

Poly(oxatetramethylene) Glycol. I. Influence of Water on Polymerization Catalysis

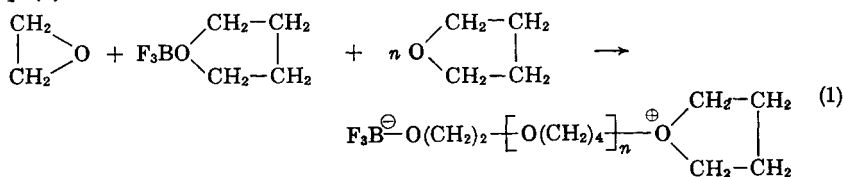
PETER R. JOHNSTON, *Chemstrand Research Center, Durham, North Carolina*

Synopsis

Tetrahydrofuran (THF) was polymerized with cocatalysts of ethylene oxide (EO) and BF_3 , using THF as the solvent. The yield of polymer, based on the amount of catalyst, was very low. With water present (0.5 mole per mole of BF_3 and EO) the yield increased fourfold. Polymerization was stopped by the addition of a large amount of water; the addition of water also provided the polymer with terminal hydroxyl groups. The polymer had a molecular weight of 1000 and was a clear, colorless, viscous liquid.

INTRODUCTION

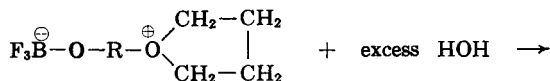
Tetrahydrofuran (THF) can be polymerized to poly(oxatetramethylene glycol). Reviews of THF polymerization have been provided by Delfs¹ and, more recently, by the discoverer, Meerwein.² To obtain a polymer with terminal hydroxyl groups, they state that polymerization should be accomplished by use of a mixture of ethylene oxide (EO) and BF_3 , as shown in eq. (1).

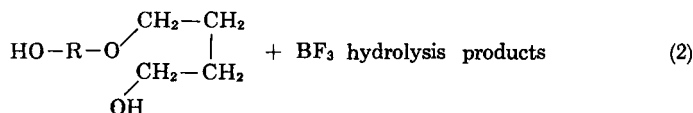


Boron trifluoride alone does not initiate polymerization.

However, only Murbach and Adicoff³ have supplied any experimental details, but they included EO in the same molar quantities as THF. They stopped the reaction by adding excess ethylene glycol, which replaced the BF_3 and left a polymer with terminal hydroxyl groups. In this manner they produced a copolymer.

It was the purpose of the present investigation to prepare a (1000 molecular weight) homopolymer by using EO in the same molar quantities as BF_3 and by using water to stop the reaction, as shown in eq. (2).





EXPERIMENTAL

Procedure

In polymer preparations the following amounts of materials were generally used: tetrahydrofuran (THF), 144 g. (2.00 moles); ethylene oxide (EO), 4.4 g. (0.10 mole); BF_3 -THF complex, 13.9 g. (0.10 mole). About two-thirds of the THF was mixed with the EO and placed in a flask that was immersed in a cooling bath and equipped with stirrer and thermometer. The remaining third of the THF was mixed separately with the BF_3 complex. Both solutions were cooled to -5°C ., after which the BF_3 solution was added to the EO solution as quickly as possible. The reaction mixture was held at -5°C . for 17 min. Reaction was stopped by adding 150 ml. of water. Unreacted THF was removed by distillation, after which 100 ml. of benzene was added to dissolve the polymer and to make easier the separation of the water. The benzene-polymer solution was washed two more times with water. The last traces of water and benzene were removed by use of a rotating vacuum flask heated with steam. The polymer was clear and colorless, had a viscosity of 5-10 cpoise at room temperature, and had a molecular weight of 1000.

All of the polymer preparation reported here followed this procedure with the exception that the amounts of EO and BF_3 were different from run to run, and in some runs, water was added in catalytic amounts to the THF-EO solution.

Materials Used

Tetrahydrofuran. Eastman White Label or du Pont technical grade THF was distilled from sodium hydroxide pellets or from lithium aluminum hydride. Polymerization results were identical with either technique. THF distilled from the completed reaction mixture contained about 8% water. The water content of this recovered THF was reduced to less than 0.08% by redistillation from sodium hydroxide pellets. This THF polymerized as efficiently as fresh THF that had been distilled from NaOH or LiAlH_4 .

Boron Trifluoride-Tetrahydrofuran Complex. According to the procedure of Osthoff,⁴ gaseous BF_3 (Matheson Co.) was passed into tetrahydrofuran until the solution became saturated as evidenced by white fumes escaping. The brown mixture obtained was distilled (b.p. 70°C . at 5 mm. Hg) to obtain a colorless, viscous liquid.

Ethylene Oxide. Ethylene oxide (Matheson Co.) was used without purification. In some experiments the gaseous ethylene oxide was condensed in a cold trap and the liquid was weighed out and added to the re-

action mixture. In other runs gaseous material was added to cold tetrahydrofuran, the increase in weight giving a measure of the amount of ethylene oxide that was added. The solution was stored at 0°C.

Analytical Methods

The water content of tetrahydrofuran was determined by gas chromatographic analysis by use of a column of Apiezon L (hydrocarbon) on Chromosorb W (silica) at 50°C.

The molecular weight of the polymer was determined from the concentration of hydroxyl groups (assuming two groups per molecule). The hydroxyl group concentration was measured by acetylation in pyridine.⁵ This method of measuring molecular weight gave results identical with those obtained from the boiling point depression of benzene, thus indicating that the polymer did contain terminal hydroxyl groups.

The intrinsic viscosity was measured in benzene solutions at 30°C. The relation between the intrinsic viscosity and molecular weight was not significantly different from what Murbach and Adicoff³ have already reported:

$$[\eta] = 2.9 \times 10^{-4} M^{0.74}$$

RESULTS AND DISCUSSION

In the absence of added water, polymerization reproducibility was poor, and essentially the same amount of polymer of 1000 molecular weight was obtained regardless of the amount of ethylene oxide and BF_3 used, even when the amount of these cocatalysts varied tenfold. These results are shown in Table I. In addition, the yield of polymer was very low. For example, when 100 moles of THF are mixed with 1 mole of BF_3 , in the presence of EO, a polymer of 1000 molecular weight will be obtained when 14 moles of THF have been consumed (molecular weight of THF is 72; $72 \times 14 = 1008$). Thus it is expected that 14% of the charge should result in polymer. The amount of polymer should increase according to the increase in the amount of BF_3 (and ethylene oxide) present.

Obviously some very important, but uncontrolled, variable was not recognized, for example, changes in the small amount of water present. In the two runs where 10 moles of BF_3 and 10 moles of EO were present, for each 100 moles of THF, 8% of the charge was recovered as polymer in one run while 35% of the charge was recovered as polymer in the other. In the run with the high yield the two separate portions of the reaction mixture had been chilled to reaction temperature but not mixed because of some difficulty with the apparatus. During this delay it is likely that moisture was absorbed from the atmosphere and it was this moisture that gave rise to the increase in yield. These results prompted deliberate addition of water to the reaction mixture.

When water was deliberately added to the reaction mixture the yield of polymer increased fourfold. Table II shows that when 5 moles of EO and

TABLE I
Yield of Poly(oxatetramethylene) Glycol
When No Water was Added

Ethylene oxide, moles/100 moles THF	BF ₃ -THF complex, moles/100 moles THF	M.W. of polymer ^a	Charge recovered as polymer, wt.-% ^b
0.5	1	920	3.0
0.5	1	1150	3.7
1	1	1300	7.4
1	1	1100	6.5
1	1	1200	7.4
2	1	900	3.4
2	1	1050	6.7
2	1	650	6.3
10	1	1100	7.4
5	5	1100	6.5
5	5	1200	6.6
5	5	720	10.8
10	5	930	7.4
10	10	800	8.1
10	10	1200	35.0

^a Determined from —OH (endgroup) analysis.

^b Weight of charge does not include the weight of BF₃ in the BF₃-THF.

5 moles of BF₃ were present for each 100 moles of THF, in the absence of water, the weight of recovered polymer amounted to 6–10% of the charge. However, when the amount of water added was 2.8 moles, the yield of polymer increased to 23–26%. When more water was added, the yield was less. However, even with water present the yield is much lower than would be expected. The reasons for such low yields are not clear.

TABLE II
Yield of Polymer When Water Was Added
to Reaction Mixture

Water, moles/100 moles THF, 5 moles BF ₃ -THF, and 5 moles EO	M.W. of polymer	Charge recovered as polymer, wt.-%
0	1100	6.5
0	1200	6.6
0	720	10.8
0.14	1050	8.7
1.4	1200	21.2
2.8	1400	25.7
2.8	1300	22.6
2.8	1300	25.5
5.0	1100	17.4

CONCLUSIONS

When tetrahydrofuran is polymerized by the use of the ethylene oxide and boron trifluoride with an excess of THF as solvent, the yield of polymer is very low. With water present as a third catalyst component the yield of polymer is increased many-fold; however, the increased yield is still lower than desirable. If an excess of water is added to stop the reaction, a polymer is obtained with terminal hydroxyl groups. This polymer which is of 1000–3000 molecular weight, is useful in the preparation of high molecular polyesters and polyurethanes suitable for spinning into synthetic fibers.

References

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Résumé

Tetrahydrofurane (THF) a été polymérisé avec l'oxyde d'éthylène (EO) et BF_3 comme co-catalyseurs. THF était le solvant. Le rendement du polymère était très bas, mais pouvait être augmenté jusqu'à quatre fois sa valeur initiale par addition d'un peu d'eau (0.5 mole pour 1 mole BF_3 et EO). La polymérisation s'arrête quand la quantité d'eau ajoutée est grande. Dans ce cas le polymère est terminé par des groupes OH. Le polymère dont le poids moléculaire est égal à 1000 était un liquide clair, incolore et visqueux.

Zusammenfassung

Tetrahydrofuran (THF) wurde in THF mit Äthylenoxyd (EO) und BF_3 als Cokatalysatoren polymerisiert. Die Polymerausbeute pro Mol Katalysator war sehr gering, konnte aber durch Zusatz von etwas Wasser (0,5 Mol pro Mol BF_3 und EO) auf das Vierfache gesteigert werden. Bei Anwesenheit grösserer Mengen von Wasser kommt die Polymerisation zum Stillstand. In diesem Fall hat das Polymere Hydroxylendgruppen. Das Polymere vom Molekulargewicht 1000 war eine klare farblose viskose Flüssigkeit.

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