

Effect of Mineral and Organic Acids on Radiation Grafting of Styrene onto Polyethylene

NASEF B. EL-ASSY

Al-Arish Faculty of Education, Suez Canal University, Al-Arish, Egypt

SYNOPSIS

A study has been made on the effect of mineral and organic acids on the radiation-induced graft polymerization of styrene onto low-density polyethylene films. Effects of different solvents and dose rate of irradiation on the grafting yield were also investigated. The influence of irradiation time and monomer concentration in the presence and absence of acid on the initial rate and grafting yield was studied. The dependence of the grafting rate on monomer concentration was found to be of the order 1.34 (in absence of acid), 0.61 (in presence of HCl), and 1.25 (in presence of oxalic acid). Such acid enhancement of the radiation grafting process is of practical importance from an economical point of view.

INTRODUCTION

Methods for increasing yields during the radiation-induced grafting of monomers to backbone polymers are important, especially in preparative terms.¹⁻⁶ The use of mineral acid as an additive for this purpose has been reported for radiation grafting of styrene to cellulose,^{3,7} polyolifins,⁸⁻¹¹ and PVC.¹² The acid effect thus appears to have general application to a wide range of grafting systems.

More recently, it was reported¹³ that the inclusion of additive amounts (ca. 1%) of polyfunctional monomers also increased the radiation grafting yields in certain systems. Thus, in the copolymerization of styrene in methanol to polyethylene films,¹³ the presence of divinylbenzene and trimethylol propane triacrylate as additives (1%) significantly enhanced the grafting yield at certain monomer concentrations, particularly in those regions where the Trommsdorff peak is observed.

In the radiation-induced graft polymerization of *N*-vinyl-2-pyrrolidone onto PE films, it was found¹⁴ that the addition of ZnCl₂ and Cu₂Cl₂ to the reaction medium effectively enhanced the grafting process and higher grafting yields were achieved.

In the present study, the effect of different mineral and organic acids in the radiation-induced graft

polymerization of styrene onto polyethylene films was investigated. The effects of dose rate and monomer concentration on the grafting yield were also studied.

EXPERIMENTAL

Materials

Low-density polyethylene films (LDPE) of thickness 75 μm (El-Nasr Co. for Medical Supplies, Egypt) were washed with methanol and dried in a vacuum oven at 50°C. Styrene (Sty), purity 99%, was stabilized with 20 ppm 4-*tert*-butyl procatechal (Merck, W. Germany).

Graft Polymerization

The direct radiation grafting method was used as a technique in the presence of nitrogen gas. Aqueous acidic solution was added to the monomer solution to enhance the grafting process. The glass ampules were subjected to ⁶⁰Co γ -rays at a dose rate that ranged from 0.15–6.4 Gy/s. The grafted films were washed thoroughly with toluene to extract the residual monomer and homopolymer occluded in the film. The films were then dried in vacuum oven at 60°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in weight as

$$\text{degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100,$$

where W_0 and W_g represent the weights of initial and grafted films, respectively.

RESULTS AND DISCUSSION

Effect of Different Acids On The Grafting Process

The correct choice of solvents is essential to the success of radiation-induced graft polymerization. Their influence on the radiation grafting process has been the subject of many studies.¹⁵⁻¹⁷ It has been established that solvents play a more important part in graft polymerization because of the significance of polymer swelling.¹⁸ The acid enhancement effect in radiation grafting of monomers onto PE and the use of these copolymers for enzyme immobilization and related reactions was reported by Garnett et al.¹⁹

In the present study, the effect of different mineral and organic acids on the radiation grafting of styrene onto PE films was investigated and is shown in Table I. It can be seen that there is a great enhancement effect for all different acids investigated. However, in the case of using mineral acids, HCl shows higher enhancement effects, and higher degrees of grafting were obtained as compared with those obtained in the presence of H_2SO_4 or HNO_3 . Oxalic acid shows also a greater effect, and much higher degrees of grafting were obtained as compared with other carboxylic acids or mineral acids.

Effect of HCl and oxalic acids concentration on the grafting process is shown in Figures 1 and 2, respectively, at two different dose rates of irradiation.

Table I Effect of (0.1 M) Mineral and Organic Acids on the Grafting of Styrene in Toluene onto PE Films

Acid	Degree of Grafting (%)
—	35
H_2SO_4	50
HCl	57
HNO_3	38
CH_3COOH	48
COOH	75
COOH	75
HCOOH	60

Total exposure dose, 20 KGy; dose rate, 0.15 Gy/s; monomer concentration, 50 wt %.

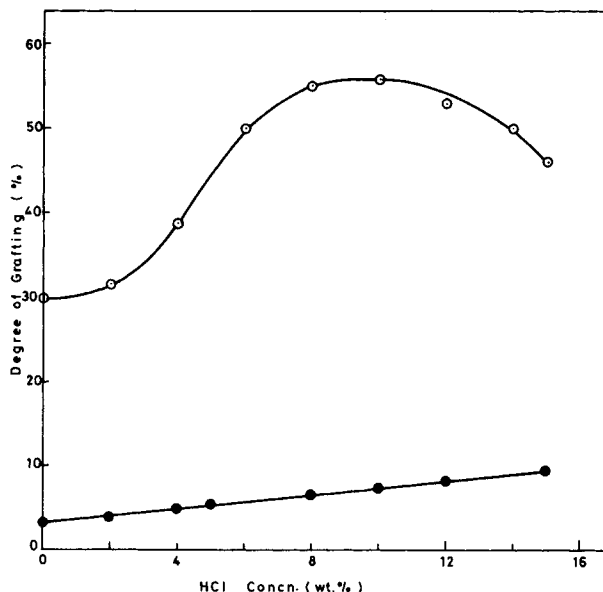


Figure 1 Degree of grafting vs. (0.1 M) HCl concentration for the grafting of styrene onto PE films, at different dose rates (Gy/s). (○), 0.15; (●), 6.41. Monomer concn. in toluene, 50 wt %; irradiation dose, 20 KGy.

It is obvious that for both acids, when the radiation grafting process was carried out at a lower dose rate, the degree of grafting increases with acid

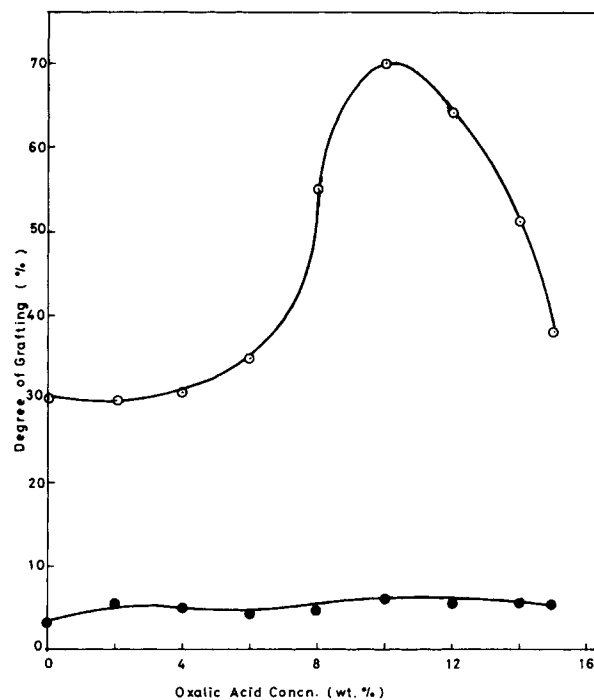


Figure 2 Degree of grafting vs. (0.1 M) oxalic acid concentration for the grafting of styrene onto PE films at different dose rates (Gy/s). (○), 0.15; (●), 6.41. Grafting conditions are the same as in Fig. 1.

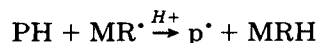
Table II Effect of Addition of Acid (10 wt %) on Radiation Grafting of Styrene (50 wt %), in Different Diluents, onto LDPE Films at Different Dose Rates

Acid (10 wt %)	Solvent (40 wt %)	Degree of grafting (%)	
		Dose rate (Gy/s) 15	641
—	MeOH	45	12.5
Oxalic	MeOH	190	6.0
H ₂ SO ₄	MeOH	350	8.0
—	Toluene	35	1.5
Oxalic	Toluene	75	5.0
H ₂ SO ₄	Toluene	50	4.0
HCl	Toluene	57	7.5
—	Benzene	29	3.5
Oxalic	Benzene	30	5.0
H ₄ SO ₄	Benzene	35	5.5

Total exposure dose, 20 KGy.

concentration to reach the maximum at 10 wt % of acid. Thereafter, it decreases gradually as the acid concentration increases. However, the degree of grafting at a higher acid concentration is still higher than that obtained in the absence of acid, i.e., in (styrene/toluene) (50/50 wt %). On the other hand, at a much higher dose rate, the grafting process resulted in much lower degrees of grafting as compared with those obtained at a low-dose rate, at a given acid concentration. Meanwhile, no significant effect of oxalic acid concentration on the degree of grafting was observed. But, in the case of HCl, a linear relationship between the degree of grafting and the HCl concentration was observed at high-dose-rate irradiation (Fig. 1).

Results suggest that the addition of small amount of (0.1 M) oxalic acid or (0.1 M) HCl (10 wt %) to the monomer solution enhanced its grafting process into LDPE films, especially at low-dose irradiation. Such acid enhancement of the graft polymerization can be explained by assuming that the acid facilitates the hydrogen abstraction reaction from an adjacent polymer molecule by styrene-toluene radicals MR to give more grafting sites by the following mechanism¹⁹



Thus, the effect of acid would appear to be due predominantly to a radiation chemistry phenomenon consistent with the observation by Bexendale and Mellows²⁰ that addition of acid to methanol increases $G(\text{H}_2)$ appreciably.

Results also showed that the dose rate has a great influence on the grafting process. Radicals formed upon irradiation at a low-dose rate can survive enough time to form growing chain radicals with the monomer molecules and the graft chains increase. Meanwhile, the diffusion of monomer solution enhanced at low-dose irradiation due to its lower viscosity compared with that at a higher dose rate due to the higher probability of homopolymer formation at the latter case. The free radicals formed upon irradiation at high-dose rate decay faster by recombination; therefore, the grafting yield is much lower than that at low-dose-rate irradiation.

Effect of Solvent

Effects of different solvents on the radiation-induced graft polymerization of styrene (50 wt %) onto LDPE films, in the presence of different acids, is shown in Table II. It is seen that the dilution of styrene with methanol enhanced its graft polymerization onto LDPE films as compared when it was diluted with toluene or benzene, at a given condition, in the absence and presence of organic or mineral acids at both low- and high-dose rates. For the grafting of styrene/methanol and styrene/benzene mixtures, the addition of (0.1 M) H₂SO₄ (10 wt %) gives higher degrees of grafting than that in the presence of oxalic acid or absence of acid. However, in the case of the styrene/toluene mixture, the

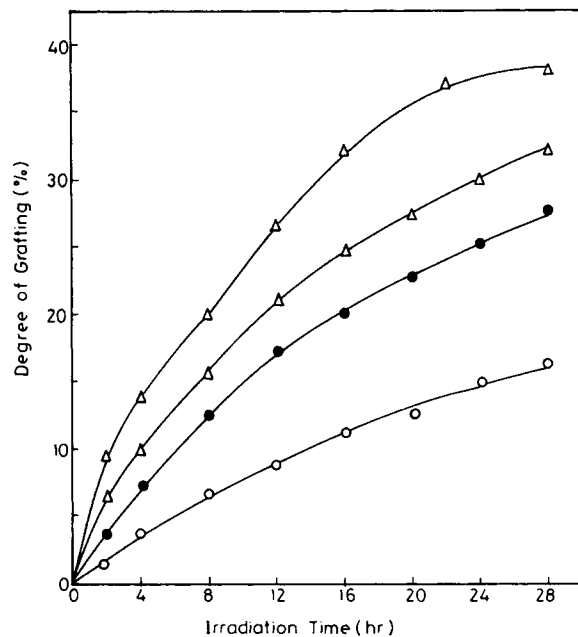


Figure 3 Degree of grafting vs. irradiation time for the grafting of different styrene-toluene concentrations (wt %). (○), 20; (●), 50; (△), 70; (▲), 90 in the absence of acid; dose rate of irradiation, 0.15 Gy/s.

grafting process enhanced in the presence of oxalic acid. Meanwhile, under any grafting conditions investigated here, the grafting process is very significantly enhanced at low-dose-rate as compared with high-dose-rate irradiation (Table II).

The aforementioned results can be reasonably understood by taking into account the resonance stabilization effect of benzene and toluene rings, which act as an energy transfer agent. Such an effect, in spite of its homopolymerization inhibition, resulted in a decrease in the grafting yield due to the consumption of the energy of irradiation. Therefore, a great difference in the grafting yield was observed when methanol was used as a diluent for styrene. Another effect may come from the enhancement of hydrogen abstraction from the polymer in the presence of methanol, which leads to the formation of active sites as compared with that in benzene or toluene.

Effect of Monomer Concentration in the Presence and Absence of Acid

Figure 3 shows the effect of Sty concentration at different irradiation times in the absence of acid.

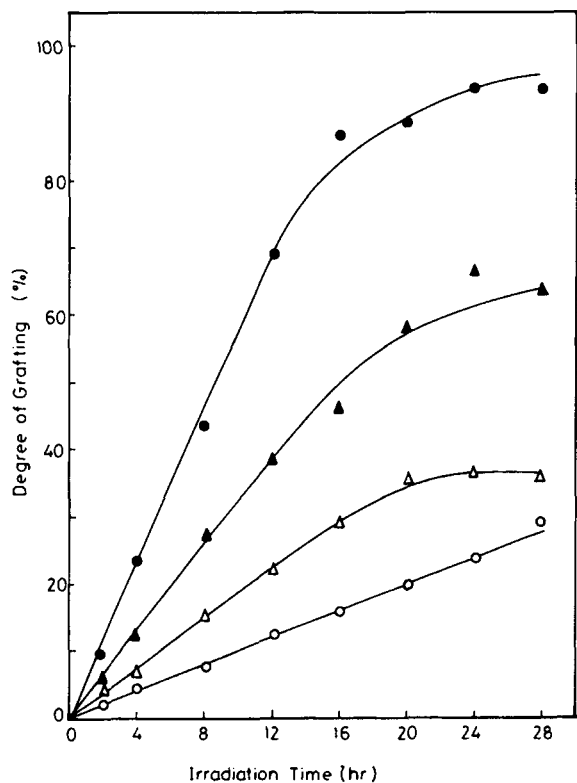


Figure 4 Degree of grafting vs. irradiation time at different styrene-toluene concentrations (wt %). (○), 15; (△), 30; (▲), 60; (●), 80 in the presence of (0.1 M) HCl (8%).

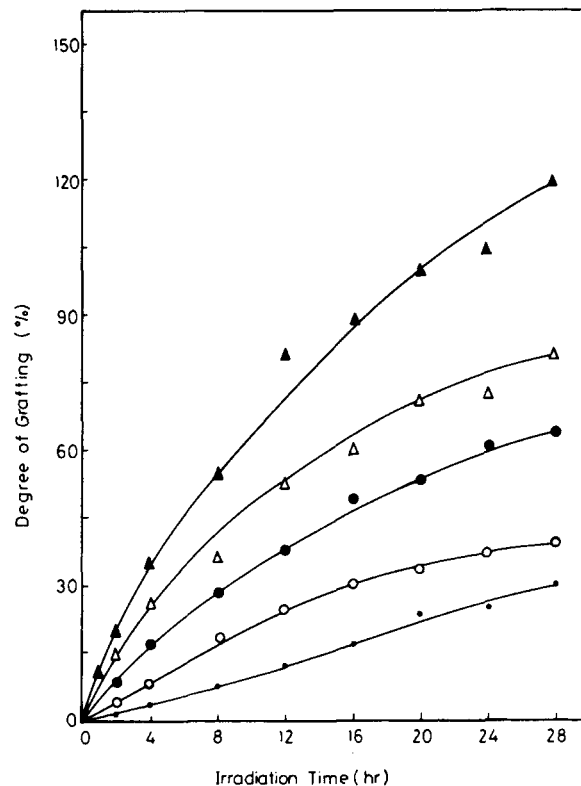


Figure 5 Degree of grafting vs. irradiation time at different styrene-toluene concentrations (wt %); (●), 15; (○), 25; (●), 50; (△), 75; (▲), 90 in the presence of (0.1 M) oxalic acid (10 wt %).

The degree of grafting increases with irradiation time for all Sty concentrations. The higher the monomer concentration, the higher the grafting yield obtained. Almost the same behavior was ob-

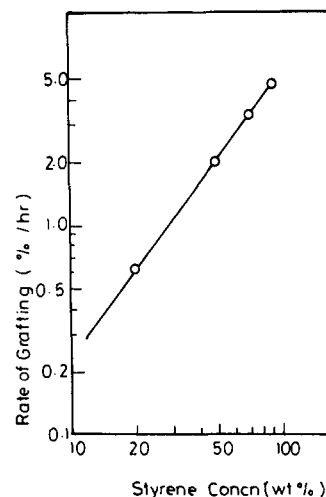


Figure 6 Logarithmic relationship between the initial rate of grafting and styrene concentration in the absence of acid.

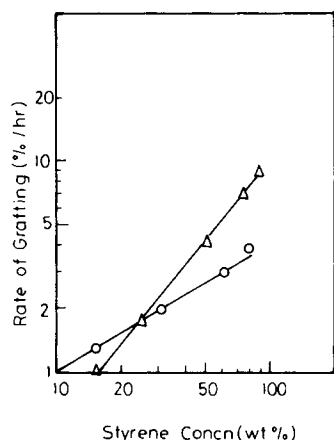


Figure 7 Logarithmic relationship between the initial rate of grafting and styrene concentration in presence of (○) HCl and (△) oxalic acid.

served for the grafting of Sty in the presence of (0.1 M) HCl (8%) or (0.1 M) oxalic acid (10%), as shown in Figures 4 and 5. However, the grafting yield is much higher for the grafting system in the presence of mineral acid (HCl) or organic acid (oxalic) as compared with that obtained in the absence of acid, at a given reaction time and Sty concentration. Meanwhile, the grafting yield in the presence of oxalic acid is somewhat higher than that obtained in the presence of HCl at a given reaction condition.

The initial rate of grafting was calculated from Figures 3, 4, and 5 and then plotted logarithmically as a function of Sty concentration and is shown in Figures 6 and 7. Such plots gave linear relationships and the dependence of grafting rate on monomer concentration was calculated to be of orders 1.34 (in the absence of acid), 0.61 (in the presence of HCl), and 1.25 (in the presence of oxalic acid).

The lower dependence on monomer concentration in the presence of HCl may be attributed to the enhancement of monomer diffusion through the polymer matrix because of lower viscous solution in such acid. However, in spite of the higher degrees of grafting obtained in presence of oxalic acid, the dependence on Sty concentration is much higher. This is due to diffusion coefficient of Sty into the trunk polymer.

It can be concluded that the addition of a small amount of mineral or organic acid into monomer solution as an additive enhances the grafting yield. This is of practical importance, especially in pre-

parative terms, and is a good achievement from an economic point of view.

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