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Radiation-Induced Ionic Grafting of Ethyl Vinyl Ether to Polypropylene Film

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ABSTRACT

The radiation-induced grafting of ethyl vinyl ether to polypropylene film in bulk has been investigated under super-dry conditions. The per cent grafting increased linearly with increasing dose without an induction period. The grafting did not take place in the presence of traces of water, indicating that the grafting proceeds by an ionic mechanism. The dose-rate dependence of the rate of grafting was found to be 0.25. The grafting was also examined in n-pentane and neopentane solutions. Although the per cent grafting in the solution system was lower than that in the bulk system, n-pentane was found to increase the grafting efficiency.

INTRODUCTION

Radiation-induced grafting of vinyl monomers to various polymers has been extensively studied. In almost every case a free-radical mechanism has been found to be involved. More recently, however, a number of examples of radiation-induced ionic grafting have been reported. These have recently been reviewed by Chapiro [1].

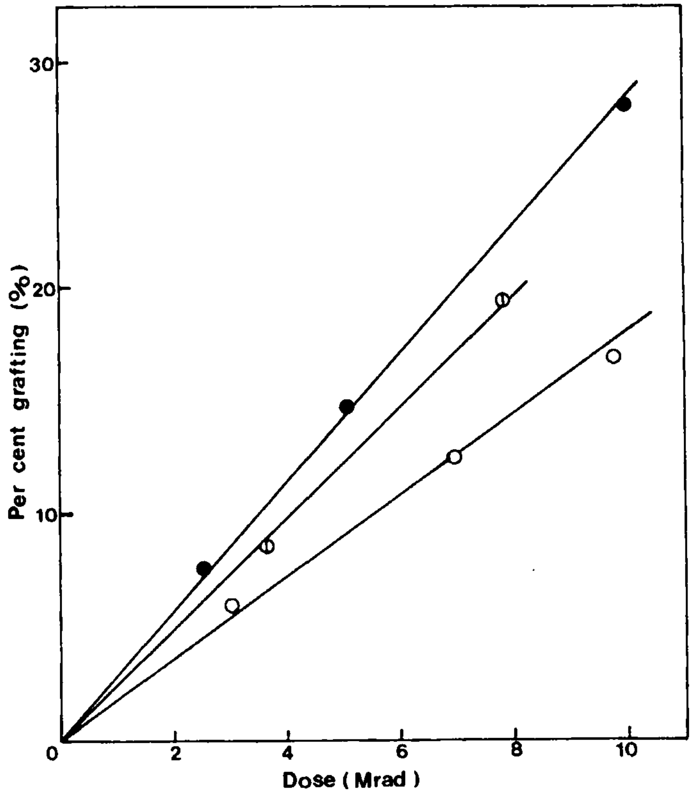

FIG. 1. Grafting of EVE to polypropylene film in bulk monomer systems at various dose rates: (●) 36.7 rad/sec; (⦶) 49.4 rad/sec; (○) 70.6 rad/sec.

Poly(vinyl chloride) responds well to such grafting, presumably due to the comparative ease of positive ion formation on the polymer chain accompanied by the production of chloride ions as discussed by Chapiro [1]. Grafting to other polymers, including polyethylene and polytetrafluorethylene, has been accomplished by using super-dry systems [2]. Under these conditions, rather substantial grafting yields of ethyl vinyl ether (EVE) have also been reported with poly(vinyl chloride) as the substrate compared with the low yields previously found [3].

In the present work the radiation-induced ionic grafting of ethyl vinyl ether to polypropylene under super-dry conditions has been

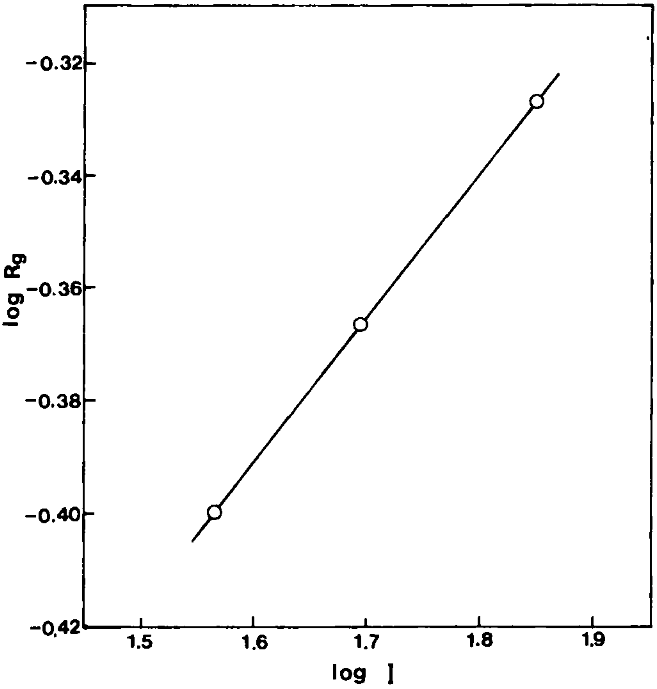

FIG. 2. Dose-rate dependence of the rate of grafting in bulk monomer system.

investigated. Two similar solvents of different free electron yields [4], n-pentane and neopentane, were studied in addition to the pure monomer. Good grafting yields were obtained but were accompanied by considerable homopolymer formation.

EXPERIMENTAL

EVE, n-pentane, and neopentane were dried and purified by the techniques described previously [3, 5-7]. The super-dry monomer and solvent were prepared by the sodium mirror method separately. In all solution graftings the concentration of the monomer was kept at a constant volume of 50%.

Commercial polypropylene film, 25 μm thick, was extracted with n-hexane and subsequently with a mixture of methanol and benzene

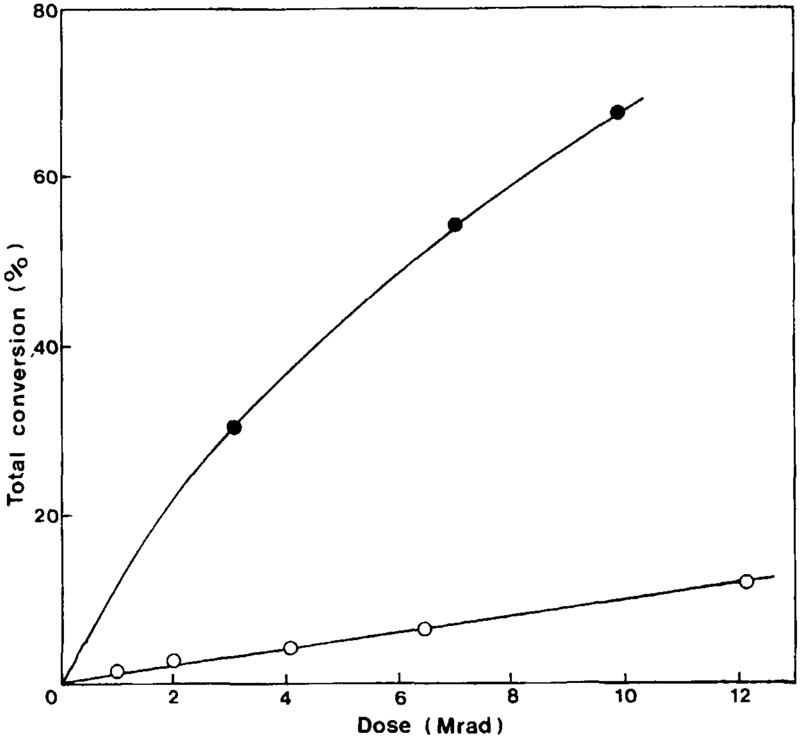

FIG. 3. Grafting of EVE to polypropylene film in (●) super-dry and (○) wet monomer systems at a dose rate of 70.6 rad/sec. Expressed as total conversions; no actual grafting was observed in the wet condition.

(volume ratio, 1:1) at room temperature for 24 hr, and then dried under vacuum. The film was stored over phosphorus pentoxide before grafting. The drying of sample ampoules containing film was carried out according to the procedure described previously [3].

Irradiations were carried out at 30°C in a cobalt-60 γ-ray source at dose rates of 36.7, 49.4, and 70.6 rad/sec. The irradiated films were extracted with methylene chloride to remove homopolymer. Some of the extracted samples were subjected to further extraction with benzene and acetone for several days, but the weight of the film was found to be unchanged. The per cent grafting was taken as the percentage of weight increase of the original film.

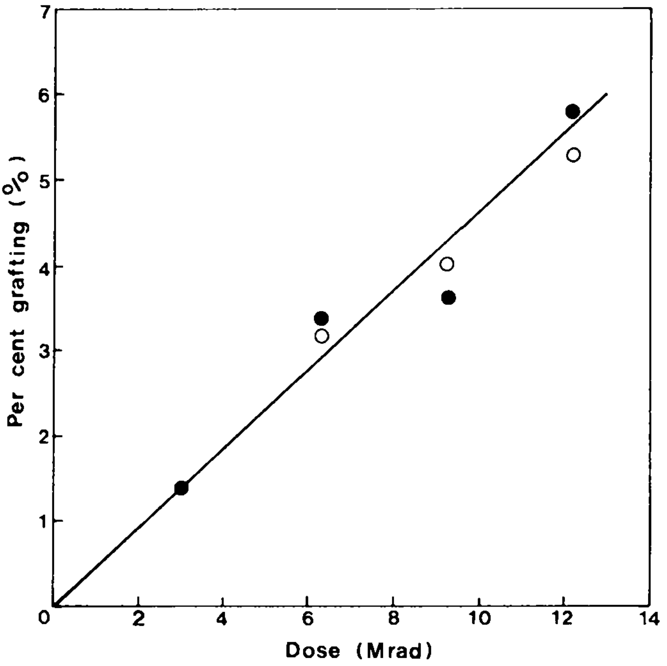

FIG. 4. Grafting of EVE to polypropylene film in (●) n-pentane and (○) neopentane solutions at a dose rate of 36.7 rad/sec.

RESULTS AND DISCUSSION

The radiation-induced grafting of EVE to polypropylene film in bulk monomer systems is shown in Fig. 1. The per cent grafting increased linearly with the dose, up to about 30% grafting was obtained under the best conditions at 10 Mrad. No induction period was observed at each dose rate, indicating that the system was indeed super-dry [3]. The dose-rate dependence of the rate of grafting was found to be 0.25 ± 0.05 as shown in Fig. 2.

Figure 3 shows the total conversion as a function of the dose in both super-dry and wet conditions. The total conversion was presented as the percentage of total weights of grafted polymer and homopolymer to weight of original monomer. The total conversion in the wet condition was much lower than that of the super-dry condition. Thus, the polymerization of EVE was largely retarded

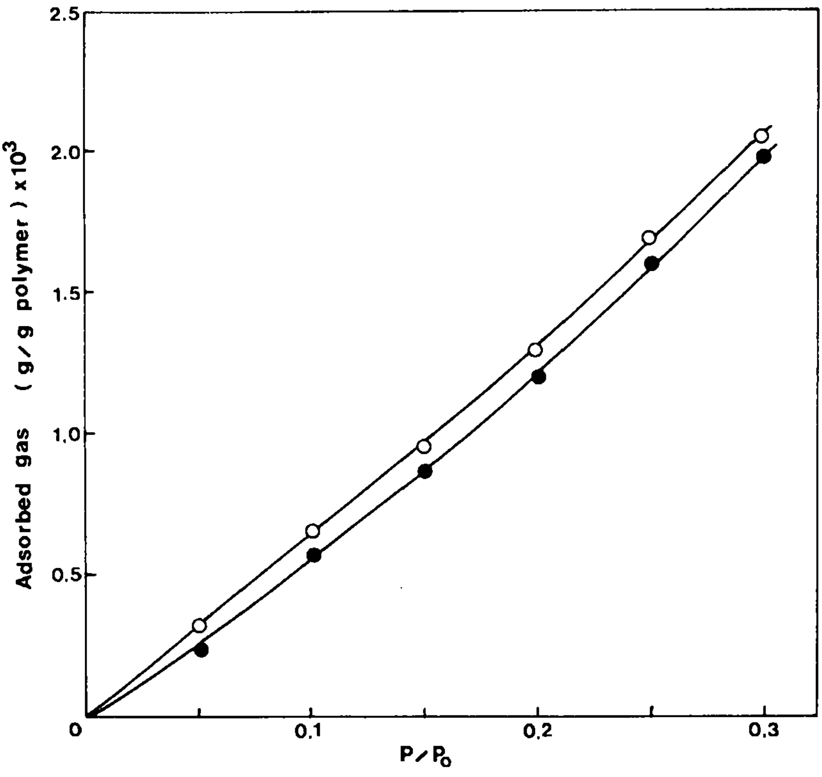

FIG. 5. Sorption of (○) n-pentane and (●) neopentane by polypropylene film at 26°C.

by the presence of water in the system. Moreover, no grafting whatever was observed in the wet condition. These facts strongly support that the grafting under the super-dry condition proceeds by a cationic mechanism. A similar sensitivity of the grafting yields to water was found in the radiation-induced grafting of EVE on poly (vinyl chloride) [3].

The 0.25 power dependence of the rate of grafting on the dose rate, shown in Fig. 2, is not unusual in heterogeneous radiation grafting. It could be due to diffusion control or to termination of the growing chains by the primary negative species. Considerably more study of the precise kinetics of the system would be needed to elucidate the reasons.

In a previous paper [7] it was reported that the rates of polymerization of ethyl vinyl ether was about twice as fast in neopentane

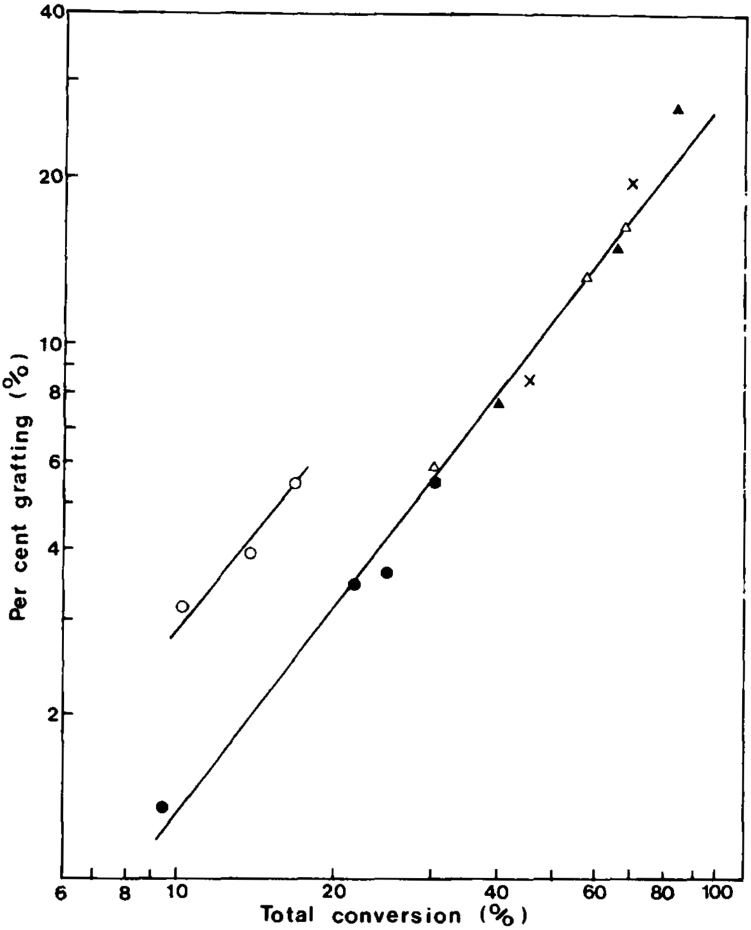

FIG. 6. Relationship between the per cent grafting and the total conversion of monomer in grafting of EVE to polypropylene film in bulk monomer system at a dose rate of (△) 70.6 rad/sec; (×) 49.4 rad/sec; (▲) 36.7 rad/sec; in solution systems: (○) in n-pentane, (●) in neopentane.

compared with n-pentane. This was ascribed to the greater free ion yield in the lower solvent. The effect of these solvents on the grafting yields was therefore investigated, and the results are shown in Fig. 4. No difference in yields were observed. This is not surprising, since the ionic species responsible for the grafting reaction must be formed on the polypropylene itself and be essentially independent of the free ion yields of the solvents used. Furthermore the degree of swelling is very similar with both solvents as shown in Fig. 5. The bulky neopentane molecules take far longer however to reach equilibrium sorption than does n-pentane.

Finally, in Fig. 6, the relationship between the percent total conversion and the percent grafting is shown in the form of a log-log plot. The percent grafting increases with the degree of conversion as does the grafting efficiency. The latter depends on the ratio of polypropylene to monomer and can reach about 40% in the best instances. The grafting in n-pentane is about twice as efficient; this is probably due to the lower rate of polymerization in this particular solvent, as reported previously [7].

In conclusion it is clear that ionic grafting of ethyl vinyl ether to polypropylene can be induced by radiation under super-dry conditions. Since the vinyl ethers do not polymerize anionically, it can be assumed that the mechanism is cationic in nature.

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