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## Radiation-Induced Polymerization of Methyl Vinyl Ether

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## **Radiation-Induced Polymerization of Methyl Vinyl Ether**

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### **ABSTRACT**

The radiation-induced polymerization of methyl vinyl ether under super-dry and wet conditions was studied. Little difference in the rates of polymerization was found. It seems clear that only an extremely slow free-radical polymerization was taking place. Possible reasons for the lack of concurrent cationic polymerization are discussed.

### **INTRODUCTION**

The radiation-induced polymerization of a number of vinyl ethers has been studied [ 1, 2]. In particular, isobutyl vinyl ether has been studied in great detail [ 3, 4]. It seems clear that the polymerization proceeds by a free cationic mechanism [ 1]. Parallel studies with stable carbonium ion salts gave rather good agreement in estimates of the absolute rate constant for propagation [ 5]. No radiation polymerization of methyl vinyl ether has been reported, however. With stable carbonium ion salts, polymerization of this monomer proceeded

but at a low rate, approximately one-tenth the rate, for example, of ethyl vinyl ether [6]. In this note, the results obtained with the irradiation of extremely dry and pure monomer are reported.

### EXPERIMENTAL

Methyl vinyl ether was obtained from the GAF Corporation and purified by washing in water potassium hydroxide solution and dried over potassium hydroxide pellets. Any traces of acetylene were removed by refluxing in a stream of dry nitrogen which was passed into Ilosvay reagent until no change of color was observed.

The purified monomer was dried over sodium mirrors and collected in baked-out ampoules and irradiated in the manner described previously [2, 7].

### RESULTS AND DISCUSSION

The radiation-induced polymerization of the super-dried methyl vinyl ether was studied at two dose rates. The conversion curves are shown as a function of dose in Fig. 1. Good linear plots were obtained, although the conversions were extremely low. The dose

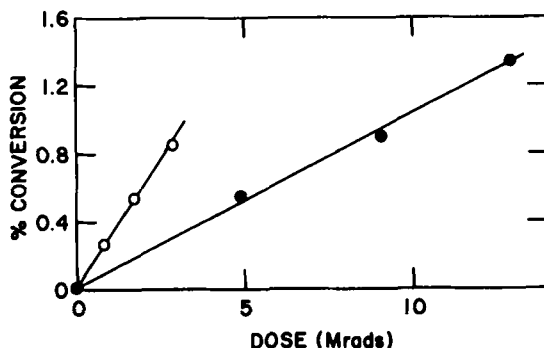


FIG. 1. Conversion-dose curves for the radiation-induced polymerization of methyl vinyl ether at  $0^{\circ}\text{C}$  at various dose rates: (•) 0.65 Mrad/hr; (○) 0.05 Mrad/hr.

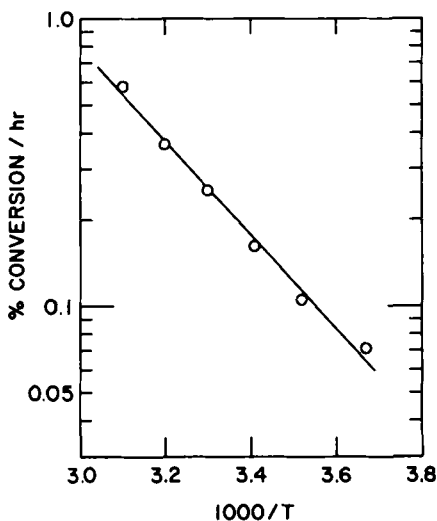


FIG. 2. Arrhenius plots for the radiation-induced polymerization of methyl vinyl ether at a dose rate of 0.65 Mrad/hr.

rate dependence of the rate of polymerization was found to be  $0.55 \pm 0.05$ .

The polymerizations of super-dried monomer were also conducted at a number of temperatures, and the Arrhenius plot of the rates are shown in Fig. 2. An activation energy of 7.3 kcal/mole was found. This compares with a value of 14.1 kcal/mole found by Ledwith et al. [6], who used "free" carbonium ion chemical initiation. The activation energy suggests, therefore, a free radical mechanism rather than free cations. A clear differentiation is possible by studying the effect of water, which completely inhibits the cationic process but should have no effect on a free radical polymerization. Thus, 10% of water was added to the methyl vinyl ether and the radiation polymerization rate measured at 30°C. Parallel measurements were conducted at the same dose rate and temperature, but with super-dried monomer. The two conversion curves are shown in Fig. 3. Close agreement was found between the two rates. It seems clear, therefore, that unlike the other vinyl ethers studied only a free radical process is observed.

Since it is known from the work of Ledwith [6] that methyl vinyl ether does polymerize by the free cation mechanism, it is puzzling

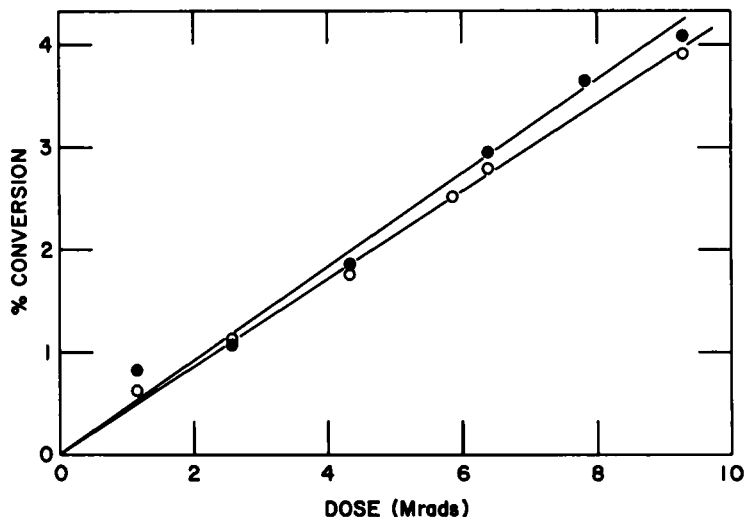


FIG. 3. Radiation-induced polymerization of methyl vinyl ether at 30° C and a dose rate of 0.65 Mrad/hr: (○) super-dry; (●) wet.

why it does not do so with radiation. The propagation rate constant is only about 1/50 that of isobutyl vinyl ether. The possible reasons for the low value has been clearly discussed by Ledwith [6]. At the highest dose rate used, isobutyl vinyl ether polymerizes at about 10%/Mrad [2]. Assuming, as is reasonable, that the initiation rate is similar for both vinyl ethers, then methyl vinyl ether should polymerize at about 0.2%/Mrad. In fact, it polymerizes at only 0.1%/Mrad, as can be seen from Fig. 1, and by a free-radical mechanism. It is suggested that, at the high doses needed to give appreciable polymerization, alcohols and other chain terminators are produced and stop the cationic reaction. A similar effect was shown to cause retardation of ethyl vinyl ether [7] polymerization. To check this a small amount of irradiated sample of methyl vinyl ether was added to a super-dry sample of isobutyl vinyl ether and irradiated. No polymerization took place even after 10 Mrad. It seems clear, therefore, that the failure of methyl vinyl ether to polymerize by a cationic mechanism with radiation is due to the slow polymerization rate per se plus the rapid concurrent production of chain terminators by the radiolysis. The higher ethers polymerize faster and have less oxygen content, and so are less prone to produce effective quantities of terminators. Ethyl vinyl ether seems to be an intermediate

case, showing retardation particularly at high dose rates. This is reasonable, since at high dose rates a larger total dose is needed leading to a greater yield of inhibitor relative to polymer. This arises since the inhibitor would be produced directly proportional to the dose rate, whereas the polymerization rate has a square-root dependence.

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