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Poly(oxatetramethylene) Glycol. II. Molecular Weight Distribution

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Synopsis

Polymer of 1200 molecular weight was prepared from tetrahydrofuran by using a catalyst mixture of ethylene oxide, BF_3, and water. Fractionation was accomplished by washing a cyclohexane-toluene solution with mixtures of methanol and water. Results, plotted on Poisson probability paper, showed that the distribution is somewhat broader than the Poisson.

INTRODUCTION

Poly(oxatetramethylene) glycol is prepared from tetrahydrofuran (THF), $\overline{\text{O(CH}_2)_4}$. Delfs[1] and Meerwein[2] have described the polymerization mechanism when ethylene oxide (EO) and BF_3 are used as cocatalysts. From such a polymerization mechanism it is expected[3] that the molecular weight distribution should follow the Poisson distribution.

Part I[4] shows how there was a large increase in yield of polymer when water was present as a third catalyst component. These results raise the question as to whether or not the polymer still had a Poisson distribution. Therefore, polymers prepared with a catalyst mixture of EO, BF_3, and water have been fractionated in order to determine the molecular weight distribution.

EXPERIMENTAL

Polymer Preparation

The general method of polymer preparation is described in Part I.[4] The polymers that were fractionated were prepared from the following amounts of materials: tetrahydrofuran (THF), 2700 g. (3.75 moles); ethylene oxide (EO), 82 g. (1.9 moles); water, 17 g. (0.9 mole); BF_3-THF complex, 262 g. (1.9 moles). Reaction was carried out at -5°C. for 17 min.; 750 g. of polymer was obtained with a molecular weight of 1200 (according to OH analysis, and boiling point depression in benzene).

Polymer Fractionation

Two separate polymers (of identical molecular weight) were fractionated by the method of Case.[5] Polymer (80 g.) was dissolved in a mixture of 900 ml. of cyclohexane and 100 ml. of toluene. This solution was shaken for 15 sec. with separate, one-liter portions of water–methanol solutions in which the methanol concentration increased from 20 to 90 vol.-% in 10% steps. The solvents were removed from the polymer fraction by evaporation in a rotating vacuum flask using steam heat.

The molecular weight of each fraction was obtained from the hydroxyl (endgroup) concentration as determined by acetylation in pyridine.

RESULTS AND DISCUSSION

In order to compare the molecular weight distribution of this polymer with a Poisson distribution it is convenient to plot the fractionation data on Poisson probability paper.[6,7] To do this it must be considered that there is at least one EO unit in each polymer chain; yet, based on the amount of EO charged to the reaction mixture and the yield of polymer, it may be that there are (on the average) three EO units to each polymer chain. Thus for a polymer of 1200 molecular weight the number of monomer units is in the range EO = 1–3, THF = 16–15, with a total of 17–18 monomer units. For the present purpose this difference is not significant (as the reader will

TABLE I
Results of Fractionating 1200 Molecular Weight Poly(oxatetramethylene) Glycol

	Fraction of polymer separated, %	Cumulative amount, %	Molecular weight[a]	No. of monomer units
Expt. 1	8.5	8.5	600	9
	5.5	14.0	700	10
	7.2	21.2	900	14
	7.9	29.1	1000	15
	16.8	45.9	1130	17
	24.0	69.9	1350	20
	19.8	89.7	1900	28
	4.8	94.5	4300	64
Expt. 2	5.9	5.9	570	9
	4.6	10.5	800	12
	6.2	16.7	920	14
	7.5	24.2	980	15
	13.1	37.3	980	15
	24.3	61.6	1230	18
	21.3	82.9	1600	24
	11.0	93.9	2200	33
	1.9	95.8	—	—
	4.3	100.1	—	—

[a] Determined by —OH (endgroup) analysis.

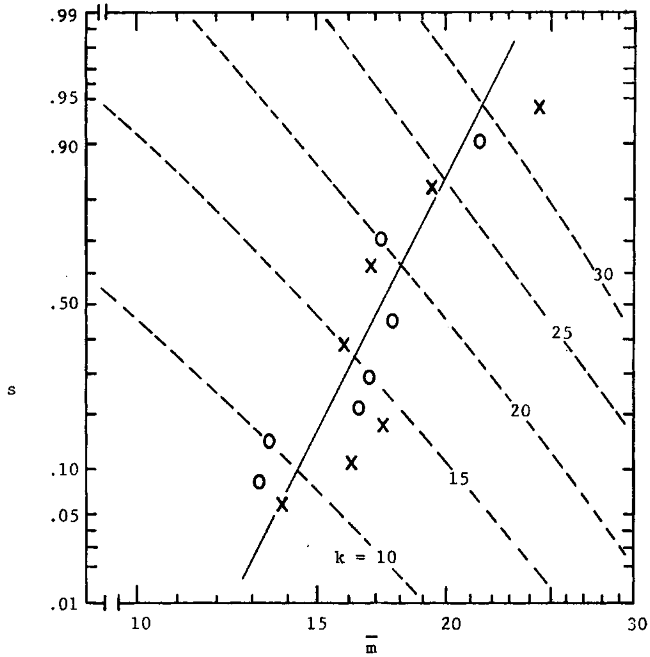

Fig. 1. Molecular weight distribution in poly(oxatetramethylene) glycol determined from a plot of fractionation data on Poisson probability paper: (O) expt. 1; (×) expt. 2. The abscissa, $\bar{m}$, is the mean value of Poisson distribution, the ordinate, s, represents the cumulative sum of Poisson terms. The curves labeled $k = 10$, 15, etc., give the probability of finding a chain length of k or less than k for any given value of $\bar{m}$ if the distribution is of the Poisson type.

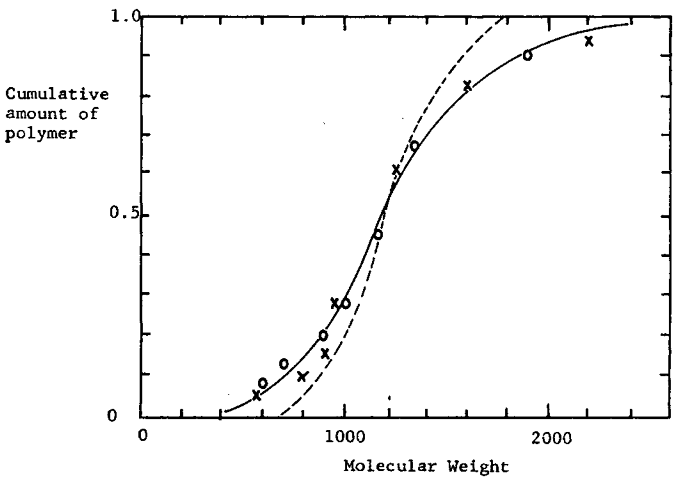

Fig. 2. Molecular weight distribution of poly(oxatetramethylene) glycol: (O) expt. 1; (×) expt. 2. The dotted curve is the Poisson distribution when the average M.W. is 1200.

see) and the molecular weight of each fraction has been converted to a value representing the number of units which have been calculated relative to the ratio: 1200/18 units.

The fractionation data are shown in Table I. Plots of these data on Poisson probability paper are shown in Figure 1. That the molecular weight distribution does not follow a Poisson distribution is indicated by the fact that the fitted line is not vertical. The fact that the line inclines to the right indicates[7] that the polymer is better described by a negative binomial[8] (or Polya[9]) distribution, or by other well-known molecular weight distributions that are broader than the Poisson (such as the Schultz or the log-normal type).

The more familiar integral molecular weight distribution curve is shown in Figure 2.

CONCLUSIONS

The molecular weight distribution of low molecular weight poly(oxatetramethylene) glycol, prepared from tetrahydrofuran by using a catalyst mixture of ethylene oxide, BF_3, and water, is somewhat broader than the Poisson distribution.

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Résumé

Un polymère de tetrahydrofurane de poids moléculaire de 1200 a été préparé à l'aide d'un mélange catalyseur formé d'oxyde d'ethylène, BF_3 et H_2O. Le produit a été fractionné par lavage d'une solution dans le cyclohexane et le toluène avec des mélanges d'alcool méthylique et d'eau. On a démontré que la largeur de la distribution des poids moléculaires surpasse celle de Poisson.

Zusammenfassung

Ein Polymeres des Tetrahydrofurans mit einem Molekulargewicht von 1200 wurde mit einer Katalysatormischung aus Äthylenoxyd, BF_3 und H_2O hergestellt. Das Produkt wurde durch Waschen einer Cyklohexan-Toluollösung mit Mischungen von Methylalkohol und Wasser fraktioniert. Es wurde gezeigt, dass die Molekulargewichtsverteilung etwas breiter als eine Poisson-Verteilung ist.

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