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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Goineau, A. M. , Kohler, J. and Stannett, V.(1977) 'Radiation-Induced Polymerization of a Series of Vinyl Ethers', *Journal of Macromolecular Science, Part A*, 11: 1, 99 – 114

To link to this Article: DOI: 10.1080/00222337708061255

URL: <http://dx.doi.org/10.1080/00222337708061255>

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Radiation-Induced Polymerization of a Series of Vinyl Ethers

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ABSTRACT

The radiation-induced polymerization of methyl, ethyl, isobutyl, isopropyl, and tert-butyl vinyl ethers was studied under super-dry conditions. Methyl vinyl ether did not polymerize at measurable rates; ethyl vinyl ether polymerized readily but with a dose rate dependence of the rate of only 0.3. The other ethers polymerized with a square-root dependence of the rate on the dose rate. Good agreement between the absolute rate constants and activation energies obtained by "free" cationic chemical initiation with those estimated by radiation was found except for tert-butyl vinyl ether, where both values were considerably lower in the case of chemical initiation. Molecular weights were higher in all cases with radiation polymerization in bulk compared with chemical initiated polymerization in methylene chloride solution. At least part of these differences can be ascribed to chain transfer to the methylene chloride. High G values were obtained in all cases except with methyl vinyl ether.

INTRODUCTION

Extensive research over the past several years has shown clearly that the radiation-induced polymerization of a number of vinyl monomers can proceed under extremely dry conditions via a "free" cationic mechanism [1]. Among the monomers which have been investigated in great detail is isobutyl vinyl ether [2-9]. A combination of conductivity and rate data led to values for the absolute rate constants for propagation which were in good agreement with those obtained by terminationless chemically induced polymerizations [10]. In this paper the radiation-induced polymerization of a number of isobutyl and other vinyl ethers under "super-dry" conditions will be described.

EXPERIMENTAL

Commercial ethyl, isobutyl, isopropyl, and tert-butyl vinyl ether monomers (EVE, IBVE, IPVE, TBVE), obtained from the Monomer-Polymer Laboratories, Borden Chemicals, were washed 7-10 times with distilled water adjusted to a pH of 8.5 with potassium hydroxide. The monomers were then dried over KOH pellets for 24 hr and refluxed over sodium metal for an additional 24 hr. The middle fractions (bp: EVE, 36.0-36.5°C; IBVE, 83-84°C; IPVE, 55-56°C; TBVE, 93-94°C) were collected and super-dried. Methyl vinyl ether (MVE), obtained from Matheson and Coleman, was treated by slow counter-current washing with distilled water in a tower filled with Raschig rings and then bubbled through a saturated solution of potassium hydroxide before condensation in a Dry Ice-cooled glass coil. The MVE was super-dried in the same manner as the other vinyl ether monomers.

The super-drying technique used was adapted from that used by Taylor and Williams [11]. Glassware used in the super-drying process was treated in a 12 kW electric oven (Gruenberg Electric Co.) equipped with an infinitely variable heater control switch. An adjustable thermostat (Barber-Colman) accommodated temperature settings up to 870°C, and a large fan mounted behind the heating coil bank provided forced air circulation, thus insuring uniform heating.

The oven, shown in Fig. 1, contained a Pyrex manifold (A) attached through a Kovar seal (B) to a metallic bellows (C). Side-arms (D) on the Pyrex manifold facilitated attachment of glassware. The bellows were, in turn, connected to a stainless-steel manifold (E). Mechanical pumping could be applied to the manifold by opening the

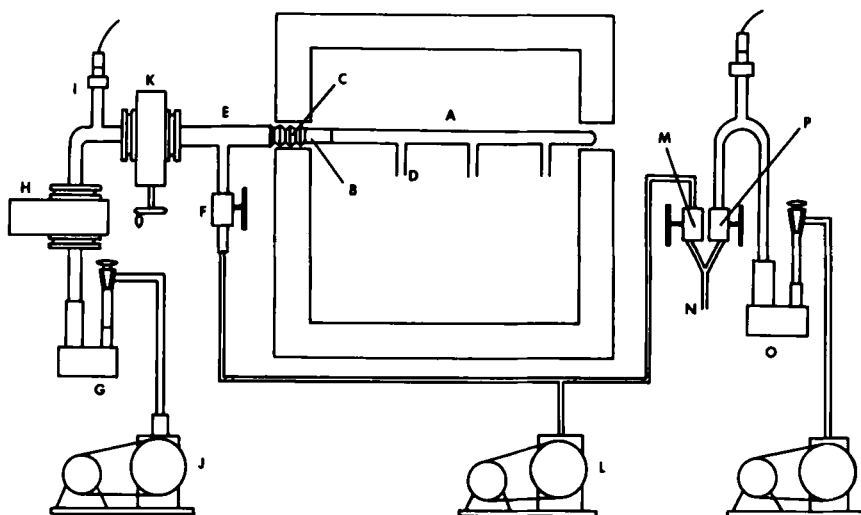


FIG. 1. Oven and equipment used for baking out and filling the ampoules.

metal valve (F). A high-vacuum unit, consisting of an oil diffusion pump (G), a metal liquid nitrogen trap (H), a cold cathode tube (I) and a mechanical pump (J), was joined to the manifold through a gate valve (Consolidated Vacuum Corp.) (K).

Operations involving monomer transfer and the preparation of sodium film flasks were conducted on a small evacuation unit next to the oven. The mechanical pump (L) common to the two systems was capable of providing a vacuum of 10^{-4} Torr. A metal valve (M) was used to isolate the pump from the monomer-handling unit. An aperture for glassware attachment (N) could be subjected to high-vacuum pumping from the oil diffusion pump by opening the metal valve (P). To safeguard against contamination by grease, metal valves were used in all regions where monomer vapor was likely to be present. The unit was designed to incorporate as small an internal volume as possible, thus permitting rapid evacuation. This system was capable of achieving a vacuum of 10^{-7} Torr.

Flasks coated with mirrors of metallic sodium were used to "super-dry" the vinyl ether monomers. A standard 200-ml round-bottomed Pyrex flask baked out overnight at 500°C under vacuum

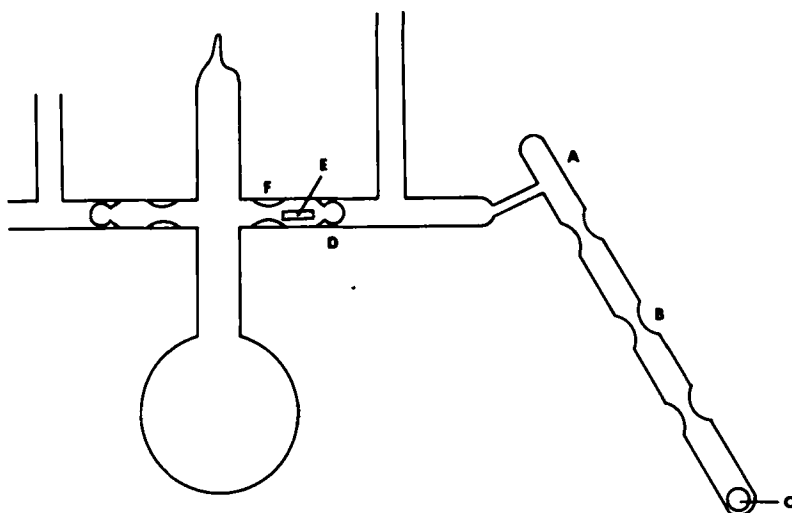


FIG. 2. Apparatus used for preparing the sodium mirror flasks.

was joined to the high-vacuum line as depicted in Fig. 2. At one end of the side-arm a Pyrex tube (A) was joined. The tube was divided into stages by a series of constrictions (B). A sodium pellet (C) was placed in the bottom of the tube, which was then sealed off and thoroughly degassed. Application of a torch flame drove the sodium higher into the tube. The distilled sodium was separated from the residue by sealing off the constrictions successively.

The breakseal (D) was crushed and a small amount of the sodium was guided into the flask with the aid of the bar magnet (E). The amount of sodium transferred was determined by the desired thickness of the film which would later be condensed on the lower part of the flask. A large flame was used to heat the upper parts of the flask including the side-arms. Sodium gradually condensed on the walls of the flask and further selective heating established a mirror on the lower half of the bulb. A vacuum of about 10^{-6} Torr was maintained throughout the operations. The flask was sealed off at the constriction (F).

Each vinyl ether monomer was degassed and transferred to a sodium film flask under vacuum and stored for several days. When the sodium mirror disappeared, the monomer was transferred to a new sodium film flask. This process was repeated until the condition

of the monomer permitted the sodium mirror to remain intact. The vinyl ether was then distilled into a manifold of sample tubes which were sealed off under liquid nitrogen and in the presence of a silica gel trap.

Sample tubes remained frozen until they were irradiated. Irradiation was carried out in a cobalt-60 γ -ray source. Dose rates were determined through Fricke dosimetry, based on the oxidation of ferrous ions into ferric ions. Low dose rates were achieved by inserting monomer sample tubes into a calibrated lead shield. In the present work, the higher dose rates were 0.72 Mrad/hr, lower dose rates 0.054 Mrad/hr. When the sample tubes had been exposed to the γ -rays for the desired length of time, the tubes were cracked open and a few drops of methanol added. Polymer yields were determined gravimetrically.

Estimates of molecular weights were made from the intrinsic viscosities determined in benzene at 30° C. The relationships used were [12, 13].

For poly(isobutyl and poly(isopropyl vinyl ether):

$$[\eta] = 7.55 \times 10^{-3} (M_v)^{0.75}$$

For poly(tert-butyl vinyl ether)

$$[\eta] = 2.04 \times 10^{-2} (M_v)^{0.64}$$

For poly(ethyl vinyl ether):

$$[\eta] = 7.6 \times 10^{-2} (M_v)^{0.60}$$

The first and third relationships were developed for poly(isobutyl vinyl ether) [12, 13] and poly(methyl vinyl ether) [14] but were thought to be suitable to give estimates of the molecular weights. In all cases, the concentration units are in g/ml.

RESULTS

Kinetics

The polymerizations proceeded smoothly and with good reproducibility provided the rigorous procedures described in the experimental

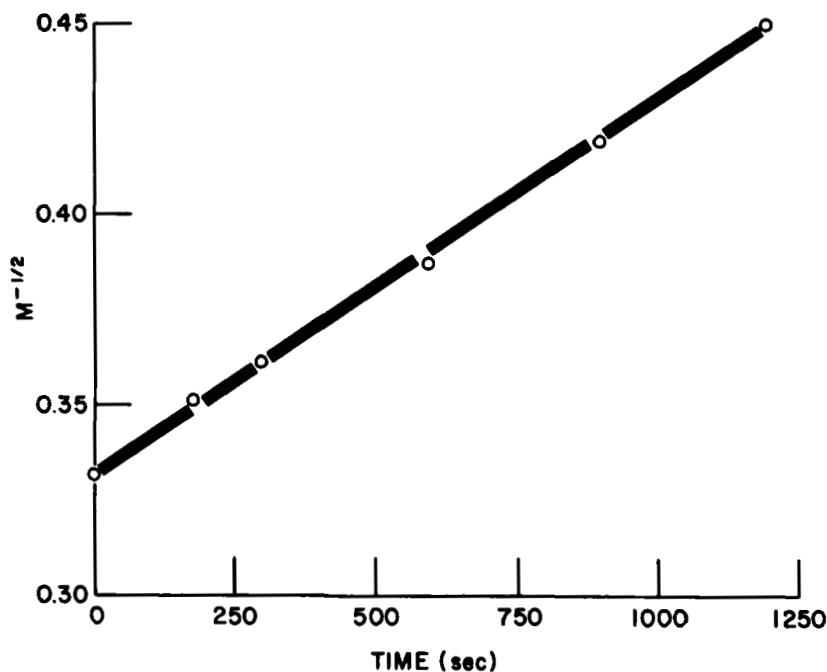


FIG. 3. Typical conversion-time data plotted as a 3/2-order reaction on monomer. Isopropyl vinyl ether at 50 C; dose rate 200 rad/sec.

section were followed. A typical conversion-time curve plotted according to a 3/2-order of the rate on the monomer concentration is shown in Fig. 3. All the polymerizations followed scrupulously both first-order and 3/2-order plots.

The kinetic scheme derived by Williams, et al. [1, 4] under completely pure (dry) conditions led to the expression

$$R_p = (R_i/k_t)^{1/2} k_p [M]$$

where R_p and R_i are the rates of propagation and initiation, respectively, k_p is the rate constant for propagation, and $[M]$ is the monomer

concentration. k_t is the termination rate constant for the recombination of the growing cations and the negative species. This reaction is believed to be diffusion-controlled. If the initiation step involves only the monomer, the rate of polymerization will be 3/2-order on the monomer concentration. If the polymer participates equally in the initiation, the rate will be first-order on the monomer concentration. Unfortunately, the maximum conversions (less than 50%) were too low to distinguish between them.

Methyl vinyl ether did not polymerize at measurable rates under the conditions used and will be the subject of a separate communication [15]. The rates obtained with the other monomers studied are presented in the form of Arrhenius plots in Figs. 4-6. Isobutyl vinyl ether has been studied extensively by Williams and Hayashi and their co-workers [4, 6] and their results, normalized to the same dose rate, are included in Fig. 5. Considering the experimental difficulties involved, the agreement is good, particularly at lower temperatures.

A key question in the work is the dose rate dependence of the rate of polymerization. Under conditions where no termination by impurities (believed to be chiefly water) occurs, the rate of polymerization is one-half order on the dose rate. As the level of impurities rises, the dependence increases. Finally, when all the growing chains are terminated by impurities, a first-order dependence will be observed. Although only two dose rates were studied, due to the limitations of the radiation sources available, a number of measurements were made and a good estimate of the dose rate dependence was possible. The results obtained together with some average polymerization rates are given in Table 1.

It can be seen that close to a square-root dependence was found for isobutyl, tert-butyl, and isopropyl vinyl ethers. Ethyl vinyl ether, however, showed about a one-third order dependence. This is believed to be due to the simultaneous production of an inhibitor. This monomer is presently being investigated in detail and will be the subject of a separate communication [16].

Williams, Hayashi, and their co-workers, used [4-6] a combination of radiation-induced electrical conductivity data and polymerization rates to calculate values for the propagation rate constants for isobutyl vinyl ether, styrene, and α -methylstyrene. The values for isobutyl vinyl ether were shown to be in reasonable agreement with those obtained by "free" cation chemical initiators [10]. If one makes the assumption that the lifetimes of the charge carriers and the initiation rates are similar with all the vinyl ethers studied in this present work to those found with isobutyl vinyl ether, propagation rate constants can also be estimated. This assumption is

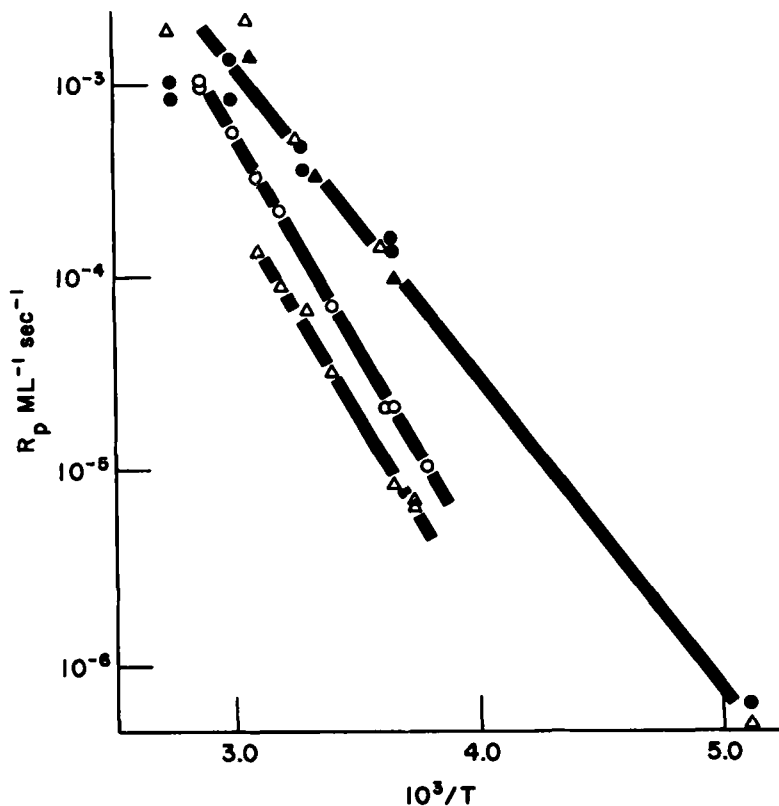


FIG. 4. Arrhenius plots of the rates of polymerization for ethyl vinyl ether (EVE) and isobutyl vinyl ether (IBVE): (Δ) EVE, 15 rad/sec; (\circ) EVE, 200 rad/sec; (Δ) IBVE, this work, 200 rad/sec; (\blacktriangle) IBVE, Hayashi et al. [6] and (\bullet) IBVE, Bonin et al. [2], both adjusted to 200 rad/sec.

probably reasonable since those found with styrene and α -methylstyrene are not too dissimilar to those found with isobutyl vinyl ether. Values calculated in this way together with the corresponding estimation energies and pre-exponential values are summarized in Table 2.

The activation energies, except for isopropyl vinyl ether, are unusually high for a free cationic vinyl polymerization; they are less than 2 kcal/mole for styrene, α -methylstyrene, isobutene, and

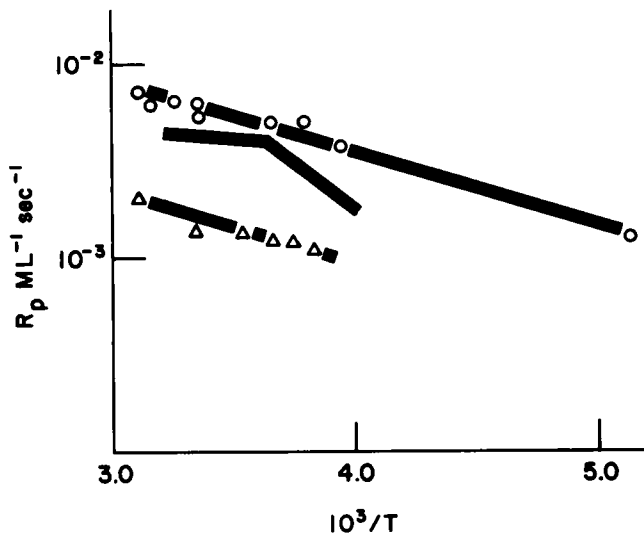


FIG. 5. Arrhenius plot of the rates for isopropyl vinyl ether: (\circ) 200 rad/sec; (\triangle) 15 rad/sec; (—) earlier work [18].

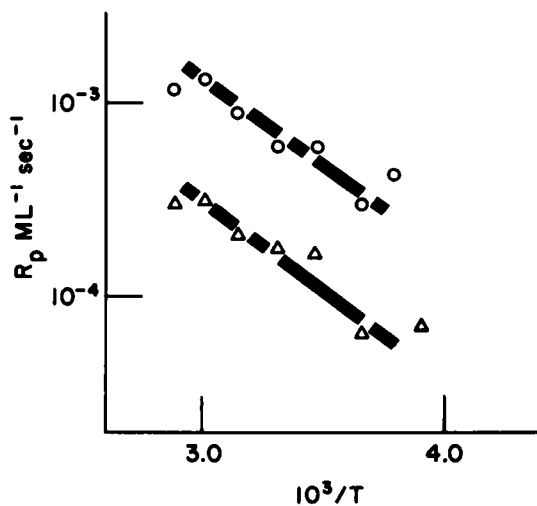


FIG. 6. Arrhenius plots of the rates for tert-butyl vinyl ether: (\circ) 200 rad/sec; (\triangle) 15 rad/sec.

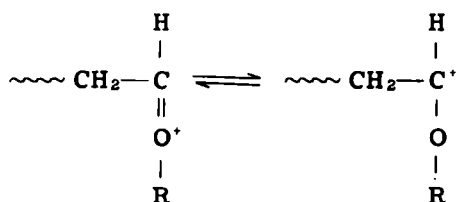
TABLE 1. Typical Polymerization Rates of Some Alkyl Vinyl Ethers and Their Dose-Rate Dependencies and Activation Energies

Temp (°C)	Dose rate (rad/sec)	Rate (liter/mole-sec)			
		EVE ^a	IPVE	IBVE	TBVE
0	200	1.9×10^{-5}	4.7×10^{-3}	2.1×10^{-4}	3.4×10^{-4}
0	15	8.0×10^{-6}	1.3×10^{-3}	5.1×10^{-5}	7.4×10^{-5}
50	200	3.2×10^{-4}	7.6×10^{-3}	1.8×10^{-3}	1.1×10^{-3}
50	15	1.3×10^{-4}	2.0×10^{-3}	—	2.4×10^{-4}
Dose- rate depend- ency		0.32 ± 0.05	0.52 ± 0.05	0.51 ± 0.05	0.59 ± 0.10

^aBelieved to be less than maximum rates.

cyclopentadiene, for example. They are, however, in agreement with those found with chemical initiation with free ions and so are not peculiar to the radiation-induced systems [10].

The high values could be due to two reasons: (1) solvation of the carbenium ion by the monomer itself; this, however, would probably lead to a zero-order of the rate of polymerization on the monomer concentration which is not observed; (2) the energy associated with the resonance stabilization of the propagating ion.



Undoubtedly any solvation would also affect the stabilization and vice versa. A careful discussion of the problem and an analysis of the activation energies associated with the copolymerization rate constants for the styrene-isobutyl vinyl ether system has been made by Hayashi et al. [17]. Based on their results it does appear that

TABLE 2. Estimated Rate Constants k_p , Activation Energies E_p , and Pre-Exponential Factors A_p for Propagation at 0°C

Monomer	k_p (liter/mole-sec) $\times 10^4$	$\log A_p$	E_p (kcal/mole)
EVE ^a	0.72 (0.51)	10.4	10.4 (9.9)
IBVE	3.8 (0.92)	11.0	7.6 (7.1)
TBVE	5.0 (0.35)	6.7	4.9 (<2)
IPVE	90.0	4.0	1.8

^aBelieved to be somewhat too high [16]. The values in parentheses are those obtained by chemical initiation.

solvation plays a role, in that the reaction Sty' + IBVE also has an activation energy of about 5.8 kcal/mole [17]. More work in different solvents is clearly needed before the causes of the high activation energies can be explained.

The pre-exponential factors are also very high compared with the hydrocarbon monomers, indicating a different structure of the transition state. Hayashi et al. [17] have suggested a five-centered coordination between the α carbon and oxygen of the carbenium ion and the α and β carbons and the oxygen of the monomer for the transition state which appears very reasonable.

The comparatively low values for E_p and A_p and the higher rates of polymerization for isopropyl vinyl ether included in Tables 1 and 2 are disturbing. Earlier work [18] with the use of the elegant dilatometer techniques of Potter and Metz [19, 20] had shown somewhat different behavior with a break in the Arrhenius plot. Above 5°C the activation energy was close to zero, whereas below it was about 7.4 kcal/mole, similar to the results obtained in the present work with the other vinyl ethers. Close to a square-root dependence of the rate on the dose rate was also found, tending to decrease at higher and increase at lower temperatures. However, the whole range was in the order of 0.44-0.56. The data are included in Fig. 5. It is interesting that the 0°C rate which fits exactly a square-root relationship is the closest to the newer ampoule data (4.0 vs. 4.7×10^{-3}). Since the newer ampoule values are higher and consistent over many determinations (Fig. 5), for example, it is believed that these are the correct values. The reasons for the lower activation energy and pre-exponential value, however, remain obscure.

Earlier studies with isobutyl vinyl ether also showed a tendency for the Arrhenius plot to curve at higher temperatures, and indeed the pioneering data of Bonin et al. [2], although scattered, showed a similar tendency as can be seen in Fig. 4. Since the highest results are probably the most valid, however, it would seem that the changes of slope are probably due to experimental artifacts. The extraordinarily rigorous nature of the experimental measurements unfortunately lends itself to such occasional anomalies in the results.

Molecular Weights

No special effort was made to study the molecular weights of the various poly(vinyl ethers) produced. However, a number of measurements were made of the intrinsic viscosities of the resulting poly(vinyl ethers). Poly(isobutyl vinyl ethers) have already been discussed [8, 9], and the poly(ethyl vinyl ethers) will be discussed in a subsequent paper [16, 21].

The molecular weights of the poly(tert-butyl vinyl ethers) and poly(isopropyl vinyl ethers) are shown graphically in Fig. 7, in the form of Arrhenius plots and at two dose rates. No great differences in the molecular weights were found over a 13-fold change in the dose rate. The largest dose used in the polymerizations was 0.8 Mrad; this results in less than 3% drop in the molecular weights due to radiation-induced degradation as discussed in a separate study [21]. The activation energies associated with the molecular weights were -4.8 and -4.0 kcal/mole for the tert-butyl and isopropyl vinyl ethers, respectively. These compare with -1.5 ± 2.5 and -5.7 kcal/mole found with the isobutyl vinyl [6] and ethyl vinyl [16] ether polymers. It is believed, at the low total doses used in this work, that the molecular weights are governed by the ratio of the rates of chain transfer to monomer and chain propagation. The lack of dependence of the molecular weights on the dose rates supports this simple picture. The scatter in the results leads to an experimental error of at least ± 1 kcal/mole, and so the results are in rough agreement for all the four vinyl ethers studied in this work. This is perhaps surprising, in view of the rather substantial differences in the activation energies for the propagation reaction, summarized in Table 2. Much more precise work including the use of osmometry or GPC studies is needed before a detailed interpretation can be made.

It is worthwhile at this stage to compare the rates and molecular weights obtained in this work to those obtained by Ledwith et al. [2] and others [10] using free cationic polymerization initiated in

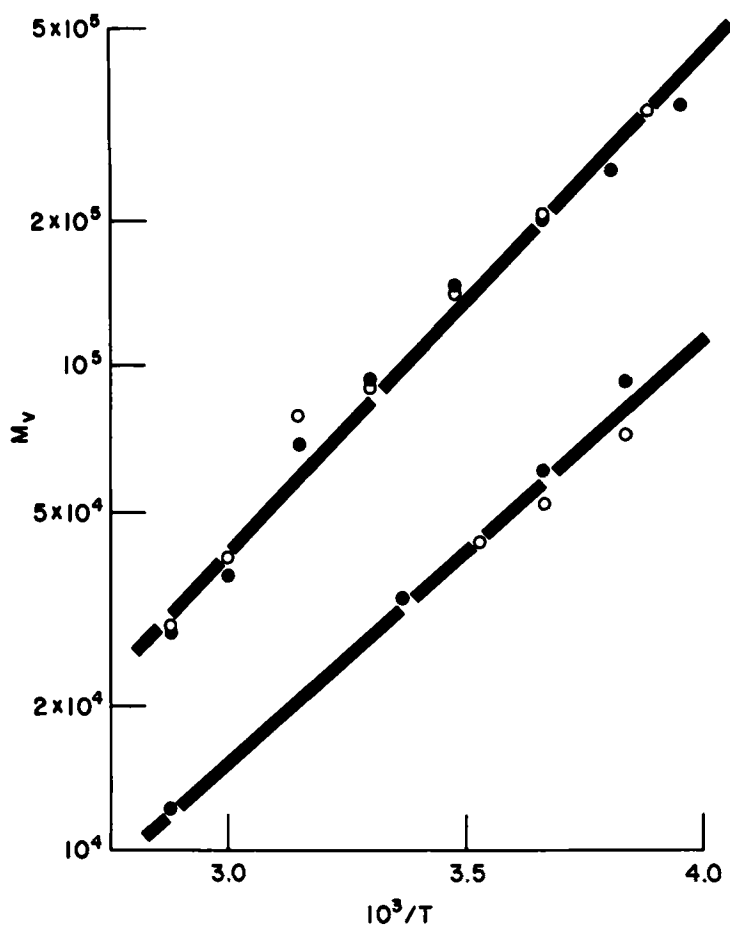


FIG. 7. Arrhenius plots of the viscosity-average molecular weight for isobutyl vinyl ether (upper curve) and isopropyl vinyl ether (lower curve): (●) 200 rad/sec; (○) 15 rad/sec.

methylene chloride solution by stable carbonium ion salts. The propagation rate constants and activation energies obtained by chemical initiation are included in Table 2. It can be seen that the values for ethyl and isobutyl vinyl ethers are in reasonable agreement with those obtained in the present work considering the experimental difficulties

TABLE 3. Typical G(-M) Values for Some Alkyl Vinyl Ethers

Temp (° C)	Dose rate (rad/sec)	G(-M) (100 eV) ⁻¹			
		EVE ^a	IPVE	IBVE	TBVE
0	200	(130)	25,000	1,300	2,000
0	15	(700)	94,000	—	7,200
50	200	(2,300)	38,000	10,000	6,600
50	15	(11,000)	160,000	—	18,000

^aBelieved to be less than maximum rates.

and assumptions involved in work of this kind. The results obtained with tert-butyl vinyl ether, however, are considerably higher with radiation and no chemical studies have been reported with isopropyl vinyl ether. It is proposed to repeat the tert-butyl vinyl ether work under super-dry conditions and to study isopropyl vinyl ether in this laboratory in the near future.

The molecular weights obtained with chemical initiation are in the 4000-6000 range [22, 23] compared with 20,000-100,000 with the radiation-produced polymers in bulk. It is believed that at least part of the differences are due to chain transfer with the methylene chloride used with the chemical initiation. In fact, the radiation-induced polymerization of isobutyl vinyl ether in methylene chloride does indeed produce polymers of much lower molecular weight [9]. A careful study [24] of the chain-transfer constants for the chemical initiation of ethyl vinyl ether at 15° C gave a coefficient for chain transfer to monomer of 7×10^{-3} , leading to an estimated weight-average molecular weight of 21,000 compared with a radiation value in bulk of 60,000. Higher molecular weights were also obtained with radiation-polymerized isobutylene compared that obtained by chemical initiation with Lewis acids [25]. Considerable further work is needed with both radiation and "free" cationic chemical initiation before these various anomalies can be interpreted clearly. Such studies are currently in progress in this laboratory.

Finally, from a practical point of view, the G(monomer) values, i. e., the number of monomer molecules polymerized per 100 eV of absorbed energy is important, since it determines the economics of the polymerization process. These numbers are presented in Table 3. Values above 10,000 are considered economically viable, and this number is exceeded in almost every case.

ACKNOWLEDGMENT

We would like to thank the Division of Isotopes Development, U. S. Atomic Energy Commission, for their support of this work.

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Accepted by editor February 23, 1976

Received for publication May 5, 1976