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Y. Suzuki^a; A. J. Chudgar^a; J. M. Rooney^a; V. Stannett^a

^a Department of Chemical Engineering, North Carolina State University Raleigh, North Carolina

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Radiation-Induced Grafting of Ethyl Vinyl Ether onto Poly(vinyl Chloride)

Y. SUZUKI, A. J. CHUDGAR, J. M. ROONEY, and V. STANNETT

Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27650

ABSTRACT

The radiation-induced graft polymerization of ethyl vinyl ether (EVE) onto poly(vinyl chloride) (PVC) was studied under a variety of conditions. Graft copolymer and homopoly(EVE) were formed in all cases. The presence of water reduced overall polymerization rates, percentage grafting, and homopoly(EVE) molecular weights. With "superdry" EVE, grafting reached 29% at a total dose of 6.9 Mrad. Grafting to PVC films was less efficient than grafting to PVC powder. Application of a relatively poor swelling agent for PVC resulted in an increase in the efficiency of grafting. From a comparison of studies of radiation-induced EVE homopolymerization and the present work, it was concluded that dry and superdry EVE are grafted to PVC by a cationic mechanism and wet EVE is grafted mainly by a free-radical mechanism.

INTRODUCTION

In 1958, Plesch [1] suggested that chemical or radiolytic methods could be used to generate macrocations from polymeric halides. These macrocations could then be used as initiators in graft

copolymerization reactions. Dreyfus and Kennedy [2] have conducted detailed studies of chemically initiated graft copolymerization involving polymeric halides. In the presence of silver salts such as AgClO_4 and AgPF_6 , polymeric halides were found to form backbone carbenium ions paired with PF_6^- or ClO_4^- counterions, while the silver halide was precipitated. High-energy radiation tends to activate molecules without regard to chemical structure, however the lability of carbon-halide bonds should render activation of certain sites through rearrangement on the polymer backbone energetically favorable, thus providing a measure of control over the initiation step in the grafting process. Radiation-induced grafting of dry isobutylene onto poly(vinyl chloride) (PVC) has been examined by Chapiro [3] and Jendrychowska-Bonamour [4]. These workers ascertained that grafting in the isobutylene-PVC system proceeded by a cationic mechanism. Percentage grafting in excess of 20% was achieved. Kabanov and Sidorova [5, 6] studied the radiation-induced grafting of "super-dry" n-butyl vinyl ether onto PVC films and other monomer-polymer systems, and demonstrated the importance of monomer dryness as a factor in controlling the graft percentage. Grafting in the n-butyl vinyl ether-PVC system proceeded without homopolymerization. The present work represents a brief study of the radiation-induced grafting of ethyl vinyl ether (EVE) to PVC under a variety of conditions.

EXPERIMENTAL

EVE, obtained from the Monomer-Polymer Laboratories, Borden Chemicals, was treated as described previously [7]. Vinyl chloride of purity greater than 99% was obtained from the Ethyl Corporation, Baton Rouge, Louisiana, distilled under high vacuum at low temperatures, degassed, and transferred to sealed ampoules. PVC was obtained by irradiating the purified vinyl chloride in the 6 kCi Co-60 γ -ray source located in the Department of Chemical Engineering of the North Carolina State University at Raleigh for 6 hr at 0°C and a dose rate of 0.12 Mrad/hr. A 78% conversion was achieved during this process. Polymer was isolated by evaporation of unreacted monomer. To remove the last traces of vinyl chloride and any impurities generated during irradiation, the PVC was dissolved completely in pure cyclohexanone and then precipitated with reagent-grade methanol. The precipitated PVC was extracted in a Soxhlet extraction column with methanol for about 100 hr. The methanol was then removed by evaporation in a vacuum oven at room temperature for 50 hr. The molecular weight of the PVC was determined from intrinsic viscosity measurements conducted at 20°C in distilled cyclohexanone by using a Ubbelohde viscometer. The viscosity-average molecular weight, calculated from Eq. (1) [8]

$$[\eta] = 1.16 \times 10^{-4} \bar{M}_v^{0.85} \quad (1)$$

was found to be 1.17×10^5 . PVC films were cast from a 5 wt % solution of the polymer in tetrahydrofuran. Film thicknesses ranged from 0.035 mm to 0.065 mm. About 0.1 g pure PVC powder or film was placed in ampoules fitted with breakseals. The PVC was dried for several days at 40°C and a vacuum of less than 10^{-5} mm Hg. Approximately 2 ml EVE was introduced onto the PVC from EVE sample tubes. Sample tubes containing "superdry," dry, and wet EVE were prepared as described previously [7, 9]. Tubes containing PVC and EVE were irradiated in the Co-60 source and the graft copolymer isolated by extraction in benzene. Percentage grafting was calculated according to Eq. (2) and graft efficiency according to Eq. (3),

$$\text{Percentage Grafting} = 100 (b - a)/a \quad (2)$$

$$\text{Graft Efficiency} = 100 (b - a)/(b + c - a) \quad (3)$$

where *a* is the original weight of PVC powder or film, *b* is the weight of PVC powder or film after irradiation, and *c* is the weight of EVE homopolymer. Molecular weights of homopoly(EVE) were determined as before [7, 9].

RESULTS AND DISCUSSION

Conversion curves for the radiation-induced graft polymerization of EVE onto PVC powder under superdry, dry, and wet conditions are presented in Fig. 1. The conversions indicated represent the total percentage of EVE consumed in both the grafting and homopolymerization reactions. The radiation-induced homopolymerization of EVE has been shown to be more complicated than the polymerization of other vinyl ethers [7, 9]. Radiolytic generation of alcohols and other species has been advanced as a possible explanation of anomalous rate behavior [7, 9]. The effect of the grafting substrate on potential side reactions is unknown, but two principal conclusions may be drawn from Fig. 1. (1) The overall rates of superdry and dry EVE polymerization are similar in the grafting system. There is, however, a small induction period with the dry system. This similarity may be caused by depression of the rate of polymerization of superdry EVE by residual impurities in the PVC.

(2) Wet EVE polymerizes at an extremely low rate in the system, indicating that the primary propagation mechanism in the dry and superdry graft polymerizations is cationic in nature.

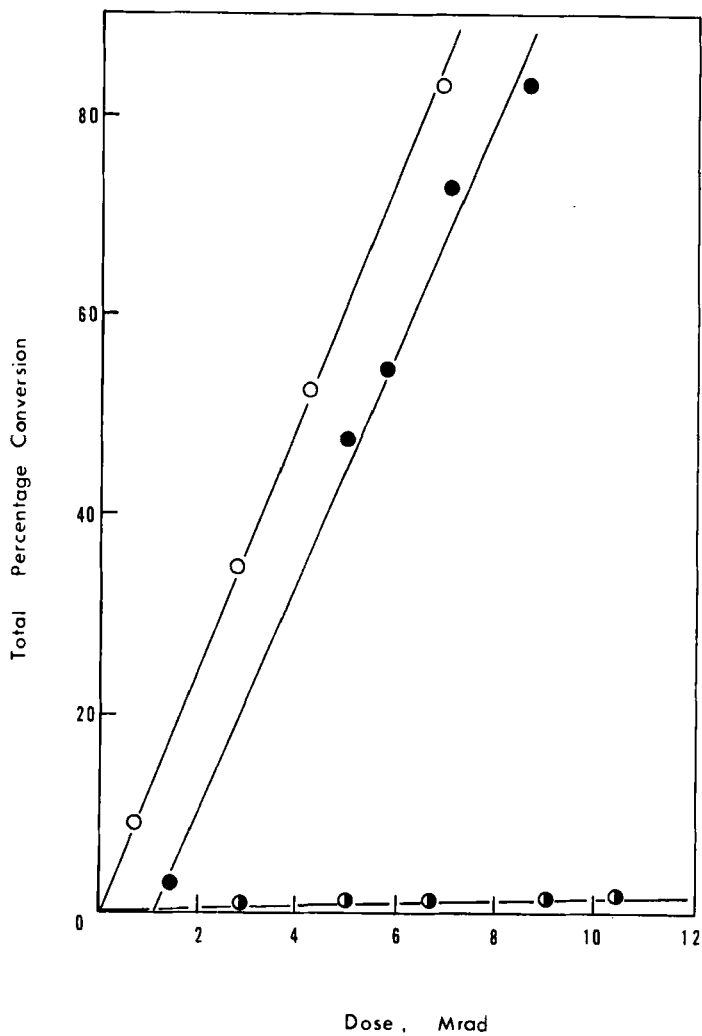


FIG. 1. Conversion curves for the radiation-induced grafting of EVE onto PVC powder at 50°C, dose rate 0.70 Mrad/hr: (○) super-dry; (●) dry; (●) wet.

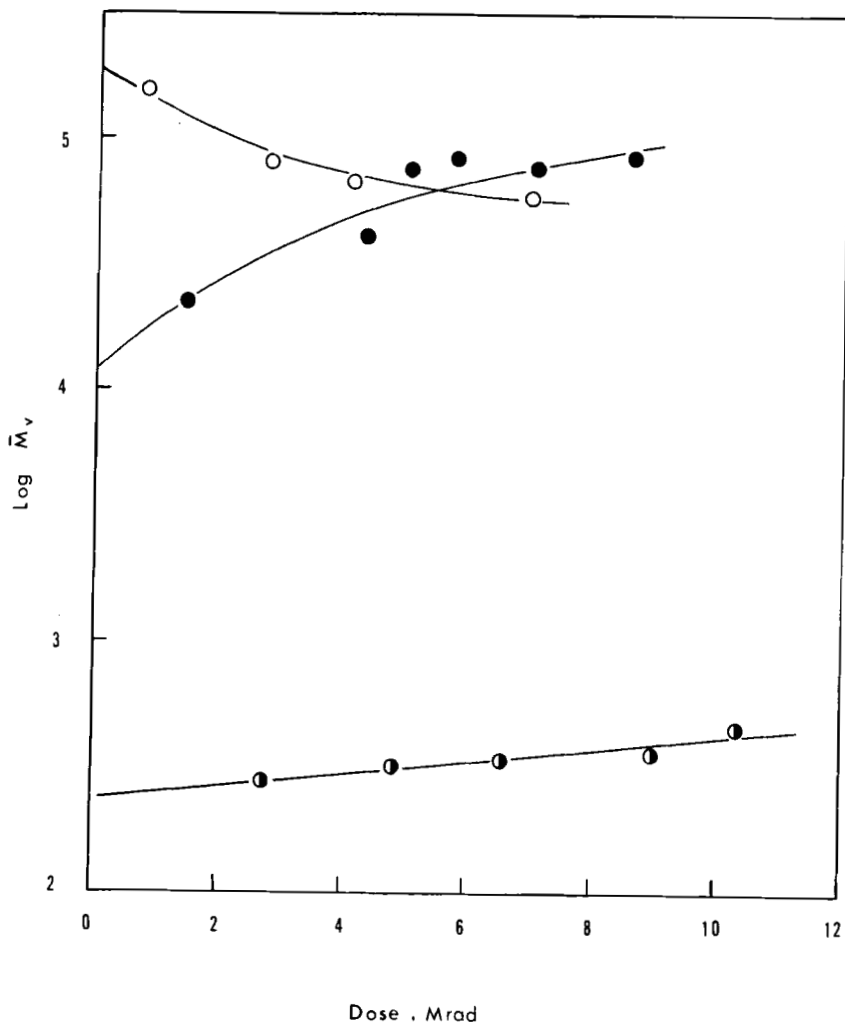


FIG. 2. Dose dependency of molecular weight of homopoly(EVE) obtained from EVE-PVC grafting system by irradiation at 50°C, dose rate 0.70 Mrad/hr: (○) superdry; (●) dry; (◐) wet.

In Fig. 2 the dependency of the molecular weight of the homopoly-(EVE) on total dose is presented graphically. Once again, a similarity in behavior between superdry and dry EVE may be observed. The viscosity-average molecular weights ranged from 58,000 to 150,000

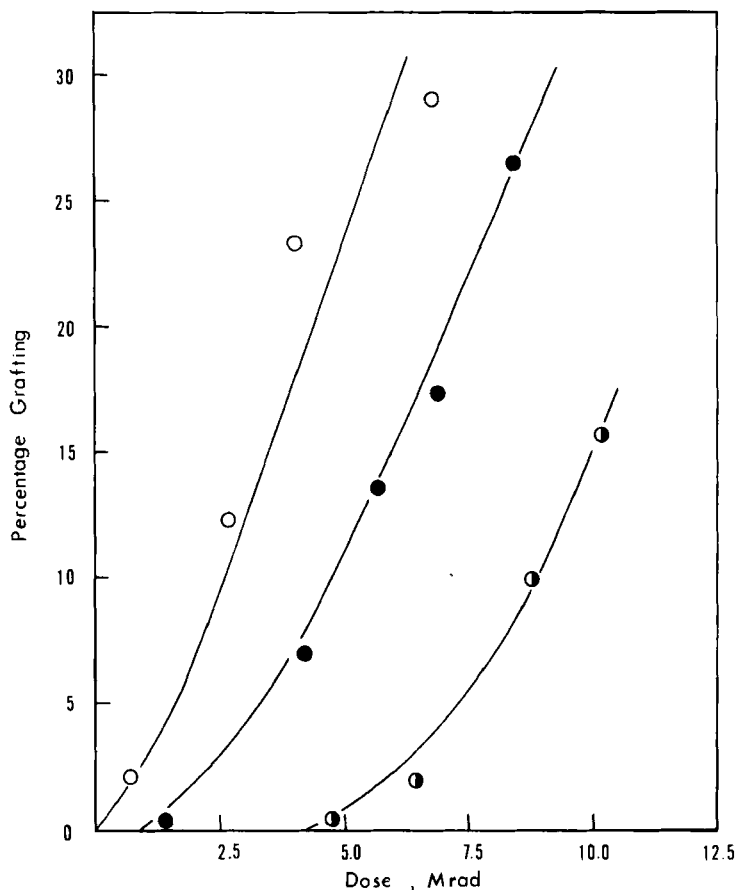


FIG. 3. Dose dependency of percentage grafting in radiation-induced grafting of EVE onto PVC powder at 50°C, dose rate 0.70 Mrad/hr: (○) superdry; (●) dry; (◐) wet.

in the former case and from 21,000 to 83,000 in the latter, while values between 273 and 457 were measured for the polymerization of wet EVE. Molecular weights of polymers obtained by irradiating wet and dry EVE in this system were found to increase gradually with increasing total dose while polymers produced from superdry EVE showed a gradual decline in \bar{M}_v with increases in the total dose. Studies on the radiation-induced polymerization of superdry EVE [7] have

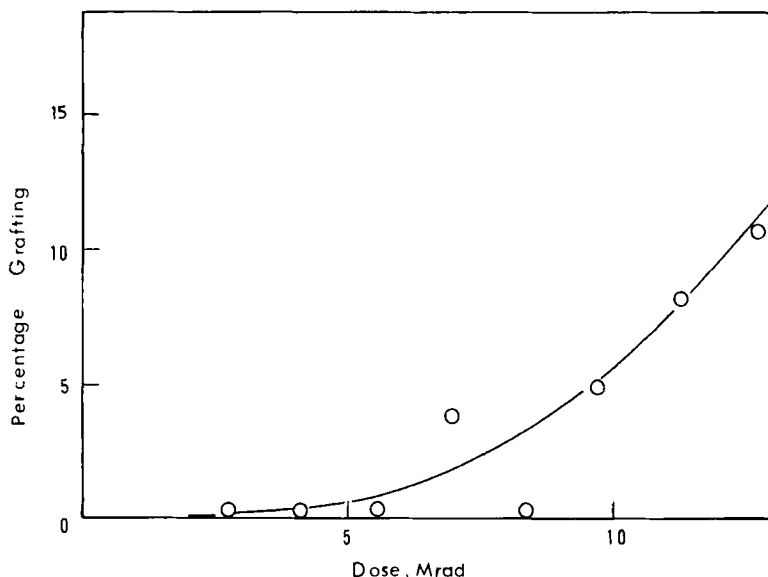


FIG. 4. Dose dependency of percentage grafting in radiation-induced grafting of dry EVE onto PVC film at 50°C, dose rate 0.70 Mrad/hr.

ascribed this decrease in molecular weight to the effects of simultaneous propagation and degradation.

The dose dependency of the percentage grafting is depicted in Fig. 3. Grafting of superdry EVE onto PVC powder proceeds without an appreciable induction period and reaches a level of 29% in 9 hr. As the moisture content of the monomer is increased, an induction period develops and the rate of grafting decreases. The physical state of the PVC was also found to influence the rate of EVE polymerization in the grafting system. Figure 4 represents a conversion curve for the radiation-induced graft polymerization of dry EVE monomer onto a PVC film. Comparison of Fig. 4 with Fig. 3 demonstrates that grafting of dry EVE to PVC films is preceded by a longer induction period and occurs at a lower rate than grafting of dry EVE to PVC powder. In theory, the rate of the grafting process may be also governed by the rate of monomer diffusion into the substrate, and the EVE molecules should require more time to diffuse into films than they require to diffuse into powder. However, the molecular weight of the homopoly(EVE) obtained by irradiating dry EVE in the presence of PVC films was found to be much lower

(4300-9500) than that achieved in the presence of PVC powder. Since the molecular weight of the homopolymer should not be affected significantly by the rate of the diffusion process, a more probable explanation of this phenomenon is that the PVC films are not as free from impurities as the PVC powder. Residual moisture and organic impurities introduced into the film during the casting process may be present in quantities sufficient to retard cationic polymerization.

In the light of these facts, application of swelling agents to the grafting substrate would be expected to produce two principal effects: (1) a decrease in the overall rate of polymerization and the rate of homopoly(EVE) formation, due to monomer dilution and (2) an increase in the graft efficiency due to the greater accessibility of active sites on the swollen substrate.

The radiation-induced homopolymerization of EVE as a 50 vol % solution in benzene, a rather poor swelling agent for PVC, is outlined in Table 1. The rate of polymerization and polymer molecular weights are significantly lower than comparable values reported for the radiation-induced bulk polymerization of dry EVE [7]. Radiation-induced grafting of dry EVE, in a 50 vol % solution, to PVC powder was conducted, and the results, presented in Table 2, are in line with

TABLE 1. Radiation-Induced Polymerization of Dry EVE in a 50 Vol % Benzene Solution at 50°C and Dose Rate 0.70 Mrad/hr

| Dose (Mrad) | Polymerization (%) | \bar{M}_v | $G_{(-m)}$ |
|-------------|--------------------|-------------|------------|
| 6.9 | 4.4 | 1100 | 85 |
| 9.0 | 6.9 | 2270 | 103 |

TABLE 2. Radiation-Induced Grafting of Dry EVE in a 50 Vol % Benzene Solution to PVC Powder at 50°C and Dose Rate 0.70 Mrad/hr

| Dose (Mrad) | Polymerization (%) | Grafting (%) | \bar{M}_v | $G_{(-m)}$ | Graft efficiency (%) |
|-------------|--------------------|--------------|-------------|------------|----------------------|
| 4.8 | 4.47 | 0 | 2640 | 124 | 0 |
| 6.9 | 7.22 | 3.7 | 7080 | 140 | 4.2 |
| 9.0 | 14.3 | 13.6 | 14600 | 213 | 7.4 |

the expectations. The overall rates of polymerization and grafting were lower than those obtained in the superdry and dry grafting systems. However the graft efficiency of 4.2% at a total dose of 6.9 Mrad was a little higher than the comparable values of 3.7% for the grafting of superdry EVE to PVC and 2.3% for the grafting of dry EVE to PVC.

The sensitivity of the grafting process to the presence of water manifested in Fig. 3 suggests that the addition of superdry and dry EVE to the PVC backbone follows a cationic mechanism: radiolysis of the PVC chains produces macrocations which initiate the polymerization of EVE monomer. The reaction scheme should be analogous to that proposed by Chapiro [3] for the radiation-induced grafting of vinyl monomers onto PVC. In a previous study [7], wet EVE was found to polymerize in bulk at a rate of about 1%/Mrad at 50°C. Number-average molecular weights ranged from 1000 to 1500, and the rate was significantly depressed by the addition of benzoquinone, a free radical scavenger. The PEVE produced in the attempted grafting of wet EVE to PVC in the present work was formed at a rate of approximately 0.5%/Mrad, yielding number-average molecular weights in the region 270-470. These similarities in rate and molecular weight behavior between the graft and bulk polymerization of wet EVE to PVC probably proceeds by a free-radical mechanism.

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