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DERIVATIVES OF AN UNSATURATED POLYESTER- POLYETHYLENE GLYCOL MALEATE

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE

Charles Dean Burton

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DERIVATIVES OF AN UNSATURATED POLYESTER - POLYETHYLENE GLYCOL MALEATE

By

Charles Dean Burton

A THESIS

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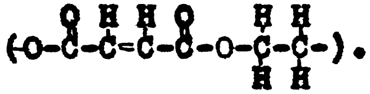
ABSTRACT OF THESIS

Polyethylene glycol maleate was prepared by heating equal molar quantities of ethylene glycol and maleic anhydride at190° C for 5.8 hours and then at 205° C. under a nitrogen atmosphere. Reduced pressure distillation was used to remove impurities. The progress of the reaction was followed by neutralization and saponification equivalents, which were used to calculate the percent reaction. The percent reaction after distillation was 91.54% and the molecular weight of the polyethylene glycol maleate was 839. The reaction rate constant at 190° C. was .0009 meq/min. and the reaction rate constant at 205° C. was .0012 meq/min. The energy of activation was 12,760. The structure was determined to be  $(-O-\overset{O}{\overset{\|}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-)$.

The polyethylne glycol maleate was reacted with hydrogen bromide, hydrogen chloride and chlorine by passing these gases through chloroform solutions of the polyester for nine hours at room temperatures. From halogen determinations, hydrogen bromide and hydrogen chloride were found to add 93.5% and 95.1% respectively to the carbon-carbon double bonds, and chlorine added to 84% of the double bonds if no substitution took place. Pure bromine was added to a chloroform solution of the polyester for one week. If no substitution took place, the bromine added to 24.5% of the double bonds. Liquid ammonia was added to the polyester and heated to 100°C in a pressure bomb. Two products, maleamide and the aminated polyester, were isolated. Hydrazine hydrate was refluxed with a chloroform solution of the polyester for four hours. The percent nitrogen was 66% of the

amount which would be found from complete addition of the hydrazine hydrate to the double bond. Nitrogen tetroxide added to polyethylene glycol maleate in a chloroform solution, and 88% of the nitrogen, which would be present for 100% addition to the double bond was found. Nitrosyl chloride was reacted with polyethylene glycol but produced only fumaric acid. Sulfur monochloride reacted with polyethylene glycol maleate in chloroform when the mixture was heated.

The unsaturation of the polyester and the derivatives produced was determined by the use of potassium bromide-potassium bromate solution in the presence of mercuric sulfate. Although this was the only unsaturation determination that could be used, it was of no value in the unsaturation determinations of the halogenated products and the hydrazine addition product.

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INTRODUCTION

Although the literature contains many references for the addition of simple molecules to olefins, relatively little has been published on the addition reactions of unsaturated polymers except in the case of additions to natural rubber. In general, double bonds might be classified into two categories, the ordinary double bonds which add HX, H_2, HOX, etc. but do not add ammonia or ammonia derivatives and those double bonds with electronegative groups attached to carbons of the double bond, which add HX, X_2, etc. with difficulty but which add ammonia more readily. The double bonds of polybutadiene and natural rubber, as expected, are inactive toward the additions of ammonia or ammonia derivatives. However, the double bonds of polyethylene glycol maleate are conjugated with carbonyl groups and might, therefore, be active. This thesis describes the preparation of polyethylene glycol maleate and an investigation of its addition reactions.

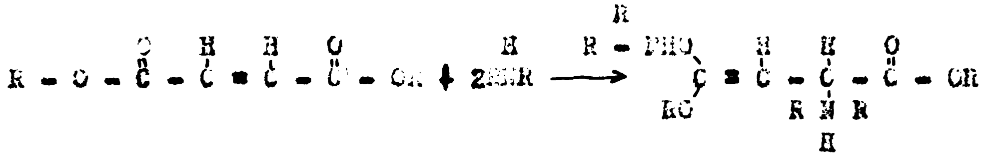
HISTORICAL

The first known formation of a polyester was accredited to Berzelius[1] who, as early as 1847, stated that polybasic acids and polyhydric alcohols formed resins when heated together. In 1914, the first U.S. patents for polyesters were obtained by Arsem[2] and Callahan[3] and in 1929, polyethylene glycol maleate and polyethylene glycol fumarate, along with several other polyesters, were produced and investigated by Carothers and Arvin.[4] Carothers stated that the fumarate was an oil and the maleate was a solid, a fact that did not agree with the work of Vorländer[5] who had produced these polyesters by the silver salt method and reported the opposite physical characteristics. Carothers produced the maleate by heating an excess of maleic anhydride with ethylene glycol at 200°C and obtained the ester as a powder which melted at 88-95°C. The moleculer weight was not determined due to the insolubility of the product but it is interesting to note that the molecular weights of other polyesters were shown to vary from 2500-5000. These values are relatively small when compared to the molecular weights of A-polymers.

Tsuzuki[6] compared the preparations of polyethylene glycol maleate and polyethylene glycol fumarate and found that while the esterification process in both cases was insignificant below 150°C, reaction could be effected at this temperature by using $ZnCl_2$ as a catalyst. At higher temperatures, this catalyst induced several side reactions and it was noted that the fumarate ester had a longer chain length and was produced in a better yield than the maleate. The molecular weights were determined by neutralization and saponification equivalents and varied from 450-1500. In a further statement, Tsuzuki showed evidence that maleic acid and its esters were transformed into the fumarate derivatives when heated above 130°C which would indicate that polyesters prepared at temperatures above 130°C should have approximately the same chain length and composition.

The conversion of maleic acid and maleic esters to the fumarate derivatives has been investigated for several years. In 1925, Meerwein and Weber[7] found that the conversion could be accomplished by such reagents as Br_2, H_2O, N_2O_3, etc. which theoretically should be capable of adding to the double bond although their mechanism for the reaction was an activation rather than an actual addition and subsequent splitting out. Horrex[8] used HCl containing some deuterium chloride to convert maleic acid to fumaric acid and found no deuterium in the product, indicating agreement with the theory of Meerwein and Weber. Kamanushi[9] found that oxygen catalyzed the conversion by acting as a paramagnetic material, but nitrogen acted as a diamagnetic material and showed no catalysis. Simamura[10] converted diethyl maleate to diethyl fumarate by the use of HX which conversion was found to proceed with or without a solvent and be unaffected by oxygen. He believed that the process involved hydrogen bonding with a resulting molecular deformation and loss of bond rigidity. Nozacki[11] catalyzed the conversion of diethyl maleate to diethyl fumarate with various amines at 25°C from which he concluded that the catalysis was a process of hydrogen bonding and coordination (having the effect of 1,4 addition) followed by decomposition to the fumarate derivative.

The rate determining step was postulated as the following:



$$R-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OR+2\overset{H}{N}R\longrightarrow\overset{\overset{R}{R-NHO}}{\underset{RO}{C}}=\overset{H}{\overset{|}{C}}-\underset{\underset{H}{R\,N\,R}}{\overset{H}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-OR$$

The mechanism shown would indicate that the conversion probably does not go to completion. Catalysis by the ions of HCl, HBr, NaBr, KCNS, etc. was believed to be the same type reaction as above with an ionic mechanism while the mechanism of conversion by H_2S and SO_2 was unknown.[12]

Conversion by heat alone was first mentioned by Carre[13] in 1927 when he converted maleic acid to fumaric acid by heating the former below the eutectic point although combinations of heat and some of the reagents previously mentioned have been used since that time.[14] Price[15] has indicated that the heat conversions probably involve an atomic free radical mechanism. Since all of those examples of the maleic-fumaric conversion show the ease of the reaction, it should be evident that the production of a pure polymaleate ester by a heat reaction is probably impossible.

Vincent[16] found that the gelation of maleate polyesters took place through the double bond and was catalyzed by heat, light and oxygen. All of the double bonds were not required for gelation since he found that a 10:1 mixture of succinate and maleate esters converted as fully as the maleate ester above. Bradley, Kropa, and Johnston[17] found that the absence of oxygen allowed the condensation to proceed further before gelation occured, but found some evidence of a small amount of conversion when the acid values of the maleate polyester approached a limiting value while the viscosity continued to increase. Catalytic conversion of polyethylene glycol maleate can be effected by heating in an air atmosphere at 1[illegible]0°C in the presence of a benzoyl peroxide catalyst, the product being an insoluble infusible solid. Kropa and Bradley[18] gelled polyethylene glycol maleate by heating it with 1/3 its weight of vinyl acetate, the gelation being accelerated by a mercury arc and proceeding with or without a benzoyl peroxide catalyst. The process was believed to be similar to rubber vulcanization.

Maleic acid and maleic anhydride have been used in many copolymers with such monomers as styrene, butadiene, etc.[19] Their extensive use in condensation reactions is due mainly to the convertibility of the resins which they form.[20] The anhydride is more freq ently used than the acid due to its lower cost, but both the acid and anhydride are produced by vapor phase oxidations of benzene, the anhydride being formed first from which the acid is made by hydrolysis.[21] The anhydride is more efficient at the start of the condensation reaction although the two rates are the same after the formation of the half ester.[20]

The addition reactions shown by the maleic acid double bond are quite different than most carbon-carbon double bonds. In 1930, Hauson[22] reacted Br^2 with maleic acid and fumaric acid, and found that the addition to fumaric acid was relatively normal while the Br^2 did not react with maleic acid in the dark at 18°C and even in the presence of light and at slightly higher temperatures, the reaction was quite slow. In the presence of HBr, the reaction was faster. In 193[illegible], Lucas and Pressman 23 suggested the use of mercuric sulfate catalyst with a potassium bromide-potassium bromate solution (as a source of bromine)for a quantitative determination of the double bonds in maleic acid and maleic anhydride. Bartlett and Nasaki[24] modified the procedure and applied it to copolymers of maleic anhydride and maleic acid with apparent success. In both of the last two procedures, the time required for reaction with maleic acid and maleic anhydride was more than four times that necessary for other unsaturates. Enkvist[25] reacted a methanolic solution of ammonia with maleic acid in a sealed tube at 100°C and found a small amount of aspartic acid. The reaction proceeded much faster in the presence of certain metal salts.

The addition of simple moleucles to other olefins proceeds without too much difficulty. Uhlrig and Levin[26] found that cyclohexene, isobutylene, diisobutylene and various fats and oils would add bromine quantitatively from a glacial acetic acid solution. Chlorine has been added to acrylonitrile by passing the gas through a chloroform solution of the nitrile at 10-60°C.[27] However, the addition of chlorine to tetrachloroethylene required an excess of chlorine at high pressures. Janz[29] added cyanogen to 1,3 butadiene while the I.G. Farben Co.[30] added cyanogen chlorides to olefins by the use of heat and pressure. Mayo and Katz[31] added HCl to isobutylene and Mayo and Savoy[32] added H Br to propylene. The Dutch found that the addition of hydrogen halides or hydrogen cyanide to an olefin was promoted by wave lengths of light of less than 300u.[33] Hydrogen cyanide has been added to acrylonitrile,[34] vinyl esters,[35] ethylene,[36] butadiene,[37] etc. the last two additions being catalyzed by Cu_2Cl_2. Organic peracids add oxygen to the double bonds of simple olefins to form epoxides,[38] while hydrogen peroxide forms the glycol with the double bond at room temperatures.[39] Ford[40] prepared ethyl dimethyl butyrate by adding CO to propylene. Schulz[41] added mercaptans and hydrogen sulfide to double bonds using the latter procedure as a method of preparation of mercaptans. Snow and Frey[42] reacted SO_2 with olefins at high temperatures to produce high molecular weight sulfones. Turner and Connor[43] added aryl sulfenyl chlorides to unsaturated compounds while Peterson and Detling[44] added tertiary halides under the influence of antimony or aluminum chlorides. Iodoform,[45] chloroform and carbontetrachloride[46] have been added to olefins under the influence of peroxides. Hamblet and McAlery[47] found that the addition of formaldehyde to butylene produced 1,3 butylene glycol. The addition products of N_2O_3 and N_2O_4 are the most widely used of the nitrogen addition compounds since they are used for unsaturation determinations. Bond[48] applied the addition of N_2O_2 to styrene and found that the gravimetric determination of styrene as the nitrosite gave results close to 100% of the theoretical. The use of N_2O_3 in this manner was applied to other olefins by Scafe and Bond[49] with good success. Most of the work on the addition of N_2O_4 to double bonds has been done by Levy and Scaife[50] who added N_2O_4 to ethylene and propylene. With other olefins, dinitroparaffins, nitroalcohols and nitro alkyl nitrates were produced in good yields. Beckham[51] added NOCl to the bonds of ethylene and propylene in the presence of $NiCl_2$, $FeCl_2$, or $Cu_2\,Cl_2$ at -22°C while Coleman and Howell[52] added NCl_3 to 1-and2-butenes in the presence of an acid sulfite to produce an amino chloride. The addition of ammonia to olefins has been of interst in the last few years. Ford[53] added ammonia to acrylonitrile at 50-150°C and produced alanine. Several patents were obtained by J. W. Teter[54] for the ammonolysis of olefins such as propylene, 1-dodecene, etc. in the presence of Ni, Co, or small amounts of water. In each case an excess of ammonia was used at temperatures as high as 800°F and pressures ranging from 800-6000 #/ sq. in.

Very little has been done on the addition of small molecules to polymers. However, it was found that rubber would react with molecules containing the $- C = C - C = O$ linkages,[55] the reaction taking place at 120°C in the absence of oxygen. It is also well known that natural rubber will add X_2, HX, S, and S_2Cl_2 to form rubber halides, rubber hydrohalides and vulcanized rubber respectively. Kumscheidt and Nie[56] subjected a butadiene polymer to mild oxidation and treated the solution with SO_2. The viscosity increased but no indication was given of the type of reaction taking place. Several types of inorganic acids and anhydrides showed the same effect.

EXPERIMENTAL

Preparation of Polyethylene Glycol Maleate.[57]

Four moles of maleic anhydride and four moles of ethylene glycol were mixed in a liter three-necked flash equipped with a motor stirrer, thermometer, gas inlet tube and a condenser set for downward distillation.

The maleic anhydride was purified by vacuum distillation, a fraction distilling at 85°C under 15 mm. pressure was collected and used while the ethylene glycol used had a refractive index of 1.4304 at 21.6°C. The system was kept under nitrogen to prevent decomposition and conversion by the oxygen of the air. The nitrogen was passed through a 10% solution of alkaline pyrogallol and a tube of concentrated sulfuric acid to remove oxygen and water. The reaction temperature was maintained at 150°C for 5.8 hours at the end of which period, the temperature was raised to 200°C for 3.5 hours.

The progress of the reaction was followed by neutralization and saponification equivalents. The saponification equivalents were determined by heating the polymer with an excess of aqueous potassium hydroxide followed by back titrations with standard hydrochloric acid while the neutralization equivalents were determined by direct titrations with methanolic potassium hydroxide. In both cases a phenolphthalein indication was used. The difference between the neutralization equivalents and the saponification equivalents was equal to the number of reacted carboxyl groups, which when divided by the saponification equivalent gave the percent reaction.

The following results were obtained:

Time (Minutes)	Temperature (Degrees C.)	% Reaction
0	60°	49
30	190°	64.8
90	190°	73.4
165	190°	78.7
240	190°	82.1
315	190°	83.1
360	190°	83.4
420	205°	85.9
495	205°	88.6
565	205°	88.8

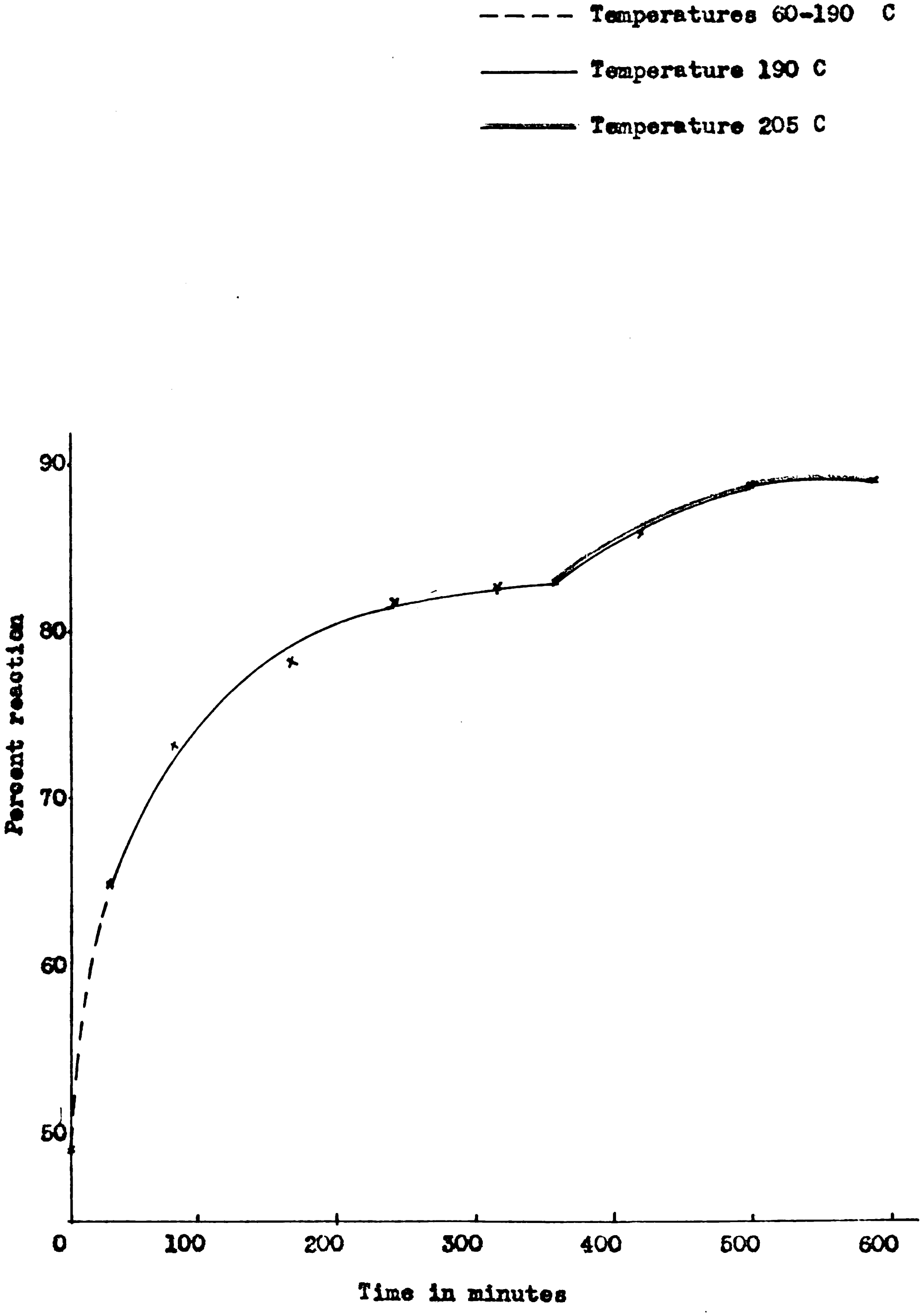
The graph of time vs. percent reaction is shown in figure #1. The percent reaction at zero time (49%) was not determined during the reaction, but it was assumed that the half ester was formed immediately when the maleic anhydride melted and a homogeneous solution was formed.[58] To prove this, .497 moles of ethylene glycol were added to .497 moles of maleic anhydride in .497 moles of acetone at 20°C and then titrated with aqueous potassium hydroxide and with a solution of potassium-hydroxide in isoprophl alcohol as soon as possible. The following results were obtained:

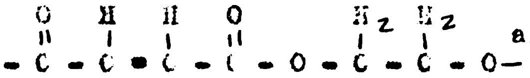
Minutes After Mixing	% Reaction
3	49.15
15	48.66

The reaction product was purified by distilling off all volatile matter at 130°C under 20-30 mm. pressure and when cooled, it was an extremely viscous resin with a slight straw color. After purification, the carboxyl groups were found to be 91.64% reacted indicating an average polymer length of approximately 12 units and a molecular weight of 839.[59] The composition of the polyethylene glycol maleate was found to be carbon - 50.64%, and hydrogen - 4.28%. The theoretical percentages for the ester

FIGURE #1

GRAPH OF PERCENT REACTION VS. TIME AT DIFFERENT TEMPERATURES



with a structual unit of 

$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{\overset{|}{C}}-\overset{H_2}{\overset{|}{C}}-O-$$

are carbon - 50.70% and hydrogen 4.26%.

Using the neutralization equivalents as the concentration of acid, the reaction rate constants (1) for the esterification reaction at 190°C. and 205°C. were determined. The reciprocals of the neutralization equivalents were plotted against the time of reaction in minutes and value of k was found from the slope of the graph. As a check on the graphical method, the values of k were calculated from the equation $\frac{1}{a-x} = kt + C$ where a is the initial mount of acid, x is the acid reacting in time t and c is a constant determined by setting x and t equal to zero. The values of k for the two temperatures were then used in the equation $\log \frac{k2}{k1} = \frac{E\ (T2 - T1)}{2.303\ R\ T2\ T1}$ (where k_1 and k_2 are the reaction rate constants, T_1 and T_2 are the absolute temperatures, and R is the gas constant (1.987) to determine the energy of activation, E. The data used and the results of these determinations are as follows:

Time (Min.)	Concentration of Acid meq./g.	Reciprocal Concentration	Calculated Value of k	Value of k from Graph
0	4.49	.223		
60	3.61	.277	.00090	.0009
135	2.82	.351	.00097	
210	2.45	.408	.00088	
285	2.31	.433	.00074	
330	2.28	.439	.00065	

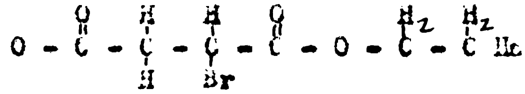
Reaction rate constants at 205°C.

60	1.97	.508	.0012	.0012
135	1.62	.617	.0013	
225	1.65	.606	.0007	

The value of the energy of activation was found to be 12,760 cal./ mole.

Addition of Hydrogen Bromide to Polyethylene Glycol Maleate

Gaseous hydrogen bromide, which had been purified by passage through copper turnings and dried through a calcium chloride tower, was passed through a solution of twenty-one grams of the polyester in 150 cc of chloroform for nine hours. The excess gas was absorbed in a water trap. During the reaction, the temperature rose to 34°C and then returned to 20°C after four hours. The product, after the solvent was removed under a vacuum of 30 mm. at 140°C for three hours, was a viscous resin which was slightly darker than the polyester. One hundred and forty-eight meq. of the polyester gained 138 meq. of H Br which is 93.30% of the theoretical amount for a polymer with the structural unit of



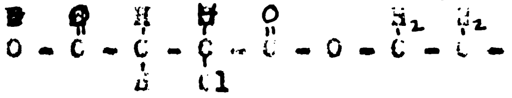
$O - \overset{O}{\overset{\|}{C}} - \underset{H}{\overset{H}{C}} - \underset{Br}{\overset{H}{C}} - \overset{O}{\overset{\|}{C}} - O - \overset{H_2}{C} - \overset{H_2}{C}$

Halogen determinations showed 33.40% bromine in the polymer which was about 93.5% of the theoretical value - (35.87%) for a polymer of the structure shown.

Addition of Hydrogen Chloride to Polyethylene Glycol Maleate.

Gaseous hydrogen chloride was purified through copper turnings and concentrated sulfuric acid and then passed through a solution (of 28.55g) of the polymer in 150 cc of chloroform for nine hours at 24°C. During the reaction, there was no change in temperature. Distillation for three hours under 40 mm. pressure at 120°C left a light yellow viscous residue which showed signs of crystalinity on long standing. Twenty-eight and fifty-five hundredths g of the polyester increased 6.97 g in weight which was 95.1% of the theoretical amount for complete addition. to the double bond of the polyester. Halogen determinations showed the polymer to contain 15.87% chlorine which was about

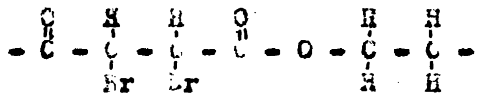
94.0% of the theoretical value (19.[illegible]7%) for a polymer with the structural unit



$-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}-$

Addition of Bromine to Polyethylene Glycol Maleate

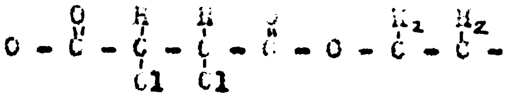
Forty-four and six tenths g of the polyester were dissolved in 200 cc of chloroform and 17.9 cc of pure bromine, and excess of the amount necessary for addition, was added, after which the flask was stopped and allowed to stand for one week with occasional shaking. The chloroform solvent and unreacted bromine were removed at 45°C and 40 mm. pressure. The product was slightly darker and less viscous than the polyester and on long standing began to show signs of crystalinity by forming a red-brown pasty material. The product contained 13.02% bromine which was only 24.59% of the theoretical value for a polymer with a structural unit of



$-O-\overset{O}{\overset{\|}{C}}-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-$

Addition of Chlorine to Polyethylene Glycol Maleate

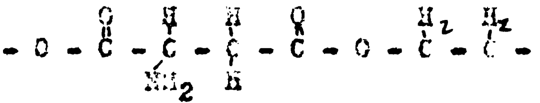
Chlorine gas which was dried through sulfuric acid, was passed through a solution of 40 grams of the polyester in 200 cc of chloroform, the excess being removed by a water trap. The temperature was 21°C, but rose to 30°C soon after the reaction started and remained there during the rest of the reaction period of nine hours. Distillation of the solvent and gases present was effected in vacuum at 100°C for $1\frac{1}{2}$ hours after which time, the product began to turn dark. On standing, a very viscous, cloudy resin formed. The percent chlorine was found to be 27.63% which was about 84% of the theoretical (33.31%) for a polymer structure of



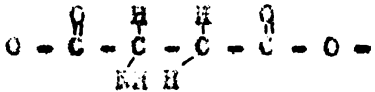
$-O-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}-$

Addition of Ammonia to Polyethylene Glycol Maleate

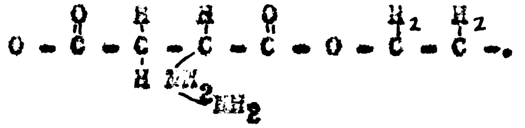
Twenty cc of Liquified ammonia were added to 54 g of the polyester which had previously been cooled in an acetone-dry ice bath. The mixture was heated to 150°C in a high pressure bomb where the highest pressure attained was 125 p.s.i. The pressure dropped steadily in about 45 minutes to zero p.s.i. although a small amount of gas was found when the bomb was opened. There were two products of the ammonolysis, one a brown resin which was soluble in dilute acid but insoluble in alkali, and a white solid which was soluble only in concentrated acids. Both products were placed in a very dilute acid solution and the white solid was filtered off. The remaining solution was made alkaline to precipitate the brown resin which was then dried under vacuum. The resin contained 11.37% nitrogen as against a theoretical value of 11.23% for a polymer which has a structural unit of



$$-O-\overset{\overset{O}{\|}}{C}-\underset{NH_2}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{\overset{O}{\|}}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-$$

It was not oxidized by potassium permanganate and showed 7% unsaturation when titrated with bromate-bromide solution. The white solid decomposed without melting at about 285°C, showed 88% unsaturation when titrated with bromate-bromide solution, and gave off ammonia when heated with alkali. The solution formed when the white solid was heated with alkali was acidified and a white solid precipitated with acetone. This solid was filtered and washed with alcohol after which the alcohol was evaporated to a small volume. This resulted in the precipitation of a white crystaline solid which melted at 130°C. i.e. the melting point of maleic acid. The percent nitrogen of the original solid was 22.86 which was about $2\frac{1}{2}$ times the theoretical for a polymer with a structural unit of  $-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{N}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}-$ and slightly less than that of maleimide (m.P. 260°C (decomp.)

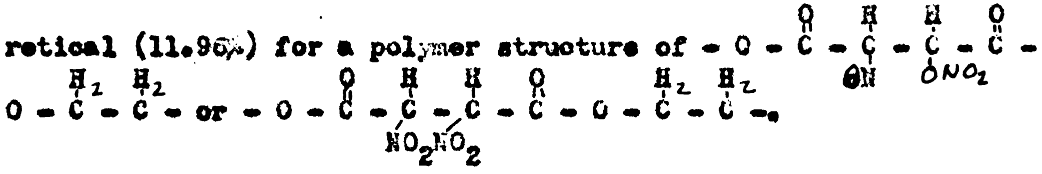
Addition of Hydrazine Hydrate to Polyethlene Glycol Maleate

Twenty-three and three tenths g of the polyester were dissolved in 100 cc of a 1:1 ratio of a chloroform-alcohol solvent, 22 g of hydrazine hydrate were added and the mixture was refluxed for four hours. Distillation at 80°C under 50 mm. vacuum for three hours resulted in a transparent bronze-colored resin which was less viscous than the polyester. Twenty-three and three tenths grams of the polyester gained 5 grams during the reaction, this value beong 61% of the theoretical amount for a polymer, the structural unit of which would be  $-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{NH_2NH_2}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}-$. The percent nitrogen was 10.34% or 64.9% of the theoretical amount (16.09%) for the structure shown. The percent unsaturation could not be determined.

Addition of Nitrogen Tetroxide to Polyethylene Glycol Maleate[67]

A solution of the 32.4 g polyester in 115 cc of chloroform was placed in a round bottom flask which was cleared of air and oxygen by passing through nitrogen. Nitrogen tetroxide was passed through the solution for five hours at which time the solution was assumed to be saturated with the gas. The nitrogen tetroxide was produced by dropping concentrated nitric acid on moist sodium arsenite and heating when necessary to produce a better volume of gas. In the early stages of the reaction, some heat was given off. Thirty-two and four tenths grams of the polyester increased

30.8 grams in weight which was a little higher than the theoretical amount. Distillation at 35°C under 50 mm. vacuum produced a yellow white semi-solid. At higher temperatures, large volumes of N_2O_4 were given off. Ten and fifty-four hundredths percent nitrogen was found in the product which was slightly less than the theoretical (11.96%) for a polymer structure of



$$-O-\overset{O}{\overset{\|}{C}}-\underset{ON}{\overset{H}{C}}-\underset{ONO_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}- \text{ or } -O-\overset{O}{\overset{\|}{C}}-\underset{NO_2}{\overset{H}{C}}-\underset{NO_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H_2}{C}-\overset{H_2}{C}-.$$

Addition of Nitrosyl Chloride to Polyethylene Glycol Maleate[63]

Thirty cc of glacial acetic acid in 20 cc of amyl nitrite were added to a solution of 22.5 g of the polyester in 150 cc of chloroform followed by a dropwise addition of 11 cc of concentrated hydrochloric acid, during the addition of which the temperature was maintained below 5°C. The chloroform solution was warmed on the steam bath for several hours. A white precipitate appeared which was filtered off and washed with chloroform but gave no tests for chlorine or nitrogen. When heated, the precipitate sublimed at 200°C, melted near 280°C, and proved to be fumaric acid.

Addition of Sulfurmonochloride to Polyethylene Glycol Maleate

Three and five tenths g of sulfurmonochloride were mixed with a solution of 5.3 g of the polyester in 50 cc of chloroform and heated on the steam bath. The yellow spongy recipitate which appeared was washed with alcohol and dried. It was found to be insoluble in all of the solvents used and no determinations could be made. The solid was air dried and placed in the hot room for several days with no destruction of the elastic properties.

ANALYTICAL

A carbon-hydrogen determination was run on the polymer by a method adapted from the macro-method of Fisher,[64] ascarite and dehydrite being used in the absorption tubes. All of the halide and halogen addition compounds were analyzed in duplicate for halogen. A weighed sample in a cellulose cup was placed in a Parr Bomb with sodium peroxide and small amounts of potassium nitrate and benzoic acid.[65] The bomb was ignited by flame and the contents dissolved in an acid solution after which the Volhand method[66] for the determination of halogen was applied. Nitro benzene was used with the chlorides rather than filtering off the silver chloride. All of the nitrogen determinations were carried out by the macro Kjeldahl method[67] with sodium sulfate and copper sulfate catalysts. The determinations of the various elements are summarized in tables 1, 2 and 3.

Several methods for the determination of unsaturation were used but only the bromide-bromate method was of any value.

Permangauate Oxidation Method for the Determination of Unsaturation

Each of the products was titrated with a saturated solution of potassium permanganate in acetone to determine the relative amounts of unsaturation or the effects of oxidation. The permanent red color of the permanganate solution was used as the end point with no outside indicator employed. The results are listed in table #4.

Mercuric Acetate Method for the Determination of Unsaturation[68]

Five grams of accurately weighed mercuric acetate were added to a solution of the sample in 25 cc of dioxane. After ten minutes, a saturated sodium chloride solution, methyl alcohol and carbontetrachloride were added and the mixture was titrated with standard potassium hydroxide to a phenolphthalein end point. Determinations were made on maleic acid, polyethylene glycol maleate, the hydrogen bromide addition product, and a blank sample. See table #5.

Hydrogenation Method for the Determination of Unsaturation

Hydrogenation was carried out on the same products as for the mercuric acetate method using low pressure hydrogenation in the presence of a palladium oxide catalyst.[69] A saturated chloroform solution of the product to be reduced was placed in the hydrogenator along with .2 grams of catalyst, 5 cc of ethyl alcohol and 2 small crystals of ferrous sulfate. The pressure gauge was calibrated with maleic acid. The results are shown in table #6.

Perbenzoic Acid Method for the Determination of Unsaturation[70]

The perbenzoic acid was prepared by the method of Braun[71] using benzoyl peroxide which had been recrystalized from absolute ethyl alcohol. Braun's method consisted of adding a cold chloroform solution of benzoyl peroxide to sodium methylate followed by acidification and extraction with chloroform. An excess of sodium methylate was used to counteract the effect of benzoic acid which seemed to be present in the peroxide. Titrations of the perbenzoic acid solution with standard thiosulfate determined the strength of the acid to be .9884 milliequivalents/ml. Twenty-five ml. of this solution were added to a chloroform solution of the sample containing about 12 milliequivalents of unsaturation after which the volume was made up to 100 ml. with chloroform. After standing for 84 hours in the cold, 10 ml. portions of the solution were titrated with standard thiosulfate solution using potassium iodide and a starchend point. The results are given in table #8.

Potassium Bromide-Potassium Bromate for Determination of Unsaturation

Two methods, those of Lucas and Pressman,[17] and Bartlett and Nosaki[18] were used in these titrations. In the Lucas procedure, an excess of KBrKBrO$_3$ and a small amount of sulfuric acid were placed in the flask followed by .2 N mercuric sulfate, the sample to be titrated, (approximately 2 milliequivalents of double bond) and 20 cc of acetic acid. After shaking the flask in the absence of light for 30 minutes, a sodium chloride solution and potassium iodide were added. The solutions were titrated with standard thiosulfate and gave extremely low results. The same method was used on two more samples although it was modified slightly by initially evacuating the flask with an aspirator. An increase in the percent unsaturation was shown, but the results were still too low to be of value. The best results were obtained by using the method of Bartlett and Nosaki. A suction flask with an attached seperatory funnel was evacuated, and a solution of the sample was run in with 5 cc of 6 NH_2SO_4 and 10 cc of water. After warming the flask for 10 minuted, an excess of the bromide bromate-solution and 20 cc of 2 N mercuric sulfate were added. At the end of 30 minutes, the excess bromide-bromate was titrated iodometrically with thiosulfate. The results are given in table #8.

DATA TABLES

Table #1 Percentages of carbon, hydrogen and oxygen in the polyethylene glycol maleate produced.

Percentages Found			Theoretical Percentages		
% C	% H	% O	% C	% H	% O
50.73; 50.55	4.16; 4.35	45.12; 45.09	50.70	4.26	45.04

Table #2 Percent halogen in the halogenated and hydrohalogenated polyester.

Addition Product	% Halogen	Theoretical % Halogen
HBr	33.43; 33.55	35.87
HCl	18.74; 18.60	19.87
Cl_2	28.10; 26.75	33.31
Br_2	13.02	52.95

Table #3 Percent nitrogen found in the addition products.

Addition Product	% Nitrogen	Theoretical % Nitrogen
NH_3 (solid)	22.84; 22.51	11.23
NH_3 (resin)	11.09; 11.54	11.23
$(NH_2)_2$	9.99; 10.68	16.09
N_2O_4	11.15; 9.93	11.96

Table #4 Relative unsaturation expressed as ml of $KMnO_4$ solution per gram.

Addition Product	Ml. of $KMnO_4$/g
Polyethylene glycol maleate	35.8
HBr	3.1
HCl	44.6
Br_2	40.0
Cl_2	5.4

Table #4 Cont.

Addition Product	Ml. of $KMnO_4$/g
NH_3 (solid)	19.4
NH_3 (resin)	2.7
$(NH_2)_2$	

Table #5 Unsaturation found by the mercuric acetate titration method.

Sample	Milliequivalents of base Used	Theoretical Milliequivalents
Maleic Acid	12.52	9.49
Polyethylene glycol maleate	.38	5.38
Polyethylene glycol maleate	.19	2.71
HBr Addition Product	1.82	4.16
HBr Addition Product	1.59	4.23

Table #6 Relative unsaturation as measured by the drop in hydrogen pressure.

Sample	Pressure Drop In lbs/sq. in./mole.	Time
Maleic Acid	90	44 min.
Polyethylene glycol maleate	50	18.8 hrs.
Polyethylene glycol maleate	62	16.8 hrs.
HBr Addition Product	0	21 hrs.

Table #7 Unsaturation measured by perbenzoic acid titrations.

Sample	Meq. of Acid Used	Theoretical Meq.
Polyethylene glycol maleate	.15	1.40
Polyethylene glycol maleate	.11	1.40

Table #8 Unsaturation measured by KB_r - KB_rO_3 titrations in the presence of $Hg\ SO_4$.

Addition Product	Meq. of Bromate Used	Theoretical Meq. of Unsaturation	Percent Unsaturation
Polyethylene glycol maleate	2.04	2.09	97.89
Polyethylene glycol maleate	2.43	2.50	97.36
HB_r	2.36	3.46	68.30
Br_2	1.40	4.22	32.97
H Cl	1.64	4.12	39.73
Cl_2	3.09	3.78	81.34
NH_3 (solid)	1.09	1.21	90.01
NH_3 (solid)	1.00	1.40	88.00
NH_3 (resin)	0.15	2.22	7.00
NH_3 (resin)	0.18	2.53	7.15
H_2	.05	1.51	3.31
H_2	.06	1.26	5.10
$(NH_2)_2$	--	An excess was used in all titrations.	

DISCUSSION

Figure #1 shows the effect of time on the consideration of maleic anhydride and ethylene glycol. The temperature was raised after 5.8 hours of esterification to effect a larger molecular weight since the reaction rate was approaching zero. This action resulted in an increased rate of esterification as shown by the graph which is in agreement with the fact that most of the water distilled off during the first $1\frac{1}{2}$ - 2 hours. It can be seen that as the reaction proceeds, the temperature necessary for condensation increases which is probably due to physical rather than chemical factors since the increasing viscosity would tend to make the collisions of hydroxyl and carboxyl groups less frequent. Stirring tends to make the mixture more homogeneous in regard to both chemical composition and temperature since in condensations where no stirring was used the gelation began earlier and, due to localized heating, the portion of the material at the edges of the flask nearest the source of heat gelled much sooner than the rest of the mixture. In all of the condensation runs made, a white, solid material was found suspended in the cooled polyester. The solid melted at 130° C and proved to be maleic acid, which sublimed off during the distillation as fumaric acid (MP. 290°C.)

No signs of the suspended maleic acid were found in the polyester at the end of the distillation process. The presence of excess acid was to be expected since a small amount of the glycol distilled off with the water during the condensation reaction. The presence of free ethylene glycol would seem unexplainable in the light of the immediate half ester formation, but at higher temperatures, an esterification-hydrolysis equilibrium is probably set up. Since mixed esters undergo ester interchange it is reasonable to assume that the hot polyester is in a dynamic rather than a static states.

Since free acid was found in the final product, the percent esterification values calculated during the reaction are probably somewhat lower than the actual percent reaction values. The molecular weight was calculated from the percent reaction by the use of the following formula which was developed by Carothers:

$$P = \frac{2}{f} - \frac{2}{fx}$$

Where P is the percent polymerization, X is the number of units in the chain and F is the functionality per molecule of monomer. Both of the monomers are considered to have a functionality of 2 since the double bond of the maleic anhydride does not take part in the esterification reaction. Substituting 91.54% (or .9154) for P and 2 for the value of X, the equation becomes: $.9154 = 1 - \frac{1}{x}$ or $.9154x-x = -1$. This gives X a value of 11.82 which when multiplied by the weight per each two functional groups (71 g) gives the molecular weight of the polymer as 839.

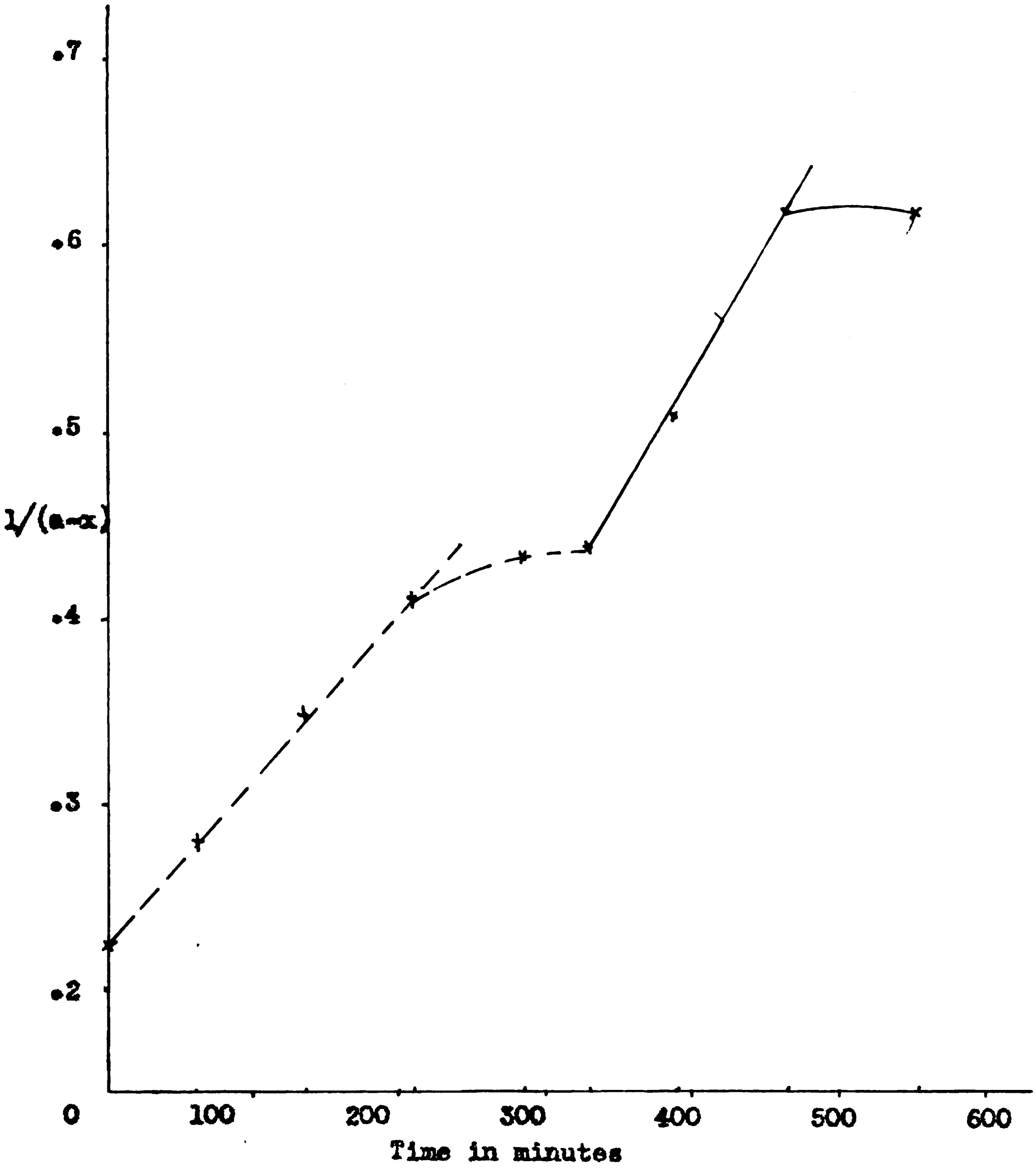
The graph of the reciprocal neutralization milliequivalents vs. time shows that the esterification of maleic anhydride and ethylene glycol is a second order reaction. The values of k at both temperatures were determined from the straight sections of the curve only, since the rate decreases considerably after several hours of reaction. This is due to the reverse reaction (hydrolysis) which takes place in all esterification reactions of this type. Although water was removed by distillation during the reaction, considerable quantities of water are probably held by the viscous

FIGURE #2

GRAPH OF RECIPROCAL
MILLIEQUIVALENTS PLOTTED
AGAINST TIME IN MINUTES

— — — Temperature 190 C

——— Temperature 205 C



mixture resulting in the hydrolysis reaction.

During the discussion it has been assumed that esterification was the only reaction taking place. However, it should be mentioned that there are several other courses which the reaction could have followed, these being A-polymerization of the acid, polyether formation and polyanhydride formation. A-polymerization and polyanhydride formation would both result in compounds which should contain only 2% hydrogen, a value much lower than the percent hydrogen found. The A-polymer would show no unsaturation and would not add any of the reagents which were added. The polyanhydride should not be formed since the half ester would tend to prevent it. Although polyether formation usually requires higher temperatures and a dehydration catalyst, it could conceivably be formed during the reaction. However, the polyether would not be hydrolyzed by the weak alkali solutions used, there would be no difference in the neutralization and saponification equivalents, and a greater percentage of hydrogen would be present in the polyether. The carbon hydrogen determinations were in very close agreement with the theoretical for esterification.

The additions of various reagents never exceeded 95% which might be due to small amounts of isolated crosslinkages through double bonds, although in most cases the remaining unsaturation was accounted for by double bond titrations.

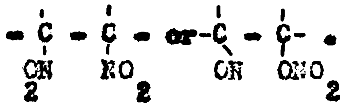
Esterification would produce a polyester which could have a chain of any one of three forms depending upon the terminating groups. The terminating groups of the molecule might be 2 hydroxyl groups, 2 carboxyl groups or 1 carboxyl and 1 hydroxyl. The half ester theory would support the last structure, but since free gylcol and free acid are known to be present, any of the three types of molecules could be formed. A cyclic structure for the polymer is rather improbable since a ring of more than eight members would have to be formed and no neutralization equivalent would be shown.

The reactivity of polyethylene glycol maleate toward halogens and hydrogen halides is in the order $Br_2 < Cl_2 < HBr < HCl$ although the difference in the reactivities of H Cl and HBr is slight. Bromine reacts very slowly and the reaction may be either substitution or addition. Chlorine reacts more easily and to a greater extent than bromine but the product formed is unstable toward heat. From the percentages of halogen present, HBr and H Cl add to the double bond nearly quantitatively. Since neither of these reagents are capable of substitution, the percent halogen gives a good indication of the unsaturation present in the polyester. As was expected, none of the halide derivatives could be checked for unsaturation by the bromide-bromate method. The bromide-bromate method depends upon the addition of bromine to the double bond and in the presence of at least three (two carbonyls and one or more halogens) strongly electronegative groups, addition would be greatly inhibited while substitution would be greatly enhanced.

The addition of ammonia to polyethylene glycol maleate resulted in two entirely different products. From the relative amounts of the products produced, it can be concluded that the primary reaction product is the aminated polyester while the secondary reaction product is maleamide. There are probably other products formed in the reaction mixture which were not isolated. With both reactions taking place simultaneously some diamide of aspartic acid should be formed. However, since the resin was precipitated from a water solution the aspartic acid derivative would be lost in this step. The percent nitrogen of the maleamide (22.67%) was lower than the theoretical value and small amounts of maleamic acid are probably present in the solid. Since these products were the results of reacting an excess (for addition) of ammonia to polyethylene glycol maleate, it would be interesting to determine what products would be formed by reacting the two in an equal molar ratio. One or the other of the reaction courses might be eliminated by running the reaction at a different temperature.

The addition of hydrazine, which should show about the same reactivity as ammonia, was only 65% complete. This is probably not due to the reactivities of the two bonds involved but may be due to the steric hinderance of large carboxyl and hydrazine groups. The addition product was easily oxidized by permanganate which would indicate the presence of a pendent NH_2 group. Various amines would probably add to the double bond of polyethylene glycol maleate but they would be restricted by steric factors to those of the smaller groups.

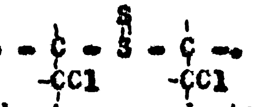
Nitrogen tetroxide adds nearly quantitatively and might be used for the gravimetric determination of the double bond. The solid product is not crystaline and apparently is not too stable to heat since some N_2O_4 was given off at temperatures slightly higher than those used to evaporate the solvent. No explanation can be given for the differences shown between the percent N_2O_4 addition and the titration of the remaining unsaturation. The structure of this derivitive could be



$-\underset{CN_2}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}-$ or $-\underset{ON}{\overset{|}{C}}-\underset{ONO_2}{\overset{|}{C}}-$.

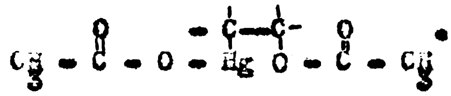
The structure is preferred since the addition of two electronegative nitro groups to the symmetrical bond should be as difficult as bromination or chlorination.

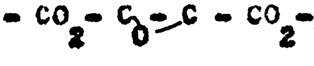
The attempt to add nitrosyl chloride to the double bond resulted in the formation of fumaric acid, and no addition was detected. Although the temperature was kept at 5°C, hydrolysis in an aqueous acid solution was not unexpected. Some tendency to add or activate the bond is indicated by the conversion of the maleate to fumaric acid, and the addition would probably take place under conditions unfavorable to hydrolysis.

The reaction of sulfur monochloride with polyethylene glycol maleate took place easily at temperatures below 100°C. The actual reaction that took place could not be determined since the polymer was insoluble in all solvents. However, due to its insolubility, the presence of a cross-linked structure was indicated. This reaction would be similar to the vulcanization of rubber and the structure would be  $- \underset{-\underset{|}{\overset{|}{C}}Cl}{\overset{|}{C}} - \overset{S}{\overset{\|}{S}} - \underset{-\underset{|}{\overset{|}{C}}Cl}{\overset{|}{C}} -$. The drying of the polymer for several days with heat was undertaken to determine whether or not the reaction product was that proposed above or hydrated sulfur. Since the elasticity was not decreased to any great extent the product could not have been the latter.

The polyethylene glycol maleate showed a self addition reaction when heated to approximately 90°C with benzoyl peroxide or ditertiary butyl peroxide, the conversion with the latter catalyst being much faster.

The unsaturation determinations by most of the methods were unsatisfactory. The presence of certain groups on the bond caused oxidation with permanganate to be as complete as that of the polyester itself. The oxidation of the hydrazine addition product was even greater than the polyester. This may have resulted in the oxidation of the pendent NH_2 group to NO_2 or N_2O_3. However, no fumes were detected.

The use of mercuric acetate for the determination gave reproducable results when like conditions were rigidly maintained but the amount of unsaturation was far below the theoretical. Also, the unsaturation of the HBr addition product was found to be much greater than that of the polyester when this method was employed. The action of the mercuric acetate depends upon the addition of mercuric acetate to the double bond followed by titration of the liberated acetic acid. One theory proposed for the structure formed from the addition of mercuric acetate to the double bond is  $CH_3-\overset{\overset{O}{\|}}{C}-O-Hg\overset{-\overset{|}{C}-\overset{|}{C}-}{\ \ }O-\overset{\overset{O}{\|}}{C}-CH_3$. The addition of methyl alcohol then hydrolyzes the polymer acetate to acetic acid and the methyl ether of the polymer. The difficulty of forming such a structure as that proposed above in the presence of the two electronegative carboxyl groups is evident.

The low results of the perbenzoic acid titrations might be expected since this reaction depends upon the addition of an oxygen atom in the form of an epoxide linkage. From the structure,  $-CO_2-C\underset{O}{\frown}C-CO_2-$, it can be seen that the tendency to form the epoxide would be very slight in the presence of the ester groups.

The addition of groups with no electronegative character was tried in the hydrogenation experiments. The results gave fairly good agreement with unsaturation found from the percentage of elements and the bromide-bromate titrations. The method could not used since the accuracy of the gauge readings for the small amount of pressure drop was very poor and a constant temperature could not be maintained.

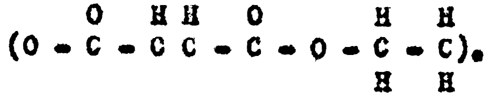
The bromido-bromate titration in the presence of air was much lower than the theoretical. In the absence of air and by employing the 10 minute heating period, results near the theoretical for addition were obtained. However, it should be noted that the presence of a substitution reaction is not impossible due to the fact that the lability of the hydrogen atoms on the double bond would be increased by heat. The action of the mercuric sulfate is not thoroughly understood but apparently its action is due to some type of coordination of the mercuric ion with the free bromine.

Most of the reactions carried out proceeded to a greater extent than has been found true of polybutadiene. Polybutadiene shows only a substitution reaction with bromine and chlorine and the extent of substitution is much greater than that which occurs in the halogenation of polyethylene glycol maleate. HCl and HBr add to polybutadiene but the reaction of the former requires 16 hours at 55°C if no catalyst is used. Polybutadiene reacts with N_2O_3 but the extent of the reaction is not known and both of the polymers will react with S_2Cl_2. The reactions of polybutadiene and positive additive groups is very difficult. The addition of ammonia to polybutadiene under a pressure of 2100 lbs./sq. in. at 420°C in the presence of a Co-Mo catalyst showed only very faint traces of nitrogen.

The effect of the electronegative ester groups on the double bond has been readily shown by the reactions carried out. Apparently the ester groups tend to pull all of the electrons around the double bond toward themselves which action results in two labile hydrogen atoms and a double bond which is very unreactive to other electronegative groups such as bromine and chlorine. Positive groups such as NH_2 and H react rather readily. Other molecules such as HBr and HCl contain one positive and one negative group and probably add through the initial attachment of the hydrogen ion followed by a shift in the double bond electrons toward the hydrogen and the final attachment of the halide group. All of the other simple molecules which added to the double bond form two groups which have different electronegativities. The approach of the two groups probably causes a slight shift of the pi electrons in one direction, destroying the symmetry of the electronic structure and allowing addition to take place more easily.

CONCLUSIONS

1. Ethylene glycol and maleic anhydride react to yield a viscous, light straw-colored resin, polethylene glycol maleate, with a probable structural unit of



$(O - \overset{O}{C} - \overset{H}{C}\overset{H}{C} - \overset{O}{C} - O - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}})$.

2. The esterification proceeds by a second order reaction which has a rate of .0009 meq/min. at 190°C, and a rate of .0012 meq/min. at 205°C.

3. The energy of activation for the reaction is 12,760 cal./mole.

4. Polyethylene glycol maleate will react with ammonia, hydrasine, hydrate, nitrogen tetroxide, sulfur monochloride, hydrogen, bromine, chlorine, hydrogen chloride, and hydrogen bromine.

5. The double bond of polyethylene glycol maleate is activated by the two carbonyl groups conjugated to it.

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