

ably as good as can be expected in view of the assumptions made and the experimental error in m_1 and m_2 .

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The Radiation-Induced Polymerization of Alkyl Vinyl Ethers

It is generally accepted that the polymerization of alkyl vinyl ethers by free-radical catalysts is "difficult."¹ Under forcing conditions substantial conversions can be achieved, but the products are polymers of low molecular weight.² Alkyl vinyl ethers are more readily polymerized by ionic catalysts such as boron trifluoride etherate,² silver perchlorate,³ iodine,³ and triphenyl methyl chloride.³ Even ionic catalysts tend to give low molecular weight material at normal temperatures. According to Schildknecht, only at low temperatures and with cationic catalysts can high polymers be obtained.²

More recently, Lal⁴ has described the stereospecific polymerization of isobutyl vinyl ether at -78° with titanium tetrachloride/aluminum trialkyl systems, to which a coordinate anionic mechanism has been attributed.⁵ The radiation-induced polymerization of alkyl vinyl ethers, other than octadecyl vinyl ether,⁶ has not hitherto been described.

We were led to study the effects of radiation on alkyl vinyl ethers following our experience with the low temperature radiation-induced polymerization of isobutene,⁷ to which a cationic mechanism was attributed.^{8,9}

The alkyl vinyl ethers were fractionally distilled through a 20-plate column packed with glass helices, the middle fraction being used, after outgassing and filtering, for polymerization in vessels cleaned as previously described.⁹ Irradiations were with Cobalt 60 γ -rays at 320–5200 rad/min. and with 2 Mev electrons from the scanned beam of a Van de Graaff generator at an instantaneous dose rate of ca 10^8 rad/min. The conversions were followed dilatometrically and the final value confirmed gravimetrically. Limiting viscosity numbers of the polymers in benzene solutions were determined at 25°C . using a suspended level dilution viscometer.

Though many attempts were made to produce polymerized ethyl vinyl ether at -78.5° , no significant yield was obtained either with γ -rays or electrons. Exposure to γ -

rays at room temperature, however, led to the formation of rubber-like transparent high polymers with limiting viscosity numbers in the range 0.5–0.6 dl./g. This contrasted markedly with the behavior of isobutene which polymerized readily when irradiated at -78.5° or lower, but not at room temperature.⁷

Closer examination of the γ -ray initiated room temperature reaction revealed induction periods, i.e., a slow initial rate of polymerization of the ethyl vinyl ether, followed by a period of acceleration, leading rapidly to about 90% conversion. The curve in Figure 1 illustrates the usual pattern. Similar curves were obtained with γ -irradiated *n*-butyl vinyl ether and isobutyl vinyl ether. This type of behavior has frequently been encountered with both catalyzed and radiation-induced free-radical polymerization and has been attributed to diffusion control of the termination rate in the gel state.¹⁰ The radiation-induced conversions of isobutene, on the other hand, showed no induction periods and were essentially linear with dose.⁹

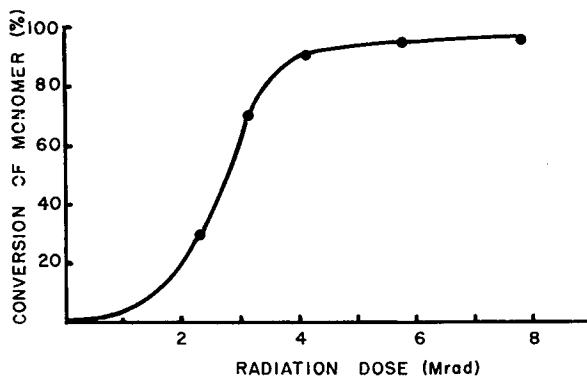


Fig. 1. Radiation-induced polymerization of ethyl vinyl ether (dose rate 1080 rad/min.).

The polymerization of ethyl vinyl ether differed also from that of isobutene in its dependence on intensity. Yields were much inferior with high dose-rate electron irradiation, whereas the conversion of isobutene was essentially independent of dose rate.⁹

Many of the characteristics of the radiation-induced polymerization of isobutene which have been previously cited in support of an ionic mechanism⁹ thus failed to apply in the case of alkyl vinyl ethers. The kinetic behavior of the latter accords with bi-molecular termination¹⁰ and a gel effect¹¹ and is suggestive rather of a free-radical mechanism. We have sought confirmatory evidence of this mechanism, but the work has been hindered by a strong variability of the induction periods, which implies that residual impurities were initially present, despite rigorous precautions, or that inhibitors or retarders were formed during irradiation. (The marked effect of traces of impurities in retarding polymerization of the lower alkyl vinyl ethers has been previously emphasized.²) Polymers isolated during the induction periods were liquids of low molecular weight (limiting viscosity numbers <0.1 dl./g.) resembling those resulting from slow polymerization under heat, light, or peroxides.²

The implication of this work, coupled with the results reported by Lal⁴ and by Fee et al.,⁸ is that various catalytic agencies serve to polymerize alkyl vinyl ethers and that it is

necessary to revise the view¹² that a cationic mechanism is essential for the formation of high polymers.

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