The POLYMERIZATION of EPOXIDES By MEANS of the GRIGNARD DERIVATIVES of t-BUTYL BROMIDE

THESIS for the DEGREE of M. S.
MICHIGAN STATE COLLEGE

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1951

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3/3/52

THE POLYCHLORINATION OF DIOXIDES BY MEANS OF THE ORTHO-ACID DERIVATIVES OF t-BUTYL BROMIDE

by

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A THESIS

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF MICHIGAN STATE COLLEGE OF AGRICULTURE AND APPLIED SCIENCE

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

1951

ACKNOWLEDGEMENT

The author wishes to express his gratitude and appreciation for the help and encouragement given by Dr. Ralph L. Guile and Dean Emeritus Ralph C. Huston during the course of this investigation.

DEDICATION

To my wife

ABSTRACT OF THESIS

by

JOHN R. PEFFER

Title: The Polymerization of Epoxides by Means of the Grignard Derivatives of t-Butyl Bromide.

Tertiary butylmagnesium bromide, anhydrous magnesium bromide, and di-tertiary butylmagnesium were investigated as possible catalysts for the polymerization of ethylene oxide, propylene oxide, butadiene monoxide, and styrene oxide.

The monomer and catalyst were combined and shaken in a closed system. The polymers were purified by dissolving them in chloroform and removing inorganic material by centrifugation. The high and low molecular weight fractions were separated by precipitating the high molecular weight material with diethyl ether from a chloroform solution. The intrinsic viscosities of the various polymers were determined. The optimum catalyst concentrations were determined and the effect of removing the catalyst solvent was studied.

Tertiary butylmagnesium bromide resulted in high yields of low molecular weight polymers of ethylene oxide. The proportion of high molecular weight polymer to low molecular weight polymer increased with decreasing catalyst concentration. An anionic mechanism of polymerization was presented. Poorer yields of polymers were obtained from the other monomers when t-butylmagnesium bromide was used as the catalyst.

Magnesium bromide caused fair yields of ether soluble, low molecular weight polymers from all the epoxides used. A cationic mechanism of polymerization was suggested.

Di-tertiary butylmagnesium was a good catalyst for the production of high molecular weight polymers of ethylene oxide. At the concentrations used, it was ineffective against propylene oxide and butadiene monoxide, and caused a poor yield of low molecular weight polystyrene oxide. A free radical mechanism was proposed.

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INTRODUCTION

Francis Evans, a graduate student in this laboratory, carried out a reaction between two moles of propylene oxide and one mole of di-t-butylmagnesium. He did not obtain the expected addition product which would hydrolyze to give 4,4,-dimethyl-2-pentanol. Instead, he separated a white gummy mass which was insoluble in ether, melted over a wide range and could not be distilled.

This phenomenon prompted this investigation to determine the optimum conditions for the polymerization of some epoxides with t-butylmagnesium bromide and its equilibrium products, di-t-butylmagnesium and magnesium bromide.

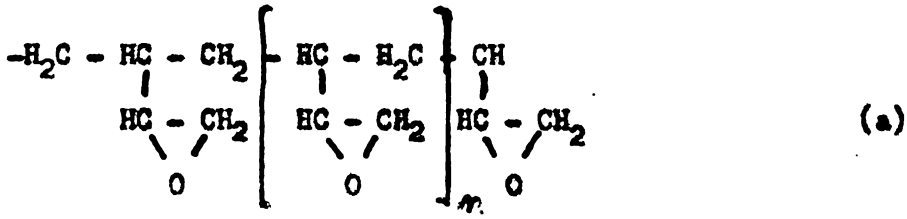
HISTORICAL

The polymerization of ethylene oxide, the simplest epoxide, was accomplished and studied by Staudinger in 1928. (1) He proposed the polymer molecule to be a linear chain with ether linkages between the individual units. Practically the same products were obtained with basic catalysts, (tertiary amines, alkali metals, etc.) and acid catalysts, (e.g. stannic chloride). The polymers were not homogeneous but were a mixture of various molecular weight homologs. By fractional precipitation the mixture was separated into polymers varying in molecular weight from 450 (a viscous liquid) to 4500 (a waxy solid). The polymers were rather stable; they decomposed only above 300° C. They were very readily soluble in organic solvents (except petroleum ether and diethyl ether) and water.

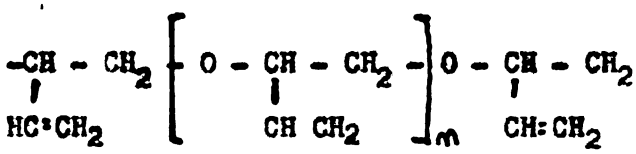
Soon after Staudinger's publication, a series of patents (2) (3) (4) (5) (6) (7) appeared on methods of polymerizing ethylene oxide. Without exception, these patents involved the use of potassium hydroxide or sodium hydroxide as catalysts. Witwer's patent (5) also takes advantage of the fact that if the solvent is a low polymer of the monomer, (e.g. diethylene glycol) further polymerization will occur to give a homogeneous product. In the United States, Carbide and Carbon Chemicals Incorporated manufactured and distributed polyethylene oxides under the trade name "Carbowax". ("Oxydwachs", German). The two principal forms are Carbowax 1000 and Carbowax 4000 (the number indicates average molecular weight) which are used in large tonnages in detergents, pharmaceuticals, and cosmetics. (8)

During his studies with ethylene oxide, Staudinger also investigated the polymerization of propylene oxide. (9) Propylene oxide polymerized under the influence of anhydrous stannic chloride with extraordinary violence. For the most part, it formed low-molecular weight polymers which were generally liquid. By fractionating, it was possible to separate a high molecular weight product which was semi-solid. This semi-solid product melted only at a high temperature and was easily soluble in benzene.

Butadiene monoxide, 3,4-epoxy-1-butene is an interesting monomer since it contains two different polymerizable groups. Thus three types of polymerization are possible; (a) exclusively through the double bond, (b) exclusively through the epoxide bond, or (c) a combination of the previously suggested means.



(a)



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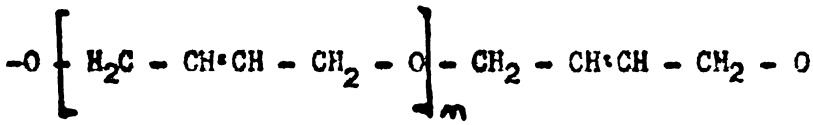


(c)

However, Bloor, in this laboratory (10) showed that butadiene monoxide was polymerizable only under conditions much more rigorous than its pseudo-diolefin characteristics would imply. He found that mass

polymerization with sodium hydroxide resulted in a polymer high in double bond content and that a sodium sand catalyst caused the formation of a polymer high in epoxide content and relatively low in unsaturation. Benzoyl peroxide, sodium formaldehyde sulfoxylate, t-butyl peroxide and zinc chloride were ineffective as catalysts while concentrated sulfuric acid caused violent polymerization and decomposition. The polymers obtained were soluble in ethyl alcohol, methyl alcohol and acetone and insoluble in ether, benzene and carbon tetrachloride.

The use of styrene oxide, 1,2-epoxyethyl benzene, as a polymerizable monomer has not been studied.

The reactions between organo-magnesium compounds and epoxides have been investigated extensively.

The investigators have shown that ethylene oxide and Grignard reagents resulted in primary alcohols. (11) (12) Substituted epoxides reacted with organo-magnesium halides to give secondary alcohols upon hydrolysis. (13) The exception was styrene oxide which gave primary or secondary alcohols depending upon the order of addition. (14)

Stevens and McCoubrey (15) and Huston and Brault (16) noted that t-butylmagnesium bromide when reacted with an epoxide gave a very poor yield of the alcohol. Huston and Brault obtained a fair yield of the bromohydrin of the epoxide and a trimer of the epoxide. They also obtained the bromohydrin by reacting the epoxide with anhydrous magnesium bromide in dry ether and hydrolyzing the precipitate.

In the reaction between epoxides and dialkylmagnesium compounds many workers have obtained gummy and resinous by-products. (17) Bartlett and Berry (18) reacted two-tenths of a mole of cyclohexene oxide

with an equivalent amount of diethylmagnesium and obtained five and one-half grams of polymer representing twenty-two percent of the starting materials. Columbic and Cottle (19) obtained 2-phenyl-1-propanol and polymer when they hydrolyzed the reaction mixture of styrene oxide and dimethylmagnesium. Huston and Tiefenthal (20) also isolated a polymeric mass when they permitted propylene oxide and di-t-butylmagnesium to react for a considerable length of time.

Grignard reagents have been investigated as catalysts for the polymerization of monomers by Beaman (21), Landler (22), and Reedel (23).

Bruylant and coworkers (24) (25) obtained large amounts of dimers and trimers when they carried out a reaction between organo-magnesium bromides and allyl cyanide.

Beaman (21) polymerized methacrylonitrile by means of butylmagnesium bromide, phenylmagnesium bromide, triphenylmethyl sodium and sodium in liquid ammonia. He obtained, from use of the Grignard reagent, a light yellow solid polymer with a molecular weight estimated at 8000.

Landler (22) polymerized methyl methacrylate with butylmagnesium bromide containing radioactive bromine. He showed that the catalyst initiated polymerization by direct action on the monomer and that termination occurred without catalyst dissociation. Both Beaman and Landler proposed ionic mechanisms for the polymerizations.

Reedel (23) achieved ethylene polymers of high molecular weight and high tensile strength by reacting ethylene with 0.005 - 5% of organometallic halides in an inert solvent such as benzene at 100° C. to 250° C. and at ethylene pressures of 400 - 1500 atmospheres.

EXPERIMENTAL

Monomers:

1. Ethylene oxide, b.p. 12° C./740 mm., obtained in cylinders from the Matheson Company.

2. Propylene oxide, b.p. 33.4 - 34.4° C./740 mm. Dow Chemical Company.

3. 3,4-epoxy-1-butene, Columbia Chemicals Division of The Pittsburgh Plate Glass Company; redistilled--b.p. 65 - 67° C./740 mm.

4. Styrene oxide, Dow Chemical Company (Technical); redistilled--b.p. 60 - 61° C./2 mm.

Reagents:

1. Tertiary butyl bromide, Eastman Kodak Company.

2. Magnesium turnings for Grignard reactions, Dow Chemical Company.

3. Anhydrous diethyl ether, C.P. dried over sodium wire for at least one week.

4. Bromine, Matheson Chemical Company.

5. 1,4-Dioxane. Eastman "Practical" was purified by the method of Fieser (26). It was kept under nitrogen and over sodium.

6. Silver nitrate, Mallinckrodt Chemical Company. Analytical Reagent.

7. Sodium thiocyanate, Mallinckrodt Chemical Company. C.P.

8. Nitrobenzene, Eastman Kodak Company.

9. Standard hydrochloric acid solution. 0.1781 N.

10. Standard sodium hydroxide solution. 0.0986 N.

Preparation of Catalyst Solutions:

1. Preparation of t-butylmagnesium bromide.

Thirty g. of clean dry magnesium turnings and 100 ml. of dry diethyl ether were placed in a dry, one liter round-bottom flask equipped with a reflux condenser, nitrogen addition tube, dropping funnel, and a mercury-sealed stirrer. The apparatus was swept with nitrogen, and while cooling in an ice bath, one mole (137 g.) of t-butyl bromide and two-hundred ml. of dry diethyl ether were poured into the dropping funnel. About five ml. of the mixture was added to the magnesium and ether in the flask and stirring was started. The reaction initiated very easily. After it had started the bromide solution was added very slowly over a period of two and one-half to three hours. The mixture was stirred in the cold for two more hours and then allowed to stand overnight.

The black solution was forced by nitrogen pressure through a tube with a glass wool plug into a nitrogen-filled bottle which was then tightly stoppered. The reagent was titrated with standard acid by Gilman's method. (27) The concentration was generally 1.2 - 1.6 M. representing a 40 - 50% yield.

2. Preparation of anhydrous magnesium bromide etherate.

Twenty-six ml. (80 g.) of bromine was added over a period of two hours to 14.5 g. of magnesium turnings in 250 ml. of dry ether. The mixture was kept under nitrogen, cooled in an ice-bath, and was well stirred. The bromine was added at such a rate as to permit gentle reflux. After addition was complete, the mixture was left standing overnight. A two layer system formed, the lower, darker one containing the bulk of the

magnesium bromide. There was also a small amount of solid precipitate. The solution was removed from the excess magnesium by forcing the liquid through a glass wool plug in a delivery tube by applying nitrogen pressure. The concentration of the $MgBr_2$ in the lower layer was found by determining the bromide ion concentration by means of the Volhard procedure. (28) The concentration of this lower phase was found to be 2.5 M.

3. Preparation of di-t-butylmagnesium solution. (29)

Three hundred ml. of freshly prepared t-butylmagnesium bromide under nitrogen was cooled in an ice bath. Seventy ml. of a solution of 50 g. of dioxane in 100 ml. of ether was added slowly with stirring and the mixture was permitted to reflux. After addition of the dioxane the thick white paste was stirred vigorously for six to ten hours. The mixture was centrifuged for fifteen minutes at 1500 rpm. If the supernatant liquid was not clear on testing, seven ml. of ether-dioxane solution was added to each bottle, and it was recentrifuged. The supernatant liquid was titrated by the Gilman (26) method and stored under nitrogen. The average concentration was 0.30 - 0.35 M. (29)

Polymerizations:

1. The reactions of epoxides with low concentrations of t-butylmagnesium bromide.*

a. The addition of t-butylmagnesium bromide to propylene oxide at atmospheric pressure (open system).

A small round-bottom flask equipped with a mercury-sealed stirrer, dropping funnel, a nitrogen inlet, and a condenser with a dry ice-acetone

* In most of the polymerizations and purifications of polymers, the various epoxides were treated alike. Thus, the procedures described are applicable for all monomers.

"finger" was cooled in an ice bath and swept with nitrogen. The required amount of propylene oxide was admitted through the dropping funnel, allowed to cool, and then the catalyst was added all at once from a pipet while the mixture was stirred vigorously. The reaction was exothermic and a white precipitate immediately formed. The mixture was stirred for twenty-four to forty-eight hours. The material in the flask was collected and the unreacted monomer was permitted to evaporate.

Yields were very low since much of the propylene oxide was lost by evaporation. Also, it was not possible to be sure that water and oxygen were excluded from the reaction. Therefore, to prevent contamination and to insure against monomer loss, it was decided to run the polymerizations in a closed system. The increased pressure of a closed system would favor formation of polymer in accordance with Le Chatelier's Principle.

b. Polymerization in a closed system.

The required amount of monomer was placed in a clean, dry pressure bottle, which was being swept with nitrogen and kept in an ice bath. The t-butylmagnesium bromide was added as rapidly as possible and the bottle was immediately capped. It was then mechanically shaken for about thirty hours at room temperature.

The best means of excluding oxygen and water from the reaction and of preventing evaporation of monomer was to add the monomer and catalyst to a pharmaceutical bottle by means of hypodermic syringes. (30) To have a true mass polymerization, the Grignard solution was injected into the nitrogen-filled bottle and the ether was removed by suction through a hypodermic needle. Then the monomer was injected all at once into the catalyst containing bottle. The bottle was mechanically shaken for about eighty hours or until polymerization was complete.

Since high pressures were built up in the bottles (especially when the monomer was ethylene oxide), the following safety precautions were taken; the flasks were well cooled during addition, glasses or goggles were worn, screens were placed around the bottles when they were not in the shaker, and a wire screen was placed over the bath containing the bottles which were being shaken. The bottles were so constructed that the rubber diaphragms could withstand considerable pressure.

2. The reactions of epoxides with anhydrous magnesium bromide etherate.

The general procedure of closed system polymerization as mentioned previously was followed. The monomer was generally added to the magnesium bromide. The reaction was vigorous.

In the equimolar reactions the following procedure for hydrolysis was followed: (31) After sixty hours shaking the bottles were cooled in ice and opened. They contained a flocculent precipitate and supernatant solvent. Fifty to 75 ml. of saturated ammonium bromide solution was added slowly with stirring. The ether solution was decanted and the magnesium hydroxide and salts were washed with three 25 ml. portions of ether. The solution and washings were combined and dried over sodium sulfate. The bromohydrin was then collected by vacuum distillation.

3. The reactions of epoxides with varying concentrations of di-t-butylmagnesium.

The previously described closed system method was followed. The reaction was not vigorous. A white cloudiness soon appeared in the solution, and if polymerization occurred it was usually evident after twelve or less hours of shaking.

Purification of Polymers

The polymer was removed from the reaction bottle and material adhering to the sides of the bottle was removed by rinsing with chloroform. A large excess of chloroform was added to the polymer until all but the inorganic material had dissolved and the solution was of a fairly low viscosity. The insoluble inorganic material was separated by centrifuging the solution for fifteen minutes at 1500 rpm and decanting. The bulk of the chloroform was distilled off. The very viscous liquid was then added with stirring to an excess of diethyl ether to precipitate the higher-molecular weight polymer fraction. The solid was collected by suction filtration or centrifuging, and the ether was driven from the liquid fraction.

Determination of Intrinsic Viscosity and Molecular Weight. (32)

Two-tenths to 0.5 g. of polymer was accurately weighed in a tared fifty milliliter volumetric flask and the flask was diluted to volume at 20° C. with the solvent. Aliquots of this solution were diluted to various concentrations between 0.1 and 2 g./100 ml. of solution.

Exactly 5 ml. of polymer solution at the above temperature was placed in the Ostwald viscometer which was immersed in the constant temperature bath. The liquid was then drawn by slight suction from an aspirator past the top mark of the viscometer. The time required for the liquid to flow between the marks was accurately measured. Viscosity readings were taken until they were constant for the solution being tested. The specific viscosities η_{sp} of four or five concentrations of the polymer solution were calculated from the equation:

$$\eta_{sp} = \frac{t_{solution} - t_{solvent}}{t_{solvent}}$$ t = time in sec.

The intrinsic viscosity $[\eta]$ was obtained by plotting η_{sp}/conc. against concentration and extrapolating to zero concentration.

The molecular weights of the ethylene oxide polymers were estimated by substituting the intrinsic viscosity in the Staudinger expression

$$[\eta] = KM$$

$$K_{benzene} = 4.1 \times 10^{-5} \qquad (9)$$

In these viscosity determinations where carbon tetrachloride was the solvent, the following expression was used:

$$[\eta] = KM + K' \qquad (32)$$

$$K_{CCl_4} = 0.83 \times 10^{-5}$$

$$K'_{CCl_4} = 0.034$$

TABLE I-A

T-Butylmagnesium bromide as a catalyst with ethylene oxide as the monomer.

Monomer		Catalyst					Insol. ether				Sol. ether				Insol. $CHCl_3$
Moles	g.	Moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)	g.	%	$[\eta]$	mol. wt. $\times 10^{-3}$	g.	%	$[\eta]$	mol. wt.	g.
1.0	44	0.05	8	34	1/0.05	80±6	1.15	2.6			28.3	65	0.021	500	8.62
0.3	13.5	0.008	1.32	5	1/0.025	>500	0.4	3	1.6	37	8.5	64	0.022	540	1.0
0.4	17.6	0.0046	0.74	10	1/0.012	80±6	6.0	34	0.035	1[c]	6.0	34	0.026	630	0.8
1.0	44	0.01	1.6	7	1/0.01	80±6	18.3	42	0.062	1.5	10	23	0.025	600	8.4
1.0	44	0.01	1.6	[a]	1/0.01	80±6	32	73	0.082	2	11	25	0.035	850	2.8
0.4	17.6	0.0023	0.37	10	1/0.006	80±6	5.9	33	0.040	1.5[c]	4.3	25	0.026	630	0.85
0.4	17.6	0.0023	0.37	5[b]	1/0.006	80±6	7.2	41	0.023	.8[c]	4.3	25	0.026	630	0.80
1.0	44	0.005	0.8	[a]	1/0.005	120±6	20.5	47	0.061	1.5	32	7	0.034	830	1.1

The temperature was maintained at 27° C. for all polymerizations except where indicated otherwise.

a. The catalyst solvent was removed by suction.

b. Half of the catalyst solvent was removed by suction.

c. CCl_4 solvent and equation (32) were unsatisfactory; the molecular weight was estimated by comparison. All other determinations were in benzene.

| | | |

TABLE I-B

T-Butylmagnesium bromide as a catalyst with propylene oxide as the monomer.[a]

Monomer		Catalyst				Insol. in ether	sol. in ether			Residue
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	g.	g.	%	[η]	g.
0.28	16.4	0.018	2.8	15	1/0.062	0	4.75	29	0.015	3.5
0.28	16.4	0.011	1.8	10	1/0.04	0	5.25	32	0.015	2.3
0.28	16.4	0.011	1.8	5[b]	1/0.04	0	6.08	37	0.015	1.8
0.56	32.8	0.010	1.6	10	1/0.018	0	4.50	13	0.011	2.8

a. The bottles containing the reaction mixture were shaken intermittantly for 200 hours.

b. Half the solvent was evaporated from the catalyst.

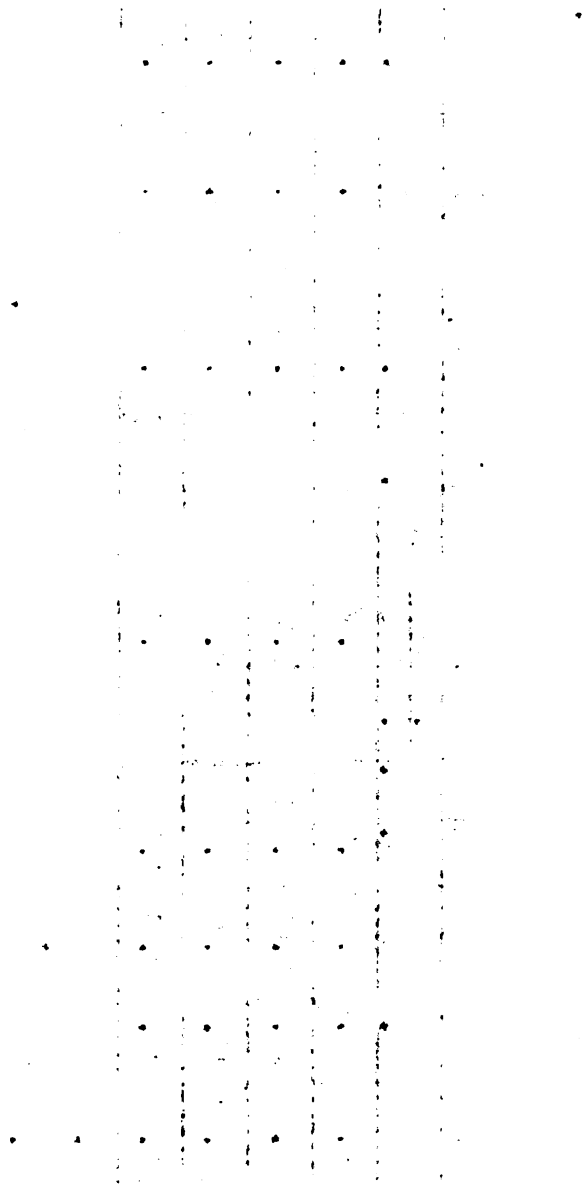


TABLE I-C

T-Butylmagnesium bromide as a catalyst with butadiene monoxide as the monomer.

Monomer		Catalyst					Insol. in ether		Sol. in ether			Residue
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time (hr)	g.	%	g.	%	$[\eta]$	g.
0.25	17.5	0.0125	2.0	8.5	1/0.05	[b]	0		6.0	34	0.025	lost
0.25	17.5	0.0125	2.0	[a]	1/0.05	80	0		17	97	0.025	1.0
0.25	17.5	0.0025	0.4	[a]	1/0.01	80	0		2.6	15		0.6
0.50	35	0.005	0.8	3.4	1/0.01	[b]	4.0	11	3.6	10	0.025	0.8

a. The ether was removed by suction.
b. The bottles containing the reaction mixture were shaken intermittantly for over 200 hours.

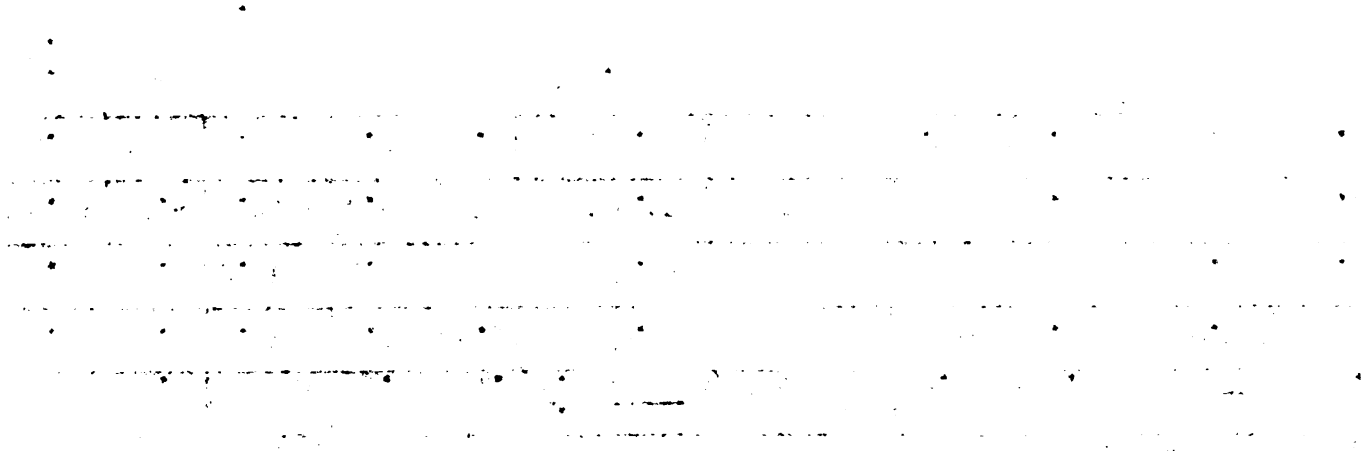


TABLE I-D

T-Butylmagnesium bromide as a catalyst with styrene oxide as the monomer.

Monomer		Catalyst					Insol. ether	Sol. ether			Insol. in $CHCl_3$
Moles	g.	moles	g.	ml.	g. monomer / g. catalyst	shaking (hr.)	g.	g.	%	[η]	g.
0.25	30	0.0125	2.0	a	1/0.05	The reaction exploded.					
0.25	30	0.0063	1.0	4.2	1/0.025	80	0	8.7	29	0.025	1.3
0.25	30	0.0025	0.4	1.7	1/0.01	80	0	7.0	23	0.021	lost
0.25	30	0.0025	0.4	a	1/0.01	70	0	6.2	21	0.020	0.2

Temp. = 27° C.
a. The ether was drawn from the catalyst by suction.

| | | |

TABLE I-D

T-Butylmagnesium bromide as a catalyst with styrene oxide as the monomer.

Monomer		Catalyst					Insol. ether	Sol. ether			Insol. in $CHCl_3$
Moles	g.	moles	g.	ml.	M. monomer / M. catalyst	shaking (hr.)	g.	g.	%	$[\eta]$	g.
0.25	30	0.0125	2.0	a	1/0.05	The reaction exploded.					
0.25	30	0.0069	1.0	4.2	1/0.025	80	0	8.7	29	0.025	1.3
0.25	30	0.0025	0.4	1.7	1/0.01	80	0	7.0	23	0.021	less
0.25	30	0.0025	0.4	a	1/0.01	70	0	6.2	21	0.020	0.2

Temp. = 27° C.
a. The ether was drawn from the catalyst by suction.

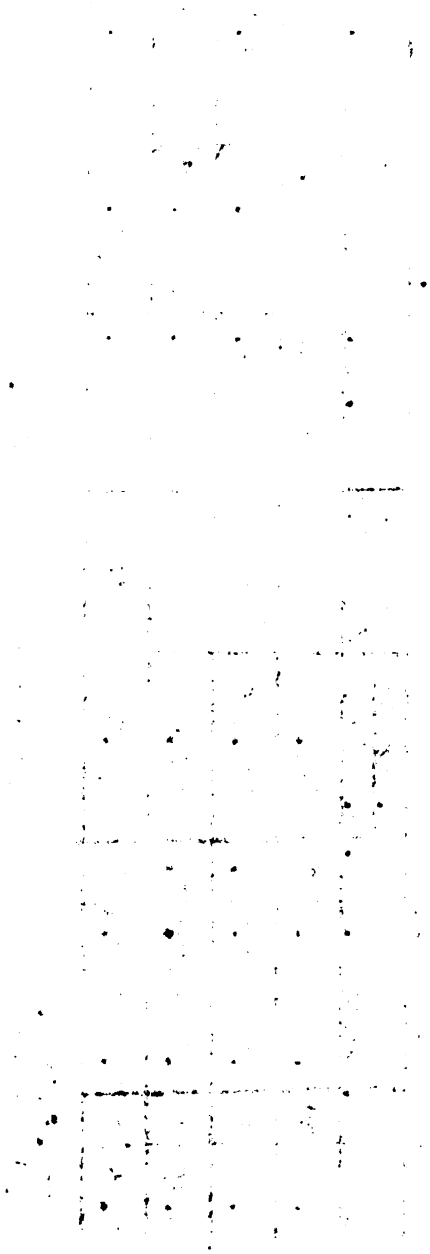


TABLE II-A

Anhydrous magnesium bromide as a catalyst with ethylene oxide as the monomer.

Monomer		Catalyst					Insol. in ether		Sol. in ether				Insol. in $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)	g.	%	g.	%	[η]	mol. wt.	g.
0.25	11	0.25	46	100	1/1	60	15g. or a 50% yield of CH_2OH-CH_2Br was obtained. b.p. = 36-38° C/2mm n_D^{20} = 1.489 n_D^{20} (lit) = 1.491						
0.5	22	0.0625	11.5	25	1/0.125[a]	80	4.5	20	11	50	0.011	270	8.45
0.5	22	0.0125	2.3	5	1/0.025[b]	60	0		20	91	0.03	730	2.6
0.5	22	0.005	0.9	2	0/0.01[b]	60	0		2.7	12	0.022	540	0.6

a. Temp. = 27°C.

b. The catalyst was added at a temperature of -70° C. and held there for twelve hours after which the bottles were shaken for fifty hours at 27° C.

TABLE II-B

Anhydrous magnesium bromide as a catalyst with propylene oxide as the monomer.

Monomer		Catalyst					Insol. in ether	Sol. in ether			Insol. in $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	Shaking time(hr)	g.	g.	%	[η]	g.
0.25	14.5	0.25	46	100	1/1	60	14g. or 40% yield of $CH_3CHOH\ CH_2Br$ was obtained. b.p.: 49-51°C./15mm.; n_D^{20}: 1.476 b.p. (lit.): 51-53°C/15mm.; n_D^{20} = 1.480				
0.50	29	0.05	9	20	1/0.1	60[a]	0	7	25	0.015	7.2
0.25	14.5	0.0125	2.3	5	1/0.05	60[b]	0	2.8	20	0.015	2.3
1.0	58	0.01	1.8	4	1/0.01	60[a]	0	0.5	<1		0.8

a. Temp.: 27° C.

b. The catalyst was added at a temperature of -70° C. which was held for 12 hours; then the bottle was shaken for 50 hours at a temperature of 27° C.

| | | |

TABLE II-C

Anhydrous magnesium bromide as a catalyst with butadiene monoxide as the monomer.

Monomer		Catalyst					Insol. ether	Sol. ether			Insol. $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time (hr)	g.	g.	%	[η]	g.
0.50	35	0.025	4.6	10	1/0.05	[a]	0	4.0	20	0.027	2.3
0.25	17.5	0.0125	2.3	[b]	1/0.05	36	0	13	70	0.025	2.0
0.25	17.5	0.005	0.9	[b]	1/0.02	36	0	6	35	0.025	0.5

a. The catalyst was added at a temperature of -70° C. which was held for 12 hours; then the bottle was shaken for 50 hours at a temperature of 27° C.
b. The ether solvent was removed by suction.

TABLE II-D

Anhydrous magnesium bromide as a catalyst with styrene oxide as the monomer.

Monomer		Catalyst					Insol. ether	Sol. ether			Insol. $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)	g.	g.	%	[η]	g.
0.25	30	0.025	4.6	10[a]	1/0.1	The reaction exploded after 5 min. shaking.					
0.25	30	0.0125	2.3	5[a]	1/0.05	76	0	18	60	0.020	1.0
0.25	30	0.005	0.92	2[a]	1/0.02	76	0	9.3	31	0.020	1.0

a. The ether solvent was removed by suction.

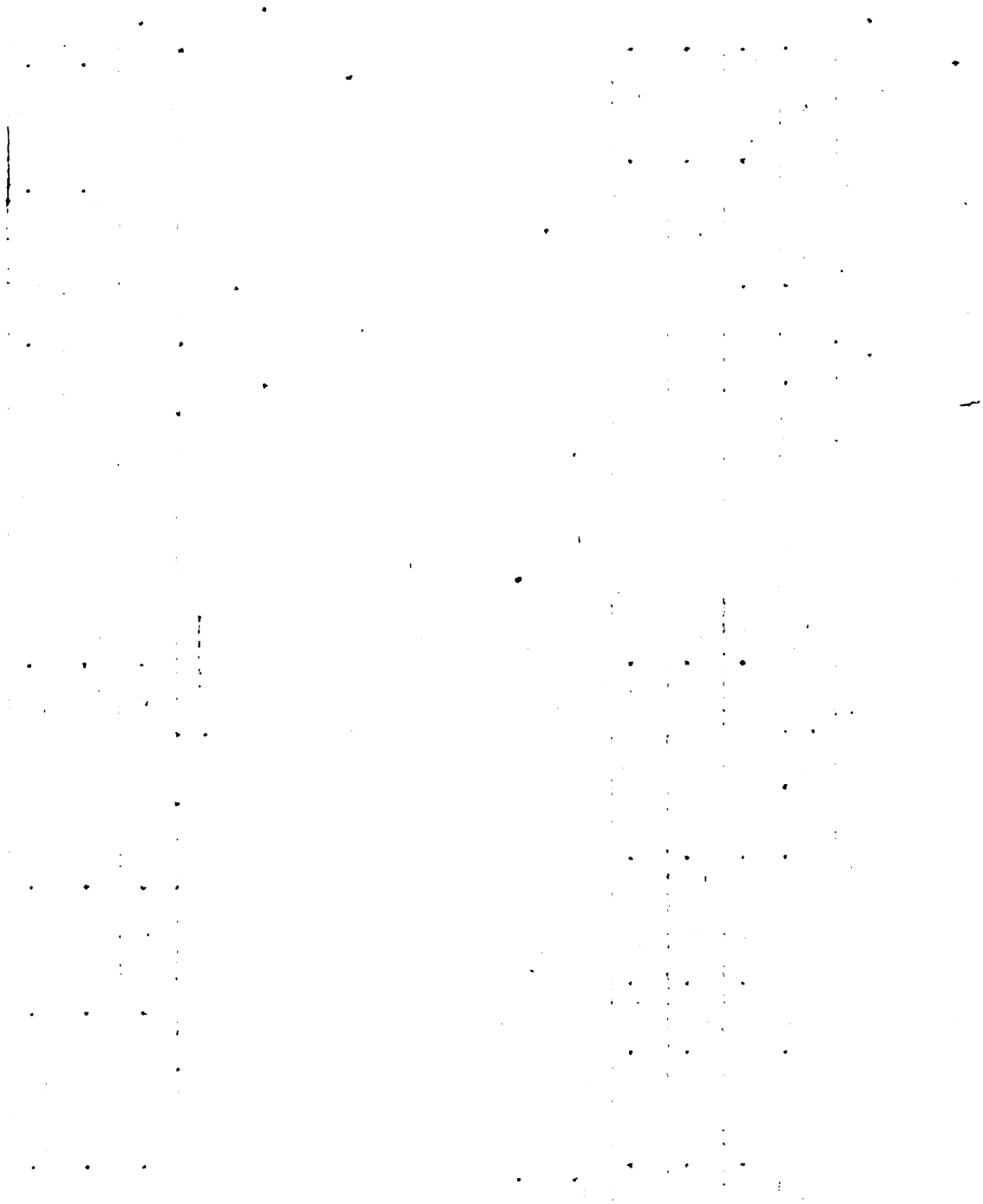


TABLE III-A

Di-t-butylmagnesium as a catalyst with ethylene oxide as the monomer.[a]

Monomer		Catalyst					Insol. ether				Sol. in ether				Insol. $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)	g.	%	$[\eta]$	mol. wt. $\times 10^{-3}$	g.	%	$[\eta]$	mol. wt.	g.
0.25	11	0.021	3	140	1/0.084	24	1.75	16	1.30	32	0.3	3			2.0
1.0	44	0.050	6.9	60	1/0.05	60	7.1	16	0.68	16.5	2.6	6	0.05	1200	4.6
0.25	11	0.0125	1.7	17	1/0.05	24	3.0	28	2.65	65	0.35	3			0.5
0.5	22	0.010	1.4	28.5	1/0.02	12	1.8	8	0.85	21	0.2	1			1.0
0.5	22	0.005	0.7	14.2	1/0.01	12	3.0	13	2.50	61	1.3	6	0.05	1200	
1.0	44	0.01	1.4	35	1/0.01	24	13.7	31	3.0	73	0.3	<1			
0.5	22	0.0025	0.35	7.0	1/0.005	12	0.8	3	0.64	15.5					0.2
0.5	22	0.0005	0.07	1.4	1/0.001	12	0.25g. total; 1% yield								
0.25	11	0.0125	1.7	[b]	1/0.05	30	4.7	43	2.00	49	3.6	33	0.013	320	1.9
0.25	11	0.005	0.7	[b]	1/0.02	30	1.5	13.5	2.10	51	2.0	18	0.015	360	0.75
1.0	44	0.01	1.4	[b]	1/0.01	80[c]	21	45	3.6	88	2.0	5			1.0
0.8	35	0.005	0.7	[b]	1/0.006	Reaction exploded.									

a. The temperature for all polymerizations was 27° C.
b. The catalyst solvent was removed by suction.
c. Polymerization appeared to be complete after shaking for approximately 24 hours.

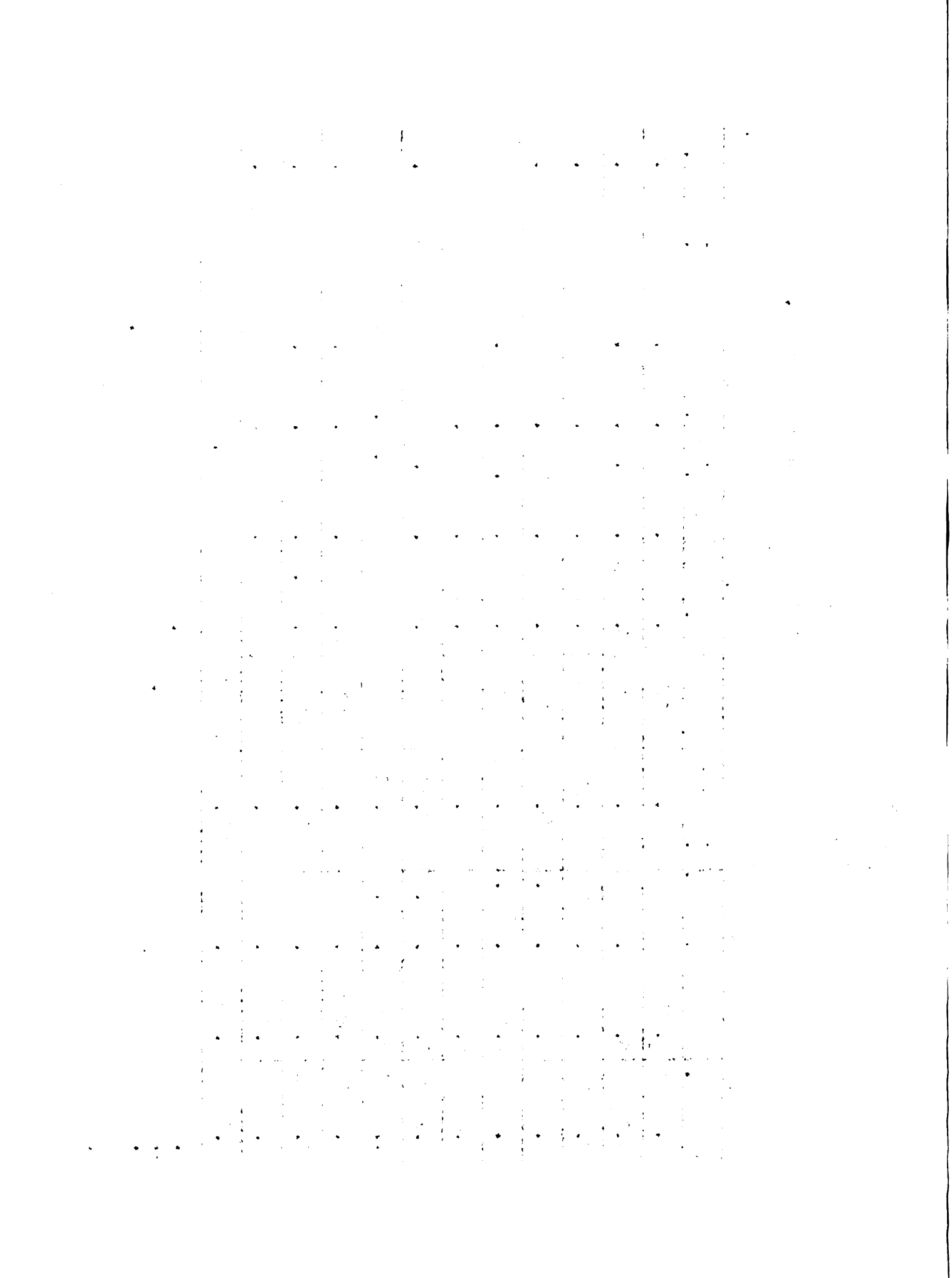


TABLE III-B

Di-t-butylmagnesium as a catalyst with propylene oxide as the monomer.

Monomer		Catalyst						
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)		
0.25	14.5	0.005	0.69	14.8	1/0.02	120	Total yield	: 1.6g.
0.25	14.5	0.0025	0.35	7.5	1/0.01	120	Total yield	. 0.6g.
0.25	14.5	0.00125	0.17	3.8	1/0.005	120	Total yield	. 0.3g.
0.25	14.5	0.00025	0.03	0.8	1/0.001	120	Total yield	: 0.2g.

TABLE III-C

Di-t-butylmagnesium as a catalyst with butadiene monoxide as the monomer.

Monomer		Catalyst					Insol. ether	Sol. ether		Insol. $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time(hr)	g.	g.	%	g.
0.25	17.5	0.0125	1.7	37.5	1/0.05	48	0	1.3	7.5	2.8
0.25	17.5	0.0050	0.7	[a]	1/0.02	48	0	1.1	6.3	0.3
0.25	17.5	0.0025	0.35	[a]	1/0.01	48	Total yield = 0.5g.			

a. The catalyst solvent was drawn off by suction.

TABLE III-D

Di-t-butylmagnesium as a catalyst with styrene oxide as the monomer.

Monomer		Catalyst					Insol. ether		Sol. ether			Insol. $CHCl_3$
Moles	g.	moles	g.	ml.	m. monomer / m. catalyst	shaking time (hr)	g.	%	g.	%	$[\eta]$	g.
0.25	30	0.0125	1.7	36.3[a]	1/0.05	48	3.7	12	9.5	32	0.021	0.25
0.25	30	0.0025	0.35	7.2[a]	1/0.01	48	Total yield = 2.0 g.					
0.25	30	0.0025	0.35	7.2	1/0.01	48	0		1.2	4	0.020	0.35

a. The catalyst solvent was drawn off by suction.

RESULTS

1. Results from the use of t-butylmagnesium bromide catalyst.

There was a very poor yield of a red oil from the open system reaction between propylene oxide and t-butylmagnesium bromide. This procedure was supplanted by the closed system method of polymerization.

Ethylene oxide polymerized most readily and yielded a semi-solid paste or waxy solid depending upon the amount of solvent and catalyst concentration. This material was fractionally precipitated into an ether-soluble viscous liquid and an ether-insoluble waxy solid. In benzene, the liquid fraction had an intrinsic viscosity of 0.02 to 0.03, proportional to a molecular weight of 500 to 650. The solid fraction had an intrinsic viscosity in benzene of 0.06 to 0.08, proportional to a molecular weight of 1500 to 2000. These polymers were readily soluble in water, dioxane, alcohol, benzene, and chloroform; they were sparingly soluble in acetone and carbon tetrachloride. Of course, high molecular weight fractions were insoluble in diethyl ether and petroleum ether.

Propylene oxide yielded primarily an ether-soluble liquid polymer fraction with an intrinsic viscosity of 0.015. It was sparingly soluble in water and dissolved readily in most organic solvents except petroleum ether.

Butadiene monoxide formed an extremely viscous, dark, semi-liquid polymer which was soluble in ethyl alcohol, chloroform, and acetone, slightly soluble in carbon tetrachloride and benzene, but insoluble in petroleum ether and water. The polymer was purified by dissolving it in ether. The unreacted monomer was distilled from the ether solution.

Polyoxystyrene in 25 to 30% yield with an intrinsic viscosity of 0.02 was produced when t-butylmagnesium bromide was used as catalyst. When more than 0.05 mole of catalyst was used per mole of monomer, the reaction became uncontrollable. All three catalysts gave very similar polymers of styrene oxide. They were all very viscous yellow gums with an intrinsic viscosity of 0.02 and were soluble in ether, benzene, and chloroform, and insoluble in water and petroleum ether. A very small amount of higher molecular weight polymer was formed from this monomer when di-t-butylmagnesium was used as catalyst.

2. Results from the use of magnesium bromide catalyst.

When magnesium bromide was used as a catalyst for epoxide polymerization, considerable difficulty was encountered in containing the reaction when the catalyst concentration was beyond 0.05 moles per mole of monomer.

A red, viscous, ether soluble liquid was obtained with ethylene oxide. The intrinsic viscosity was rather low (0.01 - 0.03) and was proportional to a molecular weight of 300 to 700. Like the other liquid polymers formed in this work, the material could not be distilled even at 150° C. and 2 mm. mercury. It was not very soluble in water. A 50% yield of ethylene bromohydrin was obtained from equimolar reaction.

The propylene oxide polymer produced with anhydrous magnesium bromide etherate was similar in appearance to the polymer from the action of t-butylmagnesium bromide. The intrinsic viscosities were identical. A 40% yield of the bromohydrin was obtained from equimolar reaction of propylene oxide and magnesium bromide.

Polybutadiene monoxide produced by means of magnesium bromide catalyst was similar in appearance, solubility, and viscosity to those butadiene

monoxide polymers produced by the action of t-butylmagnesium bromide. The yield was increased if the solvent was removed from the catalyst.

3. Results from the use of di-t-butylmagnesium catalyst.

Polyethylene oxides of a very high molecular weight were obtained in a short time when ethylene oxide was added to di-t-butylmagnesium. The ether insoluble polymer was a tough, white, fibrous material resembling crude cellulose acetate. It had an intrinsic viscosity in benzene of 0.6 - 3.6 which represents a molecular weight of 16,000 to 90,000. The polymer was soluble in water, chloroform, benzene, and dioxane and insoluble in carbon tetrachloride, acetone, diethyl ether and petroleum ether. A very small amount of ether soluble liquid was obtained. Its intrinsic viscosity was 0.05 (molecular weight = 1200.)

No polymers of propylene oxide were obtained when di-t-butylmagnesium was used as a catalyst. Higher catalyst concentrations should have been tried.

Poor yields (6 - 7%) of ether soluble polymer of butadiene monoxide were isolated when di-t-butylmagnesium was used as a catalyst.

In almost all cases it was noted that the polymer yield was increased when the catalyst solvent was removed before monomer addition.

DISCUSSION

1. Optimum conditions for polymerization.

a. Tertiary butylmagnesium bromide as catalyst.

The polymers of ethylene oxide most clearly illustrated the effect of varying polymerization conditions, such as type of catalyst, catalyst concentration, solvent effect and polymerization time.

When t-butylmagnesium bromide in ether was used against ethylene oxide the total yield was 66 - 68% between catalyst concentration of 0.6 - 5.0 moles per mole of monomer. However, the amount of ether-soluble low molecular weight polymer increased and the amount of ether-insoluble polymer decreased with increasing catalyst concentration.

The molecular weight of the ether-soluble polymer does not appear to be dependent upon catalyst concentration. No generalization can be made concerning the effect of catalyst concentration on the ether-insoluble polymers since different solvents were used for viscosity measurements.

When the monomer was added to the dry catalyst and shaken, the yield increased considerably. When the monomer-catalyst ratio was greater than 1/0.01 the polymerization was quantitative with the higher molecular weight polymer predominating.

Propylene oxide was polymerized by the action of t-butylmagnesium bromide to give a thirty to forty percent yield of a viscous red oil. (9) Preliminary experiments indicated that catalyst concentrations greater than 0.1 mole per mole of monomer resulted in little or no polymer. Instead the yield appeared to increase with decreasing catalyst concentration. The optimum catalyst concentration under the experimental

conditions set forth in Table I-B was between 0.04 and 0.1 of a mole per mole of monomer. The molecular weight ([η] = 0.015) did not appear to be dependent upon catalyst concentration.

The optimum catalyst concentration for the polymerization of butadiene monoxide is about five mole percent. Higher catalyst concentrations caused almost explosive polymerization with considerable decomposition. Poor yields were obtained when solvent was present, but true mass polymerization resulted in a quantitative yield.

The polymers of styrene oxide obtained by means of t-butylmagnesium bromide were all ether soluble and of very nearly the same intrinsic viscosity. Since this was the case, molecular weight did not seem to be a function of the catalyst concentration. The optimum catalyst concentration appeared to be between 0.02 and 0.05 of a mole of catalyst per mole of monomer. The reaction was very vigorous above a catalyst concentration of five mole percent.

b. Anhydrous magnesium bromide as catalyst.

The optimum catalyst concentration for the production of the low intrinsic viscosity polymer from ethylene oxide appears to be in the neighborhood of three mole percent. Polymerization in the cold may have had some effect in causing a higher molecular weight polymer; but since this polymerization factor was not intensively investigated, it is not at all certain whether this is the case. The decreased water solubility compared to other ethylene oxide polymers was probably due to bromine end groups on the polymer chains. (9)

The best catalyst concentration for the production of polypropylene

oxide by means of magnesium bromide was between 0.05 and 0.1 moles $MgBr_2$ per mole of monomer.

A true mass polymerization and a catalyst concentration near five mole percent appeared to be the best conditions for the polymerization of butadiene monoxide and styrene oxide by the action of magnesium bromide.

c. Use of di-t-butylmagnesium as catalyst.

The highest yield of high molecular weight polyoxyethylene was obtained at 0.01 or 0.05 of a mole of catalyst per mole of monomer. When the solvent was removed the same catalyst concentration produced still higher yields. The time required for polymerization was much shorter than when t-butylmagnesium bromide was used as a catalyst. A satisfactory shaking period seemed to be around twenty-four hours. The intrinsic viscosity roughly increased with decreasing catalyst concentration. Also, a considerable amount of ether-soluble low molecular weight polymer resulted from the true mass polymerization. The amount decreased with decreasing catalyst concentration.

Propylene oxide and butadiene monoxide did not polymerize at the catalyst concentrations used. Higher catalyst concentrations using the solvent evaporating technique should be tried.

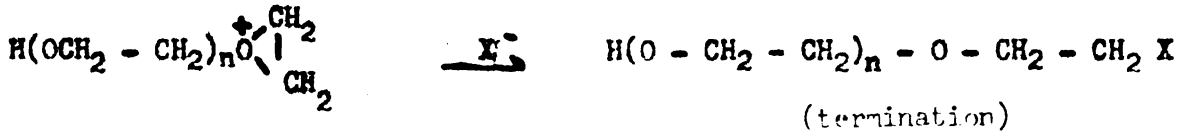
Effective polymerizations of styrene oxide with di-t-butylmagnesium would require a monomer-catalyst ratio greater than 1:0.05. It is interesting to note that polyoxystyrene produced by the use of di-t-butylmagnesium had the same intrinsic viscosity as polyoxystyrene produced by the use of t-butylmagnesium bromide, while the corresponding ethylene oxide polymers differed remarkably in that respect.

2. Possible mechanisms of polymerization.

The strained three-membered ring and the two lone pairs of electrons on the oxygen atom should be expected to give the epoxide group some chemical properties similar to those of the double bond. One of these properties is the tendency toward polymerization.

Thus, like olefins, epoxides should be polymerized both by free radical and by ionic reactions. Though these two types of polymerization reactions may be represented in quite different ways, they both operate by bringing about the addition of a univalent group to one end of a molecule, and thereby generate a univalent free radical, or free ion, whereby the addition process can be continued.

Both types occur by means of a chain reaction consisting of three main steps: initiation, propagation, and termination. The polymerization of ethylene oxide with acid catalysts such as sulfuric acid, aluminum chloride or stannic chloride probably proceeds as follows: (33)



The homolytic or free radical polymerization of ethylene oxide probably occurs in a manner analogous to the polymerization of olefins.

First, a free radical is formed from the catalyst (e.g. from a metal alkyl or organic peroxide) :

$$(C_2H_5)_4Pb \longrightarrow 4\,C_2H_5^{\bullet} + Pb$$

$$C_6H_5\text{-}CO\text{-}O\text{-}O\text{-}CO\text{-}C_6H_5 \longrightarrow 2\,C_6H_5^{\bullet} + 2CO_2$$

$$R^{\bullet} + \underset{\diagdown\,O\,\diagup}{CH_2 - CH_2} \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}O^{\bullet}$$

(initiation)

$$RCH_2\text{-}CH_2\text{-}O^{\bullet} + \underset{\diagdown\,O\,\diagup}{CH_2 - CH_2} \longrightarrow RCH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O^{\bullet}$$

(propagation)

$$R(CH_2\text{-}CH_2\text{-}O)_nCH_2\text{-}CH_2O^{\bullet} + R^{\bullet} \longrightarrow R(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_2\text{-}CH_2OR$$

(termination)

It is evident that polymerization caused by magnesium bromide etherate is ionic in nature. In the light of the work of Ribas and Tapia (34), and Huston and Agett (35), it probably proceeds thus:

$$Mg^{++} + 2\,\underset{\diagdown\,O\,\diagup}{CH_2 - CH_2} \longrightarrow Mg(OCH_2\text{-}CH_2)_2^{++}$$

(initiation)

$$Mg(OCH_2\text{-}CH_2)_2^{++} + 2n\,\underset{\diagdown\,O\,\diagup}{CH_2 - CH_2} \longrightarrow Mg\left[OCH_2\text{-}CH_2\text{-}(OCH_2\text{-}CH_2)\right]_2^{++}$$

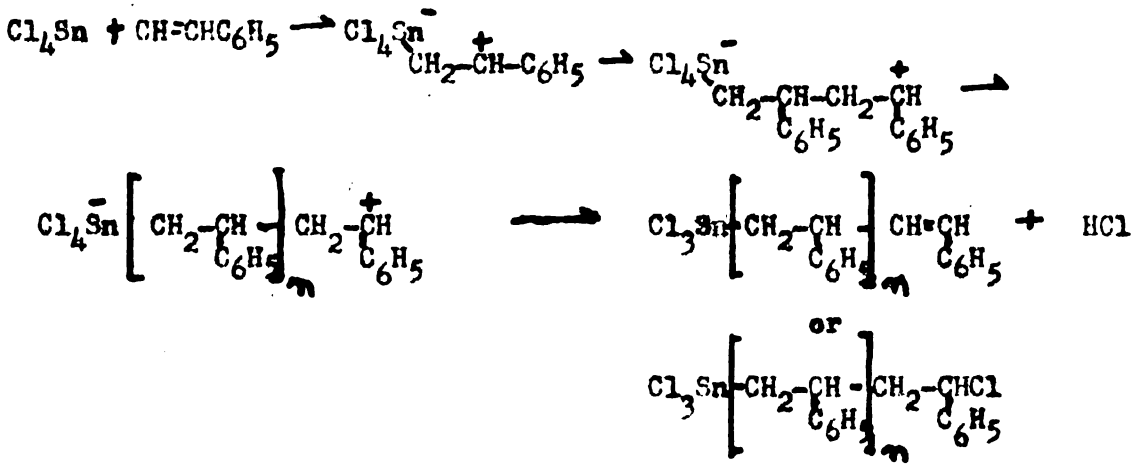
(propagation)

$$Mg\left[OCH_2\text{-}CH_2\text{-}(OCH_2\text{-}CH_2)_n\right]^{++} + 2\,Br^{-} \longrightarrow Mg\left[(OCH_2\text{-}CH_2)_n\text{-}OCH_2\text{-}CH_2\text{-}Br\right]_2$$

(termination)

In cation-catalyzed polymerization the presence of the catalyst in the molecule attached by a coordinate valence as an organometallic compound is indicated by Staudinger's observation (9) that polystyrene prepared with stannic chloride as the catalyst is difficult or impossible to

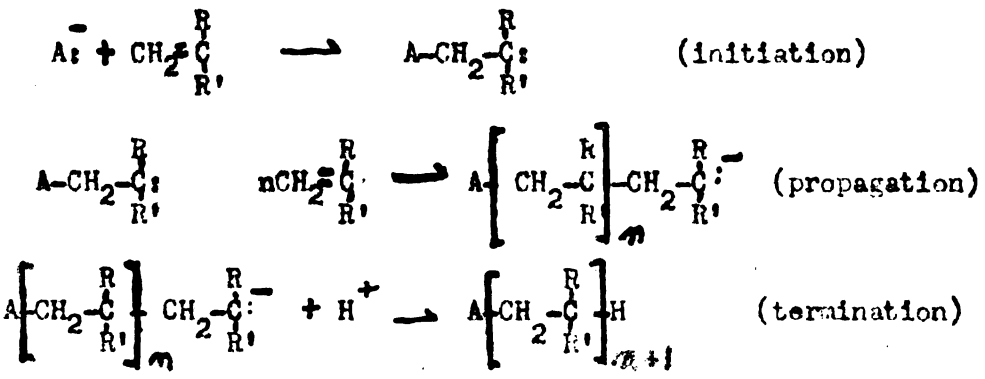
free from catalyst by precipitation from inert solvents, but the use of alcohol readily frees the polymer from tin and chlorine. This could readily be accounted for according to this formulation:



since the organometallic end group would undergo scission in a solvent containing active hydrogen, and the $SnCl_3$ group would be replaced by hydrogen. (33) The difficulty encountered in purifying the magnesium bromide-catalyzed polymers is also explainable by the preceding types of mechanism. This cationic mechanism is further verified by the fact that only low molecular weight polymers were produced. This is a distinguishing characteristic of ionically initiated polymerizations.

The type of mechanism involved in the polymerization with t-butylmagnesium bromide and di-t-butylmagnesium is not so simply ascertained. The differences in molecular weight observed in the various types of polyethylene oxides indicate that the reactions must have proceeded by different mechanisms.

Beaman (21) proposed an anionic mechanism for the polymerization of methacrylonitrile by means of butylmagnesium bromide, triphenylmethyl sodium and sodium in liquid ammonia.



(initiation)

(propagation)

(termination)

(A: = initiating negative fragment, e.g. $Ph_3C:^-$)
(R = Electron withdrawing group)
(R' = H or some other substituent)

(The termination reaction may occur in some other manner, such as elimination of $A:^-$.)

He assumed that the ionic nature of the Grignard reagent and of triphenylmethyl sodium made it seem highly unlikely that these reagents should react by homolytic cleavage to yield free radicals in the presence of highly polar monomers. Immediate and quantitative polymerization of methacrylonitrile in liquid ammonia offered more direct evidence for an anionic mechanism. He also surmised that if the reaction were free radical, butadiene and styrene would be expected to polymerize readily. The failure to obtain any polybutadiene and only low molecular weight polymer from styrene can be explained from the point of view of the anionic mechanism because of of the relatively weak electronegative character of a vinyl or phenyl group.

Application of an anionic mechanism to the polymerization of epoxides with t-butylmagnesium bromide seems applicable in light of the results of this research. Ethylene oxide is particularly noteworthy. It is highly polar with two lone pairs of electrons at the oxygen atom. This would result in carbon atoms of an electrophilic nature. The analogous mechanism

can be written thus:

$$(CH_3)_3C:^- + \overbrace{CH_2(\delta+)-CH_2(\delta+)-O}:^{\ominus} \rightarrow (CH_3)_3-CH_2-CH_2-O^-$$

$$(CH_3)_3C-CH_2-CH_2-O^- + n\ \overbrace{CH_2-CH_2-O} \rightarrow (CH_3)_3C(CH_2-CH_2-O)_nCH_2-CH_2-O^-$$

$$(CH_3)_3C-(CH_2-CH_2-O)_n-CH_2-CH_2-O^- + H^+ \rightarrow (CH_3)_3C-(CH_2-CH_2-O)-H$$

The low molecular weight of the products obtained is typical of ionically catalyzed polymerizations. Higher molecular weight products in greater yield than magnesium bromide catalyzed polymers is evidence against the cation-type mechanism. The less satisfactory results from the use of the other monomers may possibly be due to their lower polarity.

The very high molecular weight of the polymers obtained by the use of di-t-butylmagnesium on ethylene oxide seems to indicate that polymerization may have occurred by a mechanism different from that with the full Grignard.

A free-radical catalysis may have been possible since the t-butyl radical has a low free energy of formation. (36) In the absence of highly ionized magnesium bromide, this free radical formation may have taken precedence over the ionization of the alkyl. (see p. 30.)

This work is only an introduction to the subject of polymerization of epoxides by means of Grignard reagents. The results indicate that further investigations into this field should be quite worthwhile. The effects of varying temperature, pressure, and solvent concentration should be studied. The effects of higher concentrations of catalysts should be determined for those epoxides which are not readily polymerized at lower catalyst concentrations. The structure of the polymers of butadiene

monoxide would be another interesting problem. (See page 3.)

As the search for new monomers is a never-ending project, so the quest for new and different polymerization initiators will always continue as long as the desire for polymers with special properties is high.

* * * * *

SUMMARY

1. Tertiary butylmagnesium bromide, magnesium bromide etherate, and di-tertiary butylmagnesium were investigated as possible catalysts for the polymerization of certain epoxides (ethylene oxide, propylene oxide, butadiene monoxide and styrene oxide).

2. Tertiary butylmagnesium bromide was found to be an excellent catalyst for the production of low molecular weight polymers of ethylene oxide. Poorer yields of polymers were obtained when propylene oxide, butadiene monoxide, and styrene oxide were the monomers.

3. Magnesium bromide produced fair yields of low molecular weight polymers from all the epoxides used.

4. Di-tertiary butylmagnesium effected the production of high molecular weight polymers of ethylene oxide. At the concentrations used, it was ineffective against propylene oxide and butadiene oxide and caused a poor yield of low molecular weight polyoxystyrene.

5. The optimum catalyst concentrations were determined, and the effect of solvent was studied.

6. Possible polymerization mechanisms were discussed.

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