SYNTHESIS OF
POLYETHYLENE ETHER GLYCOLS

SYNTHESIS AND PROPERTIES OF POLYETHYLENE ETHER GLYCOLS

by

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INTRODUCTION

The polymerization of primary "building units" is a fundamental chemical reaction, and finds extensive application, particularly in industrial fields. Many simple chemical substances are valueless from an industrial standpoint until converted by polymerization processes into compounds which, owing to their greater stability and more desirable physical properties, have application in a great variety of industries. The most common examples are the plastic and lacquer industries where many products, formerly of very limited use, are now converted on a large scale into materials from which a great number of useful objects are manufactured. Thus a knowledge of the mechanism of polymerization and the factors governing this process is most essential to these industries.

There are also a number of natural polymers, such as cellulose and starch, which have as wide or wider an application. It is, therefore, equally important to determine their structure and to study the mechanism of their formation in the plant in order that their properties may be more fully understood and their use facilitated.

This investigation is concerned essentially with only one of these phases; viz., the determination of the mechanism of polymerization.

Polymerized ethylene oxide appeared to be a very suitable material for examination because of its solubility in most organic solvents, its stability, its ease of crystallization and its relation to pentosans, cellulose, starch, inulin, etc. However, the fractionation of polymers is generally a very difficult operation since it is almost impossible to separate quantitatively the individual high-molecular members. Inasmuch as the products of polymerization of ethylene oxide are apparently polyethylene ether glycols* (1), it seemed that a synthesis of this series of compounds and an investigation of their physical properties might yield valuable data bearing on the validity or otherwise of Staudinger's generalization.

The problem appeared all the more attractive in that certain preliminary work carried out some five or six years ago indicated the possibility of a simple step-wise synthesis of the polyethylene ether glycols. However, it was soon found that the synthesis of the higher members became increasingly difficult so that new processes had to be devised with consequent delay in the progress of the work. As a matter of fact, the better part of the last two years has been spent in developing the synthesis of the higher members, notwithstanding

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*In the literature the term polyethylene glycol has been used consistently to designate this class of compounds. The writer prefers to introduce the word "ether" into the name in order to make it more comprehensive.

the valuable preliminary work carried out by a former worker, Mr. Stanley Z. Perry.

Staudinger's investigations (3,p.287) in this field were carried out with mixtures of polyethylene ether glycols (ethylene oxide polymers) obtained by a more or less crude method of fractionation. An investigation based on the use of carefully purified synthetic products of known structure might therefore be expected to provide reliable evidence regarding the conclusions drawn from data which have been obtained from mixtures of polymers of uncertain composition. A comparison of the structure of a polyethylene ether glycol with that of polymerized ethylene oxide shows a marked similarity:

$(CH_2{-}CH_2{-}O)_x.H_2O$	$(CH_2{-}CH_2{-}O)_x$
Polyethylene ether glycol	Polyethylene oxide

In any event the synthetic, long-chain polyethylene ether glycols should serve as a valuable series of reference compounds, especially as their structure can be confirmed by the formation of various derivatives, such as dihalides, etc. Furthermore, an investigation of the physical properties, such as the viscosity, would be expected to reveal interesting data regarding chain length.

The most important outcome of the synthesis of high polymers, according to W. H. Carothers, (17) is that high molecular products can be obtained having structural configuration similar to that of the elementary building unit, and showing an analogous behaviour with organic reagents.

HISTORICAL

Polymerization - General Theories

Until recent times, the term "polymerization" was vague in meaning and generally applied to the case where two compounds have the same composition but different molecular weights. It was also applied without discrimination to many complex and little understood reactions involving loose molecular aggregates. In the past chemists were loath to study the mechanism of polymerization as it was considered to be much too intricate for comprehension. The equation for the polymerization was generally written in an empirical manner, and in the case of ethylene oxide would be:

$$n(C_2H_4O) \longrightarrow (C_2H_4O)_n$$

The intensive work carried out in the past ten years has resulted in the postulation of various theories concerning the nature of the forces binding the building units together in the polymer. These may be grouped under three headings: (i) Association, (ii) Large Ring, and (iii) Long Chain Theories.

(i) Association Theory. - The supporters of this theory contend that polymerization is brought about under the influence of residual valencies. However the nature of these valencies is ill-defined and the term itself is rather vague. A union of the structural units in this manner would, in general, be expected to be a weak one. However, it is assumed that the strength of the accumulated residual valencies is great enough to resist the disruptive powers of the solvents, etc. It has also been suggested that under favorable conditions an associated polymer may revert to the original monomer.

The association theory has practically been abandoned in recent times because of the lack of experimental evidence in its favour and also its inability to explain the process of polymerization satisfactorily.

(ii) Large Ring Theory. - For many years this theory had few supporters on account of the general acceptance of the Baeyer Strain Theory, which postulates that all rings above the six-membered would not only be unstable but their formation highly improbable.

The preparation of large stable rings by Ruzicka (2) provided the refutation of the Baeyer Strain Theory, and indicated the possibility of the existence of large ring polymers. The properties of such rings indicated that the atoms are probably not in the same plane, and hence a long flexible chain may bring the terminal groups close enough together to cause union.

(iii) Long Chain Theory. - This theory maintains that polymerization proceeds in a stepwise manner by means of normal valency forces. Depolymerization is exhibited by only a few of the known complex polymers. Thus it is assumed that the monomer loses its identity in the polymer, a conception which is well supported by the extensive work of Staudinger (3), and also by recent investigations dealing with -C-C- linkages.

Mechanism of Polymerization

This subject has been studied using a wide variety of substances and methods which may be grouped as follows:

(1) Study of cleavage and degradation products of polymers

This method has been used successfully in work on the polysaccharides and related compounds by several investigators including Haworth (4), Freudenberg (5) and Hibbert (6).

(2) Isolation of the structural unit and reconversion to the polymer

Many supporters of the association theory have attempted to isolate the structural unit, which presumably has free valencies and shows a strong tendency to associate. Among these may be mentioned Bergmann (7), Pictet (8), Hess (9), Irvine (10), and Pringsheim (11).

(3) Synthesis of the structural unit

The work on rubber is the only outstanding success in this field. But even in this instance, there is no conclusive evidence as to the mechanism.

(4) Study of the physical and colloidal properties of polymers

X-ray analysis has been of valuable assistance in determining the arrangement of the atoms or structural units in space. However, it can only be applied to crystalline structures and unfortunately many important commercial polymers do not exist in this state. Many colloidal properties of organic lyophilic sols have been studied, and some evidence as to their structure obtained. Contributions to these studies have been made by Meyer and Mark (12), Staudinger (13), and Whitby (14).

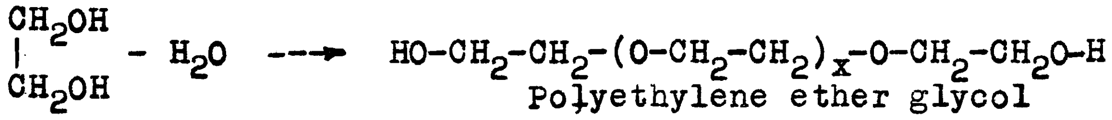
(5) Study of the different types of simple substances which tend to combine with themselves

Certain configurations such as unsaturated -C=C- linkages and oxygen bridged rings are said to provide nuclear centres for polymerization. They may be listed as (a) unsaturated, (b) polyfunctional, and (c) cyclic:

(a) $H_2C{=}O + H_2O \longrightarrow HO{-}CH_2O{-}(CH_2O)_x{-}CH_2O{-}H$

Polyoxymethylene

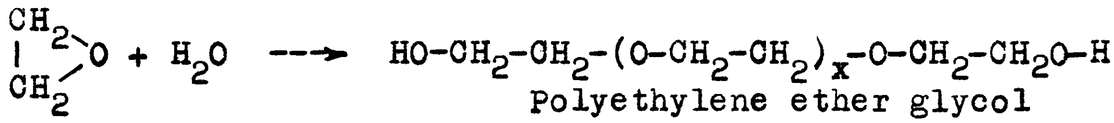
(b)



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} - H_2O \longrightarrow HO{-}CH_2{-}CH_2{-}(O{-}CH_2{-}CH_2)_x{-}O{-}CH_2{-}CH_2O{-}H$$

Polyethylene ether glycol

(c)



$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O + H_2O \longrightarrow HO{-}CH_2{-}CH_2{-}(O{-}CH_2{-}CH_2)_x{-}O{-}CH_2{-}CH_2O{-}H$$

Polyethylene ether glycol

Unsaturated linkages display the greatest effect in that polymerization often occurs with explosive violence. This type of change has been investigated by Bergmann (7) and Levene (15).

(6) Synthesis of polymers by a building process

This method probably offers the most conclusive evidence as to the mechanism of polymerization and the actual structure of the resulting polymer. By starting with a well-known compound, capable of condensing with itself by established methods, the polymerization may be controlled in such a way that only normal valency forces are involved.

Carothers (16) successfully uses this method for attacking the problem and it has also been adopted in the present investigation.

Present Theoretical Conceptions of Polymerization

The following views are quoted from Carothers (17) who has given a very complete account of practically all phases of polymerization up until 1931.

"Polymerization is a chemical union of many similar molecules, either with or without the elimination of simpler molecules (H_2O, HCl, NaCl, etc.)." "The combining action of the molecules may take place either by addition or condensation and two corresponding types of polymerization may be recognized. (The term "condensation" is used to name any reaction that occurs with the formation of a new bond between atoms not already joined, and proceeds with the elimination of elements (hydrogen, nitrogen, etc.) or of simple compounds (water, ethyl alcohol, ammonia, sodium bromide, etc...)"

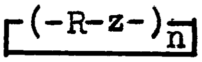
"The formation of polyoxymethylene from formaldehyde is addition or 'A' polymerization. The formation of polyethylene glycol directly from ethylene glycol is condensation or 'C' polymerization. A general class of condensation polymerizations is represented by the equation:

$$x\text{-}R\text{-}y + x\text{-}R\text{-}y + x\text{-}R\text{-}y + \ldots\ldots \longrightarrow x\text{-}R\text{-}z\text{-}R\text{-}z\text{-}R\text{-} \ldots\ldots$$

In the formula $x\text{-}R\text{-}y$, R is a bivalent radical and x and y are functional groups capable of reacting with each other to form the known functional group z. Thus if x is HO and y is COOH, z will be CO-O. The compounds $x\text{-}R\text{-}y$ are called bifunctional compounds and their reactions, bifunctional reactions. Reactions of the type, $x\text{-}R\text{-}x + y\text{-}R'\text{-}y \longrightarrow$ product, may be included in this class.

"Bifunctional reactions present the possibility of following various courses. (a) They may be intra-molecular at the first stage. The product will then be a cyclic monomer

(b) Reaction may be inter-molecular at the first stage and intra-molecular at some subsequent stage. The product will then be a cyclic polymer



(c) Reaction may be exclusively inter-molecular. In this case the product will be an open chain of the type $x\text{-}R\text{-}z\text{-}R\text{-}z \ldots \text{-}R\text{-}z\text{-}R\text{-}y$."

"Reactions of condensation are not limited to bifunctional compounds. If one of two reactants contains two functional groups and the other contains more than two, the product will be not a simple chain but a more complicated structure ..."

Examples of these are the glyptal and bakelite resins. The former is obtained by the action of phthalic acid on glycerol and the latter from phenol and formaldehyde.

The monomer may be polymerized by heat in some instances or activated to self addition by means of a catalyst. Polyethylene oxide is an example of the latter. Polymers may also be synthesized from the monomer by polyintermolecular condensation, an example of which is that of the polyethylene ether glycols.

In almost all polymerization reactions the products are generally linear; ring polymers are usually the result of specific conditions. The formation of five- and six-membered rings takes place with ease while that of the higher members proceeds only with great difficulty. Thus it is assumed that the rate of intra-molecular reaction is greater than that of inter-molecular in the case of five- and six-membered ring formation, while above that stage the positions are reversed.

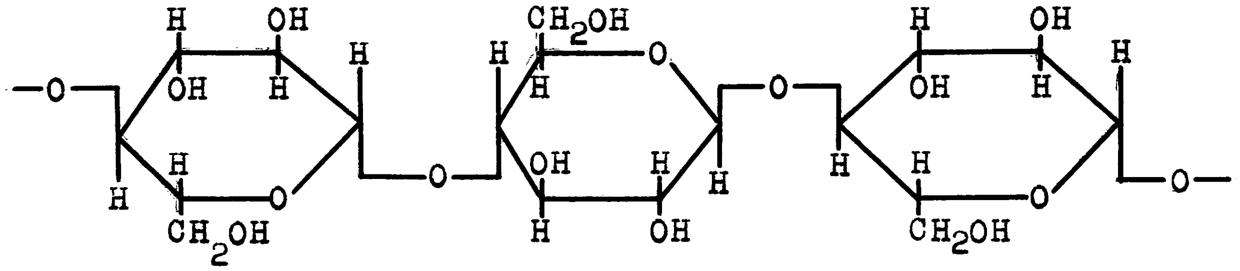
Ruggli (18) synthesized large rings containing acetylenic linkages by operating the reaction in dilute solutions in order to bring about intra-molecular condensation.

K. Ziegler (19) found that he could form large rings by carrying out polymerizations in high dilution and at a low pressure. By this procedure, the possibility of collisions of adjacent molecules is greatly reduced, thus decreasing the chances of an inter-molecular condensation; hence, more time is available for intra-molecular condensation with consequent formation of large rings.

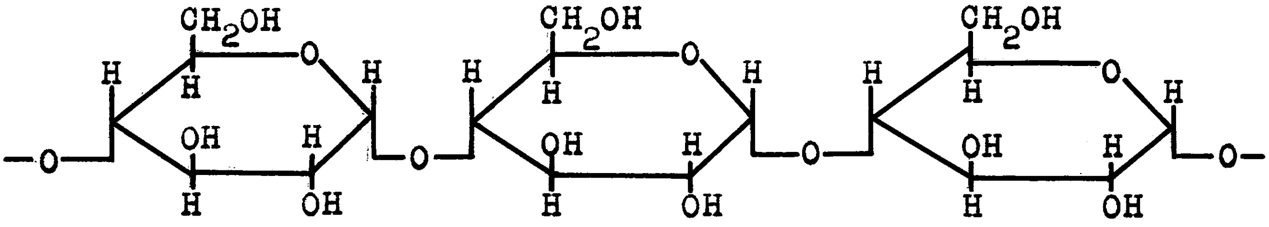
According to Dunkel (20) the cohesive forces, which oppose the separation of molecules from one another, increase with rising molecular weight in any given series. These forces reach a value in high polymers greatly in excess of that required to rupture the primary valence chain linkage. Hence, high polymers cannot be distilled without decomposition. Carothers (21) gives the molecular weight limit for distillation as in the range of about 1200-1500.

Relation of Polymerization to the Study of Natural Products

About 1924 the association theory was presented by several investigators (22) as being the most suitable explanation of the binding force in natural high polymers. Cellulose, for example, was considered to be an association of many anhydroglucose units. This theory, however, was later discarded in view of the work of Haworth, Freudenburg, Staudinger, Herzog, Meyer and Mark and others. These investigators found a similarity in physical and chemical properties between natural high polymers and the synthetic polymers, the latter of which were definitely known to have a linear structure rather than an agglomerate structure. Cellulose and starch are now well defined as linear polymers, the structural units of which are α and β gluco-pyranosides as shown below.



Cellulose



Starch

However, there are some factors which are still uncertain, as for example chain length. This has been investigated by both chemical and physical methods - chemical reactions of the terminal groups, X-ray analysis, osmosis, ultra-centrifuge sedimentation methods, and viscosity experiments. The values for the molecular weight of cellulose determined in the above manner varies from the chemical value of Haworth, 32,000, to the physical value of Staudinger, 120,000.

Staudinger's Viscosity Relationship

The mechanism of polymerization, according to Staudinger, (3, p.297) can be explained by a knowledge of three factors: (1) the mode of linkage of the building units, (2) the number of these units in the macro-molecule, and (3) the nature of the terminal groups. He examined these three factors by investigating chemical reactions of the terminal groups, cryoscopic measurements, and viscosity data on the different polymers in solution. From an extensive research on the latter, he was able to derive a relationship between viscosity and the chain length of high molecular linear polymers, as will be shown below.

The measurement of the viscosity of a solution is actually a measure of the effect of the solute on the viscosity of the pure solvent. While temperature and pressure are important factors in relating the viscosities of solutions, perhaps the most difficult factor is concentration. Many attempts have been made to obtain a mathematical relationship.

Einstein (23) derived the following equation for the relationship between the viscosity of a solution and its concentration:

$$\eta_s = \eta_0 \left(1 + K \frac{N\phi}{V}\right) \qquad (1)$$

where η_s is the viscosity of the solution, η_0 that of the pure solvent, K is a constant, N the number of particles in the volume V, and ϕ the volume of a single particle. This equation is based on the assumption that the particles are rigid spheres and that their total volume is small compared to that of the solvent. The equation, which is that of a straight line, indicates a linear increase in viscosity with concentration.

Staudinger (3, p.56) has developed a viscosity law on the basis of the Einstein equation, in which the ratio $\frac{\eta_s}{\eta_0}$ is the relative viscosity, η_r. He prefers the function specific viscosity where $\eta_r - 1 = \eta_{sp}$, because it represents the increase in the viscosity of the solvent due to the presence of the solute. In all his work, Staudinger uses η_{sp} to express viscosity.

He obtains the expression $\frac{\eta_{sp}}{c} = K$ from Einstein's equation on the rigid sphere basis as shown below. However, when this equation was applied to solutions of paraffins and colloidal products, wide discrepancies were found. Staudinger explained these discrepancies by postulating a thread-like molecule which he now treated as a rigid cylinder of length corresponding to that of the chain molecule. The equation now becomes:

$$\eta_r - 1 = \eta_{sp} = K\frac{N\phi}{V} \qquad (2)$$

When $N = \frac{a . N_L}{M}$, (where a is the amount of substance used, N_L the Loschmidt number, and M the molecular weight), it follows from (2) that:

$$\eta_{sp} = K\frac{a . N_L}{VM}\phi \qquad (3)$$

and since a/V = c, (the concentration):

$$\eta_{sp} = K\frac{c . N_L}{M}\phi \qquad (4)$$

The volume of a single thread-like molecule ϕ, may be regarded as corresponding to that of a long cylinder of diameter d, and height L. Therefore equation (4) may be written:

$$\eta_{sp} = K\frac{c . N_L}{M}\left(\frac{d}{2}\right)^2\pi . L \qquad (5)$$

Since the diameter, d, of such a molecule remains constant in a homologous series of polymers and the length, L, increases proportionately with the molecular weight, Formula (5) may be simplified since N/L and $\left(\frac{d}{2}\right)^2\pi$ can be replaced by a new constant K':

$$\eta_{sp} = K' \cdot c \qquad (6)$$

This would indicate that the specific viscosity is dependent only on the concentration and is independent of the molecular weight. Thus basic molar solutions of the different polymeric polystyrols should have the same viscosity whether the solution contains a large number of small molecules or a small number of large molecules. However, it was found experimentally that the specific viscosity of solutions of the same concentration, was proportional both to the molecular weight and the chain length. These results indicated that the dissolved thread-like molecule actually requires a larger volume than its own true volume. Viscosity measurements showed that this required volume, designated as the "effective volume" ("Wirkungsbereich"), increased as the square of the length of the molecule. It may be expressed according to Staudinger, as the volume of a shallow cylinder the height of which is the diameter, d, of the molecule and the base area $(\frac{L}{2})^2 . \pi$ Equation (4) may therefore be written:

$$\eta_{sp} = K \frac{c\, N_L}{M} \left(\frac{L}{2}\right)^2 \pi d \qquad (7)$$

Enlarging the conception of "effective volume", Staudinger considers the fibre molecule as rotating on a middle axis, but that the effective sphere includes the entire field of the thread-like molecule's rotation.

However, the length L increases in proportion to an increase of the molecular weight M with thread-like molecules, and therefore (7) becomes:

$$\eta_{sp} = K'' \frac{c\, N_L}{4} M \pi d \qquad (8)$$

But $K'' \frac{N_L}{4} \pi d$ can be absorbed in a new constant K_m, which is known as the viscosity-molecular weight constant, and by substituting in (8):

$$\eta_{sp} = K_m \cdot c \cdot M$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (9)

$$\frac{\eta_{sp}}{c} = K_m \cdot M$$

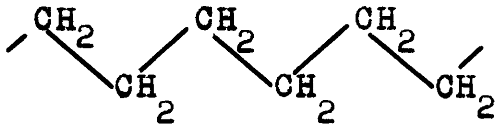
Thus Staudinger arrives at his equation for relating the viscosity to the molecular weight which in turn gives the chain length. Given K_m for any given homologous series of polymers, the molecular weight of any degree of polymerization in that series may be determined from the specific viscosity. However, as a general rule K_m is only constant in intermediate stages, while it deviates among the lower and higher members of a series. Moreover, Staudinger points out that the viscosities must be carried out in low limiting concentrations (4.4% in the case of polyethylene oxides) in order to avoid association of chains and for the same reason benzene and dioxane were generally used as solvents. The concentration, c, is expressed as base molar concentration ("grundmolare Konzentration"); i.e., in terms of building units. For example, the building unit of polyethylene oxide is $-CH_2-CH_2-O-$ with a molecular weight of 44; therefore, when c is unity, there are 44 grams of substance in one litre of solution which he calls a "4.4% solution". The relative viscosity, η_r is obtained from the expression:

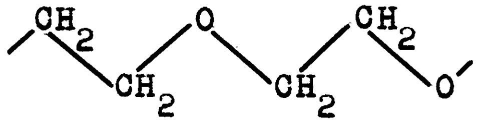
$$\eta_r = \frac{t(\text{solution})}{t(\text{solvent})}$$

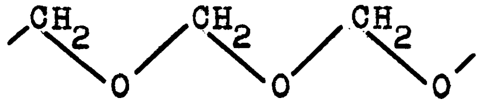
where t is the time required for a definite quantity of liquid to flow through the capillary of an Ubbelohde (24) or an Ostwald viscometer. Densities are neglected as the density of the dilute solutions are very nearly that of the pure solvent, and all viscosity measurements of a single homologous series were taken at the same concentration and temperature.

The products investigated for the purpose of applying this viscosity equation were polystyrols, polyoxymethylenes, polyethylene oxides, polyacrylic acids; also the natural polymers, rubber and cellulose.

Staudinger (3, p.293) compares polymerized ethylene oxide with polyoxymethylene and paraffin of similar solubility and melting point.

I.

Paraffin chain

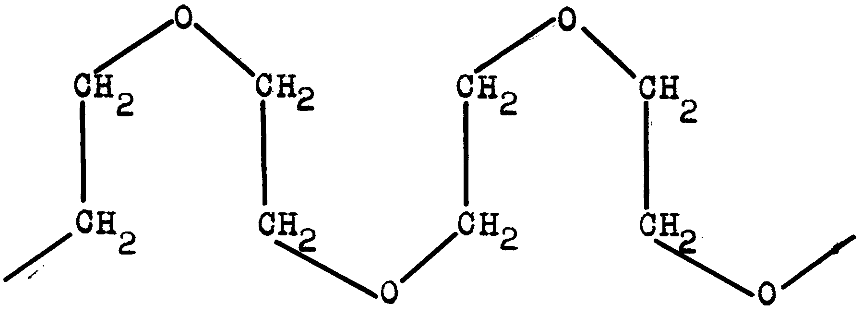
II.

Polyethylene oxide chain

III.

Polyoxymethylene chain

He found that paraffin and polyoxymethylene chains of equal length have approximately the same physical properties but on the other hand the polyethylene oxides showed a marked difference in behaviour.

Viscosity measurements have shown that the polyethylene oxide chain is shorter than indicated by Formula II and corresponds in length with a polyoxymethylene chain. In order to explain these results, he assumes that the chain is shortened by a spiral structure (25) which can be represented graphically as follows:

IV



Viscosity measurements on the acetylated derivatives of the polyethylene oxides indicated formula II as correct up to a degree of polymerization of nine, and that formula IV applies to all members above nine. However there is a great deal of uncertainty about this and it cannot be taken as definite.

Since the same differences in solubility which exist between polyoxymethylene and polyethylene oxide are also found between cellulose and starch, Staudinger assumes they are due to variation in the form of the molecule. Cellulose is an elongated chain molecule similar to polyoxymethylene and both are insoluble in most solvents. The starch molecule, on the other hand, is assumed to have a spiral structure similar to that of polyethylene oxide and their easier solubility depends on this conception.

In most of his work on the high molecular products, Staudinger used mixtures of polymers. The polymers were separated into fractions by methods which would cover a wide range of molecular weights. The viscosity measurements of the K_m constant for his equation are made upon such mixtures of polymers. The average chain length of such fractions was determined by chemical (functional group) or physical (cryoscopic) methods and this then compared with values derived from studies on their viscosities in various solvents.

Theequation of Gartenmeister (26) $\frac{\eta}{M^2} = K$, where η is the absolute viscosity coefficient, M the molecular weight, and K a constant, should apply within a homologous series. But while it is approximately correct for the paraffins, it does not hold for ethylene oxide polymers.

Ethylene Oxide Polymers

Ethylene oxide was prepared by Wurtz (27) by treating ethylene chlorhydrin with caustic potash at 125°C. He found that if the ethylene oxide contained just a trace of caustic potash, polymerization occurred on standing.

Crafts (28) prepared the dimer of the corresponding ethylene sulphide by the action of an alcoholic solution of potassium hydrosulphide on ethylene bromide.

Roithner (29) prepared ethylene oxide by the method of Demole (30), which consists in dropping ethylene chloride into hot caustic potash. He investigated the properties of ethylene oxide and obtained a polymer in the same manner as Wurtz. This polymer was described as a crystalline solid with an observed molecular weight of twenty-three to thirty times that of the original ethylene oxide. Roithner considered that the polymerization took place by the opening of the ethylene oxide ring, followed by the coupling of these units by normal valence linkages to form a large ring:

$$\left[CH_2 - CH_2 - O - (CH_2 - CH_2 - O)_x - CH_2 - CH_2 - O \right]$$

This, however, is based chiefly on negative evidence.

Careful measurements of several physical constants of ethylene oxide have been made by Maass and Boomer (31).

Faworski (32) found that under certain conditions ethylene oxide polymerizes to yield dioxane, and that the latter shows no tendency to polymerize further in the manner of six membered cyclic esters

The principal work on the polymerization of ethylene oxide is due to Staudinger and Schweitzer (1). They have shown that, when ethylene oxide is polymerized under various conditions, a homologous series of polymers is produced in which the physical properties of the individual members vary with increasing molecular weight. The catalysts used in this work were caustic potash, zinc and tin chlorides, sodium and potassium metal, sodium oxide, trimethylamine and triethyl phosphine. Ultra-violet light and Florida earth were found to be without effect. The rate of polymerization was found to depend on the quantity of the catalyst as well as such uncertain factors as degree of sub-division, hence the rates were scarcely ever reproducible. The low boiling point of ethylene oxide* (Eastman Kodak Company, b.p. 10.5 - 11.5°C.) necessitates the use of glass bomb tubes. Because of this fact, and also on account of the very rapid initial rate of polymerization when certain catalysts are used, frequent explosions occurred. This can be readily understood from a consideration of the thermal data of monomeric ethylene oxide (33).

In general an average degree of polymerization of about 50 ethylene oxide units is brought about by the various catalysts. However some catalysts, such as sodium amide, produce higher polymers averaging about 300 building units.

From the results obtained from acetylations and active hydrogen measurements, Staudinger (3, p.287) contends that these ethylene oxide polymers are linear dihydrate polymers, i.e., long chains terminated by hydroxyl groups at either end:

$$HOCH_2 - CH_2 - (O - CH_2 - CH_2)_x - O - CH_2 - CH_2OH$$

This structure is identical with that of the polyethylene ether glycols. He explains this formation by assuming that the ethylene oxide ring opens and adds on one molecule of water, the resulting glycol then reacts with another molecule of ethylene oxide, and so the chain is extended. Experimental

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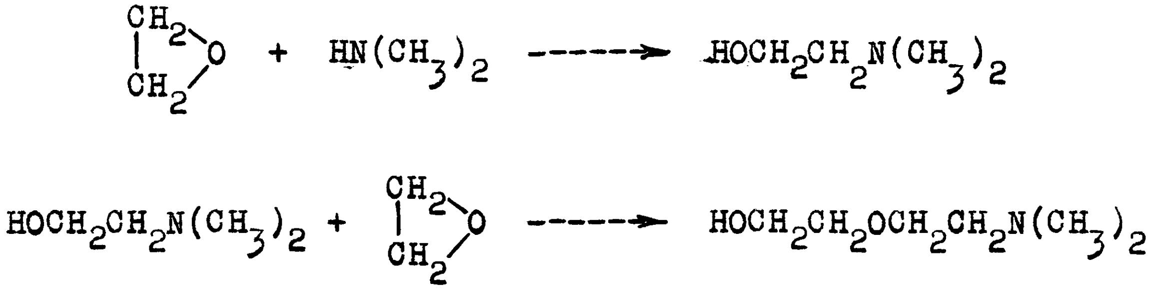
*Maass and Boomer (31) give the boiling point of pure ethylene oxide as 10.73°C.

work has shown that when glycol is introduced into such a reaction mixture, no trace of it can be detected on completion of the polymerization. However, when the polymerization was carried out with complete exclusion of water, the same polymeric products were obtained. This led Staudinger to assume that the water necessary for the formation of the chain polymer arises from the ethylene oxide itself as a result of decomposition of a small amount of it into water and acetylene:

$$\mathrm{-(CH_2-CH_2-O)_x-CH_2-CH_2-O-} \quad + \quad \mathrm{(-CH_2-CH_2-O-)}$$
$$\downarrow$$
$$\mathrm{HO-(CH_2-CH_2-O)_x-CH_2-CH_2O-H} \quad + \quad \mathrm{CH \equiv CH}$$

Since no acetylene could be detected, the assumption was made that it underwent polymerization and that the brown color, which generally occurs during this process, is caused by such a side reaction. However, since the quantity of water necessary for the formation of hydrated polyethylene oxide is so very small compared with the quantity of ethylene oxide, it is doubtful if such complete dryness of reactants and container were achieved. Furthermore, a brown color is often produced in pressure reactions in organic chemistry, so that this can scarcely be considered as an indication of the presence of acetylene. As a matter fact, Perry and Hibbert (34) find that dry potassium hydroxide does not bring about polymerization at 0°C. using an ethylene oxide dried over metallic calcium.

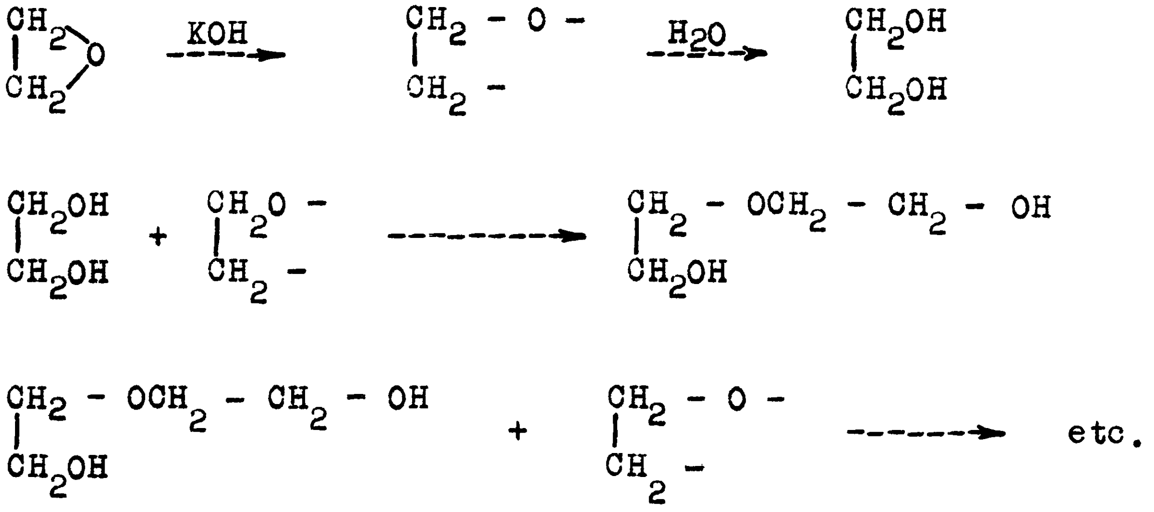
Attempts to obtain nitrogen-containing ethylene oxide polymers, using primary and secondary amines as catalysts, were not very successful, as the nitrogen content found was not in agreement with the molecular weights (cryoscopic). When large amounts of the amine were used, amino alcohols were formed:



Debye-Scherrer X-ray diagrams of the ethylene oxide polymers showed only general crystallization.

The ethylene oxide polymers are very stable and decompose only at elevated temperatures with formation of acetaldehyde, acrolein, and indefinite unsaturated compounds. Acetaldehyde is obtained with dilute hydrochloric acid at 170°C. Roithner (29) reduced ethylene oxide polymers to ethyl iodide with fuming hydriodic acid at 250°C.

Perry (34) has carried out in these laboratories a series of experiments on the polymerization of ethylene oxide using caustic potash as a ~~base~~ catalyst. He has shown that ethylene oxide will polymerize readily in the presence of caustic potash, if there is moisture, glycol, or a polyethylene ether glycol present; also that the degree and rate of polymerization is governed by time and concentration factors which is in agreement with Staudinger. When a polyethylene ether glycol was used with caustic potash, the former was found to have disappeared after the polymerization was complete. This was accepted as evidence that the polyethylene ether glycol had been used up in the building of the long chain. The polymerization of ethylene oxide under the influence of aqueous alkali is represented by Perry as follows:



$$\begin{array}{l}CH_2 \\ | \\ CH_2\end{array}\!\!>O \xrightarrow{KOH} \begin{array}{l}CH_2 - O - \\ | \\ CH_2 -\end{array} \xrightarrow{H_2O} \begin{array}{l}CH_2OH \\ | \\ CH_2OH\end{array}$$

$$\begin{array}{l}CH_2OH \\ | \\ CH_2OH\end{array} + \begin{array}{l}CH_2O - \\ | \\ CH_2 -\end{array} \longrightarrow \begin{array}{l}CH_2 - OCH_2 - CH_2 - OH \\ | \\ CH_2OH\end{array}$$

$$\begin{array}{l}CH_2 - OCH_2 - CH_2 - OH \\ | \\ CH_2OH\end{array} + \begin{array}{l}CH_2 - O - \\ | \\ CH_2 -\end{array} \longrightarrow \text{etc.}$$

Polyethylene Ether Glycols

Polyethylene ether glycols were first prepared by Lourenco (35) in 1859, by heating ethylene glycol with ethylene bromide in a sealed tube at 115 - 120°C. He claimed to have obtained and separated polyethylene ether glycols as high as hexaethylene ether glycol. His experiment was repeated by Perry (45) in these laboratories, but with no satisfactory results.

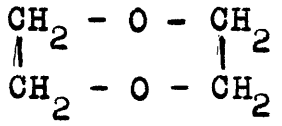
Wurtz (36) prepared polyethylene ether glycols by heating ethylene oxide with either ethylene glycol or water in a sealed tube for several weeks.

Hibbert and Bilger (47) prepared polyethylene ether glycols by heating ethylene glycol with a small amount of iodine. The iodine was found to catalyse the reaction in which two moles of the glycol unite by the elimination of one mole of water. However, the effect of the iodine declines noticeably with the higher polyethylene ether glycols.

Wurtz (37) prepared chlorhydrins by heating ethylene glycol saturated with hydrogen chloride in a sealed tube.

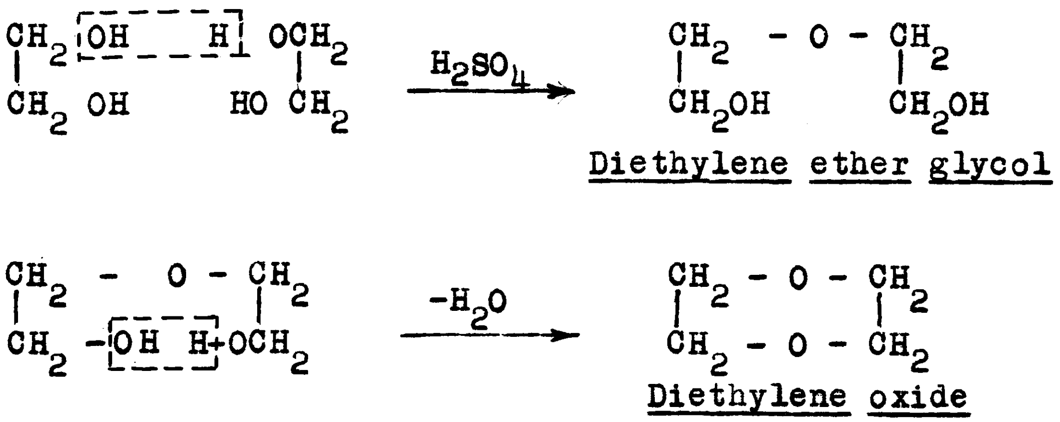
Carius (38), Fittig (39) and Ström (40) treated ethylene glycol with sulphur chloride and obtained chlorhydrins.

Polyethylene ether glycol chlorhydrins were prepared also by Lourenco (41) who passed a stream of hydrogen chloride through warm polyethylene ether glycols. He prepared the bromhydrins of the polyethylene ether glycols by treating ethylene glycol with ethylene bromide at 160°C. in a sealed tube. However, by heating these substances together at the same temperature and ordinary pressure, he obtained diethylene oxide and diethylene ether glycol bromhydrin. To the former he ascribed the formula:



$$\begin{array}{ccc} CH_2 - O - CH_2 \\ | \qquad\qquad | \\ CH_2 - O - CH_2 \end{array}$$

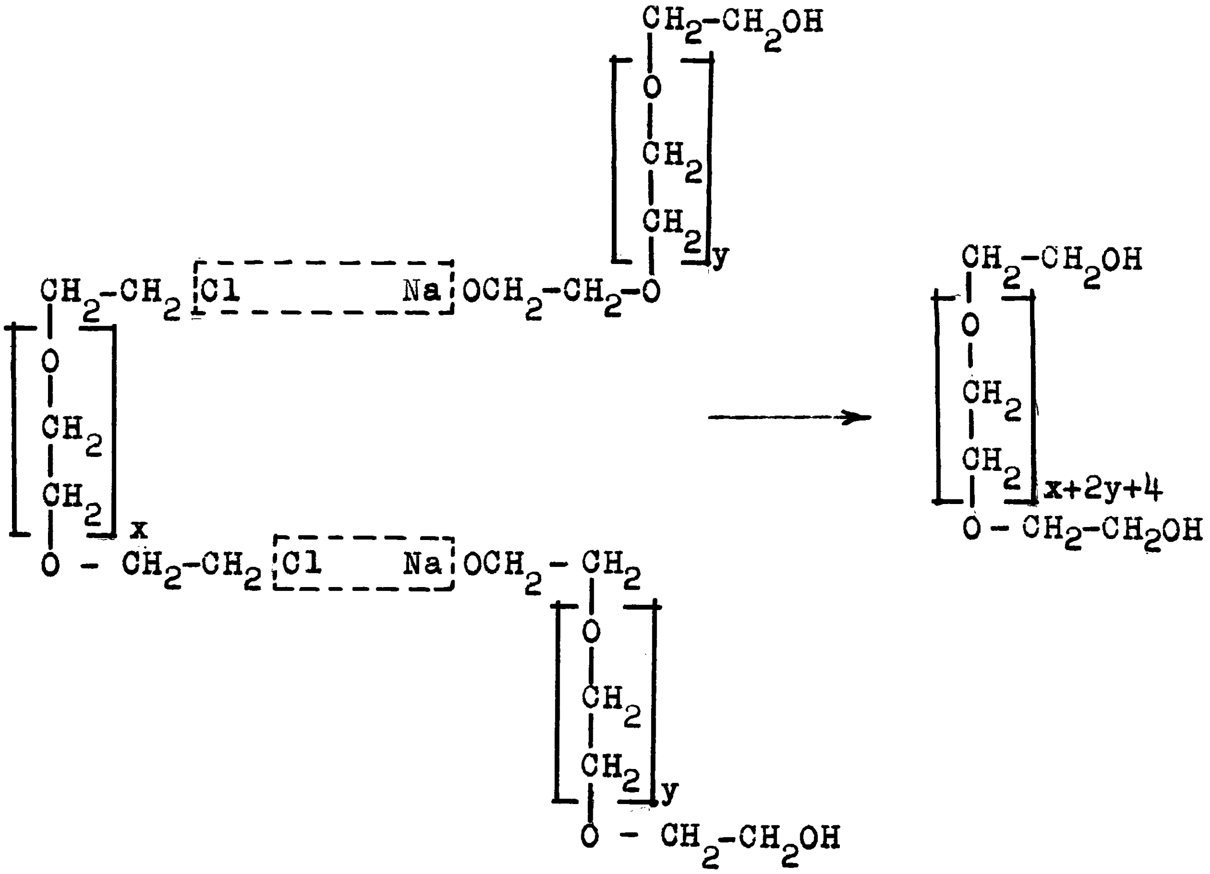
This compound was also obtained by Faworski (32) as the main product from distilling ethylene glycol with sulphuric acid. He suggested the same formula and it was confirmed by Clark (42) in 1912. Faworski's experiment lends support to the theory that polyethylene ether glycols may be dehydrated, as the above reaction obviously suggests a dehydration process. This may be assumed to take place through an intermediate stage, thus:


Diethylene ether glycol

Diethylene oxide

If this assumption is correct then treatment of diethylene ether glycol with concentrated sulphuric acid should result in the formation of diethylene oxide. Experimental evidence proved this to be the case and ethylene glycol, as well as polyethylene ether glycols, similar to those produced in the iodine condensation reaction were obtained as by-products.

Perry (unpublished work) has carried out a series of investigations in these laboratories dealing with the direct synthesis of the polyethylene ether glycols. The various methods investigated were all based on the general principle of an interaction between one mole of the dichloride of a polyethylene ether glycol with two moles of the mono-sodium salt of the same or another polyethylene ether glycol, with subsequent elimination of two moles of sodium chloride.



where x may be 1, 2, 3, 4, etc., y may be 1, 2, 3, 4, etc. and x and y may, or may not, have the same value.

A greater part of his primary research was spent in attempts to discover the best method of carrying out this reaction and isolating the resulting products. One series of experiments in his earlier work was devoted to the preparation of the metallic salt of the polyethylene ether glycol by the direct action of sodium, and a fair measure of success attained. He later modified the process, however, by using sodium methylate in place of metallic sodium. The methyl alcohol, liberated as a by-product in the modified process, was removed by distillation under reduced pressure. Perry also investigated the use of sodium hydroxide, which forms sodium derivatives when heated with polyethylene ether glycols at a high temperature. He found the sodium methylate process to be the most suitable and used it for the synthesis of a number of the lower members in the series. The preparation of the dichloride derivatives of the polyethylene ether glycols was finally based on the use of thionyl chloride as the active substituting reagent. The members of the series, prepared by Perry, were the tetra- to dekaethylene ether glycol inclusive, with the exception of the nonaethylene ether glycol. They are all colorless, odorless, viscous liquids with the exception of the dekaethylene ether glycol, which is a liquid when prepared but "sets" to a soft crystalline solid on standing. Hence this member is just on the border line between liquid and solid at room temperature (20°C.).

DISCUSSION OF EXPERIMENTAL RESULTS

I. Methods of Synthesis

Preparation, Isolation and Purification of Products

The synthesis of pure long-chain polyethylene ether glycols and their derivatives was undertaken in these laboratories five or six years ago. Since then, investigations by the writer and other workers have resulted in the preparation of a number of these synthetic polymers including the 162-membered polyethylene ether glycol.

Synthesis of the higher from the lower polyethylene ether glycols involves two main processes:

(a) Preparation of the long-chain polyethylene ether glycol dihalides,

(b) Preparation of the mono-metallic salts of the polyethylene ether glycols.

Interaction of one mole of product (a) with two moles of product (b) gives one mole of a higher member. The general scheme is illustrated in the equation on page 30.

On account of the hygroscopic nature of the polyethylene ether glycols and their derivatives, it was necessary to dry the materials, reagents, and receptacles thoroughly before use. The polyethylene ether glycols, themselves, were dried at a high temperature (110°C.) under reduced pressure (0.5 mm.). To facilitate the drying a current of dry nitrogen gas was passed through the liquid material at the same time by means of an inserted capillary tube.

(a) Preparation of the Long-Chain Polyethylene Ether Glycol Dihalides

The dichlorides were used exclusively for the synthesis of the lower polyethylene ether glycols. Inasmuch, however, as the reaction of thionyl chloride on the higher members gave unsatisfactory results, attention was directed to the dibromides. Here the methods of preparation proved even less satisfactory. An investigation of the di-iodide was then undertaken and this was found to be the best dihalide for the progressive synthesis of the higher members since it could be prepared in sufficient yield. Furthermore the analysis of the di-iodide is more reliable because of the heavier atomic weight of iodine as contrasted with chlorine and bromine.

(i) Dichlorides

The method of preparation devised by Perry, and improved by the writer, was found to be the most satisfactory. This consists of dissolving the polyethylene ether glycols in pyridine and adding thionyl chloride with rapid stirring.

The product was isolated by ~~precipitation~~ pouring into water in order to remove the pyridine hydrochloride and the resulting oil extracted with ether. The ether solution was neutralized with sodium bicarbonate, dried over sodium sulphate, shaken with both Darco charcoal and metallic mercury, filtered through a layer of charcoal, and then distilled under diminished pressure.

The optimum rate of addition of thionyl chloride and the optimum reaction temperature varied with each member; in each case, these were ascertained by carrying out a number of experiments. The treatment with mercury was introduced in order to remove colloidal sulphur, which is usually present in these reactions. The difficulties of purification became more pronounced with increasing molecular weight of the polyethylene ether glycols, and the yields were correspondingly lower.

(ii) Dibromides

A variety of methods for the preparation of these derivatives were investigated. However, only two of them gave the required product, and that in a yield much lower than was obtained in the case of the corresponding dichloride. The dibromides were therefore not used in the synthesis of the higher polyethylene ether glycols. The above-mentioned methods, however, are considered worthy of brief mention.

Phosphorus Pentabromide. - This reagent was allowed to react upon a chloroform solution of the polyethylene ether glycol. In order to eliminate the phosphorus by-products, the reaction mixture was poured into water and the material isolated from the chloroform solution as in the case of the dichloride from its ether solution, with the exception that mercury is not used in the purification. The method gives low yields and is particularly difficult of application on account of the stable emulsions which form on washing the chloroform solution. These are often gel-like in behaviour and cause a considerable loss of material.

Thionyl Bromide*. - Thionyl bromide was an obvious reagent to investigate after the success obtained with thionyl chloride. No reference to its use, however, could be found in a review of the organic chemical literature but a method of preparation was obtained from the inorganic chemical literature (Mayes and Partington (43)). In this the properties of thionyl bromide are stated to be analogous to those of the chloride with respect to inorganic reactions.

The thionyl bromide was therefore prepared according to this method (43) which consists in passing hydrogen bromide through thionyl chloride and distilling the resulting thionyl bromide. The reaction may be represented as follows:

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*This method of preparation has been forwarded to "Inorganic Syntheses" for publication.

$$SOCl_2 + 2HBr \dashrightarrow SOBr_2 + 2HCl$$

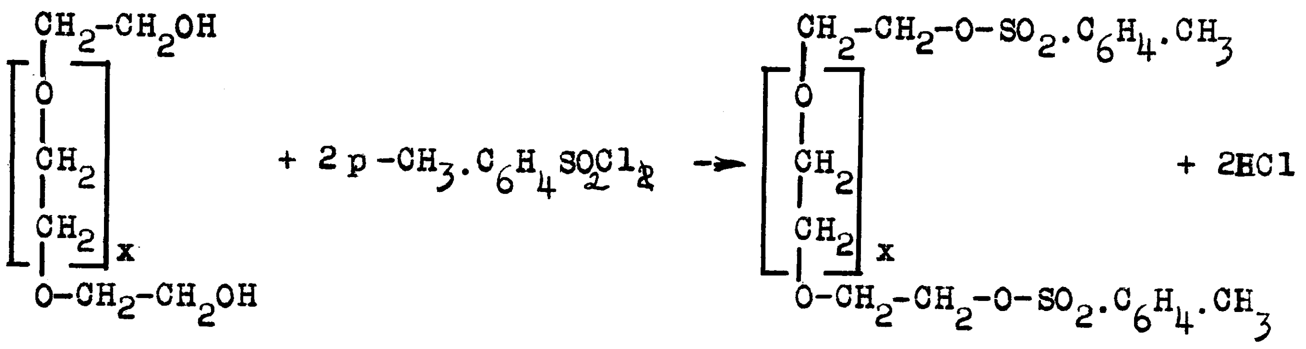
As few details of the procedure are given by Mayes and Partington, and as the method developed by the writer gives a much better yield, it has been considered advisable to give an accurate description in the experimental section. Practically a quantitative yield was obtained and no laborious fractionation required, whereas Mayes and Partington had found it necessary to purify their product by a series of fractional distillations. The bromine analysis and the boiling point over a range of different pressures agreed identically with those obtained by these authors.

The preparation and purification of the polyethylene ether glycol dibromides, using thionyl bromide, was carried out in the same manner as the corresponding chloride reactions. However, in the former case the purification is more difficult, because considerable sulphur separates out during the reaction. The yields are also much lower than those obtained by the use of thionyl chloride.

No discussion need be given of the other methods for the preparation of the dibromides investigated, because of their general unsatisfactory nature. In some cases, a cleavage of the chains was indicated by the analytical results.

(iii) Di-iodides

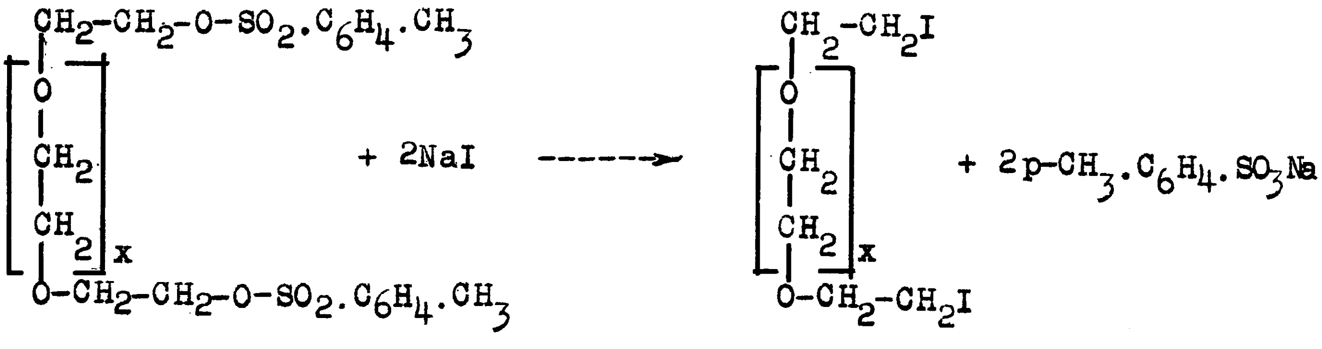
The most promising method for the preparation of the di-iodides appeared to be that used by Helferich and Himmen (44) for the synthesis of iodo derivatives of various carbohydrates. It consists of the primary formation of the ~~di~~-p-toluene sulphonic ester by the action of p-toluene sulphonyl chloride on the hydroxyl derivative, the resulting ester then being converted into the iodo derivative by interaction with sodium iodide. When applied to the polyethylene ether glycols, the reactions may be represented as follows:



$$CH_2\text{-}CH_2OH\text{-}[O\text{-}CH_2\text{-}CH_2]_x\text{-}O\text{-}CH_2\text{-}CH_2OH + 2\,p\text{-}CH_3.C_6H_4SO_2Cl \longrightarrow CH_2\text{-}CH_2\text{-}O\text{-}SO_2.C_6H_4.CH_3\text{-}[O\text{-}CH_2\text{-}CH_2]_x\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2.C_6H_4.CH_3 + 2HCl$$

Polyethylene ether glycol

Di-p-toluene sulphonic ester of the polyethylene ether glycol



$$CH_2\text{-}CH_2\text{-}O\text{-}SO_2.C_6H_4.CH_3\text{-}[O\text{-}CH_2\text{-}CH_2]_x\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_2.C_6H_4.CH_3 + 2NaI \longrightarrow CH_2\text{-}CH_2I\text{-}[O\text{-}CH_2\text{-}CH_2]_x\text{-}O\text{-}CH_2\text{-}CH_2I + 2p\text{-}CH_3.C_6H_4.SO_3Na$$

Di-iodide of the polyethylene ether glycol

This method was considered to be the most satisfactory as it provides two different means of proving the identity of the compound, viz., the sulphur analysis of the intermediate ester, and the halogen analysis of the di-iodide. The procedure was varied somewhat in order to adapt it to the different polyethylene ether glycols.

p-toluene sulphonyl chloride was added to a pyridine solution of the polyethylene ether glycol, with cooling if necessary, and the mixture allowed to stand. The time required for the reaction increased with increasing molecular weights (from 4 to 24 hours).

In order to isolate the di-iodide, water was added to the reaction mixture until it became turbid. It was allowed to stand for a short time to insure complete hydrolysis of the excess p-toluene sulphonyl chloride, and the product finally precipitated by pouring into a large volume of water with rapid stirring. The lower members were precipitated as solids, while the higher members separated as oils which generally formed emulsions with the water. The solid esters were filtered off, washed with water, and recrystallized from ethyl alcohol. The liquid esters were extracted with chloroform, the pyridine having been previously rendered insoluble in the extracting medium by conversion to pyridine hydrochloride by addition of hydrochloric acid. The chloroform solution was neutralized with sodium bicarbonate, dried over sodium sulphate, and decolorized with charcoal. The chloroform was then removed under reduced pressure and the residue dissolved in acetone. In order to remove any p-toluene sulphonic acid, the acetone solution was precipitated by pouring into petroleum ether, and the precipitated ester repeatedly washed with the latter solvent to remove the acetone.

In general, the experiments recorded in the literature relating to the formation of iodo derivatives from the above type of ester,by means of sodium iodide, were carried out at high temperatures, and in most instances under pressure. The first experiments of the writer were also carried out in this manner. However, it was later found that the reaction occurs even at room temperature and atmospheric pressure, with considerable increase in yield. This method has the great advantage of eliminating decomposition and the annoyance of liberated iodine.

The sodium iodide was allowed to react with the sulphonic ester of the polyethylene ether glycol in acetone solution. After a short time a precipitate of sodium p-toluene sulphonate formed which was filtered from the solution and the acetone then removed under reduced pressure. The residue consisted of a mixture of the reaction product with excess sodium iodide. In the case of the lower members, this mixture was extracted with ether to separate the soluble product from the insoluble sodium iodide. The ether solution was shaken with molecular silver to remove free iodine, and then distilled. Since the higher members are more soluble in dioxane than in ether, they were first extracted with the former solvent. The dioxane was removed under diminished pressure and the residue then extracted with ether. This ether solution was freed from iodine as before and the product isolated by removal of the solvent under diminished pressure.

(b) Preparation of the Mono-metallic Salts of the Polyethylene Ether Glycols

Metallic sodium or potassium was used to prepare these derivatives by the following methods: (1) without a solvent, (2) use of liquid ammonia, and (3) using dioxane as a solvent. The first method proved to be the most satisfactory in that it was by far the most convenient and gave equally good results.

Method (1)

The metal was allowed to react with the polyethylene ether glycol (in theoretical excess of the amount of metal used) in a vessel closed to the atmosphere, and nitrogen gas passed through the liquid material, which was kept at an elevated temperature. The nitrogen atmosphere, aided by the hydrogen thus evolved, prevented oxidation and the metal presented a silver lustre until all of it had reacted. Any di-metallic salt which may form presumably breaks up spontaneously to the mono-metallic derivative when an excess of the polyethylene ether glycol is present. This is borne out by the work of L. P. Moore in these laboratories, in which it was found that the formation of di-sodium salts is extremely difficult and that these are very unstable.

Method (1) is a very convenient method of synthesis, and, with proper control of temperature and rate of metal addition, the reaction goes smoothly and with a minimum of discoloration.

Method (2)

The polyethylene ether glycol was dissolved in liquid ammonia (with the higher members only partial solution takes place), and the metal then added with brisk stirring. The latter dissolved rapidly and produced an intense blue coloration in the ammonia solution. After a short time the blue color faded and the solution reverted to its original white color. This color change is an excellent indicator of the course of the reaction, since when the color disappears the reaction is complete. It was found also that,when the polyethylene ether glycol and the metal are used mole for mole,the blue color just barely disappears. The addition of a small amount of either substance will cause the color to return or disappear as the case may be. This is also an excellent indication of the ease with which the mono-metallic salt is formed, and the difficulty of forming the di-metallic salt. The salt was readily isolated by this ammonia procedure, the "end point" being shown by the color reaction, and the excess ammonia then removed by evaporation.

Method (3)

Method (3) consists in dissolving the polyethylene ether glycol in dioxane (previously refluxed over metallic potassium for some time) and then adding the metal with rapid stirring. In this manner the mono-metallic salt is obtained in dioxane solution.

Sodium was used with the lower polyethylene ether glycols and potassium with the higher on account of its greater activity. The reaction becomes increasingly sluggish as the chain lengthens.

Condensation

The condensation reaction was carried out immediately after the preparation of the mono-metallic salt (by Method(1)). The di-halide derivative was added slowly to the mono-metallic salt under the same conditions as those used in the preparation of the latter. Following the final addition the temperature was raised. In the case of the lower members a gradual precipitation of salt occurred and the reaction mixture became lighter in color; with the higher members, the amount of salt formed was so small that it remained in solution and merely a decrease in color was observable. When the basic reaction mixture became neutral, the reaction was complete.

Isolation and Purification

In order to simplify the description, the isolation and purification will be discussed under three groupings: Group I, where the initial material and final product are both liquids; Group II, where the initial material and final product are liquid and solid respectively; and Group III, where the initial material and final product are both solids.

Group I. - The crude condensation product was extracted continuously with ether until the residue consisted only of sodium chloride. The product was isolated by fractional distillation at very low pressures, obtained by use of a large oil pump in series with a Langmuir Mercury Pump. Since the lower members are viscous liquids, repeated fractionations were necessary in order to obtain a constant boiling fraction.

Group II. - When the initial polyethylene ether glycol was a liquid and the reaction product a solid, the former was removed by distillation under very low pressures. Great care was required in carrying out this distillation in order to prevent charring of the solid product. A satisfactory method was finally found in the use of a Wood's Metal bath, which was heated at a very slow rate to maintain the necessary low pressure (several microns). The distilling flask was insulated with asbestos rope as a further precaution against superheating. The solid was then purified by repeated fractional extraction with ether.

Group III. - Where both the initial polyethylene ether glycol and the reaction product were solids, the ether extraction was continued until no more of the former was extracted, as indicated by the sharp break in the rate of extraction. The residue, which consisted of the reaction product and the salt (potassium iodide), was extracted with dioxane at 100°C. in order to separate the salt. A steam-heated funnel was used for filtering the salt from the dioxane solution as it was found that the former redissolved to some extent if the solution were allowed to cool. The filtrate was decolorized with charcoal, the dioxane removed under reduced pressure, and the resulting product purified by dissolving in acetone, precipitating into ether, and washing repeatedly with the latter.

All of the above products were kept in desiccators over phosphorus pentoxide and sulphuric acid at low pressures.

Attempts to prepare derivatives of the solid polyethylene ether glycols, exclusive of the dihalides, sulphonic esters, and mono-metallic salts, resulted in oils, which would not crystallize.

The melting points of the solid members were not sharp but melted over a one degree range.

Ethylene oxide was polymerized and fractionated according to the methods of Staudinger (1). The catalysts used were, respectively, metallic potassium and potassium hydroxide. Several of these fractions were converted into p-toluene sulphonic esters; the average molecular weight of the fractions was determined from the sulphur content of these esters assuming two terminal hydroxyl groups in the polymer.

Viscosity measurements were carried out on the polyethylene ether glycols and also on the polyethylene oxides. These results are discussed in the following section.

II. Theoretical Deductions

Accurate knowledge of the molecular weight of both natural and synthetic polymers is essential to an understanding of their behavior: hence a large number of investigators have endeavored to use various properties of solutions for the determination of the molecular weight of the solute. The application of chemical end-group determinations, osmotic pressure measurements, ultra-centrifuge analyses, and viscosity measurements has provided molecular weight values which are at present regarded with considerable favor. The best method up to the present time has been that of Svedberg (48), using his ultra-centrifuge, but this method, apparently, has as yet only been applied successfully to the proteins.

However, there is a wide variation in the values obtained by the different methods for most of the polymers. While many investigators have found a relationship between the viscosity of a solution of the polymer and the molecular weight of the solute, perhaps the most outstanding generalization is that put forward by Staudinger. The values which he obtains for the molecular weight of cellulose are, however, very much at variance with those obtained by the chemical methods of Haworth (49). These discrepancies between physical and chemical methods have been pointed out and discussed by Kraemer (54)

The derivation of the Staudinger viscosity equation is given in the historical section (page 15). His conclusions are based essentially on viscosity data derived from fractionated polymers, the individual fractions of which are assumed to vary among themselves only over a comparatively limited range in chain length. However, such fractionation is at best a crude procedure (since it is carried out by a method of precipitation based on differences in solubilities) and it seems highly probable that the low molecular,soluble material influences the precipitation of the high molecular, less soluble material, tending to keep a proportion of the latter from precipitating. Staudinger (3, p.310) believes that the contrary is possible:

"When fractions are precipitated from solutions, the precipitated molecules may surround shorter molecules, which would ordinarily remain in solution, and cause them to settle out". In any event such crude fractions can hardly be considered sufficiently homogeneous for viscosity measurements upon the value of which the fundamental equation of Staudinger is based. Co-precipitation of polymers of different chain length is to be expected from a consideration of different physical phenomena such as van der Waal forces of attraction and the influence of polar molecules upon one another. Staudinger assumes that association or dissociation of the polymers does not occur in dilute dioxane or benzene solutions.

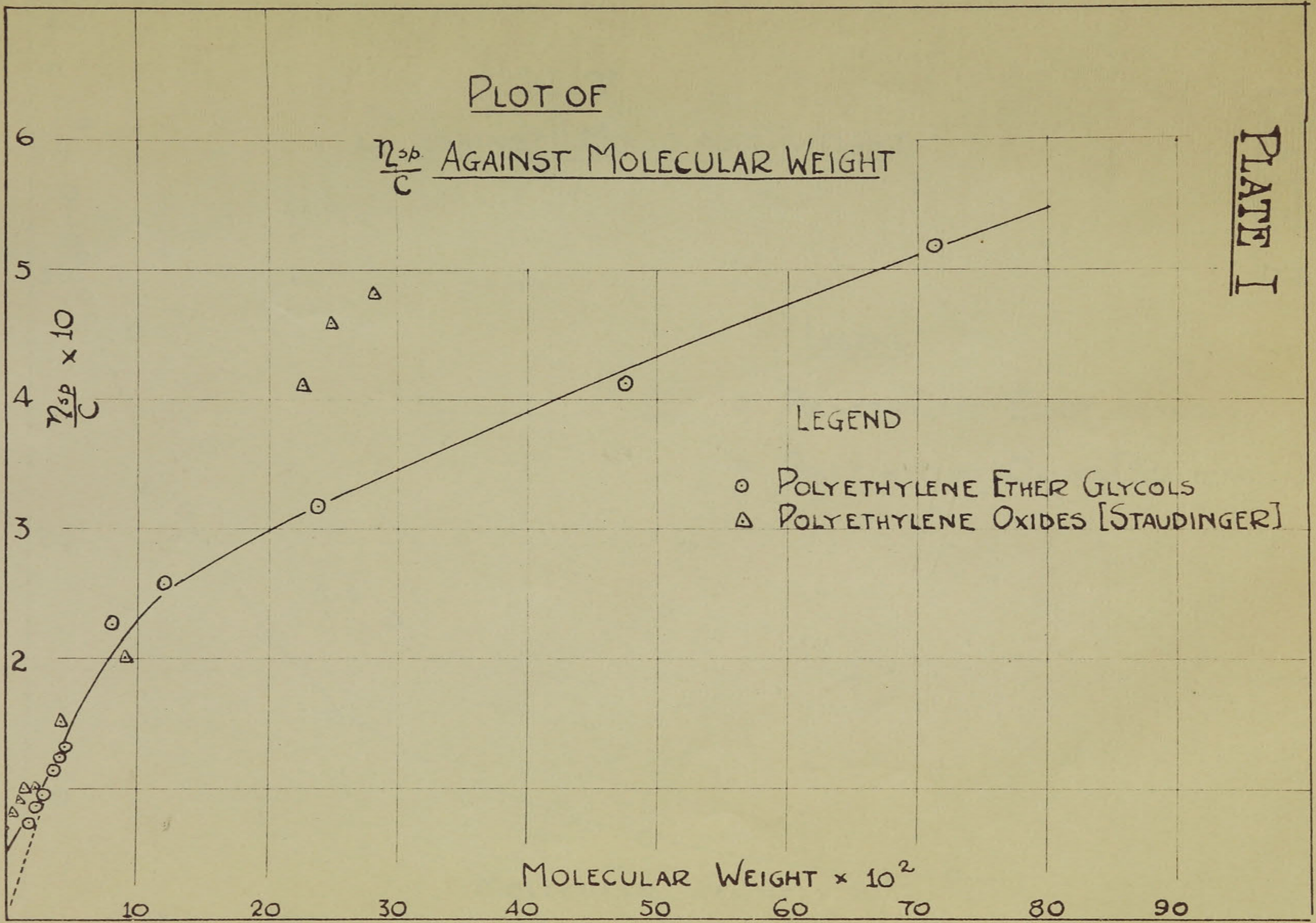
Kraemer (50) has carried out viscosity measurements on solutions of polymeric hydroxydecanoic acids ranging in molecular weight from 780 - 25,200 and finds that the quantitative equation of Staudinger does not hold for high molecular weights (above 15,000). He states: "In the light of these results, Staudinger's values for the molecular weights of rubber, cellulose, and other very high polymers are unreliable."

Relation of Polymerized Ethylene Oxide to Synthetic Polyethylene Ether Glycols

The experimental results obtained in this investigation with fractions of polymerized ethylene oxide are in agreement with those found by Staudinger. The low molecular polymers were found to form p-toluene sulphonic esters quite readily while the failure of the higher polymers to form these esters may be attributed to the sluggishness of reaction of macro-molecules in such mixtures. The ethylene oxide polymers were found to crystallize in the same manner as the solid polyethylene ether glycols and both series of compounds exhibited the same solubilities in all common solvents, a result in conformity with the work of Perry (34, 45) who has shown that ethylene oxide polymers are in reality mixtures of polyethylene ether glycols. The results obtained by Perry and those of Staudinger (acetylation experiments and active hydrogen determinations), together with those obtained in the present investigation, lead to the conclusion that ethylene oxide polymerizes to form a long linear chain terminated by a hydroxyl group at each end. The Perry-Hibbert mechanism for the polymerization of ethylene oxide is outlined in the historical section (page 27).

The viscosity and "constant" K_m values obtained with the polyethylene ether glycols in the present investigation are plotted in Graphs I and II, respectively. In Graph I the specific viscosity values have been plotted against molecular weights while in Graph II the values for K_m are plotted against molecular weight. Staudinger's experimental values (measured in 4.4% dioxane solutions), used in each graph, are quoted below. (3, p.309).

PLATE I



PLOT OF

$\frac{\eta_{sp}}{C}$ AGAINST MOLECULAR WEIGHT

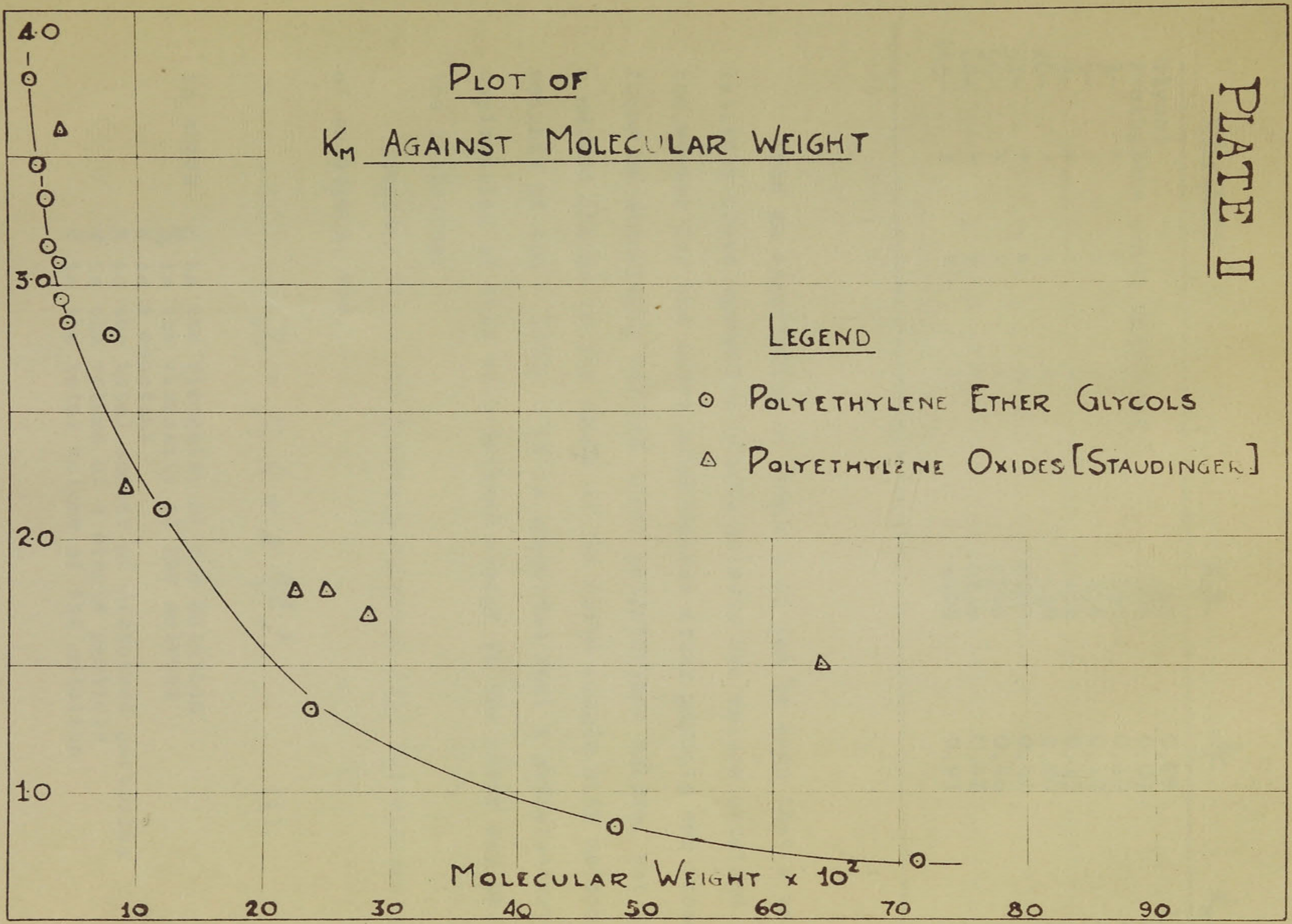


PLATE II

PLOT OF K_M AGAINST MOLECULAR WEIGHT

Substance	M.W.	$\frac{\eta_{sp}}{c}$	$K_m \cdot 10^4$
Glycol	62	0.08	13.0
2-ethylene oxide dihydrate	106	0.09	8.5
3- " " "	150	0.10	6.7
5- " " "	238	0.10	4.2
9- " " "	414	0.15	3.6
20- " " "	920	0.20	2.2
51- " " "	2260	0.41	1.8
56- " " "	2500	0.46	1.8
64- " " "	2830	0.48	1.7
145- " " "	6400	0.93	1.5

From an examination of Graph I it can be seen that a relatively close agreement exists between the values obtained by the writer for the lower polyethylene ether glycols and those found by Staudinger for the lower polyethylene oxides, but that a marked change in the slope of the curve occurs with molecular weights of 800 - 1000. It is suggested that a satisfactory explanation of this well-defined change in the curve may be the following:

Consider first the Einstein equation (23) for viscosity of solutions, viz.,

$$\eta_s = \eta_0 \left(1 + k\frac{N\phi}{V}\right) \qquad (1)$$

in which η_s is the viscosity of the solution
η_0 is the viscosity of the solvent
k is a constant
N is the total number of dissolved particles
ϕ is the volume of a single particle
V is the total volume of the solution

Equation (1) may be re-written as follows:

$$\frac{\eta_s}{\eta_0} - 1 = \eta_{sp} = K\frac{N\phi}{V} \qquad (2)$$

Staudinger assumes that the volume of a linear macromolecule may be represented as the volume of a shallow cylinder of height d (the diameter of the molecule) and a base area $\left(\frac{L}{2}\right)^2\pi$ in which L is the total length of the molecular chain (page 17) so that:

$$\phi = \left(\frac{L}{2}\right)^2\pi d \qquad (3)$$

If it is assumed that the diameter of the molecule is constant, while its length varies proportionately with molecular weight, then,

$$L = K_1 M \qquad (4)$$

in which M is the molecular weight of the solute. Substituting for L in (3), we have,

$$\phi = \left(\frac{K_1 M}{2}\right)^2\pi d \qquad (5)$$

while, substituting for ϕ in (2),

$$\eta_{sp} = \frac{N\left(\frac{K_1 M}{2}\right)^2\pi d}{V} \qquad (6)$$

or

$$\eta_{sp} = \left(\frac{K\cdot K_1^2\pi d}{4}\right)\left(\frac{M^2 N}{V}\right)$$

Since $c = \frac{MN}{V}$ (where c is the concentration of the solution,) and the grouped constants, $\frac{K \cdot K_1^2 \pi d}{4}$ may be substituted by a new constant K_m so that,

$$\eta_{sp} = K_m \cdot M \cdot c \qquad (7)$$

or

$$\frac{\eta_{sp}}{c} = K_m \cdot M$$

which is the Staudinger equation.

From equation (6),

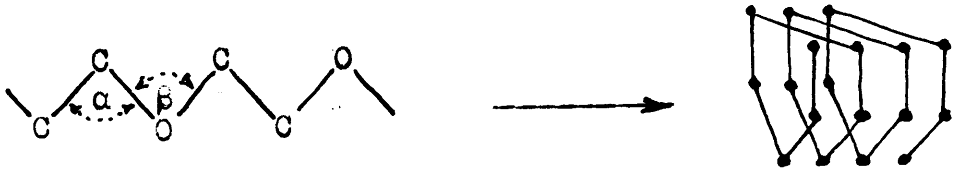
$$K_m = \frac{K \cdot K_1^2 \pi d}{4}$$

Since K is found to vary experimentally, K_1 must also vary since the other values in the equation are constant. However, K_m decreases with increase in molecular weight of the polyethylene ether glycols, so that K_1 must also decrease with increase in molecular weight.

Considering equation (4),

$$L = K_1 M$$

since K decreases with increase in molecular weight it follows that the effective length of the molecule does not increase in direct proportion to the molecular weight so that the effective length of the chain for a given molecular weight is shorter than would be expected theoretically. This relative contraction of the chain may be explained by assuming either (a) spiral grouping of the longer chains,[*] or b) a lower degree of freedom of the molecule to rotate completely in the manner assumed by Staudinger. (This lower degree of freedom may be compared to a wave-like motion created by the long chain macro molecule in its attempt to rotate as a whole.) Since no change in the valence angles (α and β) is to be expected the spiral grouping takes place about the single bonds:



It follows from this that either the distance between the planes of the spirals may decrease or the effective diameter of the molecule may increase with formation of larger spirals.

The deflection of the curve probably indicates the region where either the spiral formation acquires a marked character or departure from complete rotation becomes pronounced.

Further evidence regarding the tendency of long chains to undergo spiral formation is provided in the investigations of Pickard and Kenyon (51). These authors show that "in a series of normal esters of secondary alcohols exhibiting optical activity we may expect irregularities in the rotatory power...... and that these irregularities are due to the fact that the ester chain of carbon atoms assumes the spiral form with about five atoms in one complete turn, entire turns being completed at the point of irregularity."

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[*] Staudinger has suggested that spiralling occurs with the polyethylene oxides. (page 20)

Hibbert and Hill (52) from their investigations on cyclic acetals containing more than six atoms in the ring suggested that "cyclization in atomic chains might be expected to be a periodic function of their length, the period depending on the angles between the valence bonds, or forces, joining the atoms."

In Graph II the constant (K_m) obtained for the polyethylene ether glycols is compared with that obtained by Staudinger for his polyethylene oxides. A similarity is apparent in that the value of K_m is seen to vary sharply with the lower members but tends towards a constant value for the higher members (beyond a molecular weight of 5000). However, in the case of the polyethylene oxides the value of K_m for the period of constancy is larger than with the polyethylene ether glycols, indicating that the viscosity values for the former are too high for the molecular weights found. The high viscosity for the polymeric mixtures of relatively low mean molecular weight is probably due to the presence in each individual fraction of a small proportion of high molecular polymers. The latter increase the viscosity abnormally and at the same time cause a relatively small change in the mean molecular weight.

It is of interest that the viscosity data obtained by Kraemer (50) on the polymeric ω-hydroxydecanoic acids are in general conformity with those obtained in the present research. in that the value of K_m is relatively constant for higher molecular weights (5000 - 15000). For molecular weights below 5000 the value of K_m showed wide inconsistencies.

The results obtained in the present investigation are based on the use of long chain polyethylene ether glycols, synthesized in a step-wise manner, which are therefore of known constitution. Such compounds are obviously much more suitable for an examination of the validity of Staudinger's viscosity equation than are the non-homogeneous polymers used by him.

In conclusion, the values obtained in this research indicate that Staudinger's deductions as to chain length for the higher polymerized ethylene oxides may be incorrect to the extent of 50% and that in all probability this relative inaccuracy may also exist in the case of the molecular weight values which he assigns to natural polymers such as cellulose and rubber.

EXPERIMENTAL

Synthesis of the Polyethylene Ether Glycols*

The apparatus used for the preparation of the dichlorides consisted of a three-necked glass flask fitted with a water-cooled reflux condenser (closed with a calcium chloride tube), a mercury-sealed stirrer, and dropping funnel. All connections were made by means of ground glass joints.

The apparatus used for the preparation of the mono-metallic derivatives of the polyethylene ether glycols and the subsequent condensation reaction was similar to the above-mentioned apparatus except that the dropping funnel was combined with a gas-inlet tube, which led to the bottom of the flask.

The general scheme of synthesis of the polyethylene ether glycols is indicated below. From this it is evident that in each successive process three units are condensed, thus producing a new polymer with chain length three times the original.

$$2HOCH_2.CH_2(O.CH_2.CH_2)_xO.CH_2.CH_2OM + XCH_2.CH_2(O.CH_2.CH_2)_xO.CH_2.CH_2X$$
$$\longrightarrow HOCH_2.CH_2(O.CH_2.CH_2)_{3x+4}O.CH_2.CH_2OH + 2M.X$$

where M is the metal and X the halogen.

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* The volumetric analyses were carried out using the modified method of Stepanoff (55), the gravimetric analyses using the method of Carius.

Synthesis of Nonaethylene Ether Glycol ($HOCH_2.CH_2(O.CH_2.CH_2)_7.O.CH_2.CH_2OH$)

This member was synthesized from three moles of triethylene ether glycol. The latter was obtained commercially and purified in the following manner.

The crude product was fractionally distilled several times under diminished pressure. The final fraction boiled constantly at 115-117°C./0.5 mm., the bath temperature being held at 126-130°C. Approximately 1650 gm. of pure triethylene ether glycol were obtained from 2 kgm. of the commercial material.

(A) Preparation of Triethylene Ether Glycol Dichloride

20 gm. of freshly distilled triethylene ether glycol were dissolved in 20 gm. of pyridine and placed in the reaction flask. 40 gm. (26% excess) of thionyl chloride were added from the dropping funnel during the course of three hours, vigorous stirring being maintained throughout the reaction. The flask was surrounded by a bath kept at 40°C. during the addition. Following the addition of the thionyl chloride several pieces of porous plate were added to facilitate the evolution of sulphur dioxide. The temperature of the bath was then raised to 60°C. for a period of 30 minutes, during which time the sulphur dioxide was completely evolved.

The yellow reaction mixture was poured into three times its volume of ice-water and the resulting oil extracted several times with ether in a separatory funnel. The ether extracts were washed with water, carefully neutralized with sodium bicarbonate solution, washed again with water and then dried over anhydrous sodium sulphate.

Upon removal of the ether by distillation, the residual liquid was distilled under reduced pressure. The product obtained was a colorless, odorless liquid which distilled constantly at 80-81°C./0.5-1.0 mm. Weight, 20 gm. Yield, 80%.

0.2564 gm. substance required 27.30 cc. N/10 $AgNO_3$
0.2450 " " " 26.18 cc. " "
Found: Cl, 37.80, 37.92%
Calc. for $(C_2H_4O)_2.C_2H_4.Cl_2$: Cl, 37.97%

(B) Preparation of the Monosodium Salt of Triethylene Ether Glycol and Condensation with the Dichloride

250 gm. (92% excess) of the freshly distilled triethylene ether glycol were placed in the reaction flask and the latter then immersed in an oil bath maintained at 80°C. A current of dry nitrogen gas was bubbled through the liquid, which was stirred vigorously throughout the entire reaction. 20 gm. of metallic sodium were then added in small pieces during the course of three hours. Hydrogen gas was evolved continuously and after 12 hours the sodium had completely dissolved. A brownish-yellow solution was obtained.

85 gm. (5% excess) of triethylene ether glycol dichloride were then added through the dropping funnel during a period of

one hour, the temperature of the bath being maintained at 80°C. During the next hour the temperature was raised slowly to 160°C., the reaction mixture gradually becoming lighter in color owing to the separation of sodium chloride. The bath temperature was maintained at 160°C. for a further two hours, when the light yellow mixture reacted neutral to litmus.

The reaction product was poured into a continuous liquid extractor, in which all joints were of ground glass, and the mixture extracted with ether for about 24 hours, leaving a large residue of salt. After the ether had been removed, the residual liquid was fractionated by distillation under reduced pressure. 200 gm. of triethylene ether glycol were recovered and distillation of the residual liquid gave, on careful fractionation, a colorless distillate of the nonaethylene ether glycol, b.p. 209-212°C./0.008 mm. Weight 90 gm., yield 50%.

Synthesis of Octadekaethylene Ether Glycol $(HOCH_2.CH_2(O.CH_2.CH_2)_{16}-O.CH_2.CH_2OH)$

The crude hexaethylene ether glycol used in this synthesis had been prepared by Perry (45) using a method somewhat similar to that described above. It was purified by repeated fractional distillation under reduced pressure until the product boiled constantly at 160-163°C./0.003-0.005 mm.

(A) Preparation of Hexaethylene Ether Glycol Dichloride

70 gm. of hexaethylene ether glycol were dissolved in 40 gm. of pyridine and placed in the reaction flask. To this solution 65 gm. (10% excess) of thionyl chloride were added slowly from the dropping funnel over a period of 3 hours, with vigorous stirring. The flask was surrounded by an oil bath kept at 40°C. After the final addition, pieces of porous plate were added and the temperature of the bath raised to 80°C. for 15 minutes, during which time vigorous evolution of sulphur dioxide took place and the reaction mixture turned reddish-brown in color. It was poured into three times its volume of ice-water and the dark oil which separated extracted from the mixture repeatedly with ether. The ether extracts were washed successively with water, sodium bicarbonate solution and again with water, and then shaken continuously in the mechanical shaker for two days with Darco Charcoal and 25 gm. of metallic mercury. After this procedure the solution contained a fine black suspension of mercuric sulphide which passed through an ordinary filter. It was removed by pouring the mixture into a fine-pore, fluted filter paper, which had a layer of charcoal deposited on it from an ether suspension. The ether solution was dried over anhydrous sodium sulphate and after removal of the ether the residual pale yellow liquid was distilled under reduced pressure. The product obtained boiled constantly at 165-170°C./ 8-12 mm. On redistillation, a colorless liquid boiling at

164-166°C./9 mm. was obtained. Weight, 60 gm.; yield, 75%.

0.1984 gm. substance required 12.43 cc. N/10 $AgNO_3$
0.2108 gm. " " 13.25 " " " "
Found: Cl, 22.23, 22.32%
Calc. for $(C_2H_4O)_5.C_2H_4.Cl_2$: Cl, 22.26%

(B) Preparation of the Monosodium Derivative of Hexaethylene Ether Glycol and Condensation with the Dichloride

10 gm. of freshly-cut metallic sodium were added during two hours to 300 gm. of hexaethylene ether glycol (150% excess) in the reaction flask, the bath being maintained at 90°C. After stirring continuously for 24 hours at this temperature the sodium had dissolved completely to form a brownish solution.

65 gm. (7% excess) of hexaethylene ether glycol dichloride were added over a period of two hours at 90°C. The temperature of the bath was then raised to 180°C. during one hour and kept at 165°C. for three hours, when the mixture reacted neutral. It was then transferred to an extraction apparatus and extracted continuously with ether until all the liquid portion was removed from the sodium chloride.

The ether was removed and the residual viscous liquid distilled under high vacuum. 208 gm. of excess hexaethylene ether glycol were recovered, b.p. 176°C./0.009 mm. The temperature of the residual liquid was then raised to 220°C./0.004 mm. for 15 to 20 minutes. On cooling, it solidified to a crystalline yellow mass.

For purification this crude solid was melted, poured into a continuous extraction apparatus and extracted with ether. The first extract (taken after two hours), containing the impurities readily soluble in ether, was discarded, as was also the final fraction, which was a small residue and contained practically all of the color impurity. As the material is not readily soluble in ether, it separated out in the extraction receiver and was further purified by a second ether extraction. In this manner a small residue containing the remainder of the color impurity was removed. The pure octadeka-ethylene ether glycol was allowed to stand under ether and, after a day or two, crystallized in the form of white needles, m.p. 25-26°C. Weight, 110 gm.; yield, 63% of the theoretical.

Synthesis of the 27-Membered Ethylene Ether Glycol ($HOCH_2.-CH_2(O.CH_2.CH_2)_{25}O.CH_2.CH_2OH$)

(A) Preparation of Nonaethylene Ether Glycol Dichloride

20 gm. of nonaethylene ether glycol were dissolved in 10 gm. of pyridine and 13 gm. (13% excess) of thionyl chloride added during the course of three hours at a bath temperature of 40°C. Pieces of porous plate were then added and the temperature raised to 90°C. for ten minutes.

The product was isolated from the dark-red reaction mixture in the same manner as for hexaethylene ether glycol dichloride and distilled under very low pressure. The nonaethylene ether glycol dichloride thus obtained boiled at 183-186°C./0.005 mm. Weight, 8.9 gm.; yield, 44.5%.

0.2110 gm. substance required 9.47 cc. N/10 $AgNO_3$
0.2006 " " " 8.96 " " " "
Found: Cl, 15.92, 15.85%
Calc. for $(C_2H_4O)_8.C_2H_4.Cl_2$: Cl, 15.74%

(B) Preparation of the Monosodium Derivative of Nonaethylene Ether Glycol and Condensation with the Dichloride

0.5 gm. of freshly-cut metallic sodium were added during the course of two hours to 45 gm. (400% excess) of nonaethylene ether glycol in the reaction flask, the oil-bath temperature being maintained at 95°C. After 16 hours the sodium had all reacted to give a brownish-colored reaction mixture.

6 gm. (22% excess) of nonaethylene ether glycol dichloride were then added over a period of one hour at 95°C. After the final addition, the temperature was raised to 180°C. during the first hour and then maintained at 170°C. for a further two hours when the mixture reacted neutral.

The crude product was extracted continuously with ether until the residue consisted only of sodium chloride. The ether was removed by distillation and the residual viscous liquid fractionally distilled under high vacuum. 28 gm. of nonaethylene ether glycol were recovered (b.p. 225°C./0.01 mm.) after which the temperature of the residue was raised to 270°C./0.06 mm. for about thirty minutes. On cooling to room temperature, it solidified to a brownish crystalline mass.

This was melted and fractionally extracted with ether in the same manner as with octadekaethylene ether glycol. When the purified product was allowed to stand under ether for several days it crystallized in white needles, m.p. 30-31°C. Weight, 8 gm.; yield, 61.5%.

Determination of "Hydroxyl" in the 27-Membered Ethylene Ether Glycol

Since, at this stage of the work, no satisfactory method for preparing halogen derivatives of the higher polyethylene ether glycols had been devised, the 27-membered ethylene ether glycol was identified by its hydroxyl value. It was dried in an Abderhalden for 48 hours at 100°C. and then analysed by the method of Verley and Bölsing (53).

A solution of acetic anhydride and pyridine was made up in the proportion of 24 gm. of the former to 176 gm. of the latter. 10 cc. of this solution were added to a weighed quantity of the 27-membered ethylene ether glycol and the mixture heated on a steam bath for 15 minutes in a glass-stoppered flask. The excess acetic anhydride was converted to acetic acid by the addition of 25 cc. of water and the excess acid then titrated with sodium hydroxide.

1.1168 gm. substance required 19.1 cc. N/10 NaOH
0.8947 " " " 15.7 " " "
Found: OH, 2.91, 2.98%
Calc. for $(C_2H_4O)_{26}.C_2H_4.(OH)_2$: OH, 2.82%

Attempts to Prepare an Ester of Octadekaethylene Ether Glycol

In each of three experiments, 1 gm. of octadekaethylene ether glycol was dissolved in 3 gm. of pyridine and added to (a) 3 gm. of p-nitrobenzoyl chloride, (b) 2 gm. of p-chlorbenzoyl chloride, and (c) 1.5 gm. of 2-4-dinitrobenzoyl chloride, respectively, each of which had previously been dissolved in 5 cc. of pyridine. The reaction mixtures were allowed to stand for 24 hours at room temperature.

The addition of ice-water to each solution produced (a) an orange-red oil, (b) a white solid, and (c) a dark red semi-solid, respectively. Unfortunately it was not possible to crystallize the first and last named products while the second, crystalline in form, was found to be p-chlor benzoic anhydride.

The crude mixture (b) was filtered, washed with water, dried, and dissolved in benzene. The solution was then refluxed with charcoal, filtered and allowed to cool slowly. White needle-shaped crystals, having a silver lustre, separated from the benzene solution, m.p. 191°C. Weight, 1.2 gm.

0.0446 gm. substance gave 0.0429 gm. AgCl
0.1012 " " " 0.0970 " "
Found: Cl, 23.82, 23.74%
Calc. for $(Cl.C_6H_4CO)_2O$ (p-chlorbenzoic anhydride):
Cl, 24.06%

A mixture of the product with an authentic sample of p-chlorbenzoic anhydride melted at 194-5°C., indicating its identity.

Preparation of Octadekaethylene Ether Glycol Dichloride

20 gm. of octadekaethylene ether glycol were dissolved in 10 gm. of pyridine and 10 gm. (72% excess) of thionyl chloride added during a period of three hours, the bath being maintained at 40°C. Pieces of porous plate were then added and the temperature of the bath raised to 70°C. for ten minutes. The flask was cooled rapidly to prevent discoloration from taking place at the latter temperature.

The reaction mixture was poured into three times its volume of ice-water, thus forming an oil-water emulsion. This was placed in an extraction apparatus, extracted continuously with ether, and the dichloride isolated as described previously. Fractional extraction with ether yielded a colorless viscous liquid. Weight, 6.6 gm.; yield, 33%.

0.2200 gm. substance required 5.30 cc. N/10 $AgNO_3$
0.2124 " " " 5.18 " " " "
Found: Cl, 8.55, 8.66%.
Calc. for $(C_2H_4O)_{17}.C_2H_4.Cl_2$: Cl, 8.38%

Repeated attempts to prepare the product by the above method gave negative results in spite of variations in the technique employed. No reason can be given other than that the thionyl chloride used in the first experiment was different to that used later. It is known that minor impurities, such as traces of metallic salts, exert an influence on the behavior of this reagent.

Preparation of the Polyethylene Ether Glycol Dibromides

As the previous method for the preparation of the dichloride of the octadekaethylene ether glycol had given unsatisfactory results, and, furthermore, as the chlorine percentage decreases rapidly with the large increase in molecular weight, an attempt was made to prepare the corresponding dibromide.

The methods given below are taken from an extensive series of brominations using various methods and conditions.

Repeated attempts to prepare octadekaethylene ether glycol dibromide by using phosphorus tribromide in pyridine solution, at both low (2°C.) and high (50°C.) temperatures, led to negative results.

Use of Phosphorus Pentabromide

Preparation of the Dibromide of Hexaethylene Ether Glycol

6 gm. of hexaethylene ether glycol were dissolved in 50 cc. of chloroform and 20 gm. (9% excess) of phosphorus pentabromide added slowly at 0°C., hydrogen bromide being evolved. The mixture was allowed to stand overnight at the same temperature and then poured on to crushed ice. The chloroform layer was removed in a separatory funnel and the aqueous layer shaken with fresh chloroform. The combined chloroform solutions were neutralized with sodium bicarbonate solution, washed with water, and then dried over anhydrous sodium sulphate. The chloroform was removed under reduced pressure and the residual liquid on further distillation gave a fraction, b.p. 160-170°C./0.01 mm. Weight, 2 gm.; yield, 23%.

0.1844 gm. substance required 9.94 cc. N/10 $AgNO_3$
Found: Br, 43.13%.
Calc. for $(C_2H_4O)_5.C_2H_4.Br_2$: Br, 39.21%.

This experiment was repeated without the use of chloroform, the reaction product being diluted, however, by the addition of a mixture of benzene and ether (1:3) prior to pouring on the ice. The remainder of the procedure was similar to the above and yielded a principal fraction boiling at 165-170°C./0.01 mm. Weight, 3.75 gm.

0.2536 gm. substance required 13.44 cc. N/10 $AgNO_3$
Found: Br, 42.40%

The two fractions were combined and redistilled, yielding a colorless product, b.p. 150-155°C./0.006 mm.

0.2146 gm. substance required 10.63 cc. N/10 $AgNO_3$
0.2228 gm. substance required 11.10 cc. N/10 $AgNO_3$
Found: Br, 39.63, 39.85%
Calc. for $(C_2H_4O)_5.C_2H_4.Br_2$: Br, 39.21%

Preparation of the Dibromide of Octadekaethylene Ether Glycol

8 gm. of octadekaethylene ether glycol were dissolved in 25 cc. of dry chloroform and 11 gm. (37% excess) of phosphorus pentabromide (dissolved in 150 cc. of dry chloroform) added to it slowly at 0°C. with vigorous stirring. The reaction mixture was then allowed to stand for one hour and the resulting clear solution poured slowly into ice water and shaken well. The water was drawn off and replaced by sodium bicarbonate solution until the chloroform layer gave a neutral test with litmus and was washed with water once again. This treatment caused the formation of a persistent emulsion which sometimes formed a white gel exceedingly difficult to break. The emulsion was finally broken by centrifuging and then adding small amounts of barium perchlorate, which also dehydrated the solution. The chloroform solution was refluxed with charcoal and the solvent removed under diminished pressure. The residue was dissolved in a small amount of acetone and was precipitated in petroleum ether (30-50°C.) as a light-yellow oil, which was then washed with fresh petroleum ether.

0.3210 gm. substance required 7.25 cc. N/10 $AgNO_3$
0.2972 " " " 6.65 " " " "
Found: Br, 18.07, 17,89%
Calc. for $(C_2H_4O)_{17}.C_2H_4.Br_2$: Br, 17.10%

As the emulsions formed in the above experiment were very troublesome, causing a great loss of material, it was thought advantageous to investigate the use of another solvent. Of these, carbon tetrachloride appeared to be the most suitable.

Preparation of the Dibromide of Hexaethylene Ether Glycol

10 gm. of hexaethylene ether glycol were dissolved in 75 cc. of carbon tetrachloride and 40 gm. (33% excess) of finely divided phosphorus pentabromide added slowly and the mixture allowed to stand 24 hours at 0°C. An oil separated out and the greater part of the phosphorus pentabromide dissolved. The reaction mixture was poured into ice-water and shaken vigorously. No emulsion formed and the carbon tetrachloride layer was shaken with sodium bicarbonate solution until neutral and then washed with water. After drying over anhydrous sodium sulphate, the yellow solution was refluxed with charcoal until colorless and the carbon tetrachloride then removed under diminished pressure, leaving a colorless liquid. The liquid was dissolved in acetone and precipitated into petroleum ether (30-50°C.) (solvent ratio 1:10).

0.2570 gm. substance required 13.00 cc. N/10 $AgNO_3$
0.3362 " " " 17.05 " " " $_3$
Found: Br, 40.46, 40.56%
Calc. for $(C_2H_4O)_5.C_2H_4.Br_2$: Br, 39.21%

Hence the use of carbon tetrachloride as a solvent appeared to give better results, in that it eliminated emulsions, but its further use in attempts to prepare the dibromide of octadekaethylene ether glycol gave negative results. In general, the yields were very small and, moreover, the percentage of bromine varied to a certain extent.

The effect of a higher temperature was then investigated, with the following results:

5 gm. of hexaethylene ether glycol were dissolved in 100 cc. of carbon tetrachloride and 20 gm. (31% excess) of finely divided phosphorus pentabromide added slowly at room temperature. The mixture was refluxed for three hours in an all-glass apparatus and a clear solution resulted which changed in color from orange to brown. This carbon tetrachloride solution, when cool, was treated in the same manner as in the previous experiment, and yielded 1-1/2 gm. of a pale yellow liquid. The product was dissolved in acetone (5 cc.) and precipitated into petroleum ether (30-50°C.) (100 cc.), then washed with fresh petroleum ether.

0.3340 gm. substance required 16.35 cc. N/10 $AgNO_3$
0.2962 " " " 14.45 " " " $_3$
Found: Br, 39.16, 39.03%
Theoretical: Br, 39.21%

Repetition of the experiment did not result in a higher yield so that it was finally considered impractical.

Another method investigated consisted in suspending the polyethylene ether glycol in ether and adding an ether solution of phosphorus pentabromide. As the polyethylene ether glycol is only slightly soluble in ether, it was considered that the rate of solution would provide an indication of the rate of the reaction. However, the reaction did not take place even after refluxing the reaction mixture for several hours.

Use of Hydrogen Bromide

Even though it was considered that the chain might be broken, the action of hydrogen bromide upon octadekaethylene ether glycol was investigated.

The following three methods were used: (1) The action of a saturated solution of hydrogen bromide in acetic acid at 0-20°C., (2) Primary acetylation with acetic anhydride followed by the same procedure as that used in the first method, (3) Primary acetylation with acetic anhydride, using zinc chloride as a catalyst, and subsequent saturation with hydrogen bromide at 0-20°C.

A series of experiments was investigated in which each of the above methods was used. In all cases the bromine percentages varied over a wide range, thus indicating ruptures in the chain of the molecule, the extent of which depends upon the conditions employed.

Use of Thionyl Bromide

Preparation of Thionyl Bromide

Thionyl bromide was prepared according to the method of Mayes and Partington (43). The hydrogen bromide used was prepared catalytically by mixing the vapors of bromine with an excess of hydrogen and passing the mixture over a glowing platinum wire. The resulting hydrogen bromide, free from bromine, was dried by leading it through a tower filled with calcium chloride and phosphorus pentoxide.

The hydrogen bromide was passed into 50 cc. of thionyl chloride (technical) for 12 hours at 0°C. yielding a reddish liquid which on distillation under diminished pressure in an all-glass apparatus gave 50 cc. of a reddish liquid boiling constantly at 69-70°C./62 mm. This result was surprising inasmuch as Mayes and Partington obtained a product boiling over a wide range and containing considerable unchanged thionyl chloride. Although redistilled many times the entire amount of the product obtained by the above procedure always came over at a constant temperature. The last distillate taken boiled at 48°C./20 mm. and was orange-yellow in color.

Mayes and Partington give the boiling points of their pure product over a wide range of pressures and the product obtained above had the same boiling point at the different pressures quoted.

Analysis (Volumetric):

0.3020 gm. substance required 28.94 cc. N/10 $AgNO_3$
Found: Br, 76.67%

Analysis (Gravimetric):

0.1876 gm. substance gave 0.3388 gm. AgBr
Found: Br, 76.85%
Calc. for $SOBr_2$: Br, 76.88%.

Mayes and Partington give few details of the method employed but it is evident that the technique described above gives a higher yield of a product having the same boiling point.

Preparation of Diethylene Ether Glycol Dibromide

The apparatus was the same as that used for the preparation of the dichlorides.

10 gm. of diethylene ether glycol were dissolved in 30 gm. of pyridine,and 45 gm. of thionyl bromide (15% excess) added over a period of one hour at 0°C. with constant stirring. A yellow solid separated during the addition, which did not disappear when the solution was warmed to 60°C. The contents of the reaction flask were cooled and poured on to crushed ice. A light-brown precipitate was obtained which was insoluble in ether, water, and alcohol. On crystallization from carbon disulphide, it formed yellow crystals, m.p. 114°C., and was therefore concluded to be sulphur.

The filtrate was extracted with ether, neutralized with sodium bicarbonate, washed with water, and then shaken with metallic mercury and charcoal (which removes any free sulphur and decolorizes the solution, respectively). The ether was removed and the residual oil found to boil constantly at 55°C./2 mm. yielding a colorless liquid having a slight ethereal odor.

0.3296 gm. substance required 28.48 cc. N/10 $AgNO_3$
0.2424 " " " 21.03 " " "
Found: Br, 69.11, 69.40%
Calc. for $(C_2H_4O).C_2H_4.Br_2$: Br, 68.96%

Preparation of Hexaethylene Ether Glycol Dibromide

5 gm. of hexaethylene ether glycol were dissolved in 4 gm. of pyridine and 10 gm. (26% excess) of thionyl bromide added during one-half hour without cooling. The mixture was poured into ice-water and treated as above. A colorless liquid was obtained, b.p. 130°C./0.15 mm.

0.2318 gm. substance required 12.00 cc. N/10 $AgNO_3$
0.2394 " " " 12.33 " " "
Found: Br, 41.42, 41.20%
Calc. for $(C_2H_4O)_5.C_2H_4.Br_2$: Br, 39.21%

Owing to the fact that free sulphur separates during the reaction, also that low yields are obtained and bromine percentages show a discrepancy, the method was discarded.

Investigation of New Methods for the Synthesis of the Polyethylene Ether Glycols

Various methods were investigated in order to advance the series of the polyethylene ether glycols. Several examples of these methods are given below, using triethylene ether glycol as a base since this glycol and its dichloride are readily available.

Attempts to Prepare Nonaethylene Ether Glycol

(A) Preparation of the Monosodium Salt of Triethylene Ether Glycol

The apparatus consisted of a two-necked round bottom flask, fitted with a mercury-sealed stirrer and soda-lime tube. All connections were made by means of ground glass joints.

Ammonia gas was purified and dried in the following manner. It was passed through a train, consisting of pure heavy liquid petroleum and potassium hydroxide flakes successively, and condensed on metallic sodium, from which it was distilled directly to the reaction flask.

10 gm. of triethylene ether glycol were dissolved in 50 cc. of liquid ammonia and 1.5 gm. of freshly cut metallic sodium added in small pieces during a period of 30 minutes; vigorous stirring being maintained. The sodium dissolved in the ammonia and formed the usual clay-blue coloration, which slowly faded and, after several minutes, disappeared entirely.

When all the sodium had been added, the solution was colorless. Small pieces of sodium were then added until the blue color, which reappeared, had faded but had not entirely disappeared. At this point a drop of triethylene ether glycol was added and the solution slowly became colorless.

The product was isolated by carefully distilling off the ammonia, first at atmospheric pressure and finally at 0.5 mm. at 50°C.

The salt is a white solid and very hygroscopic. It is very soluble in water and alcohol, soluble in hot dioxane and slightly soluble in hot benzene and anisol.

(B) Condensation of the Monosodium Salt of Triethylene Ether Glycol with the Dichloride

The apparatus was the same as that used for the preparation of the dichlorides.

5 gm. of the monosodium salt of triethylene ether glycol were dissolved in 75 cc. of dioxane. 2.75 gm. (theoretical) of triethylene ether glycol dichloride, dissolved in 15 cc. of dioxane, were added through the dropping funnel over a period of 15 minutes, rapid stirring being maintained. The solution was refluxed for three hours and sodium chloride separated. This salt was filtered from the solution, the dioxane removed under reduced pressure and the residue distilled. The greater part distilled at 130°C./0.7 mm. and no nonaethylene

ether glycol was obtained.

The above experiment was repeated without the use of dioxane as a solvent. The apparatus consisted of a long, cylindrical, round-bottomed flask with a side-arm outlet near the top. The flask was fitted with a magnetic stirrer for operation under diminished pressure.

5 gm. of the monosodium salt of triethyleme ether glycol were mixed with 2.75 gm. (theoretical) of triethylene ether glycol dichloride and placed in the reaction flask.

The flask was connected to a vacuum pump and the pressure reduced to 1 mm. The temperature was slowly raised to 150°C. and held at this temperature for two hours, stirring being maintained throughout the reaction. The reaction began as soon as the sodium salt melted and proceeded rapidly. However, some decomposition occurred and the method was therefore unsatisfactory.

<u>Use of Dioxane as a Medium for the Condensation Reaction</u>

The apparatus was the same as that used in the case of the dichloride preparation.

1.3 gm. of metallic potassium were added in small pieces during the course of one hour to 5.5 gm. of triethylene ether glycol, dissolved in 50 cc. of dioxane (previously refluxed over potassium and distilled), in the reaction flask. During the addition the bath temperature was maintained at 80°C. and the potassium dissolved rapidly under the influence of vigorous stirring.

After the potassium had all dissolved, 3.12 gm. (theoretical) of triethylene ether glycol dichloride, dissolved in 15 cc. of dioxane were added through the dropping funnel during a period of 15 minutes. The bath temperature was then raised to 115°C. and kept at this temperature for three hours, during which time salt precipitation occurred. The salt was filtered from the solution, the dioxane removed under diminished pressure and the residue distilled. Two fractions were obtained, the first distilling at 105°C./0.7 mm. while the second and larger distilled at 135°C./0.3 mm., and both contained chlorine. Only 1 gm. of high boiling residue remained. Hence these methods are all highly unsatisfactory.

Preparation of Triethylene Ether Glycol Di-iodide

(a) Preparation of the Di-p-toluene Sulphonic Ester of Triethylene Ether Glycol

20 gm. (100% excess) of p-toluene sulphonyl chloride were dissolved in 50 gm. of pyridine in a glass-stoppered flask, and 4 gm. of triethylene ether glycol added. The reaction temperature was controlled by shaking the flask under running tap water. After about 20 minutes, pyridine hydrochloride separated from the solution and the mixture was then allowed to stand for three hours at room temperature.

The contents of the flask were diluted to turbidity with ice-water and allowed to stand for one hour. They were then poured in a fine stream into 500 cc. of rapidly stirred ice-water. The resulting precipitate was filtered off, washed repeatedly with water, and dried in a desiccator. The dry solid was dissolved in alcohol, refluxed with charcoal, and filtered. A white crystalline solid separated from the alcohol solution upon cooling; this solid was filtered off and the crystallization from alcohol repeated, m.p. 82°C. Weight, 10 gm.; yield, 82%.

0.2128 gm. substance gave 0.2154 gm. $BaSO_4$
0.2095 " " " 0.2134 " "
Found: S, 13.88, 14.00%
Calculated for $(C_2H_4O)_3.O(C_7H_7SO_2)_2$: S, 13.97%

(b) Preparation of the Di-iodide from the Ester

4 gm. of the di-p-toluene sulphonic ester of triethylene ether glycol were mixed intimately with 9 gm. (200% excess) of anhydrous sodium iodide, 30 cc. of acetone added and the mixture heated in a bomb-tube at 90°C. for six hours.

The reaction mixture was filtered and the precipitated sodium p-toluene sulphonate washed repeatedly with acetone. The acetone solution was evaporated to dryness under reduced pressure and the residue extracted with ether in a Soxhlet. The reddish ether solution was decolorized by shaking with a small amount of "molecular" silver, after which the ether was removed by distillation and the residue distilled under reduced pressure. The product obtained was a colorless liquid, b.p. 110°C./0.025 mm. Weight, 2 gm. Yield from ester, 62%.

0.3800 gm. substance required 20.37 cc. N/10 $AgNO_3$
0.2762 " " " 14.86 " " "
Found: I, 68.08, 68.35%
Calc. for $(C_2H_4O)_2.C_2H_4.I_2$: I, 68.64%

Synthesis of the 54-Membered Ethylene Ether Glycol

$HOCH_2.CH_2(O.CH_2.CH_2)_{52}O.CH_2.CH_2OH$

(A) Preparation of Octadekaethylene Ether Glycol Di-iodide

(a) Preparation of the Di-p-toluene Sulphonic Ester of Octadekaethylene Ether Glycol

42 gm. of octadekaethylene ether glycol were divided among four separate experiments of 10.5 gm. each, and treated as follows:

10 gm. of octadekaethylene ether glycol, dissolved in 10 cc. of pyridine, were added to 10 gm. (200% excess) of p-toluene sulphonyl chloride, dissolved in 10 cc. of pyridine. The solution was allowed to stand 12 hours at room temperature.

The contents were diluted to turbidity with ice-water and allowed to stand one hour. They were then poured in a fine stream into 200 cc. of rapidly stirred ice-water. 60 cc. of cold 1:1 hydrochloric acid were added to the resulting oil emulsion and it was extracted immediately with chloroform.

The chloroform extracts from all four experiments were combined and washed successively with water, sodium bicarbonate solution and water. The solution was then dried over sodium sulphate, filtered and refluxed with activated charcoal. The charcoal was filtered off and the chloroform removed under reduced pressure. The residue was dissolved in 25 cc. of acetone and poured through a capillary dropping funnel into 250 cc. of rapidly stirred 30-50°C. petroleum ether. The resulting oil was allowed to stand in the solvent for one hour and then washed repeatedly with fresh petroleum ether. It was then separated from the petroleum ether and placed in a vacuum desiccator. Weight, 34 gm.; yield, 58.7%.

0.2304 gm. substance gave 0.0988 gm. $BaSO_4$
0.2102 " " " 0.0859 " "
Found: S, 5.88, 5.60%.
Calc. for $(C_2H_4O)_{18}\cdot O\cdot(C_7H_7SO_2)_2$: S, 5.72%

(b) Conversion of the Di-p-toluene Sulphonic Ester of Octadekaethylene Ether Glycol to the Di-iodide

33.5 gm. of the above-mentioned ester were dissolved in 50 cc. of acetone and added to a solution of 30 gm. (200% excess) of sodium iodide in 150 cc. of acetone. The mixture was allowed to stand at room temperature for 48 hours, during which period sodium-p-toluene sulphonate separated in a practically quantitative yield.

The reaction mixture was filtered and the precipitate washed repeatedly with acetone. The acetone was removed under reduced pressure and the residue extracted with dioxane by rapidly stirring with the latter at 80°C. This procedure yielded a reddish dioxane solution of the product and left a white solid residue consisting of sodium iodide. The solution was cooled to 20°C, filtered, and the filtrate shaken first with a small amount of "molecular" silver and then with activated charcoal. It was filtered again and the dioxane then removed under reduced pressure. The residue was extracted with ether and the ether solution shaken with a small amount of "molecular" silver until colorless. Upon removal of the ether under reduced pressure, a pale yellow liquid was obtained. Weight, 27 gm.; yield from the ester, 87.5%; overall yield, 53.4%.

0.1498 gm. substance gave 0.0693 gm. AgI
0.1942 " " " 0.0895 " "
Found: I, 25.09, 24.90%
Calc. for $(C_2H_4O)_{17}.C_2H_4.I_2$: I, 24.67%

(B) Preparation of the Monopotassium Salt of Octadekaethylene Ether Glycol and Condensation with the Di-iodide

1.92 gm. of freshly cut metallic potassium were added in small pieces through the condenser during the course of one hour to 41.8 gm. (4.5% excess) of octadekaethylene ether glycol in the reaction flask. The flask was surrounded by a bath at 95°C. and a constant stream of nitrogen was passed through the liquid, with vigorous stirring continued throughout. The reaction product turned brown and after three hours (the potassium having all reacted) the product was allowed to cool to room temperature.

26.6 gm. (5% excess) of octadekaethylene ether glycol di-iodide, dissolved in 100 cc. of ether, were added during a period of 15 minutes. The ether was removed by distillation and the temperature slowly raised to 100°C. where it was maintained for two hours. During this period the color faded steadily until it became light-red. The contents of the flask reacted neutral to litmus, Congo and phenolphthalein. The reaction mixture was poured into an extraction apparatus and extracted continuously with ether. As an indication of the rate of extraction it was observed that during the first 8 hours the level of the material in the extractor dropped 2 cm.; in the following 8 hours, 1 cm.; in the next 6 hours 2 mm.; and 2 hours later no change occurred. The first fraction gave a test for halogen while the other fractions were halogen-free. At this point, the ether was removed under reduced pressure and the residue refluxed in dioxane for 15 minutes. This resulted in a dioxane solution of the product and a separation of the potassium iodide as a precipitate, which was removed by filtering through a steam-heated funnel. The solution was refluxed with activated charcoal, filtered and the dioxane removed under reduced pressure, leaving a pale yellow crystalline residue which was halogen-free. Weight, 28.9 gm.; yield, 49%.

The crude product was obtained as a white crystalline powder by dissolving it in acetone (1 vol.) and precipitating first in ether (20 vol.) at 0°C. and then in petroleum ether (30-50°C., 10 vol.) at -30°C. After washing repeatedly with the cold petroleum ether it was dried in a desiccator over phosphorus pentoxide and sulphuric acid under vacuum, m.p. 37-38°C.

Synthesis of the 162-Membered Ethylene Ether Glycol

$HOCH_2.CH_2(O.CH_2.CH_2)_{160}.O.CH_2.CH_2OH$

(A) Preparation of the 54-Membered Ethylene Ether Glycol Di-iodide

(a) Preparation of the Di-p-toluene Sulphonic Ester of the 54-Membered Ethylene Ether Glycol

10 gm. of the 54-membered ethylene ether glycol, dissolved in 10 cc. of pyridine, were added to a solution of 4 gm. (300% excess) of p-toluene sulphonic chloride in 10 cc. of pyridine and the mixture allowed to stand 24 hours at room temperature.

The solution was diluted with water until turbid, the contents of the flask allowed to stand one hour at room temperature and then poured in a fine stream into 200 cc. of rapidly stirred ice-water. The product was isolated in the same manner as in the case of the p-toluene sulphonic ester of the 18-membered derivative and was identical in appearance. Weight 8 gm.;

yield, 71%.

0.1886 gm. substance gave 0.0394 gm. $BaSO_4$
0.2238 "   "   " 0.0430 "   "
Found: S, 2.86, 2.63%
Calc. for $(C_2H_4O)_{54}.O.(C_7H_7SO_2)_2$: S, 2.37%

(b) Conversion of the 54-Membered Di-p-toluene Sulphonic Ester into the Di-iodide

7.5 gm. of the above-mentioned ester, dissolved in 60 cc. of acetone were added to a solution of 5 gm. (500% excess) of sodium iodide in 40 cc. of acetone and the entire solution allowed to stand 48 hours at room temperature. The solution of the di-iodide was filtered from the sodium p-toluene sulphonate and the product isolated as already described for the 54-membered derivative. This was obtained as a white, crystalline solid. Weight, 5.5 gm.; yield from the ester, 75.8%; overall yield, 50%; m.p. 29-30°C.

0.2358 gm. substance required 1.88 cc. N/10 $AgNO_3$
0.1876 "   "   " 1.48 "   "   "
Found: I, 10.12, 10.00%
Calc. for $(C_2H_4O)_{53}.C_2H_4.I_2$: I, 9.72%.

(B) Preparation of the Monopotassium Salt of the 54-Membered Ethylene Ether Glycol and Condensation with the Di-iodide

0.09 gm. of metallic potassium were added through the condenser during the course of one hour to 6 gm. (10% excess) of the 54-membered ethylene ether glycol in the reaction flask which was surrounded by an oil bath at 80°C. Vigorous stirring was maintained throughout. After two hours the potassium had all reacted and the contents of the flask were allowed to cool to room temperature.

3.5 gm. (20% excess) of the 54-membered ethylene ether glycol, dissolved in 150 cc. of ether, were added to the reaction mixture through the dropping funnel and the ether removed by distillation. The bath temperature was slowly raised to 100°C. during the course of one hour and kept at this temperature for a further hour. The contents of the flask became lighter in color and at the end of this period reacted neutral. The product was isolated and purified in the same manner as in the case of the 54-membered ethylene ether glycol. However, in the present experiment the rate of extraction was much slower. The purified product is a white crystalline, somewhat hygroscopic solid, m.p. 48-49°C. Weight, 4.1 gm.; yield, 50%.

Preparation of the 162-Membered Ethylene Ether Glycol Di-iodide

(a) Preparation of the Di-p-toluene Sulphonic Ester of the 162-Membered Ethylene Ether Glycol

2 gm. of the 162-membered ethylene ether glycol, dissolved in 5 cc. of pyridine, were added to a solution of 1 gm. (500% excess) of p-toluene sulphonyl chloride in 5 cc. of pyridine and the mixture allowed to stand for 24 hours at room temperature.

The contents of the flask were diluted with ice-water until the solution was turbid and then allowed to stand one hour.

It was poured in a fine stream into 100 cc. of rapidly stirred ice-water, 30 cc. of cold hydrochloric acid (1:1) were then added, and the mixture immediately extracted with chloroform. The product, isolated in the usual manner, was obtained as an extremely viscous liquid. Weight, 1.4 gm; yield, 67%.

0.2866 gm. substance gave 0.0236 gm. $BaSO_4$
0.1938 " " " 0.0176 " " "
Found: S, 1.13, 1.24%
Calc. for $(C_2H_4O)_{162}.O(C_7H_7SO_2)_2$: S, 0.86%

(b) Conversion of the Di-p-toluene Sulphonic Ester of the 162-Membered Ethylene Ether Glycol to the Di-iodide

0.8 gm. of the above-mentioned ester, dissolved in 10 cc. of acetone, were added to a solution of 1 gm. (25 times excess) of sodium iodide in 5 cc. of acetone and the mixture allowed to stand 48 hours at room temperature. The separation of the sodium p-toluene sulphonate was slower than in the case of the 54-membered ethylene ether glycol.

The product was isolated as in the previous experiments and was obtained as a white crystalline solid, m.p. 38-39°C.

0.1934 gm. substance required 0.60 cc. N/10 $AgNO_3$
0.2424 " " " 0.75 " " "
Found: I, 3.93, 3.82%
Calc. for $(C_2H_4O)_{161}.C_2H_4.I_2$: I, 3.45%

Weight, 0.6 gm. ; yield from ester, 75%

POLYMERIZATION OF ETHYLENE OXIDE

Since phosphorus pentoxide and calcium chloride react with ethylene oxide (29), the latter was dried with soda lime. A bomb tube, to be used as a receiver, was dried by warming with a flame while under reduced pressure.

Ethylene oxide, b.p. 10.5 - 11.5°C., was distilled through a horizontal tube 5 feet in length charged with freshly fused soda-lime. The vapor was condensed directly into a dry bomb tube (closed to the atmosphere by means of a soda-lime tube) surrounded by a bath of solid carbon dioxide in alcohol kept at -70°C. The following examples are typical of a number of experiments.

Use of Potassium as a Catalyst

50 cc. of liquid ethylene oxide were collected in a bomb tube and 0.4 gm. of metallic potassium (cut into several pieces and weighed in petroleum ether) was rapidly dried by rolling in filter paper and added to the contents of the bomb tube. The bomb tube was closed by a soda-lime tube and allowed to stand at 0°C. for two hours in order that the first vigorous action would occur at ordinary pressure. It was re-cooled to -70°C. and sealed, then gradually allowed to come to room temperature and kept there for six days. After cooling to -50°C. the tube was opened.

The product, a brown crystalline solid, was dissolved in 200 cc. of benzene and the solution filtered. The fractionation of the product was carried out by pouring successive portions of ether, in a fine stream, into the rapidly stirred benzene solution and filtering off the resulting precipitates. To the 200 cc. of benzene solution, ether was added as shown below.

Ether	Fraction
260 cc.	(a) yellow solid
100 "	(b) white solid
350 "	(c) white solid

Upon evaporation of the final filtrate under reduced pressure only a trace of residue was obtained.

The three fractions were further divided as shown below.

Fraction (a) was dissolved in 200 cc. of benzene and the solution refluxed with charcoal, filtered, and ether added.

Ether	Fraction		Weight
150 cc.	I-K	white solid	12.9 gm.
100 "	II-K	" "	7.0 "
400 "	III-K	" "	1.9 "

Fraction (b) was dissolved in 175 cc. of benzene and fractionated with ether.

Ether	Fraction		Weight
170 cc.	IV-K	white solid	7.5 gm.
100 "	V-K	" "	3.4 "
400 "	VI-K	" "	0.2 "

Fraction (c), being a small quantity (0.5 gm.), was not further fractionated. This is designated as Fraction VII-K.

Attempts to form the p-toluene sulphonic esters of the above-mentioned fractions gave negative results.

(B) 25 cc. of ethylene oxide were collected in a bomb tube at -70°C. and 0.2 gm. of metallic potassium added as in Experiment (A). The bomb tube was closed with a soda-lime tube, allowed to stand at 0°C. for 2 hours, cooled to -50°C. and then sealed. It was allowed to stand at 0°C. for one day and at room temperature for 7 days, then cooled to -50°C. and opened.

The product, a soft, brown crystalline mass, was melted, poured into an extraction apparatus, and extracted continuously with ether. Four arbitrary fractions were obtained, each being removed after six hours' extraction. The ether was removed from each fraction in turn and the residues dissolved in benzene and refluxed with charcoal. Each fraction, after filtering, and removing the benzene under reduced pressure, solidified to a soft crystalline mass on standing. The following yields were obtained: Fraction I-K', 5.0 gm.; Fraction II-K', 3.5 gm.; Fraction III-K', 3.0 gm.; Fraction IV-K', 3.0 gm.

The first three fractions were converted into the p-toluene sulphonic esters in the manner described for the polyethylene ether glycols.

Heat was evolved, pyridine hydrochloride separated from the solution, and the mixture was then allowed to stand for 12 hours at room temperature.

Fraction	Pyridine	p-toluene sulphonyl chloride	Yield of ester
I-K', 3.5 gm.	20 cc.	4 gm.	2.6 gm.
II-K', 1.0 "	10 "	1 "	0.6 "
III-K', 1.5 "	10 "	2 "	1.0 "

Analyses of the p-toluene sulphonic esters

Fraction I

0.2130 gm. substance gave 0.0826 gm. $BaSO_4$
0.3038 " " " 0.1178 " " "
Found: S, 5.32, 5.31%

Fraction II

0.2364 gm. substance gave 0.0764 gm. $BaSO_4$
0.1866 " " " 0.0632 " " "
Found: S, 4.43, 4.64%

Fraction III

0.1992 gm. substance gave 0.0622 gm. $BaSO_4$
0.2060 " " " 0.0662 " " "
Found: S, 4.28, 4.40%

These results may be compared with the theoretical sulphur analyses for the corresponding polyethylene ether glycols:

	Fractions		
	I-K'	II-K'	III-K'
%S polyethylene oxide ester	5.32, 5.31	4.43, 4.64	4.28, 4.40
%S polyethylene ether glycol ester	5.30	4.49	4.35
Member	20	25	26
M.W. of corresponding polyethylene ether glycol	900	1120	1160

The residue in the extractor would not form a p-toluene sulphonic ester when treated in the same manner.

It was found that when the polymerization was carried out in containers that were merely closed by soda-lime tubes, a large loss of ethylene oxide occurs even at 0°C. owing to the heat of the reaction.

It was also found that the polymerization proceeded much more readily when the surface of the potassium metal was not appreciably oxidized. This was accomplished by cutting the metal into small strips over the mouth of the bomb tube and allowing the pieces to drop into the liquid ethylene oxide. On warming even to 0°C. the reaction became very vigorous and, in one instance, exploded at 20°C. two hours after the bomb tube was sealed.

Use of Potassium Hydroxide as a Catalyst

50 cc. of ethylene oxide were collected in a bomb tube at -70°C. and 14 gm. of pure potassium hydroxide, in the form of a single stick moistened with ethylene glycol, were added and the tube sealed. It was allowed to stand in a vertical position at room temperature for 20 days. The ethylene oxide adjacent to the catalyst polymerized to a solid in 2 days but the entire amount solidified only after 14 days.

The contents of the tube were divided into two parts: (α) the brown material which had been in direct contact with the catalyst; (β) the light-yellow material which had been above the catalyst.

Part (α) was dissolved in 125 cc. of benzene and the potassium hydroxide removed by filtration. Ether was then added to the benzene solution as shown below.

Ether	Fraction
100 cc.	A-α yellow solid
150 "	B-α white solid
450 "	C-α " "

Upon evaporation of the final filtrate under reduced pressure only a trace of residue was obtained.

Fraction A-α was dissolved in 100 cc. of benzene and the solution decolorized with charcoal. The fractions were precipitated from the benzene solution with ether.

Ether	Fraction		Weight
100 cc.	I-α-KOH	white solid	7.3 gm.
100 "	II-α-KOH	" "	1.0 gm.
300 "	-	trace	-

The final filtrate was evaporated under reduced pressure but no product was obtained. Fraction II-α was dissolved in 100 cc. of benzene and ether added to the solution.

Ether	Fraction		Weight
75 cc.	III-α-KOH	white solid	1.8 gm.
100 "	IV-α-KOH	" "	2.3 "
200 "	-		-

No product was obtained upon distillation of the final filtrate under reduced pressure.

Fraction III-α now becomes V-α-KOH (0.2 gm.) and was not further fractionated.

Part (β) was dissolved in 125 cc. of benzene and ether added.

Ether	Fraction	
100 cc.	A-β	light yellow solid
150 "	B-β	white solid
400 "	-	trace

Only a trace of polymer was obtained from the final filtrate.

Fraction I-β was dissolved in 150 cc. of benzene and ether added.

Ether	Fraction		Weight
175 cc.	I-β-KOH	white solid	9.2 gm.
100 "	II-β-KOH	" "	2.4 "
200 "	-	trace	

Fraction B-β now becomes Fraction III-β-KOH (2.0 gm.) and was not further fractionated.

VISCOSITY MEASUREMENTS

The viscosity measurements were all carried out in a Jones-Veazy (46) modification of an Ostwald Viscometer. All precautions were taken to avoid contamination of the liquids by means of a suitable dust-cap for the viscometer. The thermostat was maintained at 25°C. with an accuracy of ± 0.05°C. For each determination the maximum deviation from the mean of five readings was ± 0.1 sec. Benzene was used as the solvent and the concentration of the solutions was the same in all cases, 4.4% or 1"basic molar". (This concentration was chosen since it is the one at which Staudinger measures the viscosity of the low molecular polyethylene oxides.)

Staudinger's viscosity measurements were carried out at 20°C. whereas the present measurements were taken at 25°C. A comparison, however, can readily be made between the two as the relative viscosity is not appreciably affected by a 5-degree difference in temperature.

15 cc. of liquid were pipetted into the viscometer and the latter placed in the thermostat for 30 minutes before any readings were taken. The volume of liquid which flowed through the capillary was approximately 10 cc.

When measured at the same temperature, the densities of both solutions and solvent are approximately the same for the same low concentration. These densities were therefore neglected by Staudinger and also in the present investigation. Hence the relative viscosity was determined from the equation:

$$\eta_r = \frac{t_{(solution)}}{t_{(solvent)}}$$

where η_r = relative viscosity, and t = time of flow of the liquid through the capillary. η_{sp} was obtained from the expression $(\eta_r - 1) = \eta_{sp}$. (see p.15).

By inserting the values for $\frac{\eta_{sp}}{c}$ (where c = 1, in terms of "basic molarity") and M in Staudinger's equation,

$$\frac{\eta_{sp}}{c} = K_m \cdot M$$

the value of the constant K_m was obtained.

In the following table are shown the viscosity results for the polyethylene ether glycols.investigated.

Note: Time of flow of pure benzene = 89.6 secs.

Polyethylene ether glycol	Mol. Weight	Time of flow in sec.	$\frac{\eta_{sp}}{c}$	$K_m . 10^4$
4-membered	194	96.2	0.0737	3.80
5- "	238	97.0	0.0826	3.47
6- "	282	98.0	0.0938	3.33
7- "	326	98.8	0.1027	3.15
8- "	370	99.8	0.1138	3.08
9- "	414	100.5	0.1214	2.94
10- "	458	101.3	0.1306	2.85
18- "	810	109.9	0.227	2.80
27- "	1206	112.5	0.256	2.12
54- "	2394	118.0	0.317	1.32
"108"- "	"4770"	126.4	0.411	0.86
162- "	7146	136.1	0.519	0.73

Of the above polyethylene ether glycols, members 4,5,6, 7,8, and 10 were prepared by Perry in these laboratories (45). The member signified by "108" represents a 1:1 mixture of the 54- and 162-membered ethylene ether glycols.

Viscosity measurements on a number of ethylene oxide polymers are given below.

Note: Time of flow of pure benzene = 89.6 secs.

Polymer	Time of flow in secs.	$\frac{\eta_{sp}}{c}$	$K_m . 10^4$	Mol. weight*
I-K	176.6	0.97	-	-
II-K	173.5	0.94	-	-
III-K	151.4	0.69	-	-
IV-K	172.5	0.93	-	-
V-K	162.6	0.81	-	-
I-K'	109.0	0.22	2.4	900
II-K'	112.6	0.26	2.3	1120
III-K'	115.9	0.29	2.5	1160
I-α-KOH	172.0	0.92	-	-
III-α-KOH	175.0	0.95	-	-
IV-α-KOH	141.8	0.58	-	-
I-β-KOH	172.3	0.92	-	-
II-β-KOH	162.4	0.81	-	-
III-β-KOH	155.7	0.74	-	-

*The molecular weights were determined from the sulphur analysis of the p-toluene sulphonic ester derivative.

SUMMARY

1. Polyethylene ether glycols have been synthesized in a step-wise manner by the interaction of one mole of the dihalide derivative of a lower polyethylene ether glycol with two moles of the corresponding monometallic salt, followed by subsequent elimination of two moles of the metal halide.

2. The methods of preparation of the dihalides and monometallic salts were investigated. The molecular weights of these polyethylene ether glycols were determined from the halogen content of the dihalide derivatives as well as from the sulphur content of the p-toluene sulphonic ester derivatives.

3. Details for the preparation of thionyl bromide in almost quantitative yield have been given.

4. Ethylene oxide was polymerized and fractionated by the method of Staudinger. The presence of hydroxyl groups was shown by the formation of the p-toluene sulphonic ester derivatives and thus further evidence provided for the conception that ethylene oxide polymerizes to form long chain polyethylene ether glycols.

5. Viscosity measurements were carried out on both series of compounds and compared with those of Staudinger on the polyethylene oxide.

6. Polyethylene ether glycols, used in this investigation, were of known constitution and therefore considered to be more suitable for investigating the validity of the Staudinger viscosity equation than polyethylene oxide mixtures. It was found that this equation does not hold for polyethylene ether glycols with molecular weight below 5000.

7. From these results it was concluded that the values which Staudinger assigns to natural high polymers, such as cellulose and rubber, are unreliable.

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