

Copolymerization of Ethylene Oxide and Propylene Oxide by Anhydrous Potassium Hydroxide

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Synopsis

Ethylene oxide and propylene oxide have been copolymerized at low temperatures in the presence of anhydrous potassium hydroxide. The monomer reactivity ratios were found to be $r(\text{ethylene oxide}) = 6.5$ and $r(\text{propylene oxide}) = 0.5$.

INTRODUCTION

Little information exists concerning copolymerization rates of monomers catalyzed by ionic species. In the case of epoxides there has been one report, by Bailey and France,¹ covering the copolymerization of ethylene oxide and propylene oxide. Catalysis was effected by bases such as metal alkoxides and the reactions were carried out at elevated temperatures. As has been pointed out by St. Pierre and Price,² these monomers will also polymerize at room temperature in the presence of potassium hydroxide. Accordingly, a number of copolymers have been prepared using this catalyst under these conditions; and the results, including the relative reactivity ratios, are reported here.

EXPERIMENTAL

Materials

Ethylene oxide (Matheson Company) was dried by passing it through potassium hydroxide pellets, silica gel, and ascarite. It was then distilled at low temperature under high vacuum.

Propylene oxide (Fisher Scientific Company) was refluxed with potassium hydroxide for 4-6 hr at atmospheric pressure and was fractionally distilled through a calcium hydroxide-packed column at a reflux ratio of 10:1. This dried propylene oxide was then distilled at low temperature under high vacuum.

Catalyst Preparation. Since the polymerization of epoxides occurs in the presence of solid KOH, it was necessary to take special precautions to reproduce the degree of dispersion of the KOH in each run. In order to

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do this, the catalyst was prepared by dispersing reagent-grade potassium hydroxide in reagent-grade benzene by means of a Waring blender. Measured amounts of this dispersion were titrated against a standard solution of hydrochloric acid in order to determine the amount of potassium hydroxide per ml present in the dispersion. Three ml of this dispersion (0.011 mole of KOH) were introduced into the polymerization ampoule by means of a specially built buret having a long delivery tube. Each time a dispersion was taken from the buret, the delivery tube was washed with a few ml of benzene. At no time was the dispersion allowed to dry or come in contact with the atmosphere. The ampoules containing potassium hydroxide dispersion were then quickly attached to a vacuum line for stripping off the benzene.

This method of introducing potassium hydroxide-benzene dispersions improved the precision to 2%–5% in fixing the amount of potassium hydroxide present in a reaction.³ The vacuum-stripped potassium hydroxide was further dried by flaming the ampoules with a gas-oxygen flame.

Polymerization

All experiments reported in this investigation were conducted under high vacuum conditions. All experimental conditions were designed to rigorously exclude oxygen, moisture, and carbon dioxide. Polymerizations were carried out at 25°C for a time sufficient to effect a conversion of less than 5%.

The isolation of polymer samples was accomplished by breaking the ampoules and stripping off the highly volatile monomers under vacuum at room temperature. The product polymer and the potassium hydroxide were then dissolved in methanol and the solution was passed through a methanol-conditioned Dowex 50-X8 cationic resin column to remove the base. The solvent was removed from the polymer by holding the sample under vacuum at room temperature for several days.

The compositions of the copolymers so obtained were determined by elemental analysis.

RESULTS AND DISCUSSION

Figure 1 shows the plot of ethylene oxide in the copolymers as a function of feed compositions. The curve is analogous to the typical copolymerization curve⁴ for $r_1 > 1$, $r_2 < 1$, i.e., with monomer 1 (ethylene oxide) being more reactive than monomer 2 (propylene oxide).

One of the three general methods used for the calculation of monomer reactivity ratios, the Fineman and Ross⁵ method, has generally proved to be most useful and has been used here. In most copolymerization reactions, the composition is determined primarily by propagation, since initiation and termination reactions occur far less frequently than do propagation

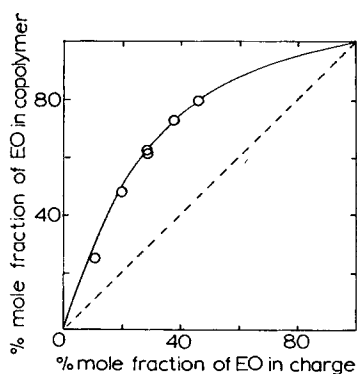


Fig. 1. Copolymer composition versus feed composition.

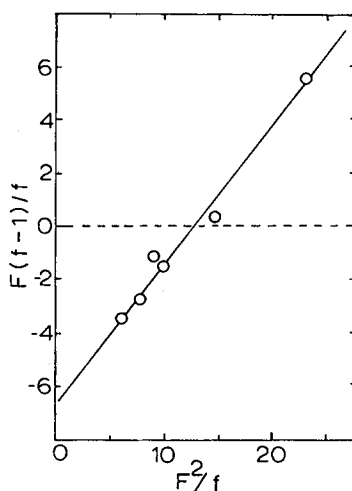


Fig. 2. Fineman and Ross plot for ethylene oxide-propylene oxide copolymer.

reactions. Thus, under steady state conditions, the composition of monomers is given by

$$\frac{d(M_1)}{d(M_2)} = \left(\frac{M_1}{M_2} \right) \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (1)$$

where M_1 and M_2 represent the molar concentrations of the respective monomers, and r_1 and r_2 are the reactivity ratios of the two monomers. At very low conversions, $d(M_1)/d(M_2) = m_1/m_2$ where m_1 and m_2 refer to copolymer composition. We may now write the copolymer composition equation in the form

$$\frac{m_1}{m_2} = \left(\frac{M_1}{M_2} \right) \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (2)$$

Substituting F for M_1/M_2 and f for m_1/m_2 , the following equation results:

$$\left(\frac{F}{f}\right)(f-1) = r_1\left(\frac{F_2}{f}\right) - r_2. \quad (3)$$

Thus a plot of $(F/f)(f-1)$ versus F^2/f should be a straight line with the slope equal to r_1 and intercept $-r_2$.

Figure 2 shows the above plot for the system under study here, and the reactivity ratios of ethylene oxide and propylene oxide are found to be 6.5 and 0.5, respectively. The product r_1r_2 gives an indication of the nature of the copolymer;⁶ when this product is unity, the copolymer is composed primarily of random sequences of comonomers. If $r_1r_2 < 1$ or > 1 , then block sequences are present. Although the r_1r_2 product has generally been found to be close to unity or less than unity, in the case of anionic polymerization it has occasionally been reported to be greater than unity.⁷ In the present case the product is about 3, indicating that short blocks of ethylene oxide are randomly distributed along the chain.

The results reported here, showing that ethylene oxide is more reactive than propylene oxide, support the mechanism proposed by Bailey and France¹ for polymerizations of this type.

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Received January 9, 1970