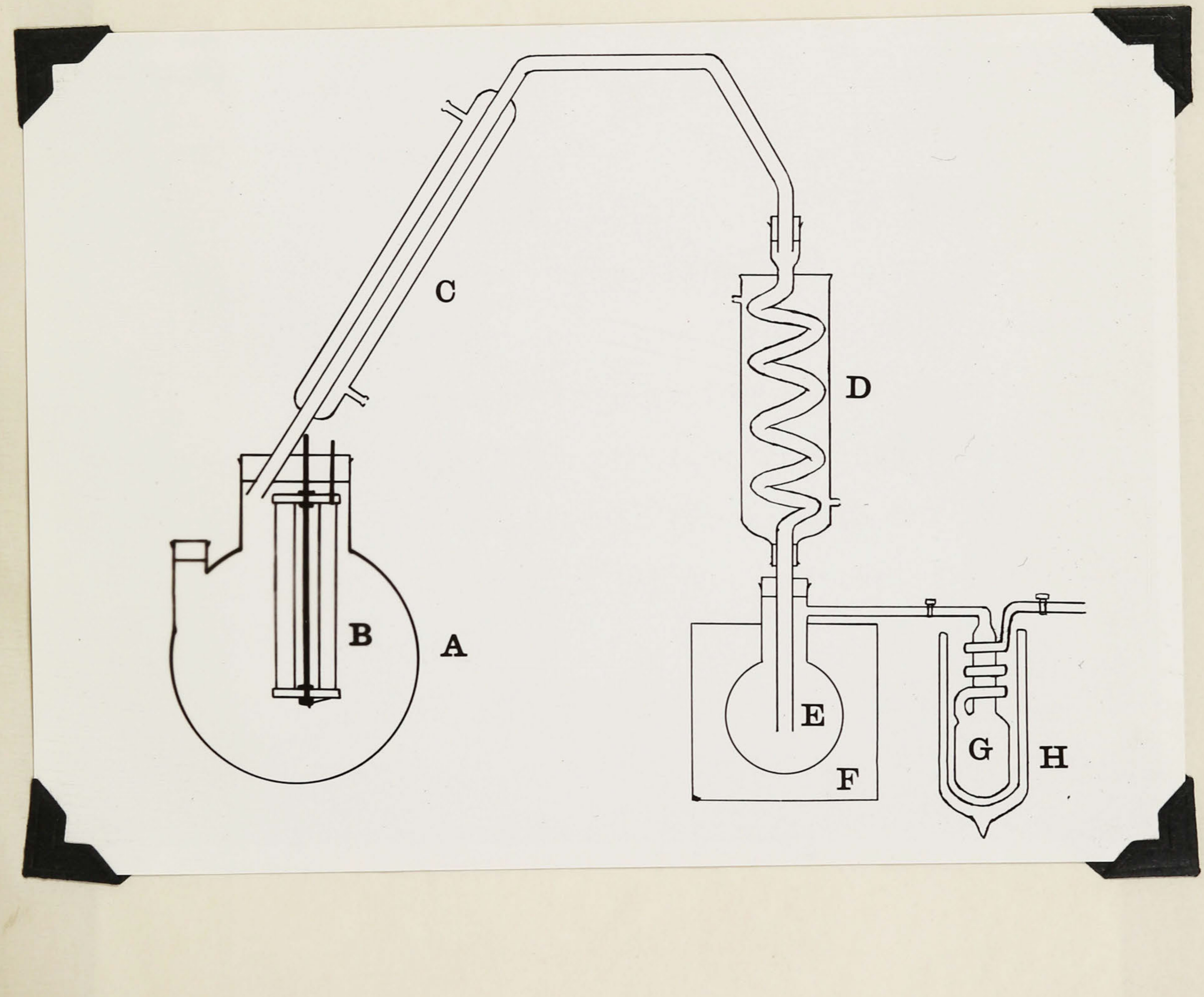
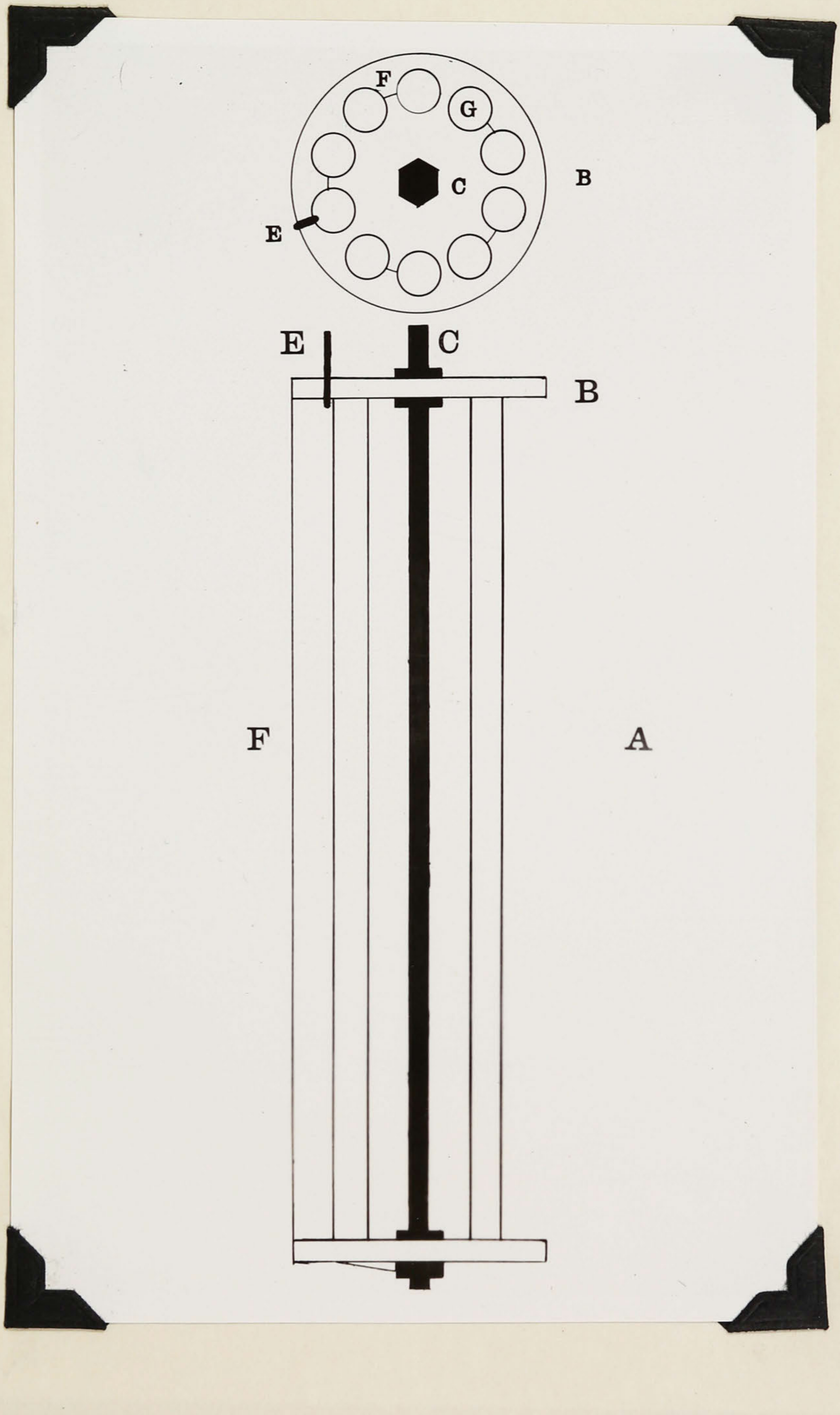


Figure 2.



top plate.

The element consists of 6 feet of No.28 gauge platinum wire (F) threaded through holes in two perforated disks of asbestos slate (B) 4.75 inches apart. This gives 11 vertical strands of wire in all. (The wire used was circular. It is probable that if it had been flattened better not results would have been obtained).

The asbestos slate plates were 0.125 in. in thickness and 1.5 in. in diameter. (Or of such diameter as to leave sufficient clearance in the neck of the flask for the liquid refluxing back from the condenser to flow into the flask without coming in contact with the hot plate or wires). The holes in the plates for the passage of the wire should be as large as the strength of the plates will permit, in order to allow of the free passage of vapors.

The plates are attached to a heavy copper wire, (C), 0.125 in. in diameter, by means of nuts soldered to the rod on either surface of each plate. This rod acts as one terminal. The other terminal (E) is attached to the end of the platinum wire which has been brought over the edge of the upper plate.

Another apparatus, which was similar to that used by Staudinger, was prepared. In this, the principle is the same as in the above lamp, but the decomposition takes place under reduced pressure. A diagrammatic sketch of the apparatus is shown in "Synthetic Rubber", by J.P.Schotz (1926), page 94. However, as this was found to be considerably more inconvenient and troublesome than the original lamp, it was not used.

Also it might be mentioned that a nichrome element could not be used as in a very few minutes it became heavily coated with carbon.

OPERATION

Only 450 cc. of dipentene (From the Hercules Power Company) were charged into the flask. This volume was used as it was found after trying quantities varying from 350-600 cc. that the apparatus worked most efficiently with such a charge. This was brought to the boiling point; and, after it seemed certain that the air in the flask had all been displaced, the heating coil was brought to, and maintained at, a dull red heat, (7.5 to 8.5 amps., D.C., 110 volts required) while the dipentene in the flask was kept boiling fairly rapidly.

It was found that, as the run proceeded, the platinum gradually became coated with carbon, with the result that its efficiency fell off. Hence each morning before starting a run the platinum was cleaned by heating the coil to a bright red heat for one or two minutes.

Further, as the run proceeded the concentration of resins in the liquid left in the conversion flask rose; and this also caused the rate of isoprene formation to fall off. Hence before each run, the flask was cleaned out thoroughly and dried. The residue which was thus rejected of course contained some unchanged dipentene, but for our purposes it did not seem worth while to recover it by separating it from the resin which it contained.

The distillate contained unchanged dipentene as well as isoprene. The former could of course be used again.

The following shows the results of a representative run:- 450 cc. of dipentene boiled as described for 7 hours left a residue of 160 cc. in the conversion flask and gave a distillate of 270 cc. On fractionation the distillate gave an isoprene fraction (boiling 27.5 to 37°C.) of 190 cc. the balance being dipentene.

PURIFICATION OF ISOPRENE

Approximately 4 liters of isoprene were obtained in the manner indicated. This was dried over calcium chloride and fractionated several times. The first method used for the purification of this product was one described by Ostromysslensky (35). 1500 cc. of isoprene, (B.P. 33°-36°C.) were allowed to stand at room temperature over 16 grams of sodium wire and 135 grams of barium peroxide for at least two days. This mixture was then refluxed for one hour ~~and bour~~ and distilled. After fractionation the volume of isoprene (B.P. 33° to 35°) was 1300 cc. This isoprene which was used in the first part of the work as Ostromisslensky claimed that after such treatment the product would be 90-100% pure and would contain no unsaturated compounds other than isoprene.

Finally the purification was carried further than this by a second method used by Ostromisslensky (35). From the isoprene purified as above, the tetra bromide was made by the Mokiewsky (36) method in which bromine is added to a cooled dilute solution of isoprene in chloroform. The isoprene was removed from this by treatment with zinc dust. According to Gustavson's method (37) the actual procedure used was as follows, 100 cc. of isoprene were dissolved in 100 cc. of chloroform. The solution was introduced into a 2 liter flask fitted with a reflux condenser, dropping funnel and mechanical stirrer. The flask was cooled in an cc. ice-salt bath to about -10°C. Then a solution of 320 grams of bromine in 500 cc. of chloroform, previously cooled, was added, drop by drop, to the isoprene-chloroform solution. It was found after five or six experiments that these concentrations were the most convenient, for though some substitution took place it was not very great. In more concentrated solutions, the theoretical quantity of bromine could not be added without a considerable quantity of hydrogen bromide being given off.

The solution of bromides thus obtained was then washed with an aqueous soda solution, till it was colorless. The chloroformic layer was then dried over anhydrous potassium carbonate. The mixture was filtered and the chloroform distilled off. The concentrate, generally brown in color, was then distilled in vacuo. Three main fractions were obtained. The first boiled at 60°-70°C. (under a pressure of 12 mm. of mercury); the second at 88°-94° and the third at 155°-160°. The first fraction, containing amylene bromides, was discarded. The presence of such a fraction as this shows that Ostromisslensky's first method was not as efficient as was claimed, for, according to him, isoprene, purified in that manner, would contain no unsaturated compounds other than isoprene. The yield of the second and third fractions, isoprene dibromide and tetrabromide respectively, was about 75-80%. It was very difficult to get these fractions in a pure state, but after three or four distillations in vacuo, colorless, or almost colorless, products, were obtained. As these went dark on standing they were used immediately in all cases. The relative amounts of the two fractions varied, but when the above procedure was adhered to only a small amount of dibromide was obtained. If however an insufficient quantity of bromide was added the second fraction was larger as of course would be expected.

The regeneration of the isoprene from the tetra bromide was conducted first according to the procedure recommended by Ostromisslensky. Isoprene tetrabromide, 320 grams, was slowly added by means of a dropping funnel to 300 cc. of alcohol in which 262 grams of zinc dust (twice the theoretical quantity) were suspended. The reaction was very slow in the cold but when the alcohol was kept boiling gently, it proceeded very rapidly. To the flask (of the three-necked type) was attached a reflux condenser which was kept at such a temperature, 45°-50°C., that only the alcohol was condensed, while the isoprene passed through it and was condensed in a second condenser. This apparatus was similar to that used in the preparation of the crude isoprene. The traces of alcohol carried over with the isoprene were removed by washing. The yields by this method, even before the product had been dried and distilled, were low, 40% being a maximum. During the reaction the alcohol became very dark, and on cooling a hard black resinous mass separated out. Also much of the zinc dust did not react as it became caked and crusted in the bottom of the flask. In the final procedure adopted a larger quantity of alcohol, 450-500 cc. was used. The zinc dust was added in three portions and kept in a state of constant agitation by means of an electrically driven stirrer passing through one neck of the flask, and sealed with mercury in the usual manner. The yields by this method were very good, 85 to 90% of the theoretical quantity of isoprene being recoverered.

The same general procedure was applied to the dibromide. In this case 75 to 85% of the theoretical quantity of isoprene was recovered.

The isoprene obtained this was then dried over calcium chloride and distilled. The distillate was then allowed to stand over sodium wire for several days and re-distilled. The boiling point of the pure isoprene was 33.4 to 33.9 at 744 mm.

PREPARATION OF 2-3-DIMETHYLBUTADIENE -1-3.

Preparation of Pinacone Hydrate

For the preparation of pinacone hydrate 200 grams of 20-mesh aluminium were placed in a perfectly dry 3-liter flask. Then a solution of 30 grams of mercuric chloride in 300 ccs. of acetone was added rapidly with agitation. This was left undisturbed for 15-20 minutes. Then 10 grams of finely divided zinc chloride and 100 ccs. of acetone were added. After this addition the mixture was allowed to stand for one and a half to two hours with frequent shaking. The shaking had to be as vigorous as possible to prevent the caking of the aluminium at the bottom of the flask. Then 500 cc. of acetone and a solution of 30 grams of mercuric chloride in 600 cc. of acetone were added drop-wise over a period of four hours, at such a rate as to keep the liquid at its boiling point. It was found necessary to alternate the addition of these two reagents so as to cut down the vigor of the reaction, ie. 100 cc. of one and then 100 cc. of the other. A large excess of acetone is used to keep the aluminium complex in solution. The flask was then covered with a cloth and allowed to stand overnight. Generally it was found refluxing slowly in the morning. It has been found that stirring is not necessary as long as the aluminium is kept in a loose condition. In all the reaction took 35-40 hours. The flask was then heated on a water bath for two hours. Then 1200 cc. of water were added gradually to decompose the complex and the mixture boiled for two hours. When it had cooled to about 40°C. it was filtered and the mass extracted with four 1000 cc. portions of acetone. The filtrate and washings were concentrated to about 2000 cc. and the supernatant oil removed with a separating funnel. The aqueous liquid on standing overnight in an ice box deposited crystals of pinacone hydrate. The oil, which consists of mesityl oxide, isophorone, etc., deposited crystals of pinacone. The total yield of pinacone hydrate was about 350 grams.

It was necessary during the reaction to exclude all moisture. The acetone had to be carefully dried over calcium chloride and fractionally distilled. Small amounts of impurities in the acetone greatly reduced the yield of hydrate and on two occasions prevented the reaction from going at all.

The hydrate was purified by dissolving it in an equal weight of boiling water, filtering and cooling the filtrate in ice. The crystals deposited were removed by filtration. Two recrystallizations were generally enough to give a very pure product.

Removal of Water of Crystallization from the Pinacone Hydrate

Pinacone hydrate when distilled gave up practically all its water under 135°C. This carried over 10-15% of the pinacone present. This however was recovered from the distillate. For this preparation a long air condenser is used with a well cooled receiver. The yield of anhydrous pinacone was 85-90% of the theoretical.

Potassium hydroxide and potassium carbonate were tried as dehydrating agents but were not as convenient to use as the method described.

Dehydration of Pinacone to 2-3-Dimethylbutadiene-1,4

Anhydrous pinacone was treated with 2% of sulphonilic acid (38) and heated with a free flame so that the vapors passing off registered a temperature of about 90°C. Half of the pinacone was added through a separatory funnel so as to maintain the concentration of the catalyst more or less constant as the reaction progressed. The distillate consisting of two layers was separated and the hydrocarbon layer dried and distilled. The fraction distilling below 90° was fractionated again and the liquid boiling from $68-72^{\circ}$C. taken as diene. Yield about 45% of the theoretical.

The above experiment was repeated but 10% of potash alum (39) was used instead of the sulphanilic acid. The yield obtained was very low (about 30% of the theoretical) most of the hydrocarbon boiling above 72°C.

Dehydration was then attempted using potassium bisulphate (40). After drying and fractionating the hydrocarbon, which was obtained, the yield of diene boiling between 68° and 73° amounted to 40% of the theoretical.

Then 500 grams of pinacone were treated with 2 grams of 48% hydrobromic acid (41) under the same conditions as before. The reaction proceeded very slowly but after 24 hours most of the pinacone had reacted. After the first fractionation, the yield was only 55% of the theoretical. However it was found that by repeated fractionation of the apparently higher boiling portions, the yield of the dimethylbutadiene could be raised from 55% to between 70 and 80%. In all 3000 grams of anhydrous pinacone gave 1600 grams of pure dimethylbutadiene.

As the impurities in the dimethylbutadiene were mainly pinacoline, they were removed by treating the carefully dried and fractionated product with sodium. After two or three such treatments, the product was considered pure as its refractive index was found to agree quite closely with Kandakow's value.

$N_D^{20} = 1.4375$ - Kandakow's value (42).

$N_D^{20} = 1.4376$ - Whitby and Macallum (43)

$N_D^{22} = 1.4370$ - Found for one sample

$N_D^{24} = 1.4367$ - Found for a second sample

The boiling point varied between 69.5° 70.5°C.

The Preparation of Dimethyl-2-4 Pentadiene-2-4.

This compound was prepared according to Grignard's method (44) by the action of methylmagnesium iodide on mesityl oxide in ethereal solution.

The methyl iodide was prepared by the method of Dumas and Peligot (45). 72 grams of methyl alcohol and 20 grams of red phosphorus were mixed in a flask to which was attached a reflux condenser. 200 grams of iodine were added slowly. After this addition, the mixture was allowed to stand over night and then distilled from a water-bath. The distillate was shaken with dilute sodium hydroxide, dried over anhydrous calcium chloride and redistilled. The yield of the pure product was 180 grams.

The mesityl oxide was prepared from diacetone alcohol by distilling the latter in the presence of iodine (45). The diacetone alcohol had been prepared by refluxing acetone against barium hydroxide in the usual manner (46).

The actual procedure used in preparing the diene was as follows. 34 grams of magnesium turnings were introduced into a 2 liter flask, which had connected to it a reflux condenser and dropping funnel. Then enough of an ethereal solution of methyl iodide, which contained 202 grams of the iodide dissolved in an equal volume of pure anhydrous ether, was added to cover the magnesium. A vigorous reaction immediately set in, and the flask had to be cooled with running water. Then 550 cc. of ether were added and the rest of the iodide solution was allowed to run in slowly through a dropping funnel. When the addition was complete, the mixture was heated on a water bath for one hour. Then a solution of 127 grams of anhydrous mesityl oxide dissolved in an equal quantity of ether was added slowly through the dropping funnel. The rate of addition of the methyl iodide and mesityl oxide solutions had to be controlled carefully on account of the vigor of the reactions. After the addition of the mesityl oxide the mixture was heated for half an hour on a water bath and then allowed to stand over night. In the morning the flask was cooled in crushed ice and slightly over the theoretical quantity of a 10% acetic acid solution, previously cooled with ice, was added. The ether layer was then separated from the aqueous layer and the latter washed once with ether. The ethereal layer and extract were washed with dilute sodium hyrdoxide solution, then with dilute sodium bisulphite solution and then with distilled water. The solution thus obtained was concentrated on a water bath. The distillation was continued at atmospheric pressure. At about 70° C. the dehydration process began and the mixture of water and hydrocarbon distilled almost completely at 80° C. The residue consisted of unchanged mesityl oxide and a dimer of the diene. The hydrocarbon was dried with calcium chloride and fractionated carefully. The boiling point found was 92° C. at 749 mm. The boiling point found by Grignard was 92-93° at 750 mm. The yield of pure hydrocarbon was 50% of the theoretical.

The Preparation of Methyl-2-pentadiene-2-4.

The starting point in this preparation is diacetone alcohol. Diacetone alcohol is reduced to 2-methyl-pentandiol-2-4 which is then dehydrated to give the desired diene.

Two methods for the reduction of diacetone alcohol have been tried but neither has proved satisfactory.

Zelinsky and Zelikoff's procedure (47) has been followed carefully but very poor yields have been obtained. According to this method an aqueous solution of diacetone alcohol is reduced by means of 3% sodium amalgam. Various concentrations of the amalgam have been used but the yields have always been low — between 30 and 40%.

The second method, the reduction of the diacetone alcohol by the action of sodium on moist ether, gave poor results also. A 30% yield was the highest obtained.

The reduction by electrolytic means is now being attempted. The method being followed is that of Read and Fletcher (48).

The dehydration of the diol has been carried out very successfully, on a small scale anyway, by means of hydrobromic acid as described by Kyriokides (49).

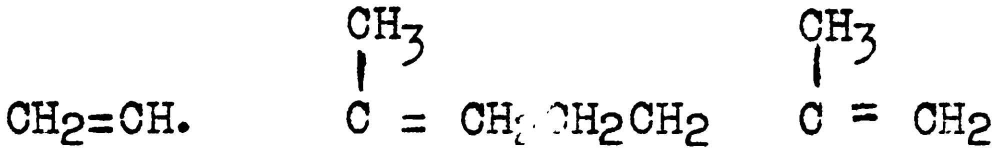
The Polymerization of Isoprene and the Examination of its Lower Polymers.

Experiment A

In the first polymerization of isoprene, the procedure followed was that given by Ostromisslensky for the preparation of β myrcene (19a). 200 grams of isoprene were heated in an iron autoclave for 5 days at a temperature varying between 85° and 95°C., but for the most part at 92°C. The isoprene used in this experiment had only been purified by the first method described, i.e. with sodium and barium peroxide. At the end of the 5 days, the autoclave was opened and the colorless syrupy liquid siphoned off. The solution was concentrated by distilling off the unchanged isoprene from a water bath. The isoprene recovered amount to 56% of the total weight used. The concentrate was then distilled with steam and 65 cc. (27.7% of the total weight of isoprene used) of a clear, colorless oil, and 30 grams (15% of the total weight)of a rubber-like product were obtained. The oil had a peculiar odor, unlike a stock sample of dipentene. It was then diluted with ether and dried over anhydrous sodium sulphate for 137 hours. The solution was then poured off; the sodium sulphate remaining extracted with dry ether, and the ether then removed from the original solution and the extract by fractional distillation. The oil left was distilled under a pressure of

10.5 mm. of mercury. The temperature rose very rapidly to 53.5°C., and from there rose very slowly till at the end of the distillation the temperature registered was 56.5°C. The boiling point of this fraction corresponded with that given by Ostromisslensky for B-myrcene. There remained in the distilling flask a small residue of a very viscous, colored oil. When this was treated with alcohol, a fine crystalline precipitate formed. Its constitution was not determined.

Ostromisslensky's formula for B-myrcene is:



$$CH_2{=}CH.\overset{\overset{CH_3}{|}}{C}=CH_2CH_2CH_2\overset{\overset{CH_3}{|}}{C}=CH_2$$

This shows the presence of three double bonds, two of which are conjugated in the molecule. So in order to determine the unsaturation of the above oil, a standard sodium thiosulphate solution and a Hanus solution were prepared. The following procedure was used. A weighed quantity of oil (about .15 grams) was dissolved in 10 cc. of chloroform. To this was added twice as much Hanus solution as would be required to saturated the oil if it was pure B-myr~~e~~cene. The whole was let stand in the dark in a glass-stoppered bottle for varying lengths of time. After the period of absorption 10 cc. of a 15% potassium iodide solution and

100 cc. of water were added. the unabsorbed iodine was then titrated with sodium thiosulphate, starch being used as an indicator. The amount of iodine absorbed, and from this the number of double bonds saturated, were calculated. In each case of course a blank was also run.

Period of Absorption	No. of Double Bonds Saturated
1/2 hour	.69
5 hours	1.8
5-1/2 "	1.8
7-1/2 "	1.9
24 "	2.1

Evidently then the oil contained two double bonds unless the theoretical absorption would not take place on account of the presence of conjugated linkages. But as a sample of isoprene which was not specially purified absorbed the equivalent of 1.5 double bonds on treatment with the same solution of iodine bromide for 7 hours, conjugation would not seem to cause such an effect.

The molecular weight of the oil was determined by the cryoscopic method using benzene as the solvent.

Molecular weight calculated for $C_{10}H_{16}$	136.2
" " found	139.9

Ostromisslensky had shown that B-myrcene (19a) and in general compounds with conjugated double bonds on treatment with a concentrated aqueous solution of sulphur dioxide give rise to a white amorphous precipitate. This was tried, but the oil gave only a trace of such a precipitate even after several days.

To see if the oil would polymerize to a high polymer it was heated with metallic sodium and barium peroxide in a sealed glass tube for 3 days at 100°. The tube was opened and the contents examined. There was no evidence of any polymerization having taken place. B-myrcene under such conditions gave, according to Ostromisslensky, a rubber-like polymer.

The index of refraction of the oil was then taken and was found to be very close to that of dipentene under the same conditions. A source of white light was used, with an Abbé refractometer in each case. The temperature was kept constant at 14.5°C.

Oil	1.4769
Dipentene	1.4765

Ostromisslensky's B-myrcene gave a much higher value than dipentene, i.e. n_D^{26} 1.53681.

As it now seemed almost certain that the oil was not B-myrcene it was thought safe to distil it at atmospheric pressure. This of course could not be done with B-myrcene because under such treatment it would polymerize. In this case, however, after distillation there were no signs to indicate that polymerization had taken place.

Fraction	(1)	Up to 172°C. (corr.)
	(2)	172 - 174
	(3)	174 - 176
	(4)	176 - end.

On distillation of a sample of dipentene most of the oil came over between 174° and 176°C. (B.P.of pure dipentene 175-176°C.). But in this case fractions (2) and (3) were of equal volumes and included most of the oil. It looked therefore, as though some other oil were present besides dipentene (which was identified later).

The following values for the refractive index of dipentene and the different fractions of this oil were obtained when a source of white light was used with an Abbé refractometer.

Dipentene	(B.P.174.0-176.0)	n_D 1.4745	at 18.6°C.
Oil	(B.P.172 -174)	1.4750	at 16.5
Oil	(B.P.174 -176)	1.4753	at 16.5

These results were in each case the mean of at least four different readings.

Preparation of Tetrabromide

Small samples (1-2 cc.) of each fraction of the oil and of dipentene (B.P.174-176°C.) were taken and treated with four parts of absolute alcohol and four parts of absolute ether and saturated in the cold with bromine. These were allowed to stand in an ice box for two weeks.

The solutions were evaporated. The residue in each case consisted of crystals mixed with a very viscid oil. In the case of dipentene however the proportion of oil to crystals was much less than with the fractions of the other oil. After several recrystallizations from ether, the oil was removed from the dipentene tetrabromide and its melting point found to be 125°C. The original melting point ranged between 103°-115°C. After 12 recrystallizations the melting point of the tetrabromide from the unknown oil was found to have risen from between 90° and 105°C. to 124° - 125°C. Dipentene by this method was shown to be present in each fraction of the oil.

Attempts to prepare a nitrosite from the 3 fractions of the oil resulted only in the formation of very viscid oily products from which no crystals could be separated. The dihydrochloride too could not be prepared in a crystalline form.

This oil then was not B-myrcene or an open chain dimer of isoprene intermediate between it and its caoutchouc-like polymers, but a mixture of cyclic dimers consisting mainly of dipentène.

Experiment B.

As it was known now that the isoprene used in the above experiment was not as pure as thought originally, the procedure was repeated using isoprene purified by the tetrabromide method. 50 cc. of this pure isoprene was introduced into each of 6 Pyrex tubes. The iron container was not used in this experiment as Ostromisslensky had on one occasion definitely specified glass. The tubes were about the size of an ordinary Carius tube. These were cooled by means of solid carbon dioxide and sealed carefully. They were then heated on a water bath at 85°C. for 98 hours. Thus all the details given by Ostromisslensky (19a) have been adhered to closely. At the end of the period mentioned, the tubes were opened and the colorless syrupy solution removed. The unchanged isoprene was recovered from this by distillation at atmospheric pressure. The residue consisted of a rubber-like polymer and an oil. The latter was separated from the high polymer by distilling it off first at a pressure of 9 mm. of mercury and then at 1 to 2 mm. The distillate was collected in a flask cooled in solid carbon dioxide moistened with ether. The distillation was continued till the weight of the undistillable residue remained constant. Both distillations were carried out on a water bath in order to prevent any further polymerization or change in the character of the products.

The oil, amounting to 19.5 grams, obtained this way was dried over calcium chloride and then redistilled from a water bath under a pressure of 7 mm. of mercury.

The boiling point of the mixture rose rapidly to 53°C. and then very slowly till at the end of the distillation it had reached 54°C. Only a very slight residue remained in the distillation flask. The mixture was fractionated under the same pressure as before. Two fractions were obtained.

Fraction and Weight	Boiling point at a pressure of 7 mm. of mercury	Index of refraction
#1 7.3 grams	Up to 53°C. mainly at 52-53°C.	N_D^{25} = 1.4540
#11 11.4 grams	53°-54°C.	N_D^{25} = 1.4713
#111 75 grams	residue	not determined.

The table shows that fraction #1 had very low refractive index. This was proved later to be due to the presence of isoprene in it. The refractive index of fraction #11, however, was close to, but slightly lower than that of dipentene under the same conditions. The refractive index of the residue was not measured.

These three fractions were then distilled at atmospheric pressure. The fractions obtained and their properties are listed in the following table.

Fraction	Boiling Point	Index of Refraction at 26°C.	Remarks.
1	Up to 128°C.		Consisted mainly of isoprene. Gave a heavy white precipitate with aqueous solution of sulphur dioxide.
2	128°-171° (mainly between 160° -171°)	1.4667 to 1.4670	Slight precipitate with an aqueous solution of sulphur dioxide.
3	171°-174°	1.4705 1.4710	Very slight white precipitate with aqueous sulphurdioxide.
4	174°-175°	1.4723 to 1.4726	No precipitate with aqueous sulphur dioxide solution
5	residue	1.4827 to 1.4820	A viscid oil. Slightly brown in color.

The residue was then distilled under reduced pressure and a few drops of a clear, colorless oil were obtained. The index of refraction of this was measured at 25°C. and found to be 1.4730. The residue from this was a dark brown and very viscid oil. It dissolved in benzene but when treated with absolute alcohol a very small quantity of fine crystals separated out. The oil obtained from residue #5 became very viscid on standing in the presence of air and when treated with absolute alcohol gave a crystalline precipitate closely resembling the above. The quantity of thse crystals was very, very small so that analysis was impossible but the conditions under which they were formed indicate that they were probably an oxidation product of the original oil. The other fraction showed a marked increase in refractive index even on standing in corked test tubes, but did not give any crystalline precipitate with absolute alcohol.

This oil too showed no tendency towards polymerization when treated with sodium and barium peroxide for 3 days at 100°C.

The above data shows then that the oil obtained in experiment B was practically identical with that obtained in experiment A.

The above experiment was repeated at a higher temperature (experiment C). 60 cc. of pure isoprene were heated in a Pyrex tube for 12-1/2 hours at 145°C. + 1.5°C. The dimer was separated from the rubber-like polymer and unchanged isoprene by distillation first at atmospheric pressure and then under reduced pressure as in experiment B. Distillation of this oil under reduced pressure and at atmospheric pressure gave fractions whose boiling points and refractive indices were the same as those of the corresponding fractions obtained from the oils formed in experiments A and B. When pure isoprene was heated for 5-1/4 hours at this temperature the same oil was obtained (experiment D).

Experiment E.

In a second method given by Ostromisslensky (19a) for the preparation of B-myrcene, pure isoprene (1 kilogram) was heated with benzoyl peroxide (50 grams) for 10 days at 90°C. This procedure was repeated but, as in all previous experiments, too, smaller quantities had to be used. 50 cc. of pure isoprene and 1.71 grams of benzoyl peroxide were introduced into each of three Pyrex tubes and sealed up carefully. These tubes were then heated on a water bath for 10 days at or within a degree or so of 90°C. In this case, too, most of the isoprene remained unchanged. The solution was distilled on a water bath to get rid of this isoprene and the residue treated with steam. The oil,which distilled,was separated from the layer of water and dried over calcium chloride. It was then distilled under reduced pressure. At 10.5 mm. of mercury the boiling point rose rapidly to 61.5°C. and remained constant there till the distillation was finished. The boiling point in this case was slightly higher than that of the previous samples of oil. Two fractions were obtained.

Fraction	Boiling point (10.5-11 mm.)	N_D^{25}	d_4^{25}
1	Up to 61.5 C. (mostly at 60-61.5°C.)	1.4710 to 1.4713	.832
11	61.5	1.4727	.838

In its action towards an aqueous solution of sulphur dioxide it behaved like the previous oils.

Thus, though isoprene has been polymerized under the various conditions mentioned, the oily polymer obtained in each case seems to be the same. Molecular weight determinations have shown it to be a dimer or a mixture of dimers. It has been shown too that it possessed two double bonds per ($C_{10}H_{16}$) unit. The fact that it gave only a slight precipitate with an aqueous solution of sulphur dioxide proves that these double bonds are not conjugated. Thus the possibility of the presence of any open chain dimer of isoprene in this mixture in more than traces, is eliminated. The fact that the oil was a mixture was proved by the fact that it could be distilled and fractions of different boiling points and refractive indices obtained. These constants indicated the presence of dipentene. This was proved when dipentene tetrabromide was isolated from the products,obtained on brominating the oil. The low refractive index of the oil and the fact that it did not polymerize on being heated with sodium and barium peroxide also showed that neither B-myrcene nor any other product, intermediate between isoprene and its rubber-like polymer, were present.

Though nothing further can be said definitely concerning the composition of this oil, a comparison between the physical constants and general properties of its various fractions (experiment B) with those of the compounds in the following table brings out the close resemblance between them and Lebedeff's and Aschan's dimers. In fact the main fraction obtained corresponds closely to Aschan's 'diprene' which was obtained in a similar way. A small fraction too has been isolated which corresponds roughly to Lebedeff's dimer in boiling point and refractive index. The constants of the oil also resemble those of myrcene and Harries(dimer but it has been shown that these cannot be present, as they are open chain dimers, each containing three double bonds, two of which are conjugated.

It is expected that when a larger quantity of this oil has been accumulated a closer study may remove some of the doubt as to the nature of its undetermined constituents.

Compound	Boiling point	N_D	Density	Remarks
B-myrcene	58°C. (13 mm)	1.5368 at 26°C.	d_4^{20} .8472	Gives a white precipitate on addition of an aqueous sulphur dioxide solution. On being heated with sodium and barium peroxide it gives a rubber-like polymer.
Myrcene	56-7 (12 mm)	1.47065 (20°C)	d_4^{20} .7962	Can be distilled without polymerizing. B.P.16 (260mm). Gives a white precipitate with aqueous sulphur dioxide solution. Naturally occurring.

Compound	Boiling point	N_D	Density	Remarks
Harries' crude open chain (?) dimer (12)	63-5 (14 mm)	1.47408 (18°)	d_{18}^{18} .8451	Forms an oily tetrabromide
Lebedeff's cyclic dimer (31)	44°C. (9 mm)	1.4638 (20°C)	d_{0}^{20} .8331	B.P.160-1(760mm) Forms a tetrabromide.
Aschan's dimer(32)	171.5 to 173°C. at 752mm.	1.46960 (23.4)	d_{4}^{20} .8481	Gives an oily tetrabromide. Does not polymerize to a rubber-like polymer.
Dipentene 58°(9.5mm) →	175.6° (760mm)	1.47428 (at 20°C)	d_{0}^{20} .8454	Gives a crystalline tetra bromide.

The Polymerization of Dimethylbutadiene and the Examination of its Lower Polymers.

In order to find out if any compound comparable to B-myrcene could be isolated from the products of the polymerization of dimethylbutadiene,the following experiments were carried out.

In experiment #1 two tubes, each containing 50 cc. of pure dimethylbutadiene were heated in a water bath at 85°C. for 101 hours. At the end of this time the tubes were opened and the clear syrupy liquid poured into a flask. The unchanged diene was removed from the rest of the solution by distillation at atmospheric pressure. The oily polymer was then distilled from the rubber, under reduced pressure, in the same way as described in experiment B. The amount of oily polymer formed in this case was very small, so this experiment was repeated in experiments 11 and 111 but the period of heating was increased to 154 hours and 250 hours, respectively. The analyses of these tubes were carried out separately and showed that there was an increase in the amount of oil formed as the time of heating was increased but that it was still very small. Accordingly 375 cc. of pure dimethylbutadiene (experiment IV) were heated in 5 sealed tubes in a water bath at 85°C. for 120 hours. The oily polymer formed was isolated as before and added to that already obtained.

The crude product, 5 or 6 cc. in all, was distilled at a pressure of 10 mm. and its boiling point found to be about 80°. Its index of refraction at 26°C. was 1.4775. It gave no precipitate with an aqueous solution of sulphur dioxide. On being heated at 100°C. in a sealed tube for 4 days, the oil became slightly viscid (N_D^{26} 1.491) and colored but gave no precipitate when added to alcohol.

In experiment V, 100 cc. of pure dimethylbutadiene were heated at 145°C. for 12-1/2 hours. The oily polymer was separated in the usual manner. After purification it gave no precipitate with an aqueous sulphur dioxide solution. When boiled at a pressure of 748 mm. of mercury it showed a very sharp fraction at 198°-200° C. Its refractive index at 21° C. was 1.4799.

The following table gives the physical properties of the above oils and those of the dimer isolated by Lebedeff (31) and Aschan (32) from the polymerization of dimethylbutadiene. The same compound was isolated by Kandakow (50) and also by Richards (51) from the pyrogenic decomposition products of dimethylbutadiene rubber.

	BOILING POINT	NO.
Lebedeff's compound	205° C. (750 mm.) (85° at 13 mm.)	1.47716 at 19.7° C.
Aschan's compound	200.5 201.3 (87° at 12 mm.)	1.47915 at 20° C.
Richards	205° C.	1.47786 at 25° C.
85° Polymer	Approx. 80° C. (10 mm.)	1.4775 at 25° C.
145° Polymer	198-200 (748 mm.)	1.4799 at 21° C.

The oil obtained at both temperatures is obviously the same. Its properties agree well with those of the dimethyldipentene described by the above-mentioned workers.

Thus, too, by the polymerization of dimethylbutadiene, no open chain compound intermediate between the diene and the high polymer has been obtained.

The Effect of Temperature and Time of Heating upon the Polymerization of Dimethylbutadiene.

In order to determine the effect of temperature on the rate of polymerization and the yield of dimers and high polymer, dimethylbutadiene was kept in tubes, sealed at atmospheric pressure for different lengths of time, at temperatures varying from 45°C. to 145°C. After this treatment was over the tubes were opened and the contents transferred to a tared-flask. The unchanged diene was removed by distillation, from a water-bath, at atmospheric pressure. Then the diene was distilled from the residue under reduced pressure and collected in a flask cooled with solid carbon dioxide moistened with ether. This distillation was carried on till the flask and its contents no longer lost in weight. The flask was reweighed. The difference between this weight, and that of the flask alone, was taken as the weight of high polymer. To determine the yield of dimer the product obtained from the vacuum distillation was evaporated under reduced pressure till no more diene came off, or else distilled in vacuo and fractionated. The results obtained are tabulated in the following table.

Weight of diene used	Reaction carried on for	Reaction carried on at	% of diene polymerized	% of diene converted to high polymer	% of diene converted to dimer*	Experiment
725.	80 days	room temperature	3.45%	3.45%	None	VII
174.5	10 days 12 hours	45° approximately	19.25	19.25	Traces	VIII
72.7	4 days 5 hours	85° approximately	11.4	10.5	.9	I
72.7	6 days 10 hours	85°C.	15.3	13.8	1.5	II
72.7	10 days 10 hours	85°C.	22.3%	19.6	2.7	III
14.5	37 days 11 hours	85°C.		49.7%	Not determined	VI
72.7	12-1/2 hours	145° 1.5°C.	26.7%	15.6%	11.1%	V

The polymer in experiment VII was formed in a sample of dimethylbutadiene which had been standing in a sealed pyrex flask in the laboratory. In experiments I, II, III, VI and VIII the tubes were heated in a water-bath, but in experiment V the heating was carried on in a bomb furnace. In all cases the tubes were of the same size (volume 105 cc.) and the same amount of liquid (50 c.c.) was put into each. This was found to be an important factor as the amount of air in the tube greatly influenced the rate of polymerization.

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* The dimer obtained in these experiments (and #4) has been described in a previous section.

In Experiment IV, when a larger type of tube (volume 250 c.c.) was used, 272.5 grams of diene (75 c.c. in each tube) when heated at 85°C. for 120 hours, gave 50 grams of rubber-like polymer -- (18.3%). This yield is much higher than the data in the table would indicate. However, these results are not surprising as it is a well known fact that oxygen, oxides, ozonides, peroxides and other oxidizing agents, exert a definite catalytic influence on the polymerization of such dienes as this.

In experiments I, II, and III the ratio of the amount of oil to the amount of rubber-like polymer is not a constant. This however cannot be taken to disprove Lebedeff's rule as the experimental error in handling these small quantities (.7-2 grams) was relatively great. Also as in these cases the oil was not distilled, any impurity in the original diene would be concentrated here. It has been shown by Lebedeff, Harries and others that after a certain point has been reached the rate of polymerization decreases. In the present work, experiments I, II, III and VI bear out this fact.

The effect of temperature on the rate of polymerization of dimethylbutadiene is also brought out in this table. This is shown for instance in experiments VIII and III where a difference in temperature of 40°C. causes a difference of 99-1/2 days in the time of heating required to bring about approximately the same percentage conversion of diene to high polymer. The yield obtained at 145°C. is quite in accord with the results of Lebedeff (31) who found that when dimethylbutadiene was heated for 5 hours at 150°, 15.1%

of the diene was polymerized and for 15.5 hours at the same temperature 38.4% was polymerized. At these higher temperatures, as Lebedeff, Harries and others have already noticed, the yield of dimer is greatly increased. It should be mentioned that the tubes used in the polymerization at 145°C. were 165 c.c. in volume but the volume of diene (50 c.c.) was the same.

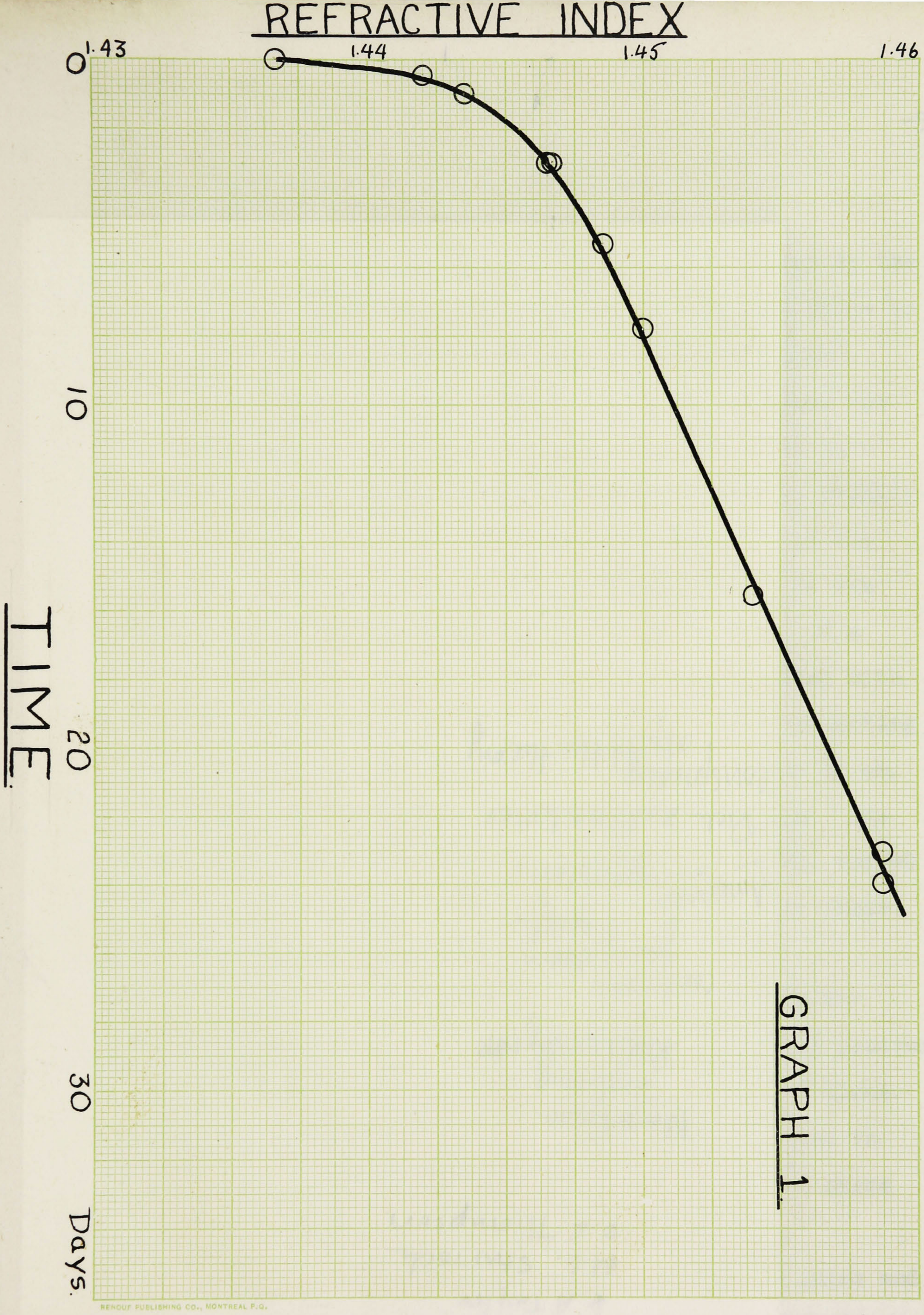
The Effect of Polymerization upon the Refractive Index and Density of Dimethylbutadiene.

In order to determine the effect of polymerization upon the index of refraction and density of dimethylbutadiene a number of small tubes, the volume of each being about 15 c.c., were made up and 5 c.c. of pure diene introduced into each. These were cooled in solid carbon dioxide moistened with ether, and sealed off. They were then hung, by means of a copper wire cage, into a constant-temperature bath. This was kept at 85° + 2.5°C. by means of an electric heater and thermo-regulator, and was stirred efficiently. This temperature was chosen as it was known to cause comparatively rapid polymerization of the diene to high polymer with only but a small amount of dimer formation. After the period of heating was over the tube~~s~~, whose refractive index and density was to be measured, was removed from the bath and allowed to cool. It was then opened and its contents transferred to a weighing bottle. The refractive index of the solution was measured with an Abbé refractometer kept at 24°-25°C. The weighing bottle and its contents were placed in a ther~~m~~mostat kept at 25° +.02°C. and allowed to come to this temperature. The density of the solution was then measured. For this determination a small pipette, about 1 c.c. in volume, had been previously standardized. This pipette and a tube, which was made fit closely over the outlet of the pipette in order to prevent evaporation, were weighed. Then the solution was drawn into the pipette till the meniscus had reached the graduation mark. The tube was then slipped over the outlet of the pipette and the whole reweighed. The density was calculated from the difference between the two weights. The results obtained are shown in the following table.

Time at 85°C.	N_D^{25}	$D_{4^\circ}^{25^\circ}$	
0	1.4367		
12 hours	1.4420	.7335	
12 hours	1.4420		
1 day	1.4435	.7372	
3 days	1.4460	.7400	8.3% of diene polymerized to high polymer
3 days	1.4468	.7394	
5 days 7.25 hours	1.4486	.7457	11.2% polymerized to high polymer
7 days 18.75 hours	1.4500	.7469	
15 days 12 hours	1.4540	Too Viscous to be determined.	19.82 calculated
22 days 22 hours	1.4590		25.5 calculated
24 days 2 hours	1.4590		
*16 days 22.5 hours	1.4500	.7469	
*12 days	1.4499		

The variation in refractive index with time is shown graphically on the following page (Graph I). The change in density with time of heating was not plotted but does show the same general type of curve.

Two anomalous results were obtained in the experiments



GRAPH 1

marked with an asterisk. Polymerization, as measured by the change in refractive index and density measurements seems to have stopped. The cause of this deviation is not known.

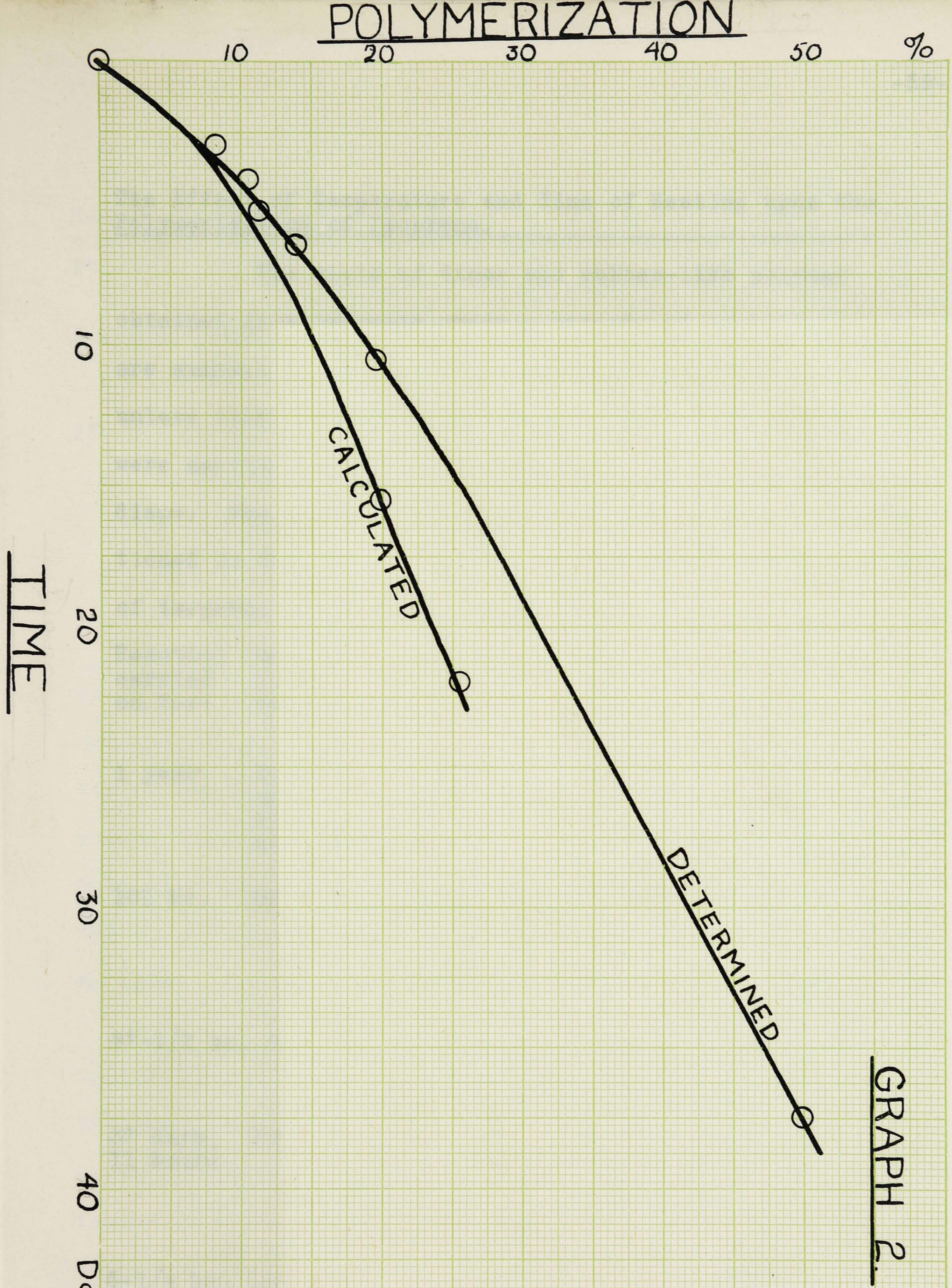
The effect of the air present in a tube upon the rate of polymerization of the diene and consequently upon the index of refraction of the resulting solution is readily seen in the two experiments which follow. 10 c.c. of the diene were sealed in a glass tube, volume 25 c.c., in the ordinary manner. At the same time 10 c.c. were put in a similar tube, cooled in solid carbon dioxide moistened with ether in the usual manner, but then evacuated, by connecting it to a water pump, till the pressure was reduced to 10 mm. The tube was sealed off while still at this pressure. The two tubes were then heated in the thermostat at 85°C. for 40 hours. At the end of this time they were opened and their refractive indices measured.

N_D^{26} = 1.4440 - For solution in tube filled with air.
N_D^{26} = 1.4420 - For solution sealed under reduced pressure.
N_D^{25} = 1.4267 - Original refractive index of the diene.

Thus though the increase in refractive index in neither case is great, the difference between the two cases is very noticeable.

The results, obtained from the refractive index and density measurements, emphasize a point which has already been mentioned. This is -- that polymerization generally proceeds rapidly up to a certain point and then slows down.

The change in refractive index also serves as a measure of the extent that the diene has polymerized to the high polymer provided that the amount of dimer formed is small, otherwise of course a correction would have to be made for this. The actual concentration of high polymer present in the diene has only been determined in two cases, but has been roughly calculated in two other cases and the results, with those of experiments I, II, III and VI, plotted (Graph II). The calculations were made as follows. The refractive index of pure methyl rubber, as determined by Whitby and Macallum (43) is 1.525 (at 20°C.) and that of the pure diene from which it was prepared was 1.4377 (at 20°C.) Thus 100% polymerization caused a change in index of refraction of .0873. Then, having assumed that 1% polymerization would cause a change of .000873 in the refractive index, the concentration corresponding to the refractive indices of 1.4540 and 1.4590 were calculated. The curves can not be expected to agree very closely as the calculation is only very approximate. Also it might be noted that in experiments I, II, III and VI the temperature was only roughly controlled. So it may be concluded that on the whole refractive index measurements serve as a convenient method for following the polymerization of the diene to high polymer provided that the amount of dimer being formed is not too great.


POLYMERIZATION
10
20
30
40
50
%
10
20
30
40
Days.
TIME
CALCULATED
DETERMINED

GRAPH 2.

The Effect of Temperature and Time of Heating upon the Polymerization of Isoprene.

The yield of dimer and rubber-like polymer obtained from isoprene under a variety of conditions are summarized in the following table. In all cases, unless otherwise stated, the experiments and analyses were carried out in the same way as with dimethylbutadiene. The quantitative results of the experiments mentioned in the section on the examination of the dimers of isoprene are included in this table.

Reaction carried on for-	Reaction carried on at-	% of diene polymerized	% of diene converted to high polymer	% of diene converted to dimer	Remarks
1 year	Temp. of an ice-box, approximately 10°C.	.015	.010	.005 (crude dimer)	Isoprene in a glass stoppered bottle. Exp. H.
101 hr.	85° ± 2°C.	24.15	16.25	7.9	30 cc. of diene heated in a tube, 90 cc. in volume. Expt. G
97-1/2 hr.	85° ± 2°C.	26.12	17.05	9.07	50 cc. in a 165 cc. tube Expt. B.
37 days, 11 hours	85° ± 2°C.		35.3		Dimer as gel undetermined 50 cc. in a 165 cc. tube. Expt. F.
5-1/4 hr.	145° ± 2°C.	48.23	10.03	38.20	50 cc. of isoprene in a 165 cc. tube Expt. D.
12-1/2 hr.	145° ± 2°C.	70.4	15.56	54.7	60 cc. in a 165 cc. tube. Expt. C.

Reaction carried on for-	Reaction carried on at-	% of diene polymerized	% of diene converted to high polymer	% of diene converted to dimer	Remarks
5 hours	150°C.	53.			Results obtained by Lebedeff
15 "	150°C.	79.			Result obtained by Lebedeff
	92°C.	42.7	15	27.7	Expt.A. Carried out in an iron autoclave

The above table shows clearly the great effect of temperature on the velocity of polymerization. Also, a comparison of these results with those obtained on the velocity of polymerization of dimethylbutadiene shows that an increase in the number of methyl substituents diminishes the ease of polymerization. This fact has also been pointed out by Lebedeff (31) and more recently by Whitby and Macallum (52).

In the case of isoprene too, an increase in the temperature employed for the polymerization greatly increases the amount of the dimer formed. However, at a constant temperature, the ratio between the amount of dimer and high polymer formed is a constant. This is evident from the results obtained at 145°C. The presence of a catalyst, as pointed out by Lebedeff, may change this ratio. From these results it is seen too that the tendency of isoprene to polymerize to its dimer is greater than in the case of dimethylbutadiene.

Viscosity and Molecular Weight Measurements of the Dimethylbutadiene Polymers

After the analyses of the samples, which had been prepared in order to measure the rate of polymerization of dimethylbutadiene, there were left in the distillation flasks rubber-like residues. It was on these residues that the following experiments were carried out. Previous to their use, they had to be carefully purified. This was done by allowing them to dissolve in pure anhydrous benzene and then precipitating them with absolute ethyl alcohol. This was repeated at least twice. Then, when the greater part of the liquid absorbed by the precipitated polymer had been expressed, it was placed in a vacuum desiccator, and the remaining benzene and alcohol removed by means of a water-pump. After the first 10 or 12 hours of this treatment, the desiccator was connected to a Hyvac pump for several hours. This procedure was carried on for 4-5 days, or till such a time that all traces of liquid had been removed from the polymer. This was naturally most important as the presence of a very small amount of a foreign liquid would have been sufficient to affect seriously a molecular weight determination, since the depression of the freezing point of the solvent was only .04° to .1°. It was found too that the polymers were very susceptible to oxidation and, when not actually being used, had to be kept in a vacuum desiccator where the pressure was 9 to 10 mm. Even under these conditions they oxidized rapidly and so all measurements and solutions had to be made as soon as the polymers were dry.

In the preparation of solutions for viscosity measurements a definite procedure has been followed. A weighed quantity of polymer was put into a small bottle, which had been carefully cleaned and dried, and 20 cc. of anhydrous thiophene-free benzene was added. The bottles used were about 50 cc. in volume and were in all cases stoppered by a cork covered with tin foil. They were then placed in a dark cupboard for eight days. During this time they were shaken once a day. Viscosity measurements were then made as follows: 5 cc. of the sol were transferred, by means of a pipette, to an Ostwald viscosimeter which was placed in a water-bath kept constant at 30.1° ± .02°C. When the sol had reached this temperature its time of flow was measured. The time of flow relative to the time of flow of the pure solvent (called here the relative viscosity) was calculated. The same viscosimeter was used throughout, the time of flow of pure benzene through it at 30.1°C. being 24.4 seconds.

The solutions for the molecular weight determinations were prepared in the same manner as the above, pure benzene being used as the solvent. For comparative purposes the same amount of solvent (20 cc.) and approximately the same amount of polymer (about .68 grams) have been used. At the same time as the solutions were made up 20 cc. of pure benzene was put in a bottle under exactly the same conditions as the sols. All were then put in a dark cupboard and, except for occasional shaking, were allowed to remain there for 4 days. The freezing points of the pure benzene and the sols were then measured in the usual way. The difference between the freezing point of the benzene and that of the sol was taken as dT in the ordinary formula,

$$M = K \frac{w}{dT\ W}$$

where M = the molecular weight of the dissolved substances.

w = the weight of the dissolved substance.

W = the weight of the solvent

K = 5120

dT = the depression of the freezing point

It was found that mechanical stirring assisted greatly in obtaining consistent results and also in preventing excessive supercooling. As this never exceeded .2° to .3° it was not corrected for when the calculation of molecular weight was made.

The results obtained from relative viscosity and molecular weight measurements are given in the following tables. The experiments have been numbered here, as throughout the whole work.

<u>Dimethylbutadiene</u>

<u>Experiment I</u> - Polymer prepared by heating dimethylbutadiene at 85°C. for 101 hours. Total polymerisation: 11.4%.

Concentration in grams per 20 cc.of solvent used	Relative Viscosity	Concentration in grams per 20 cc.of solvent used.	Molecular Weight found
.6677	3.69	.2121	1443
.5161	2.80	.3542	2110
.3231	1.96	.7700	3400
.1881	1.53		
.0862	1.24		

<u>Experiment II</u> - Polymer prepared by heating dimethylbutadiene at 85°C. for 154 hours. Total polymerization: 15.3%

Concentration in grams per 20 cc.of solvent used.	Relative Viscosity	Concentration in grams per 20 cc.of solvent used	Molecular Weight
.0819	1.27	.2230	1973
.2632	1.87	.6788	3982
.3181	2.15	.6713	4017
.4974	2.93	.8597	4067
.6713	3.82		
.6788	3.83		
.7147	4.11		
.8088	4.64		
.8597	5.08		
.9076	5.36		

<u>Experiment III</u> - Polymer prepared by heating dimethylbutadiene at 85°C. for 250 hours. Total polymerization: 22.3%.

Concentration in grams per 20 cc.of solvent used	Relative Viscosity	Concentration in grams per 20 cc.of solvent used.	Molecular Weight found
.2121	1.78	.2615	2402
.3270	2.25	.6971	4645
.4600	3.00		
.6454	3.93		
.6971	4.55		
.8143	5.17		
.8990	6.38		

The point with a relative viscosity of 4.55 does not fall on the curve. This is probably due to a slight evaporation having taken place during the molecular weight determinations for which it was also used.

Experiment V - The polymer was prepared by heating dimethylbutadiene at 145°C. for 12-1/2 hours. Total polymerization: 26.7%.

Concentration in grams per 20 cc. of solvent used.	Relative Viscosity	Concentration in grams per 20 cc.of solvent used.	Molecular Weight found
.2363	1.41	.6804	2100
.4537	1.81	.6885	2175
.6804	2.30		
.6885	2.34		
.8626	2.84		

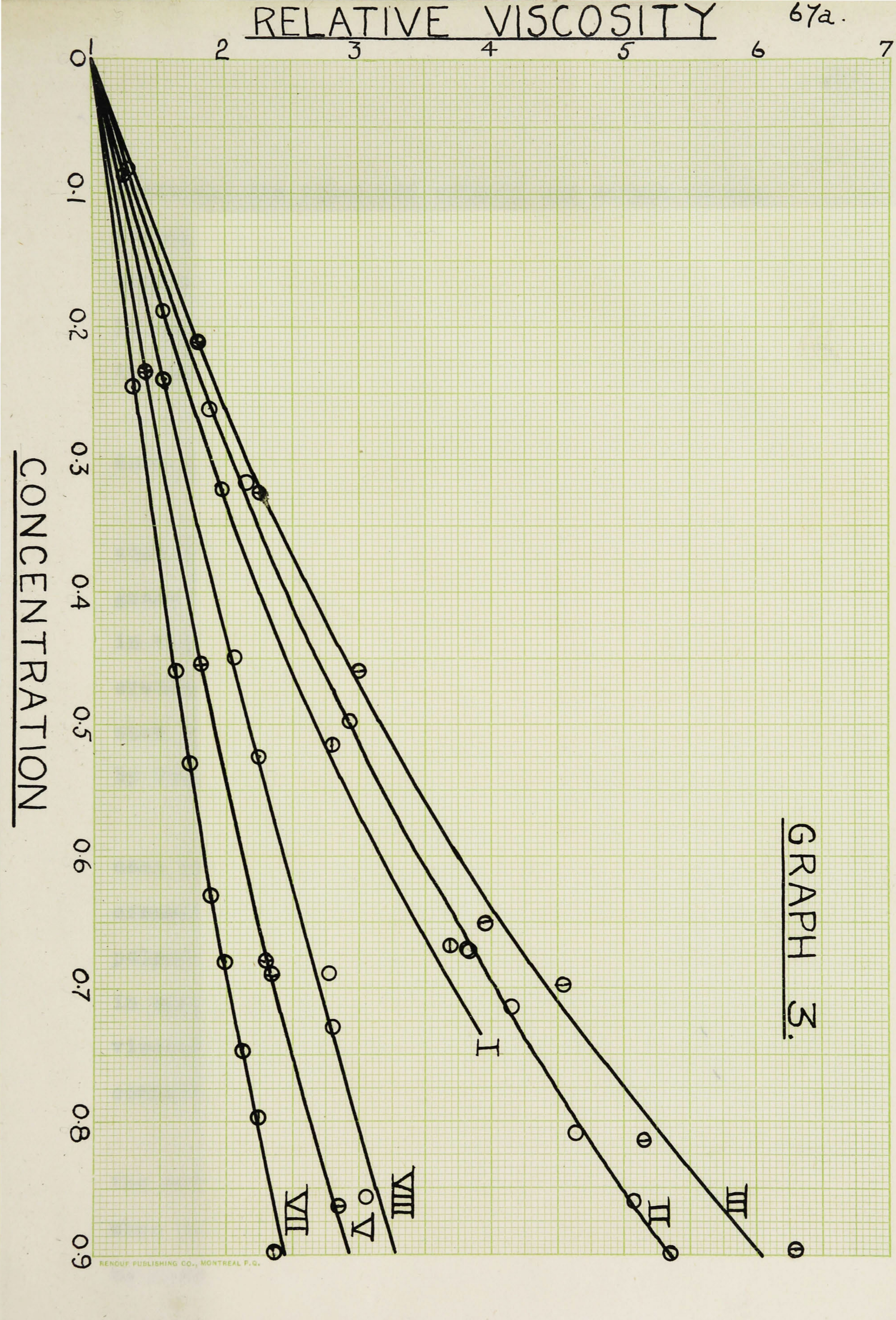
Experiment VII - This polymer was formed at room temperature. Total polymerization after 80 days: 3.45%.

Concentration in grams per 20 cc.of solvent used.	Relative Viscosity	Concentration in grams per 20 cc.of solvent used.	Molecular Weight found
.2435	1.31	.6838	1700
.4705	1.62	.6612	1799
.5345	1.72	.6922	2278
.6305	1.87		
.6813	1.99		
.7477	2.11		
.7961	2.23		
.9031	2.33		

Experiment VIII - In this experiment the polymer used was prepared by heating dimethylbutadiene at 45°C. for 10-1/2 days. Total polymerization: 19.25%.

Concentration in grams per 20 cc.of solvent used	Relative Viscosity	Concentration in grams per 20 cc.of solvent used.	Molecular Weight found
.2418	1.53	.2418	529
.4489	2.06	.6883	1923
.5255	2.24	.7315	2102
.6883	2.76	.8570	2294
.7315	2.79		
.8570	3.05		

It will be noticed that in some cases, solutions which were used in the molecular weight measurements were used again when the viscosities were being taken. This previous


RELATIVE VISCOSITY
1
2
3
4
5
6
7
CONCENTRATION
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
I
II
III
V
VII
VIII
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GRAPH 3.

treatment was in general without any effect on the viscosity of the solution. It was found that cooling, even to the temperature of solid carbon dioxide for 12 hours, has no permanent effect on the viscosity of the sol.

The above concentration and relative viscosity data are plotted on Graph 3.

The curves show that for a given concentration, such as has been used throughout, that is about .6 - .7 grams $\overset{20}{\text{per}}$/cc. of solvent used, there is a definite increase in viscosity as the molecular weight of the polymer increases. This has also been shown to be the case with such polymers as polyindene, meta-styrene and poly-anethole, by Staudinger (33) and Whitby and Katz (34).

Whitby and Katz have also shown that in the case of indene, the molecular weight of the polymer increased as the preparation of indene which had undergone polymerization increased. Experiments I, II and III are in agreement with these results and show an increase in viscosity and molecular weight as percentage of diene converted to the high polymer increased.

It has also been shown by these workers that the molecular magnitude of the polymer ultimately attained when polymerization was practically complete, appeared to be lower the higher the temperature employed, When polymerization was in its early stages this was not necessarily true. The first observation is borne out by the difference in molecular weight and viscosity, when in solution, shown by the polymers prepared at 145°C. and 85°C. The lower viscosity and molecular weights of polymers prepared at 45°C. and at room temperature bear out the second observation.

There is also a noticeable difference in solubility between polymers of different molecular magnitudes. The products with low molecular weights have a much greater solubility than the higher polymers. This is particularly noticeable in the case of a product which was obtained from the diene by autopolymerization at room temperature. Though at the moment of writing, it has been standing under benzene in the dark for 3-1/2 weeks and is now in a very swollen condition, it has not dispersed. It is evidently then a very high polymer as even the products obtained at 85°C. dissolved in 2 or 3 hours. It appears then that dimethylbutadiene too conforms to the observation made by Whitby and by Staudinger, that as polymerization approaches completion the polymers obtained at low temperatures show much higher molecular weights than those prepared at a higher temperature.

That the molecular weight of the polymer has a great effect on the viscosity of its solutions has already been pointed out. So it might be expected, since the viscosity of a sol decreases rapidly with decrease in the concentration of the polymer, that the molecular weight of the polymer, too, would decrease. The results tabulated above show that such is the case. These experiments on polymerized dimethylbutadiene then,agree well with the work of Pummer, Nielsen (25) and Gündel, who have found such to be the case with purified natural rubber. Their results indicate 520-620 as the lowest value for the molecular weight of caoutchouc. This corresponds to a molecule containing 8 isoprene units. The present work, though not complete enough to permit any definite statement to be made, also indicates for the dimethylbutadiene polymer, a molecule containing about the same number of basic units.

Viscosity and Molecular Weight Determinations of the Isoprene Polymers

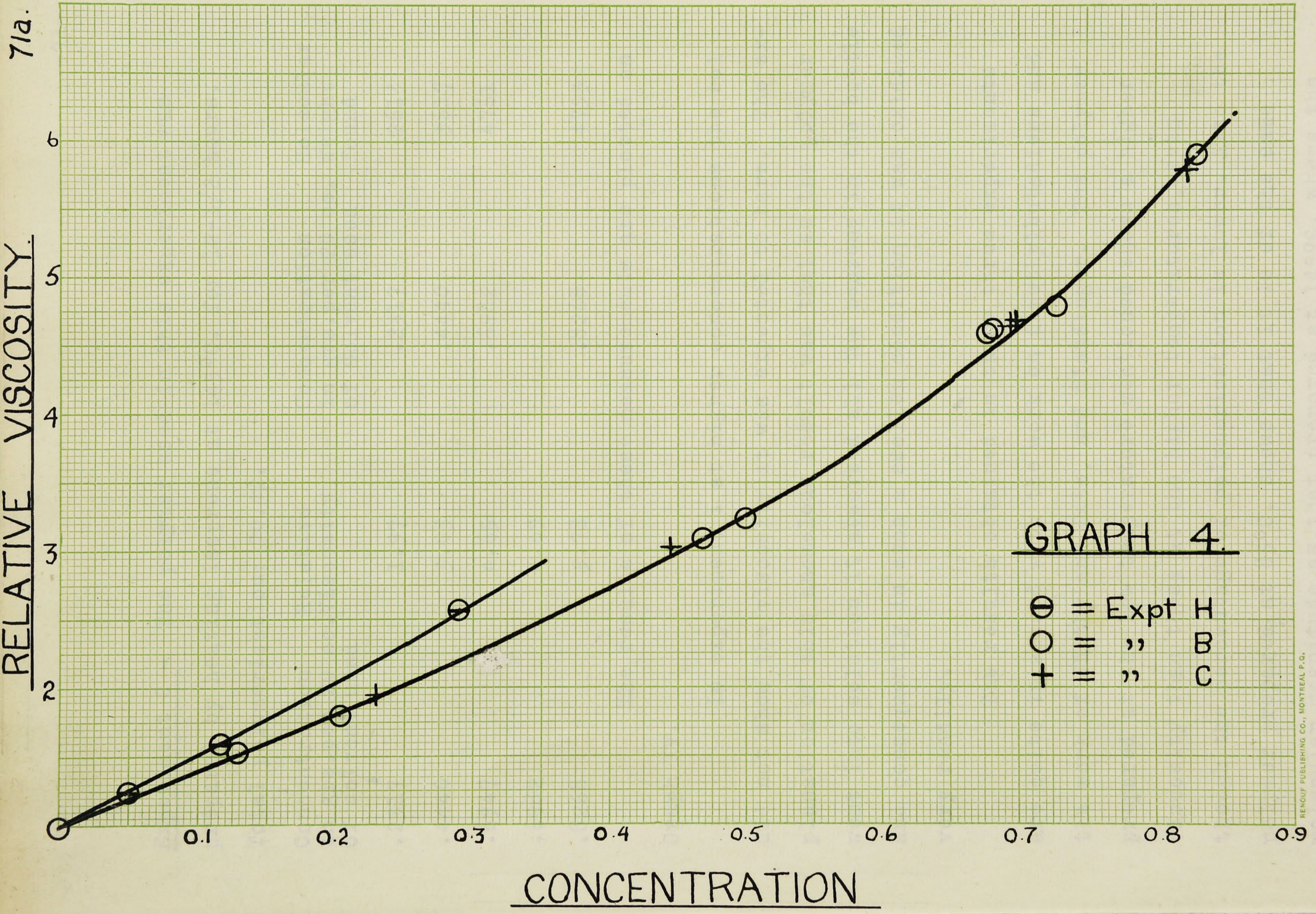
Upon the rubber-like polymers obtained from experiments B, C, and H, molecular weight measurements have been made by the cryoscopic method using benzene as the solvent. Also the relationships between viscosity and concentration have been determined for solutions of these polymers in benzene. Exactly, the same procedure has been followed with these as with dimethylbutadiene polymers. The results obtained have been tabulated in the following tables.

Experiment H - Polymer obtained by the autopolymerization of isoprene at 10°C. over a period of one year. Total polymerization: .015%.

Concentration in grams per 20 cc. of solvent used	Relative Viscosity (at 30.1°C.) (measured after 21 days in this case)
.0512	1.24
.1172	1.60
.2912	2.57
.4920	6.13

Experiment B - This polymer was prepared by heating isoprene at 85°C. for 971/2 hours. Total polymerization: 26.12%.

Concentration in grs.per 20 cc. of solvent used.	Relative Viscosity	Concentration in grs.per 20 cc. of solvent used	Molecular Weight found
.1290	1.54	.2627	3348
.2025	1.81	.6808	4870
.4710	3.10	.6810	4893
.4997	3.24	.6862	5158
.6810	4.62	.8292	4680
.6862	4.66		
.7285	4.79		
.8292	5.92		
.9316	6.44		



GRAPH 4.

RELATIVE VISCOSITY.
2
3
4
5
6
CONCENTRATION
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
⊖ = Expt H
○ = " B
+ = " C
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Experiment C - The polymer used in this experiment was prepared by heating isoprene at 145°C. for 12-1/2 hours. Total polymerization: 70.4%.

Concentration in grs.per 20 cc. of solvent used	Relative Viscosity	Concentration in grs.per 20 cc. of solvent used	Molecular Weight found
.2317	1.97	.2317	2613
.4440	3.03	.4440	3617
.6947	4.65	.6982	4761
.6982	4.69		
.8268	5.78	.8268	4753

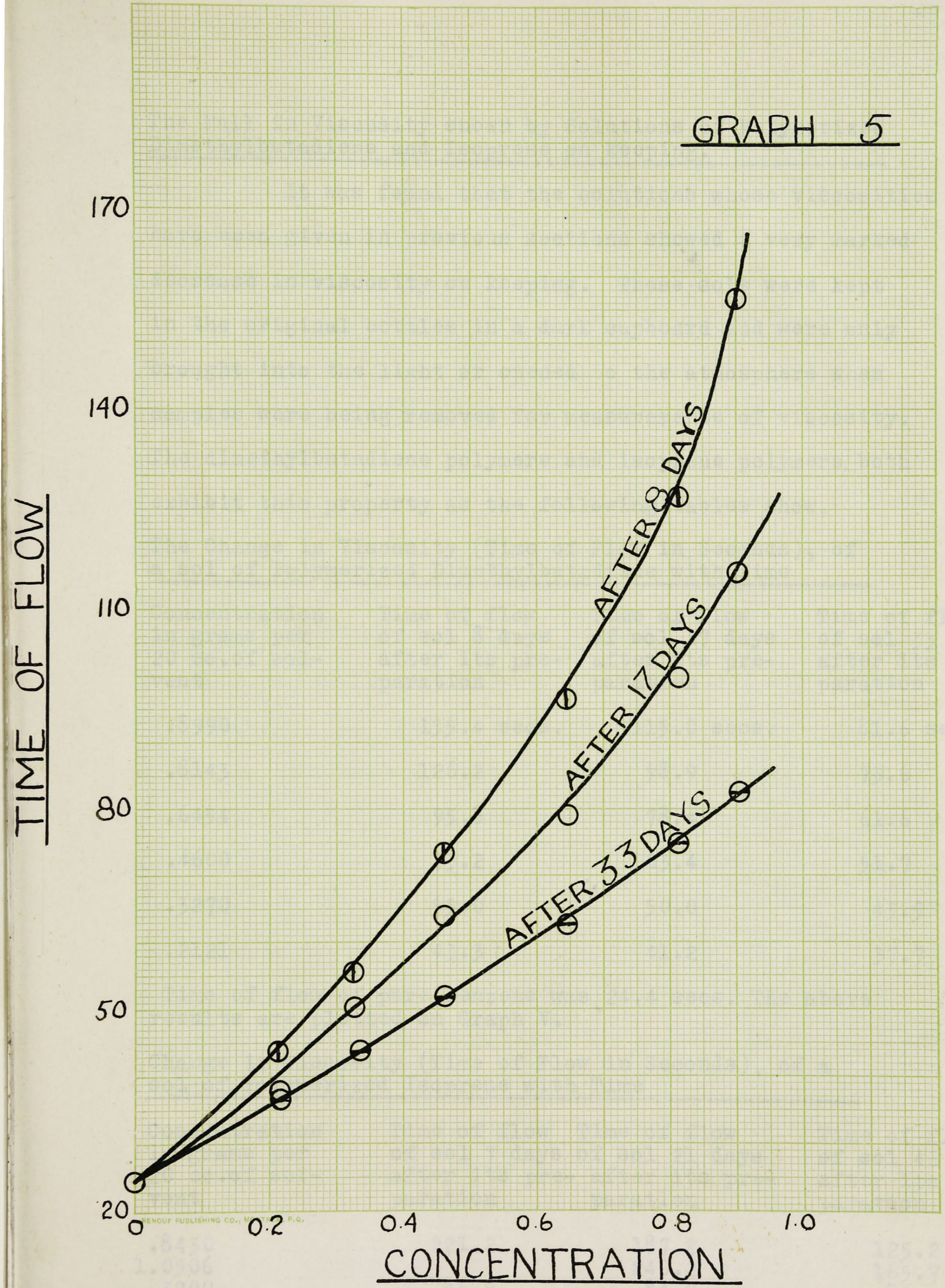
The results of these measurements are plotted on Graph IV.

In experiment I at higher concentrations the sol did not show the viscosity it was expected to have. The explanation of this anomalous result was that, as the polymer went into solution, it absorbed all the benzene in the bottle and consequently in such a swollen condition it was oxidized very readily.

The results obtained in these three experiments are quite in accord with the work on dimethylbutadiene and the work of Whitby and Katz, and Staudinger. The polymer prepared at the low temperature mentioned shows a higher viscosity than those at the higher temperatures, even though the percentage of polymerization is lower. Also the polymer prepared at 85°C. shows that it is of the same molecular magnitude as that prepared at 145°C. where the percentage of polymerization was much greater. So, as the molecular weight of a polymer is known to increase as the time of heating at a constant temperature is increased, it is reasonable to believe that, the ultimate product obtained at 85°C., would be much greater than that prepared at 145°C.

The variation of the molecular weights of these polymers with the concentration employed in their determination is similar to the results obtained on dimethylbutadiene and also with those of Pummerer and his co-workers on natural rubber.

Further experiments on these points have been started, but, at the moment of writing this thesis, are not ready for measurement.



GRAPH 5

170
140
110
80
50
20
0
0.2
0.4
0.6
0.8
1.0
TIME OF FLOW
CONCENTRATION
AFTER 8 DAYS
AFTER 17 DAYS
AFTER 33 DAYS

The Fall in Viscosity shown by Solutions of Polymerized Dimethylbutadiene and Isoprene on keeping.

It was found that the solutions whose viscosities have been given in previous sections showed a very marked decrease in viscosity on keeping. These sols were kept in the original bottles in a dark cupboard and were only brought into the light or opened to the atmosphere when samples were being removed for measurements of viscosity. The dimethylbutadiene polymers and isoprene polymers, both exhibit this property as the following tables show.

The Change in Viscosity (Time of Flow in Seconds), of a sol of Polymerized Dimethylbutadiene with Time

Concentration in grams per 20 cc.of solvent	Time of flow of sol 8 days after its preparation	Time of flow of sol 17 days after its preparation	Time of flow of sol 33 days after its preparation
.8990	155.4 secs.	115.0 secs.	81.6 secs.
.8143	126.2	98.9	73.6
.6454	95.8	78.4	61.6
.4600	73.2	63.4	51.7
.3270	55.0	50.0	43.9
.2121	43.3	41.2	37.7

Time of flow of pure benzene was 24.4 secs. The above results are plotted on Graph V.

Change in Viscosity (Time of Flow in Seconds), of a sol of Polymerized Isoprene with Time

Concentration in grams per 20 cc.of solvent	Time of flow of sol 7 days after its preparation	Time of flow of sol 21 days after its preparation	Time of flow of sol 46 days after its preparation
.8430	221.2	187.2	125.2
1.0506		240.2	165.7
.3900	86.9	84.9	80.2

It is evident from this data that the higher the original viscosity the greater is the initial decrease. Also as time goes on, the decrease in the viscosity of the sol per unit of time becomes less.

In order to find out whether or not the change in the properties of the sol resulted from a permanent change in the polymer, the following experiments were carried out. A solution containing .7147 gr. of polymerized dimethylbutadiene to 20 cc. of solvent, whose relative viscosity was 2.23 (at 30.1°C) and whose viscosity 53 days previous to the experiment was 4.23, was poured into absolute alcohol. As the precipitate would not coagulate the mixture had to be evaporated at room temperature. Even when dry the residue was sticky and entirely different from the originally tough, elastic product. A solution was then made up to exactly the same concentration as the original, and its viscosity measured on the next day at 30.1°C. The relative viscosity found was 2.23. The experiment was repeated with a sol whose relative viscosity was 2.38 and whose viscosity 53 days previous to this was 4.65. After evaporation the residue in this case was dissolved in benzene and reprecipitated. It was then dried and made up to the same concentration as the original sol, i.e. .8088 grams in 20 cc. of solvent. The relative viscosity was found to be 2.40, in this case too, the same as that of the sol, immediately preceding the experiment. The change then is evidently permanent because for the same concentration, the initial relative viscosity cannot be attained. Knowing the susceptibility of the polymer itself, to oxidation a probable cause of such a change would be oxidation due to the presence of the air in the containing bottle. So it was decided to introduce into a sol an antioxidant to see if this would prevent the decrease in viscosity from taking place. Accordingly 10 cc. of a benzene solution of polymerized dimethylbutadiene were placed in a small bottle. This was stoppered well and placed in a dark cupboard. At the same time 10 cc. of the same solution of dimethylaniline were placed in a similar bottle and put away. The dimethylaniline solution contained 2.3148 grams of dimethylaniline per 20 cc. of benzene. The two solutions were allowed to stand for 6 days. Then to the first sol 1 cc. of dimethylaniline solution was added. After 12 hours the viscosities of the two sols were measured in the same viscosimeter. It was found that the time of flow of the solution, which had the dimethylaniline present in it during the whole time, was 46.6 seconds while that of the other was 44.4 seconds. Unfortunately this sol, which was the only one available at the time, had a low viscosity so no great difference between the two could be expected. But even this result indicates that oxidation of the polymer is the cause of the fall in viscosity that these sols undergo on keeping.

The Surface Tension of Benzene Solutions of Polymerized Dimethylbutadiene

For the measurement of the surface tension of solutions of polymerized dimethylbutadiene in benzene a Du Nouy apparatus was used. The concentration used varied between .0862 to .6677 grams of polymer in 20 cc. of benzene, but the results obtained showed that the polymer had no effect on the surface tension of the solvent. All measurements were made at 21.6°C.

The Unsaturation of Polymerized Dimethylbutadiene

The polymer upon which the measurement of unsaturation was made, had been prepared by heating pure dimethylbutadiene at 85°C. for 101 hours. It then was purified by dissolving it in pure benzene and precipitating it with alcohol several times and finally by prolonged drying in a vacuum desiccator. The method of A.R. Kemp (59) was followed closely and, as full details are given in the original paper, they will not be repeated here. The iodine numbers obtained were, 309.1, 307.8, 298.6 and 297. These values correspond very closely to the calculated value (309.1). This calculation is based on the assumption that there is present in the molecule, one double bond for each (C_6H_{10}) unit. Determinations of unsaturation then indicate that the polymer is a ring compound. This method gives similar results with natural rubber; that is, it indicates the presence of one double bond per (C_5H_8)

unit. But as Pummerer has pointed out it is doubtful if such methods as this are accurate enough to differentiate between an open-or-closed-chain compound containing say, 6 to 10 isoprene molecules. The same, of course, would apply to polymerized dimethylbutadiene.

The Fractionation of a Polymerized Dimethylbutadiene

The method used for this purpose was that of fractional precipitation. 5.5 grams of the polymere were dissolved in 50 cc. of pure benzene. Then a solution of 80 parts of absolute alcohol to 20 parts of benzene was added till a faint cloudiness appeared in the solution. This mixture was allowed to stand over-night. In the morning it was found that two layers had separated out. The upper one (Fraction 1) was quite fluid but the lower one (Fraction II) was very viscid. The two layers were separated and the polymer precipitated from them by the addition of absolute alcohol. The precipitate was dried carefully in vacuo. It was found that the heavy layer contained most of the polymer. Solutions of the two fractions were made for viscosity measurements. The concentration used was .8544 grams per c.c.

The residue from Fraction II was dissolved in benzene, using approximately the same concentration as before, and again fractionally precipitated. Two layers, the upper one (Fraction III) and the lower one (Fraction IV) were separated and treated as before. The solutions for the viscosity measurements were prepared as in the previous case. The viscosity of the four fractions was then measured.

Fraction	Time of flow
I	55.4 secs.
II	72.1 "
III	67.8 "
IV	81.3 "

The remainder of Fraction IV was not treated further.

It is evident that in the case of polymerized dimethylbutadiene too the product is a mixture of polymers of different molecular magnitude. This was shown by Whitby and Katz, and Staudinger to be true of the polymers they dealt with.

The Influence of Various Reagents on the Polymerization of Isoprene

The following table gives the qualitative results obtained when 1/2 cc. of isoprene was treated by the reagents mentioned.

Reagent	Result
2 drops $SnCl_4$	Completely polymerized in 3 hours. Product was a clear amber colored mass and was not elastic. On warming it becomes elastic as shown by compression between fingers and less clearly by stretching. Product swells in benzene but does not dissolve.
2 drops $SbCl_5$	Violent reaction. Product a pitchy material, soluble in benzene.

2 drops $SbCl_5$ (isoprene cooled in solid carbon dioxide)	Product very similar to that obtained by $SnCl_4$
5 drops of a 20% solution of $SbCl_5$ (in chloroform)	Orange colored product, very similar to that obtained with $SnCl_4$
A little finely powdered $SbCl_3$	Violent reaction accompanied by charring
The same to isoprene cooled in solid carbon dioxide	Product similar to that with $SnCl_4$
Finely powdered $FeCl_3$	Only slight effect even after standing 2 days. Solution bluish green color.
Finely powdered $FeBr_3$	Only slightly polymerized after 12 hours. Product a dark brown gel with the consistency of a weak vulcanized oil.
Finely powdered thorium bromide	No evidence of polymerization
5 drops of a 20% $B\ Cl_3$ solution (in chloroform)	Slight evidence of polymerization after standing 24 hours
5 drops of a 20% $B\ Br_3$ solution(in chloroform)	Slight evidence of polymerization after 24 hours
Finely powdered $Al\ Cl_3$	Completely polymerized to a yellow flaky mass after 24 hours. Very slightly soluble in benzene.
2 drops of $ChCl_2COOH$	No evidence of polymerization even after standing 2 days.

In all cases mentioned here even when there was no evidence of the formation of a polymer while isoprene was present, a polymer was precipitated out on the addition of alcohol. In the cases of ferric chloride and bromide, thorium bromide, dichloracetic acid, boron trichloride and bromide the amount of polymer formed after two days was small. The polymers precipitated by alcohol resembled one another in appearance very much, being all white or light colored substances and in most cases quite unlike rubber. They are evidently isomers of rubber.

Products similar in appearance to these were obtained when a 3% solution of rubber in benzene was treated with the following catalysts:- $SbCl_5$, $SnCl_4$, $SbCl_3$, $Al\ Cl_3$ and $FeBr_3$. Highly colored complex products were formed first, but on addition of alcohol the catalyst is split off and snow white or very pale yellow powders were obtained. These for the most part were but very slightly soluble.

Similar results to these have been obtained by the action of antimony pentachloride and stannic chloride on dimethylbutadiene.

The Polymerization of Dimethyl-2-4-pentadine-2-4

In an attempt to polymerize this compound by heat alone, 5 cc. were sealed in a glass tube and heated at 85°C. for 4 days and 16 hours. After this period the tube was opened and the refractice index measured. The difference between the refractive index before and after heating was only .0028. Evidently the tendency of this dimethylpentadiene to polymerize at this temperature is very small. This was to be expected to a certain extent, as the fact that methyl substition decreases the ease of polymerization of butadiene, has been already pointed out.

That this dimethylpentadiene can be polymerized had been shown by Grignard (44) when through the action of sulphuric acid he obtained a dimer which he proved to be a ring compound. This same compound was obtained, during an attempted preparation of the dimethyl-2-4-pentene-2-ol-4 by Grignard's method (44), when an ethereal solution of the above alcohol was concentrated in the presence of traces of sulphuric acid. It boiled at 98°-100°C. in 12 mm. and 216°-217.5° at 760 mm. The index of refraction found, N_D^{26} = 1.4800, agreed with Grignard's value, N_D^{10} = 1.48483.

The diene is polymerized by stannic chloride to a very viscous sticky oil. This product is quite unlike that obtained from isoprene and dimethylbutadiene which are white flaky compounds. The oil is probably a similar compound but in a lower state of polymerization. Thus, though the polymerization of this diene is much slower than in the case of isoprene and dimethylbutadiene, it seems certain that, under suitable conditions, high molecular compounds may be obtained from it too.

V. SUMMARY

An apparatus for the preparation of isoprene has been made and is described in this thesis. The results obtained by different methods of purification have been discussed and the best one is indicated. The methods for the preparation of 2-3-dimethylbutadiene-1-3, of 2-4-dimethylpentadiene-2-4, and of 2-methylpentadiene-2-4 have been described and the experimental results considered.

In regard to the polymerization of isoprene no indications of an open-chain compound intermediate between the monomer isoprene and its high rubber-like polymer have been obtained. Though the directions given by Ostromisslensky for the preparation of B-myrcene, the only compound of this type mentioned in the literature, have been followed carefully, it has not been found among the products formed during the reactions. Its presence, even in traces, has been shown to be very doubtful, in spite of the fact that Ostromisslensky has described it as the principal product of the reaction.

The oil, which has been obtained, has been proved to be a mixture. Dipentene has been detected definitely, and fractions corresponding to the general properties of Aschan's and Lebedeff's compounds, have been isolated.

From the polymerization products of dimethylbutadiene a dimer has been isolated which has been proved to be the 4-6-dimethyldipentene obtained by Lebedeff, Aschan, Kandakow and Richards. In this case too, no open-chain compound intermediate between the monomer and its high polymer was found.

Thus, though the polymerization of these dienes to high polymers probably takes place due to the intermediate formation of open-chain compounds, there must be of a very transitory nature as it has been definitely shown, by Lebedeff and by this work, that no such compound can be isolated.

Isoprene and dimethylbutadiene have been polymerized at different temperatures, and the analyses show that as the temperature used for polymerization is increased, the yield of dimer is increased, but for a constant temperature the ratio of dimer to high polymer is a constant. This is in agreement with the previous work of Lebedeff.

A comparison of the rates of polymerization of these two compounds and of the trimethylbutadiene shows that an increase in the number of methyl substituents decreases the ease of polymerization of the diene.

It has been found too that the refractive index measurements may be used very conveniently to follow the course of polymerization of a diene if such conditions, as are mentioned, are adhered to.

It has been shown, too, that oxygen has a definite catalytic effect on the polymerization of dimethylbutadiene.

This has not been noticed in the case of isoprene probably because, after the first experiences with dimethylbutadiene, conditions were kept more nearly standardized.

From measurements of the relative viscosities of benzene solutions of polymerized dimethylbutadiene and isoprene and of the molecular weights of the polymers it was found that at a given temperature the apparent molecular weight increased as the proportion of diene which had polymerized, increased. The results also indicated the fact that the higher the temperature at which polymerization was brought about, the lower the molecular weight of the product ultimately obtained. Further experiments are being carried out to obtain more definite data on this point.

The molecular weight measurements themselves indicated that in all cases the polymer being dealt with was an association product of a basic hydrocarbon. Molecular weight measurements gave as a lowest value 529 in the case of the dimethylbutadiene polymer. This corresponds to a basic molecule with about six (C_6H_{10}) units in it. As to the nature of the basic hydrocarbon little can be said, but at present the indications are that it is a ring compound, as it has been shown by unsaturation measurements that it contained one double bond per (C_6H_{10}) unit. But, though the results obtained agreed well among themselves it is doubtful if this method is accurate enough to show the difference between the number of double bonds in a ring on open-chain compound of this size.

The rubber-like products obtained by the polymerization of dimethylbutadiene was shown by fractionation to be a mixture of polymers varying in molecular magnitude. Then, in this respect, the polymerized product resembles those obtained from styrene, indene, etc.

Solutions of polymerized isoprene and dimethylbutadiene have been shown to drop in viscosity very rapidly even though kept at room temperature in the dark and in carefully sealed bottles. It has been shown that this effect is caused by a permanent change in the polymer. It has been suggested, and some experimental proof has been advanced to support the suggestion, that this change is due to oxidation.

The surface tension of solutions of polymerized dimethylbutadiene in benzene has been measured. The polymer was found to have no effect on the surface tension of the solvent. Some qualitative experiments have been done in connection with the action of various catalysts on isoprene and dimethylbutadiene.

In regard to the polymerization of the dimethylpentadiene it has been shown that the presence of a small quantity of sulphuric acid readily converts it to the dimer. It has also been shown that this compound is only polymerized with difficulty at 85°C. by the action of heat alone. However, from the indications at present it is expected that it could be polymerized to a product of higher molecular weight by the action of stannic chloride under suitable conditions.

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APPENDIX I

The Oxidation of Caoutchouc.

Recently in this Laboratory H. N.Stephens has studied the oxidation by air of resin free caoutchouc in solution in xylene at 100°C. By varying the periods of oxidation he was able to control the process to a certain extent. His reaction mixtures he divided into two parts: petrolic ether soluble, and petrolic ether insoluble. From the first he aucceeded in separating seven substances whose molecular weights ranged from 4809 to 1040, and whose carbon-hydrogen ratios approximated closely to the value 10/16. From the petrolic ether insoluble material his results were unsatisfactory as he was not able to isolate, in any case, what appeared to be a homogeneous product. Also, in the time at his disposal he was unable to m ake any attempt to determine the constitution of the apparently homogeneous products. So it was with the object of attacking this problem that the present research was undertaken.

In the present work it was thought advisable to get the rubber in as pure a state as possible before proceeding with the preparation of the oxidation products required.

The rubber first used was crepe sheet. As a sample, 100 grams of rubber were extracted with 1000 cc. of a 1-1 acetone-petroleum ether mixture. The solution was changed every 24 hours for the first three extractions and then after every 48 hours for the last two. By this time the extract left no residue on evaporation. The rubber was allowed to stand for a few days till the excess of solution had evaporated off, then 10 grams were treated with 100 cc. of commercial benzene. After allowing this to stand for a week some of the solution was decanted off and filtered with suction through a cotton and glass wool filter. The resultant clean solution was poured into acetone and the rubber precipitated out. This gave a very pure colourless product, giving a negative test for nitrogen. However, it was found that crepe rubber disintegrated to a large extent in benzene, so that the protein became suspended throughout the whole solution and was very difficult to remove.

Accordingly, 1500 grams of smoked sheet were treated as above, but the extractions were carried over 15 days. By this time the extract was quite colourless and left no residue on evaporation. 950 grams of this rubber were removed, dried and placed in 47 litres of commercial benzene. This mixture was allowed to stand for 15 days with occasional gentle shaking. The liquid was decanted off and filtered by suction. The filtrate was then poured into acetone and the rubber precipitated out. This was allowed to dry, in a vacuum, for a week. The resulting rubber, though slightly amber in colour, gave no test for nitrogen and was resin-free. The yield of rubber was approximately 75-80%.

486 grams of the purified rubber were then put in a large pyrex flask and 4050 cc. pure xylene added. Xylene was chosen as the medium for oxidation as it has fair solvent properties and a comparatively high boiling point. The flask was then heated in an oil bath with temperature regulating device, at a temperature of 99-100° C., a tall reflux condenser being used to prevent loss of solvent. The heating was continued for 2 days, to ensure complete solution, and then a gentle stream of air, dried by $CaCl_2$, concentrated H_2SO_4 and soda-lime, was passed through the solution for 22 days, this being the time found by Stephens to be necessary for complete oxidation under such conditions.

At the end of the above period a large amount of resin had separated from the solution. The clear reddish solution was decanted off this insoluble matter and filtered by suction. The resins in solution were precipitated by petrolic ether (B.P.35-60°), after the solution had been distilled under reduced pressure to a volume of one litre.

The distillate obtained had a very sharp penetrating odour resembling that of formic acid. This was tested for by boiling a water extract of the distillate with mercuric chloride - a copious precipitate of Hg_2Cl_2 was formed, proving the presence of formic acid.

As it was noticed that the amount of resins (petrolic ether insoluble material) was very great, a qualitative test was made, taking aliquot portions of a concentrated solution of the products of the reaction, to determine the relative amounts of the products soluble in petrolic ether and those insoluble. It was found that the amount of soluble products - those whose constitution it had been hoped to examine - was too small to do anything with. Evidently then, the removal of the proteins before oxidation, rather than after the oxidation, as was done by Stephens, has caused the reaction to go much further, with the result that the rubber was oxidized almost completely to resins insoluble in petrolic ether.

These resins, after precipitation, were very thoroughly washed with petrol ether. They were as yet in the form of a red oil, traces of solvent still being present. When they were dried on a steam bath under reduced pressure they were found to yield a dark red gum, which was soon further oxidized on the surface to a glass. They were very soluble in acetone, chloroform, alcohol and methyl alcohol, less soluble in aromatic hydrocarbons and insoluble in carbon disulphide and petrolic ether.

A rough separation of the resins was made by dissolving them in chloroform and bringing about fractional precipitation with petrolic ether. These fractions were twice fractionally precipitated and yielded gums varying gradually in colour from a very dark red to a bright orange. They were all soluble in caustic alkalies with varying degrees of care. In all cases, though, heating for a considerable length of time was required to effect solution. These solutions were dark brown and opaque. The solubilities of the various samples obtained were so similar that no separation could be effected. On mixing two resins of altogether different appearance it was impossible to separate them again by the selective action of solvents. Also no separation of the resins could be made by steam distillation.

The molecular weight of one of the resins, the first fraction obtained by precipitation with petrolic ether, was determined in benzene by the cryoscopic method. This gave a value of 744, though probably the real value was considerable lower than this as a small part of the solid did not go into solution. However, such a molecular weight as this has no significance as the resin was not homogeneous.

All the solid resins, soluble in acetone, have a strong reducing power on Fehlings solution on boiling. With phenyl hydrazine, however, no crystalline products could be obtained.

Though there was but a very small amount of petrolic ether soluble matter present, a few qualitative tests were made upon it to see if it resembled in any way that obtained by Stephens. A concentrated solution of these products was treated with an excess of ethyl alcohol, but instead of a light red gum as was expected, a very light yellow wax was obtained. The solution remaining after this separation was again concentrated under reduced pressure and treated with an excess of methyl alcohol. Again, instead of a red gum, a light yellow wax was obtained. Both of these compounds came down as flaky precipitates and if they had been present in a greater quantity they could no doubt have been obtained in a fairly homogeneous state. No further separation was attempted, but there still remained in solution a red oil which was left as a residue when the alcoholic solution was evaporated under reduced pressure.

It was quite apparent that to obtain anything like the results of Stephens the whole oxidation would have to be repeated, following this time his method of purification of the raw rubber, or cutting down the period of oxidation of the purer form. Instead of doing this it was decided that to attempt to follow the polymerization process of such a diene as isoprene would be really a more suitable way of attacking the problem.