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Radiation-Induced Polymerization of Ethyl Vinyl Ether

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ABSTRACT

The radiation-induced polymerization of ethyl vinyl ether has been studied in bulk under conditions of extreme dryness and saturated with water. Drying was found to increase the rate by nearly thirty times. Water produced a similar reduction in the molecular weights of the polymers. Some evidence was found for the concurrent production, by radiolysis, of inhibiting species, probably alcohols. When this was corrected for by taking initial rates, a clear square-root dependence of the rate of polymerization on the dose rate was found with the super dry monomer system. Similarly, by extrapolating the molecular weight data to zero dose, a measure of the chain transfer to monomer constants could be obtained. By using the electrical conductivity values obtained by Hayashi, Williams and co-workers, an estimate of the rate constants for propagation were obtained. These compared well with those obtained in parallel studies with a "free" cationic chemical initiator.

INTRODUCTION

The earliest report of the radiation-induced polymerization of vinyl ethers appears to be that of Pinner and Worrall [1], who studied ethyl vinyl ether (EVE) in bulk. Lengthy induction periods and a dose-rate dependence of the rate of less than unity led the authors to postulate a free radical mechanism. Research into the radiation polymerization of various vinyl ethers, particularly isobutyl vinyl ether, has established that a cationic mechanism predominates when sufficiently pure and extremely dry monomers are used [2-6]. Techniques for obtaining "super-dry" monomers have been developed by Metz [7, 8], Williams [9] and their co-workers, and others [5, 6, 10, 11]. Combinations of polymerization rate studies and electrical conductivity measurements have established values for the absolute rate constants for propagation by free ions [3, 5]. These values appear to be in reasonable agreement with corresponding chemical measurements [12].

The kinetic behavior of the radiation-induced polymerization of EVE has remained largely unexplored until now and the present work represents such a study.

EXPERIMENTAL

Ethyl vinyl ether, obtained from the Monomer Polymer Laboratories, Borden Chemicals, was washed 7-10 times with distilled water adjusted to a pH of 8.5 with potassium hydroxide. The monomer was then dried over KOH pellets for 24 hr and refluxed over sodium metal for an additional 24 hr. A middle fraction (bp 36.0-36.5°C) was collected. Wet conditions for radiation-induced polymerization were achieved by adding 10% by volume of water to the pure EVE monomer in the ampoule before degassing. Dry conditions were achieved by treating the EVE with molecular sieves in the manner described by Stannett et al. [10]. The procedures used in preparing "super-dry" EVE are discussed in detail in a separate communication [6].

Polymerization reactions at high dose rates (0.7 Mrad/hr) were carried out in the 6 kCi cobalt-60 γ-ray source of the Department of Chemical Engineering of the North Carolina State University at Raleigh. Irradiations at low dose rates (0.05 Mrad/hr) were conducted in the same source by enclosing the monomer ampoules within a calibrated lead shield.

Viscosity measurements were carried out on benzene solutions of poly(ethyl vinyl ether) at 30°C in a Ubbelohde capillary viscometer.

Viscosity-average molecular weights were estimated from intrinsic viscosities according to an equation developed for methyl vinyl ether [13]:

$$[\eta] = 7.6 \times 10^{-2}\,\overline{M}_w^{\;0.6}$$

where concentration is in g/ml.

Number-average molecular weights were estimated by assuming that the chain lengths follow the "most probable" distribution and that $\overline{M}_w = 2\overline{M}_n$ [14].

RESULTS AND DISCUSSION

Some effects of the susceptibility of γ-ray-initiated poly(ethyl vinyl ether) chains to termination with protic impurities such as water can be observed in Fig. 1. Super-dry monomer samples achieve high conversions in much shorter periods of time than dry or wet samples. The difference in behavior between dry and super-dry samples is much more pronounced than the difference between dry and wet samples, indicating that only minute traces of water are required to retard the polymerization dramatically. High sensitivity to the presence of water is characteristic of radiation-induced cationic polymerizations [2-11].

The preparation of super-dry liquid monomers has been discussed by Taylor and Williams [9] and others [7, 8], and the modified procedures used in the present work are outlined in a separate communication [6]. Despite the most stringent precautions, small amounts of both gaseous and liquid impurities may remain in the monomer ampoule and are probably also produced during the irradiation. The effects of gaseous impurities should be magnified as the volume ratio of monomer to dead space in the ampoule decreases. However, increasing the ampoule volume fifty times was found to have no influence on the rate. Deterioration in kinetic behavior would also be expected to occur as a result of impurity-catalyzed decomposition reactions and desorption of water from the glass during lengthy storage periods prior to irradiation leading to lower rates of polymerization. Figure 2, however, shows that the differences in rate behavior between samples stored for 2 months prior to irradiation and samples irradiated immediately after preparation are very slight. A small amount of polymerization had occurred, however, on storage. The decrease in polymerization rate at higher doses shown in Fig. 2

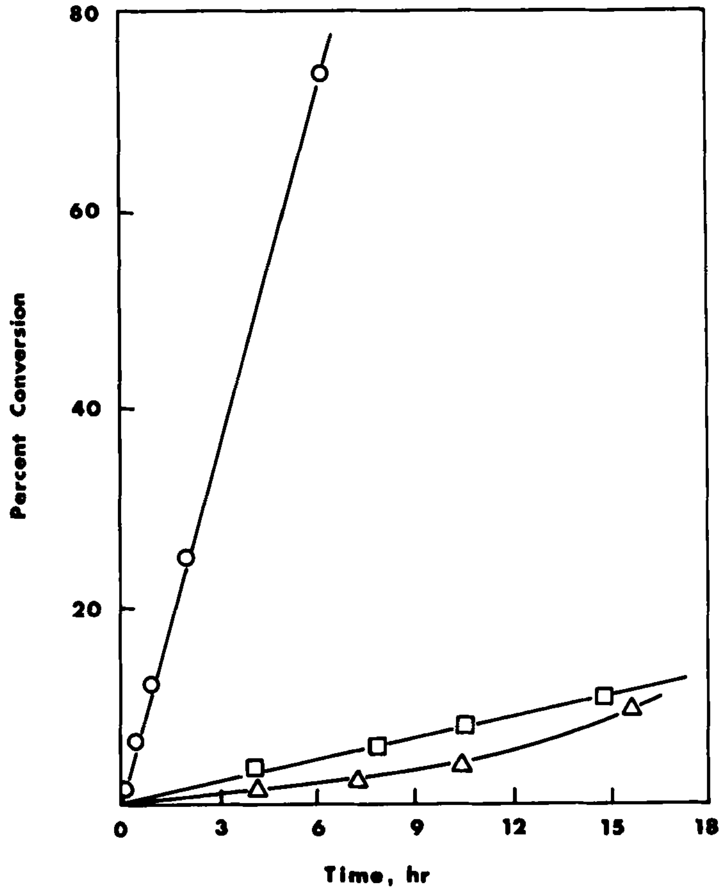

FIG. 1. Conversion curves for the radiation-induced polymerization of EVE at 50° C; dose rate 5.7×10^{15} eV/g-sec: (○) super-dry; (□) dry; (△) wet.

was found repeatedly with the "super-dried" experiments. A typical plot of this type is shown in Fig. 3; it can be seen that at higher doses a curvature begins to occur. There seems to be some dose rate dependence; this is logical, since the production of alcohols, for example, could be linear with dose rate, whereas polymerization rates proceed proportional to the square root of the dose rate. This would lead to a lower than 0.5 power dependence of the rate on the dose rate

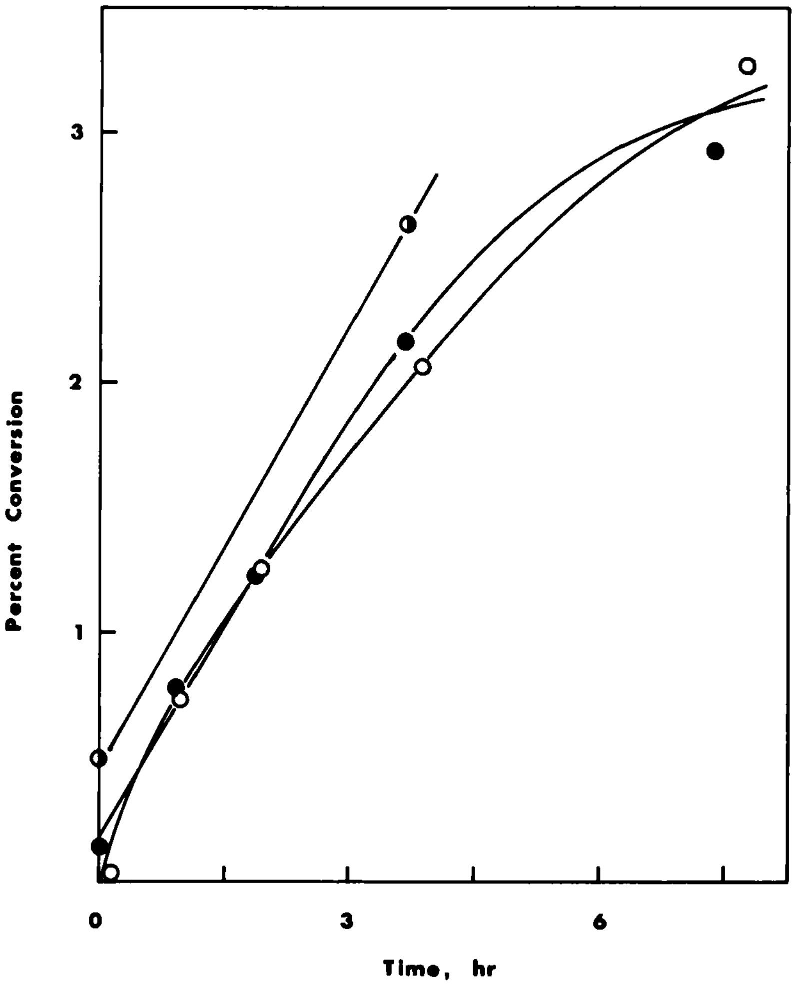

FIG. 2. Conversion curves for the radiation-induced polymerization of super-dry EVE at 0° C; dose rate 5.4 × 10^{15} eV/g-sec: (○) irradiated immediately after preparation; (●) stored 2 months in Dewar flask at room temperature; (◑) stored for 2 months in open laboratory.

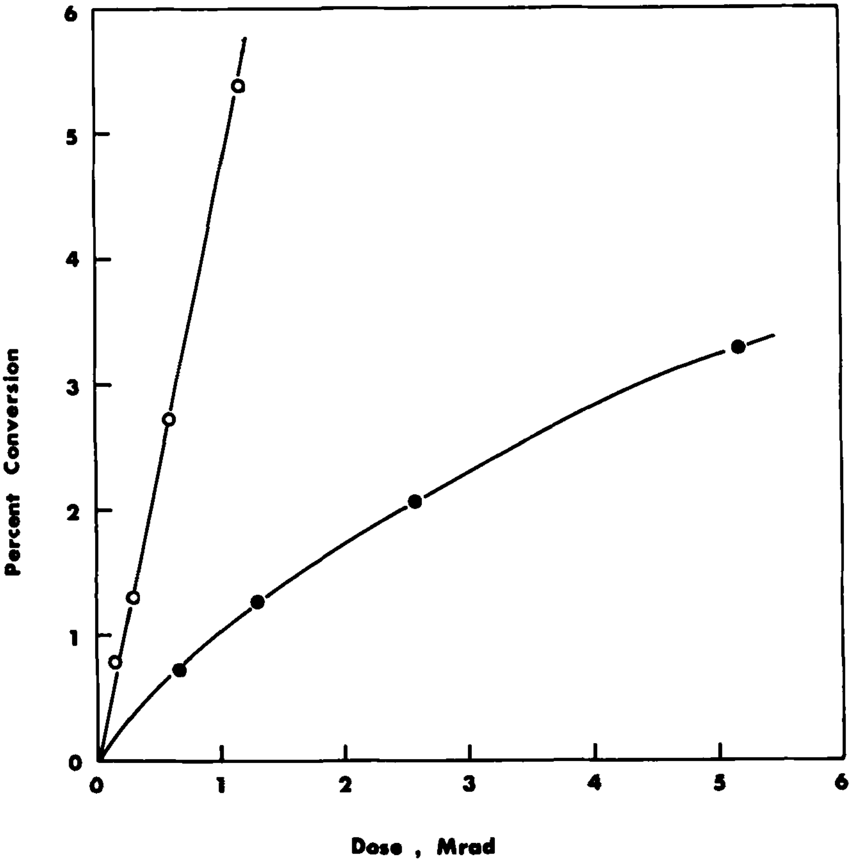

FIG. 3. Conversion curves for the radiation-induced polymerization of EVE at 0° C: (○) dose rate 0.65 Mrad/hr; (●) dose rate 0.05 Mrad/hr.

unless initial rates are used. This was, indeed, the case in the work of Goineau et al. [6]. This is believed to be due to the traces of inhibiting alcohols formed during the radiolysis; such alcohols are known to be formed in the radiolysis of aliphatic ethers. Initial rates were always taken in such cases. Methyl and ethyl vinyl ethers would be particularly vulnerable to such effects owing to their higher oxygen contents.

Irradiation of EVE is thought to generate cation-radicals. Under wet conditions, the cationic active species will terminate rapidly with

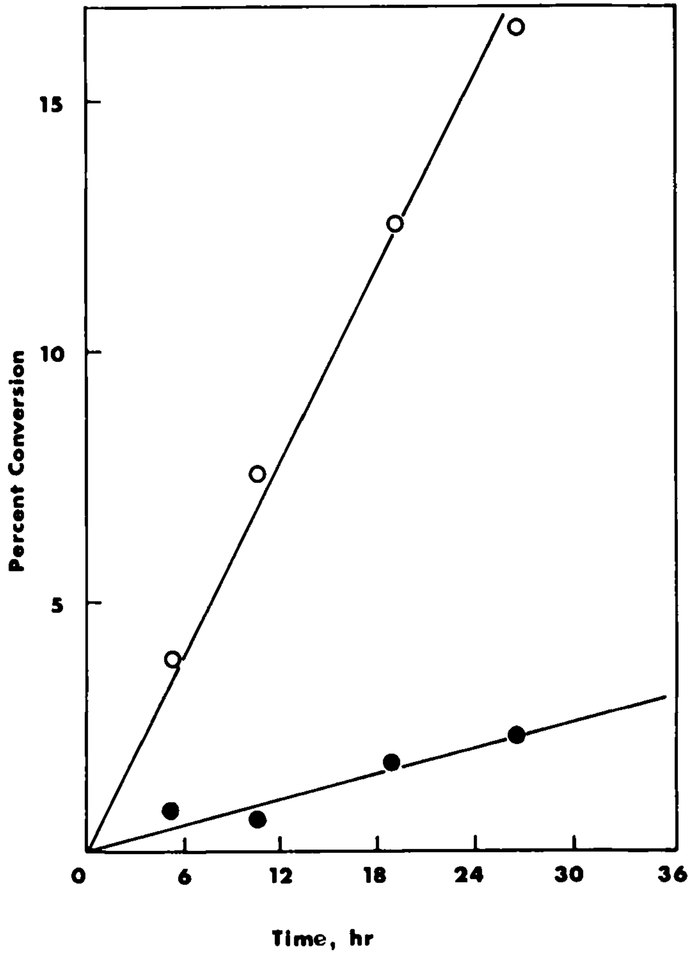

FIG. 4. Conversion curves for the radiation-induced polymerization of wet EVE at 0° C; dose rate 5.7 × 10^{15} eV/g-sec: (o) wet EVE; (•) wet EVE + benzoquinone.

water molecules. Polymerization then proceeds at a rate chiefly governed by free-radical propagation. As a test of this hypothesis, benzoquinone, a free radical scavenger, was added to wet EVE prior to irradiation. In Fig. 4 rate curves for the polymerization of EVE with and without benzoquinone are presented. The significant depression

TABLE 1. Regenerative Chain Transfer to Monomer in the Radiation-Induced Polymerization of Super-Dry EVE at 50° C and a Dose Rate of 11.0×10^{15} eV/g-sec.

$\overline{DP}_n$	G(-m)	G(polymer)[a]	N_{tr}[b]
1195	2095	1.8	11.9
1083	2260	2.1	14.1
1056	2410	2.3	15.4

[a] Calculated from G(polymer) = G(-m)/$\overline{DP}_n$.

[b] The average number of regenerative chain transfer steps occurring during the kinetic lifetime of each carbenium ion; calculated from G_i = 0.14 and G(polymer); N_{tr} = G(polymer)/G_i - 1.

of the rate due to the presence of the scavenger suggests that free radical propagation contributes greatly to the overall rate of polymerization of wet EVE.

In view of the close structural similarities between EVE and IBVE, it seems reasonable to assume that EVE polymerization may be described by Williams' model for radiation-induced ionic polymerization [3, 4]. Previous studies [5, 11] demonstrated that regenerative chain transfer to monomer plays an important role in determining the molecular weight of poly(isobutyl vinyl ether). The same phenomenon is evident in the radiation-induced polymerization of EVE. Values of G(-m)/$\overline{DP}_n$ provide a measure of the relative importance of the chain-transfer reaction. From Table 1 it can be seen that at 50° C the ratio G(-m)/$\overline{DP}_n$ is approximately 2.1. If it is assumed that G_i is ca. 0.14 for EVE [5], it follows that about 14 chain-transfer steps occur during the kinetic lifetime of each propagating carbenium ion. This prevalence of chain transfer to monomer has been noted in studies on chemically initiated carbenium ion polymerizations of EVE [12, 15] and IBVE [16]. Since the chemically initiated systems are unequivocally cationic in nature, similarities in behavior between these systems and radiation-induced polymerizations of super-dry vinyl ethers lend additional support to the theory that the latter processes are also cationic.

By invoking appropriate assumptions concerning the reactivity of the propagating ions, the electrical charge balance and steady-state kinetics, the expression (1) for the overall rate of polymerization may be derived from the Williams model [3]:

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

Since R_i is directly proportional to I, the dose rate, the relationship between R_p and I is determined by the relative magnitude of $k_{tx}[X]$, where k_{tx} is the rate constant for termination with impurities and $[X]$ is the concentration of the impurities. If $k_{tx}[X] \gg (R_i k_t)^{1/2}$, then $R_p \propto I^{1.0}$, whereas if $(R_i k_t)^{1/2} \gg k_{tx}[X]$, then $R_p \propto I^{0.5}$. Consequently, the dose rate dependence of R_p may be used as an indication of the level of impurities in the polymerization system. Although the rates were studied at only two dose rates, a number of careful measurements were made. The rates were found to be 2.20×10^{-5} mole/liter-sec and 0.593×10^{-5} mole/liter-sec at 0.65 and 0.050 Mrad/hr, respectively. This leads to a dose rate dependence of 0.51, close to the correct dependence for completely dry monomer. Similar dependencies have been found [5, 6] for other vinyl ethers under super-dry conditions.

If one assumes that the initiation rates and termination rates with EVE are similar to those found by Williams et al. [3] and by Hayashi et al. [5] with IBVE, then the absolute value of k_p can be calculated as 8.3×10^3 liter/mole-sec. This compares well with the value of 5.1×10^3 liter/mole-sec found with chemical initiation by unpaired ions in methylene chloride solution [12]. The radiation value is higher than that reported previously [12] because of the use of initial rates. Since this leads to a square root dependency of the rate on the dose rate, these are believed to be more reliable values.

The temperature dependence of the rates of EVE polymerization are presented in Fig. 5. The activation energy remains constant at a value of 9.3 kcal/mole over the entire temperature range for both dose rates studied. This overall activation energy may be approximated for super-dry systems by the sum of the activation energies of the fundamental processes [3]:

$$E_{total} = (E_i/2) + E_p - (E_t/2) \tag{2}$$

where E_i and E_p represent activation energies of initiation and

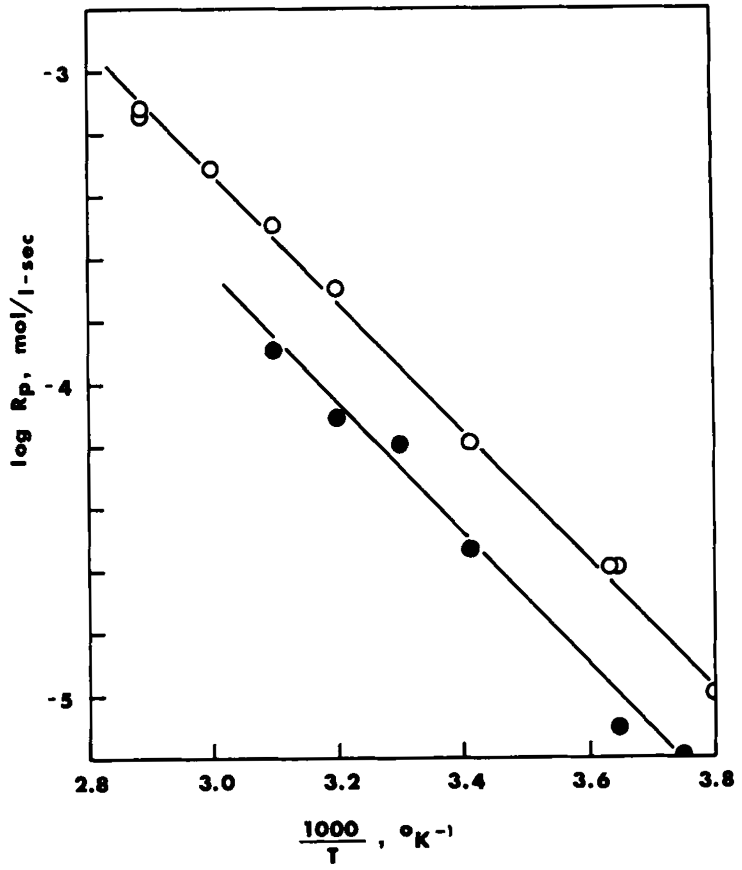

FIG. 5. Arrhenius plots for overall rate of polymerization of super-dry EVE: (○) dose rate 11.28×10^{15} eV/g-sec; (●) dose rate 8.68×10^{14} eV/g-sec.

propagation respectively, and E_t is the activation energy of termination by charge neutralization. Assuming values of ca. 0 kcal/mole for E_i and ca. 3 kcal/mole for E_t leads to a value of 10.8 kcal/mole for E_p. This value of E_p is very close to the value of 9.9 kcal/mole observed for the propagation of unpaired poly(ethyl vinyl ether) cations in methylene dichloride [12]. Methylene dichloride is known to provide a high degree of solvation for carbenium ions and the similarity in activation energies between the chemicall initiated solution polymerization of EVE and the bulk radiation polymerization suggests that solvation processes are also at work in the latter system.

The surprisingly high activation energies in the free cationic polymerization of isobutyl and ethyl vinyl ether have been ascribed to the solvation of the ions plus their resonance stabilization and have been discussed in detail [5, 6, 18].

Number-average molecular weights of the polymers produced by irradiating "super-dry" EVE ranged from 10,000 to 300,000- values significantly higher than those obtained in studies on chemically initiated EVE polymerization [12, 15]. The disparity is puzzling but could be attributable to the greater frequency of charge transfer to monomer in chemically initiated systems and the possibility of transfer reactions involving solvent molecules in solution polymerizations [19, 20].

The ratio of the rate constant of transfer to monomer k_f to the rate constant of propagation k_p may be determined from the equation

$$1/\overline{DP}_n = [G_i/G(-m)] + k_f/k_p \tag{3}$$

Figure 6 presents an Arrhenius plot of the ratio k_f/k_p. The calculations were made on assuming a G_i value of 0.14 over the entire temperature range. Values of k_f/k_p are lower than the values calculated for solution polymerization of EVE [18, 19] and also slightly lower than comparable ratios extracted from data on radiation-induced IBVE polymerizations [5]. In the latter case, a steady increase in k_f/k_p with temperature was observed for irradiation temperatures in excess of 30° C, and this trend is noticeable in the present EVE polymerization data. From the slope of the plot, the value of the activation energy difference (E_p - E_f) is found to be -5.7 kcal/mole. This compares with -1.5 ± 2.5 kcal/mole found by Hayashi et al. [5] with IBVE.

Striking differences in behavior between IBVE and EVE are manifest in the dose dependence of the polymer molecular weights. The number-average molecular weight of the polymer produced by irradiating super-dry IBVE at 0° C was found [11] to rise rapidly with increases in total dose, reaching a maximum $\overline{M}_n$ of 120,000. Further

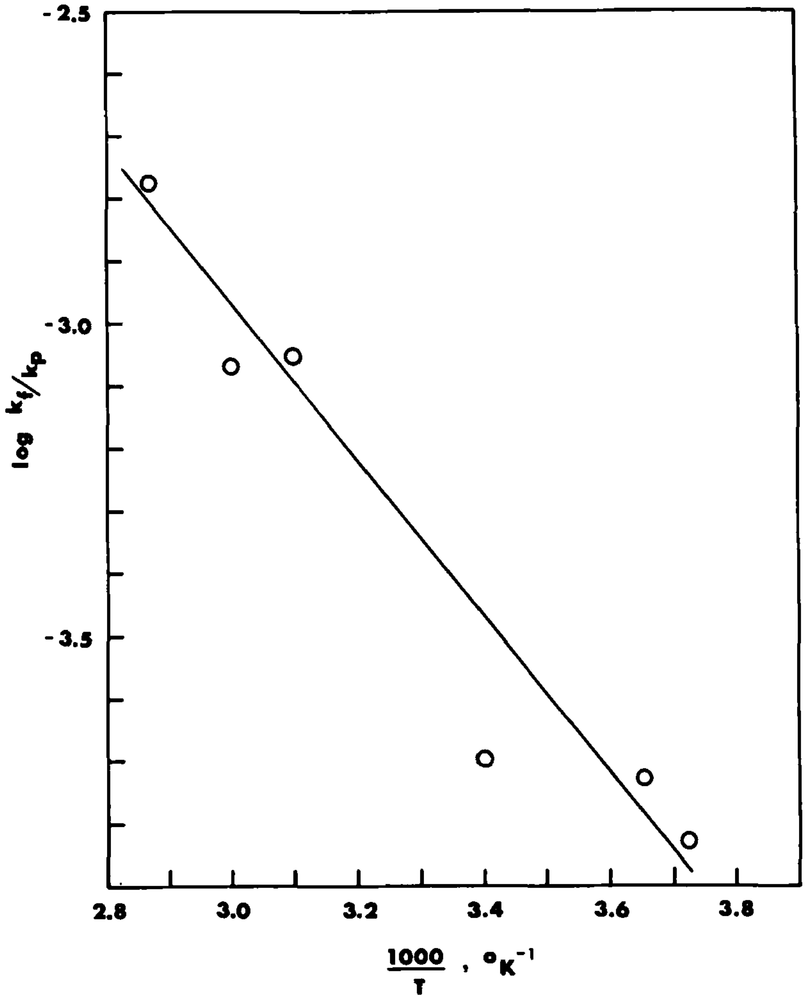

FIG. 6. Relative importance of processes of chain transfer and propagation in the polymerization of super-dry EVE as a function of temperature.

increases in dose resulted in degradation of the polymer, as shown by a slow decrease in $\overline{M}_n$. In Fig. 7, the number-average molecular weight of polymer prepared by irradiating super-dry EVE is plotted as a function of irradiation time. The highest molecular weights are

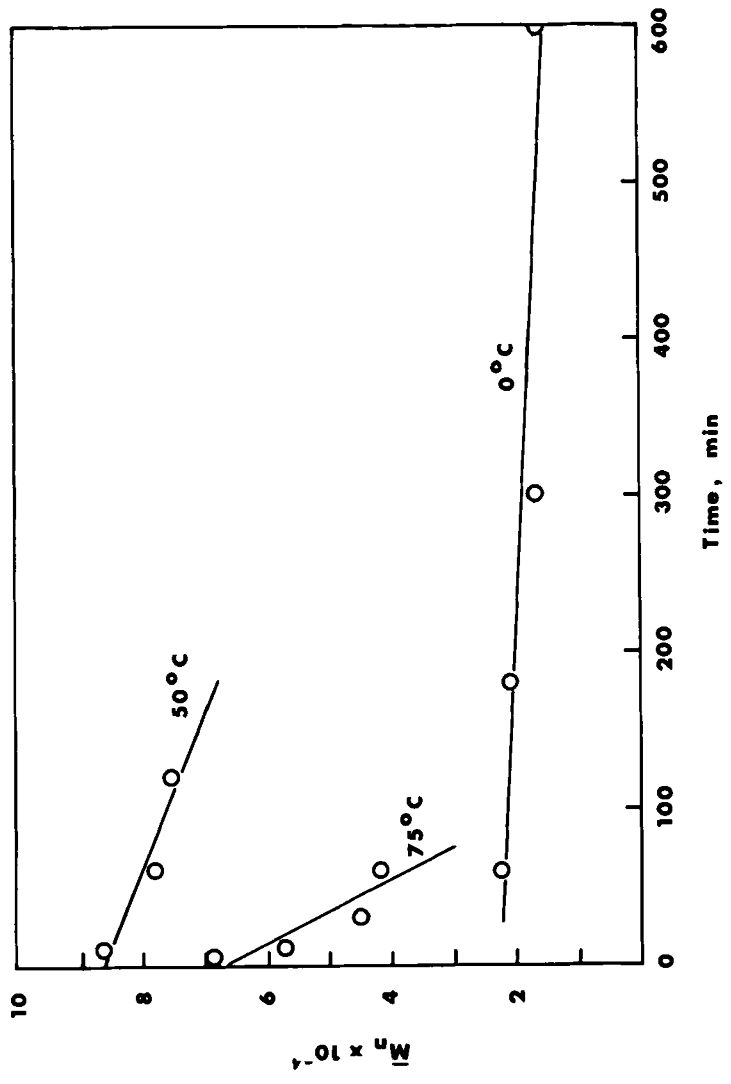

FIG. 7. Number-average molecular weight of poly(EVE) as a function of irradiation time; dose rate 5.5×10^{15} eV/g-sec (super dry).

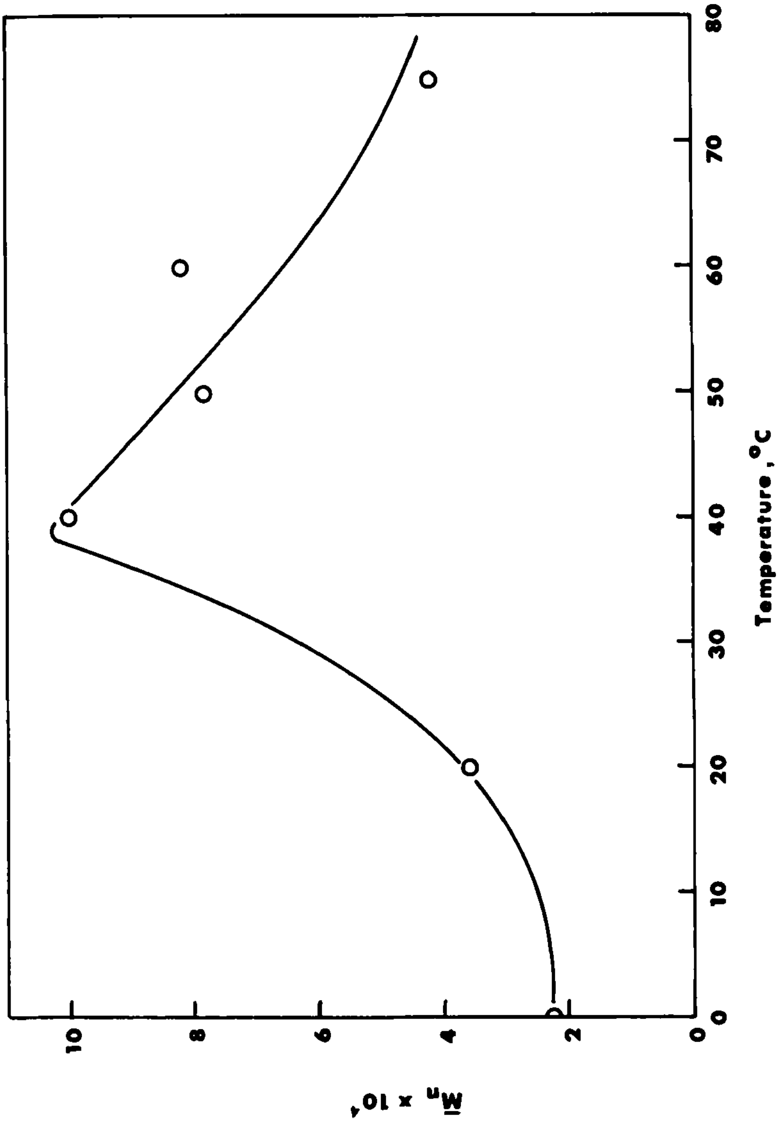

FIG. 8. Number-average molecular weight of poly(EVE) as a function of irradiation temperature; dose rate 5.5×10^{15} eV/g-sec; total dose 2.0×10^{19} eV/g (super dry).

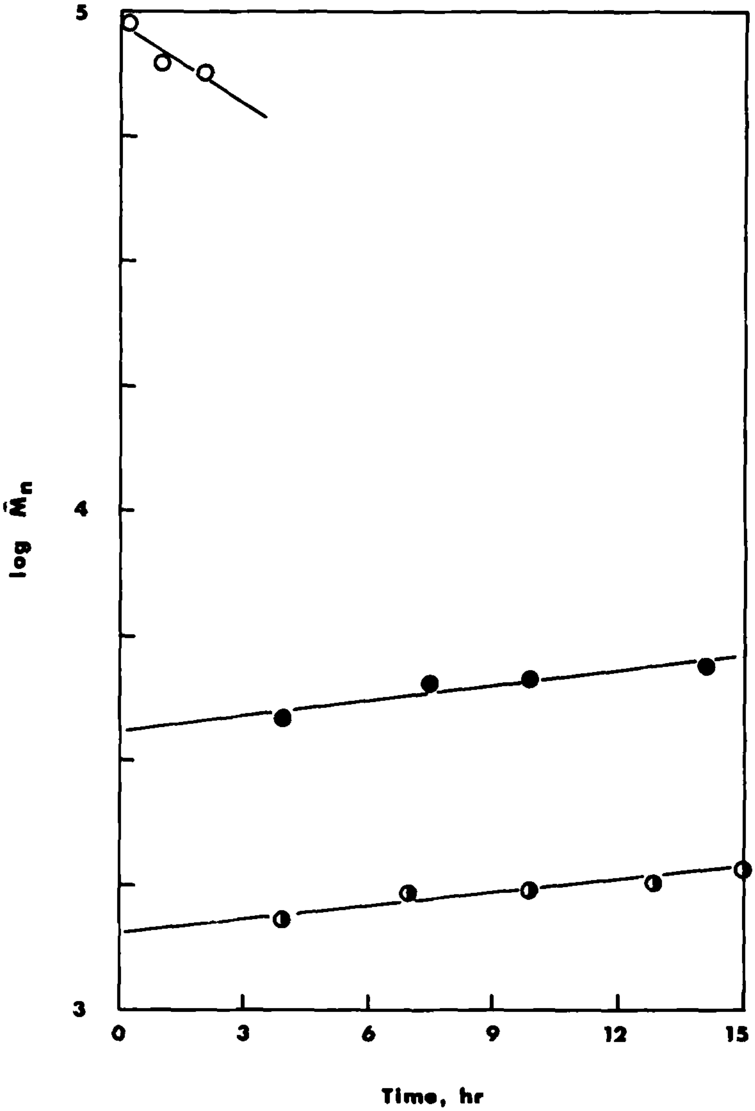

FIG. 9. Influence of the level of monomer dryness on the number-average molecular weight of poly(EVE) prepared at 50° C; dose rate 5.5×10^{15} eV/g-sec: (○) super-dry; (●) dry; (◑) wet.

obtained at low doses, with increased doses producing a steady decline in molecular weight. Increasing the irradiation temperature hastens the rate of decrease in molecular weight. A separate communication concerning the degradative process in irradiated EVE systems is being submitted for publication [21].

An earlier study [11] noted that the molecular weight of polymer produced by irradiating super-dry IBVE attained a maximum at an irradiation temperature of about 35°C at a fixed dose. This behavior can be attributed to the influence of competition between the chain transfer and propagation reactions and the increase in radiation-induced degradation at higher temperature [21]. The shape of the molecular weight versus temperature curves are similar for both IBVE and EVE, as shown in Fig. 8 and Fig. 5 of a previous paper [11].

The level of monomer dryness exerts a profound influence on the molecular weight of radiation-initiated poly(ethyl vinyl ether). The data in Fig. 9 indicate that super-dry EVE polymerizes to molecular weights almost two orders of magnitude higher than those obtained from wet EVE. Molecular weights resulting from polymerization of dry EVE are only slightly higher than those resulting from polymerization of wet EVE, implying that only minute quantities of water are required to reduce the molecular weight of radiation-induced poly(ethyl vinyl ether) drastically by termination with water molecules.

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REFERENCES

[1] S. H. Pinner and R. Worrall, J. Appl. Polym. Sci., 2, 122 (1959).
[2] M. A. Bonin, M. L. Calvert, W. L. Miller, and F. Williams, J. Polym. Sci. B, 2, 143 (1964).
[3] F. Williams, K. Hayashi, K. Ueno, K. Hayashi, and S. Okamura, Trans. Faraday Soc., 63, 1501 (1967).
[4] F. Williams in Fundamental Processes in Radiation Chemistry, P. Ausloos, Ed., Interscience, New York, 1968, pp. 515-598.
[5] K. Hayashi, K. Hayashi, and S. Okamura, J. Polym. Sci. A-1, 9, 2305 (1971).

[6] A. M. Goineau, J. Kohler, and V. Stannett, to be published.

[7] R. C. Potter, C. L. Johnson, D. J. Metz, and R. H. Bretton, J. Polym. Sci. A-1, 4, 2295 (1966).

[8] R. C. Potter, R. H. Bretton, and D. J. Metz, J. Polym. Sci. A-1, 4, 2295 (1966).

[9] R. B. Taylor and F. Williams, J. Amer. Chem. Soc., 91, 3728 (1969).

[10] V. Stannett, T. A. DuPlessis, and A. M. Goineau, J. Appl. Polym. Sci., 16, 2847 (1973).

[11] T. A. DuPlessis, V. Stannett, and A. Goineau, J. Polym. Sci. Polym. Chem. Ed., 12, 2457 (1974).

[12] Y. J. Chung, J. M. Rooney, D. R. Squire, and V. Stannett, Polymer, 16, 527 (1975).

[13] J. A. Manson and G. J. Marquette, Makromol. Chem., 37, 187 (1960).

[14] K. Ueno, K. Hayashi, and S. Okamura, Ann. Repts. Japan. Assoc. Rad. Res. Polym. 8, 55 (1966-7).

[15] A. Leswith, E. Lockett, and D. C. Sherrington, Polymer, 16, 31 (1975).

[16] C. E. H. Bawn, C. Fitzsimmons, A. Ledwith, J. Penfold, and J. A. Weightman, Polymer, 12, 119 (1971).

[17] S. W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960, p. 499.

[18] K. Hayashi, K. Hayashi, and S. Okamura, Polym. J. 4, 426 (1973).

[19] J. M. Rooney, D. R. Squire, and V. Stannett, J. Polym. Sci. Polym. Chem. Ed., 14, 1877 (1976).

[20] T. A. Duplessis, V. Stannett, and A. M. Goineau, J. Macromol. Sci.–Chem., A8, 1361 (1974).

[21] Y. Suzuki, J. M. Rooney, and V. Stannett, J. Macromol. Sci.–Chem., in press.

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