Radiation-Induced Degradation of a Series of Poly(vinyl Ethers)

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ABSTRACT

The degradative effects of γ-radiation on diethyl ether solutions of poly(alkyl vinyl ethers) under a variety of conditions were studied by polymer molecular weight measurements. Poly(methyl vinyl ether) (PMVE), poly(ethyl vinyl ether) (PEVE), poly(isopropyl vinyl ether) (PIPVE), and poly(isobutyl vinyl ether) (PIBVE) exhibited similar degradative behavior, with $G_{(SC)}$ values between 0.3 and 0.9 scissions/100 eV at 0°C. Chemically polymerized and radiation-polymerized PEVE samples gave comparable results. Chain degradation was much more pronounced for samples of poly(tert-butyl vinyl ether) (PTBVE) which yielded a $G_{(SC)}$ value of 3.6 at 0°C. Degradation experiments conducted on PEVE in air resulted in significantly higher rates of scission: $G_{(SC)} = 5.6$ scissions/100 eV at 0°C. Chain scission was not measurably influenced by changing the solvent from diethyl ether to di-isopropyl ether. Increased polymer concentration was found to reduce the rate of polymer degradation.

INTRODUCTION

The poly(vinyl ethers) belong to the class of polymers which degrade when exposed to high energy radiation. When the vinyl ethers are polymerized with radiation initiation it is clear that concurrent degradation must also take place. A similar phenomenon occurs with isobutylene polymerization [1, 2]. The final molecular weight of the polymer is governed by various competing factors, including chain transfer to monomer, the relative rates of propagation and termination, and the concurrent radiation-induced degradation. During the course of a rather extensive series of studies of the radiation-induced polymerization of a number of vinyl ethers, it was decided to conduct a brief parallel study on the effect of dose and temperature on the radiation degradation of the poly(vinyl ethers) themselves. In particular, this information is useful in predicting the amount of concurrent degradation accompanying the polymerization reaction. The present paper describes the results of such a study.

EXPERIMENTAL

Samples of poly(ethyl vinyl ether) (PEVE), poly(isopropyl vinyl ether) (PIPVE), poly(isobutyl vinyl ether) (PIBVE), and poly(tert-butyl vinyl ether) (PTBVE) were obtained by irradiating "super-dry" monomer in the Co-60 γ-ray source located in the laboratories of the Department of Chemical Engineering of North Carolina State University. Irradiation temperatures were controlled by means of a Lauda thermostat. The preparation of super-dry vinyl ether monomers is described in detail elsewhere [3]. Chemically initiated PEVE was prepared by adding a solution of triphenylmethyl hexachloroantimonate in methylene dichloride to super-dry EVE monomer at -10°C under vacuum. Poly(methyl vinyl ether) (PMVE) was obtained from the General Aniline and Film Corporation.

Polymer samples were dissolved in spectroscopic grade diethyl ether, forming a solution of 10% by weight. The solution was degassed and transferred to ampoules which were then sealed off under a vacuum of about 5×10^{-5} Torr. Irradiation of the ampoules was carried out in the γ-ray source mentioned above. After exposure to the γ-rays, the ampoules were cracked open and the solvent evaporated. Intrinsic viscosity measurements were conducted on benzene solutions at 30°C. Viscosity-average molecular weights were calculated from the formulas used in the related polymerization studies [3]. The corresponding number-average molecular weights were estimated from the exponents of the Mark-Howink
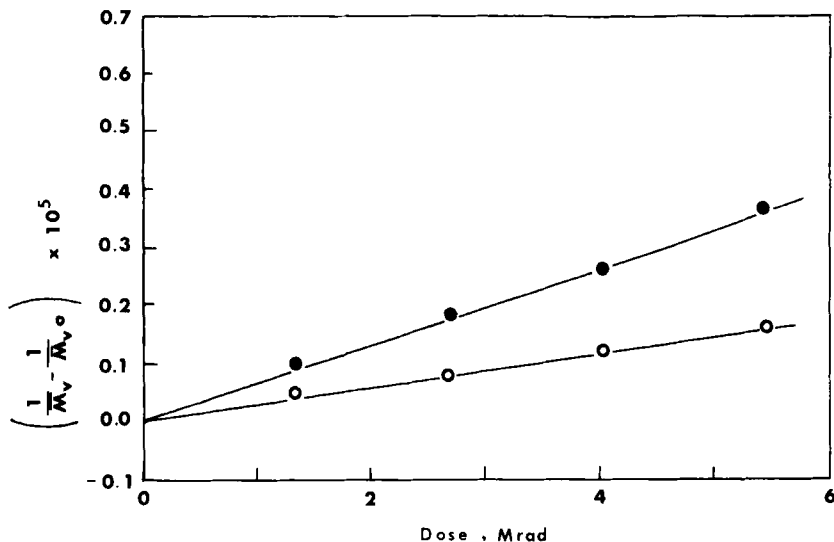
FIG. 1. Radiation-induced degradation of chemically polymerized poly(MVE) in diethyl ether: (●) at 75°C; and (○) at 0°C; dose rate 0.68 Mrad/hr.

equation by the method described by Charlesby [4], a random distribution being assumed.

The G (scission) values were calculated from the equation [5]:

$$G \text{ (scission)} = (9.6/W)\{(10^5/D) [(1/\overline{M}_n) - (1/\overline{M}_{n0})]\}$$

where W is the molecular weight of the monomer unit, D is the absorbed dose in Mrad, and $\overline{M}_n$ and $\overline{M}_{n0}$ are the number-average molecular weights initially and after the absorbed dose D.

RESULTS

The degradation of PMVE, PEVE, PIPVE, PIBVE, and PTBVE as a function of total dose and at least two temperatures are presented in Figs. 1-5, respectively. The samples were irradiated in diethyl ether solution under high vacuum. In the case of PEVE a plot of the degradation versus dose in air is included as well as data for both
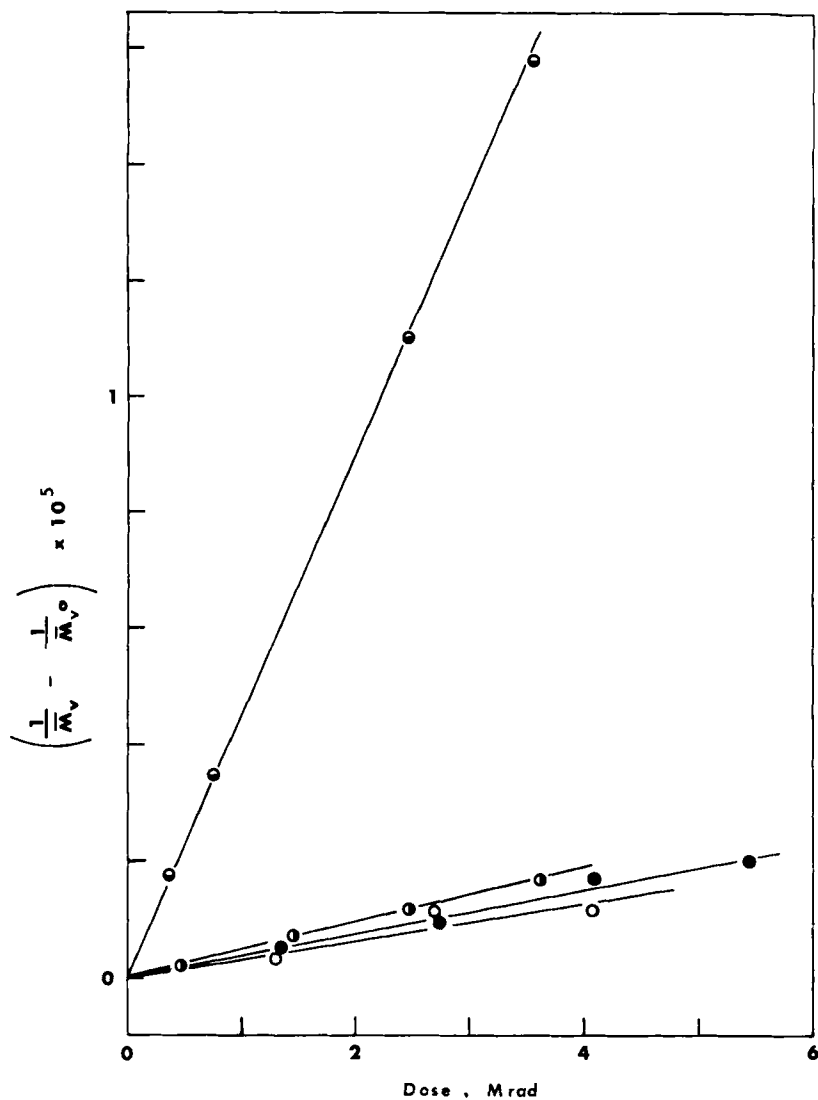
FIG. 2. Radiation-induced degradation of poly(EVE) in diethyl ether (•) poly(EVE) radiation-polymerized at 75°C (•) and (○) 0°C; (◑) degraded in air at 0°C; (○) chemically polymerized poly(EVE), degraded at 30°C.

FIG. 3. Radiation-induced degradation of poly(IPVE) in diethyl ether (●) at 75°C and (○) at 0°C.

FIG. 4. Radiation-induced degradation of poly(IBVE) in diethyl ether: (●) at 75°C; (◐) at 20°C; (○) at 0°C; (◓) in diisopropyl ether at 0°C.
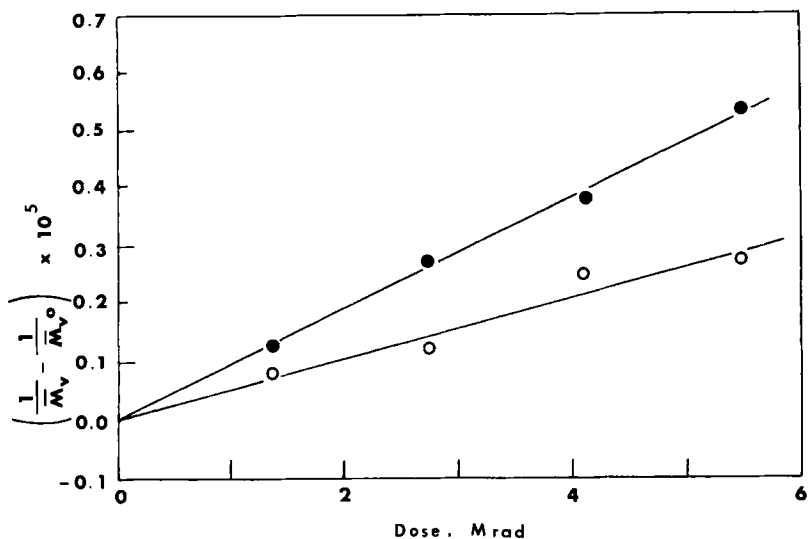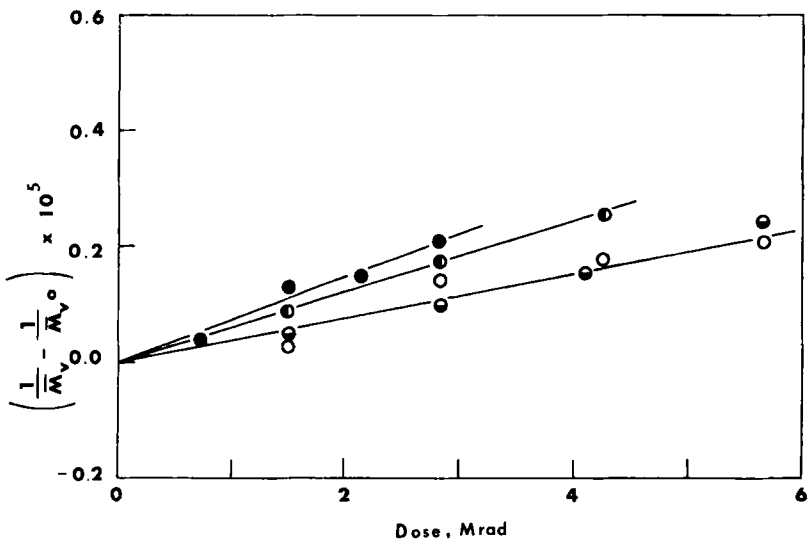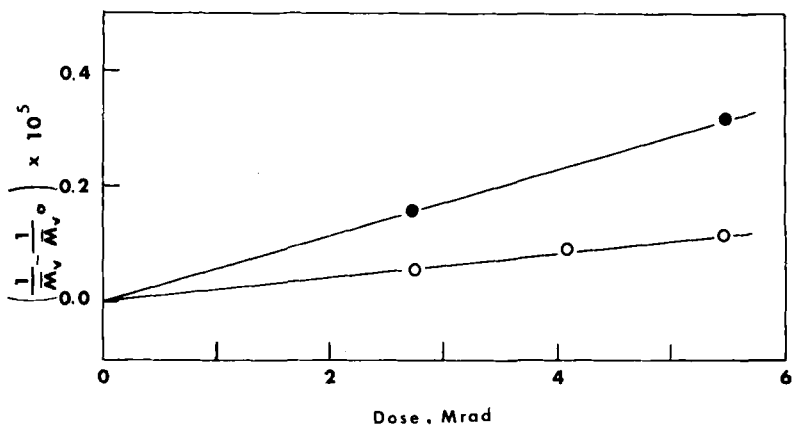
FIG. 5. Radiation-induced degradation of poly(TBVE) in diethyl ether at (●) 75°C and (○) 0°C.

chemically and radiation produced samples. Good linear plots of the reciprocal of the viscosity average molecular weight versus dose were obtained. This enabled the calculation of reasonable estimates of the G (scission) values within the limitation of the viscosity-average molecular weight measurements, rather than direct number-average measurements. The results are plotted in a normalized manner as $(1/\overline{M}_v) - (1/\overline{M}_{v0})$. Although the effect of the initial molecular weight of the polymer was not investigated in detail, two samples of PEVE, one of $\overline{M}_v = 150,000$ and one of $\overline{M}_v = 350,000$ were studied, and identical G (scission) values obtained. The molecular weights of the polymers used are included in Table 1 together with the G (scission) values and the activation energies. The effect of the polymer concentration was also studied and the results are presented in Fig. 6. The amount of degradation decreased, only slightly with increasing PIBVE concentration up to about 20% by weight. At higher concentrations, the degradation was markedly reduced. All other experiments reported were on 10% solutions by weight. Finally similar degradation experiments were conducted in diethyl ether and diisopropyl ether with PIBVE; the results are included in Fig. 4. No difference in the degree of degradation was found within the experimental error.

TABLE 1. G (Scission) Values and Activation Energies for the
Radiation-Induced Degradation of Poly (Vinyl Ethers) in Vacuo; Dose
Rate-0.68 Mrad/hr

Polymer	Initial MW	G (scissions) (no./100 eV)		E_a (kcal/ mole)
		0°C	75°C	
Poly(methyl vinyl ether)	72,000	0.31	0.64	1.8
Poly(ethyl vinyl ether)	150,000	0.36	0.50	0.8
	350,000	0.36	0.50	0.8
Poly(ethyl vinyl ether)[a]	150,000	5.6	-	-
Poly(isopropyl vinyl ether)	57,000	0.86	1.50	1.4
Poly(isobutyl vinyl ether)	86,000	0.39	1.73	3.8
Poly(tert-butyl vinyl ether)	86,000	3.6	10.3	2.7

[a]In air.

DISCUSSION

The results presented in the previous section are similar in many
respects to those reported for polyisobutylene and other degrading-
type polymers. The effect of air is quite characteristic and is
normally attributed to oxidative chain degradation. The poly(vinyl
ethers) seem more affected by air than polyisobutylene or poly(methyl
methacrylate), for example. Since the poly(vinyl ethers) are rather
easily oxidized this is, perhaps, not surprising.
    The effect of increased polymer concentration in reducing the
amount of degradation has been reported by Okamura et al. [6], but
conflicting results were obtained by Henglein et al. [7]. The effects
of solvent are complex and can include chain transfer and energy
transfer mechanisms. A reasonable additional explanation would be
that polymer-polymer radical recombination reactions become more
important at higher concentrations.
    The G (scission) values together with the activation energies are
presented in Table 1. Both quantities are subject to some errors,
since only viscosity-average molecular weights were measured and
only three temperatures, at most, were used. The molecular weight
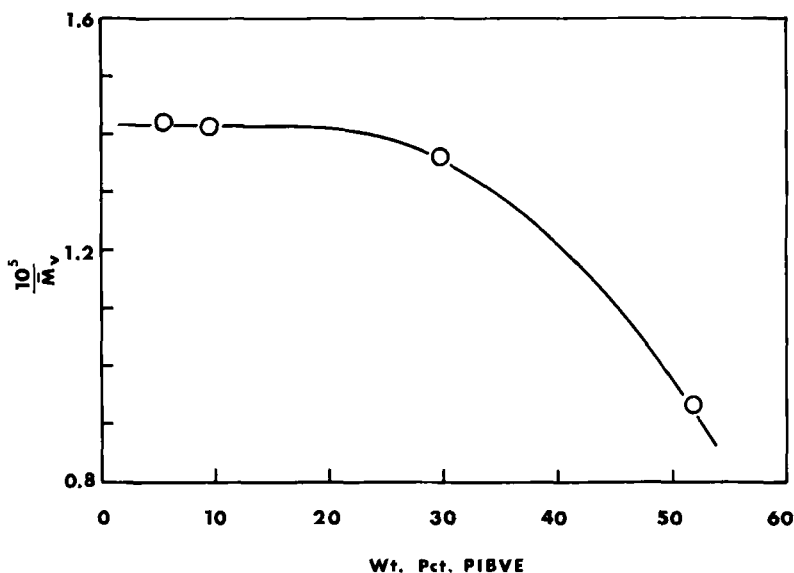distributions tend towards the most probable distribution with

FIG. 6. Effect of polymer concentration on the radiation-induced degradation of poly(IBVE) in diethyl ether at 75°C; dose rate 0.68 Mrad/hr; total dose 2.72 Mrad.

increasing dose which could also cause an error if the original distributions were different. This could account for example for the G (scission) values of 0.61 and 0.45 at 30°C found with polymer polymerized chemically and with radiation, respectively, although structural differences could also be responsible. In spite of these difficulties the values presented in Table 1 are believed to be reasonable estimates. They are quite low, polyisobutylene for example has a G value for scission of 3.4 at room temperature [1]. The low values are probably related to the low degrees of strain in the poly(vinyl ether) molecules. This is reflected in their higher heats of polymerization which are in the range of 17-23 kcal/mole [8, 9] compared with 13 kcal/mole for polyisobutylene. The high value for PTBVE is puzzling; it could be due to steric strain caused by the bulky tert-butyl group, but the reported heat of polymerization is similar to those of the other vinyl ethers [8].

Finally the data presented can be used to estimate the amount of degradation encountered during the polymerization reactions. The similarity between the results obtained with diethyl ether and diisopropyl ether solutions lend credence to this approach. On the

assumption of a linear conversion-dose plot the final polymer sample will have been subjected, on the average, to one half the total dose. It can be seen from the polymerization data presented previously [3, 10] that, where super-dry monomer is used, molecular weight reductions during polymerization are relatively insignificant at $0°C$ but could be more pronounced at higher temperatures.

ACKNOWLEDGMENT

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