

Graft Polymerization of Acrylic Acid onto Polyethylene Film by Preirradiation Method. II. Effects of Oxygen at Irradiation, Storage Time after Irradiation, Mohr's Salt, and Ethylene Dichloride

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Synopsis

In the grafting of acrylic acid onto polyethylene by preirradiation method, the irradiation in air gave a higher rate of grafting than in N₂, since the diffusion rate of monomer is larger for less cross-linked polyethylene. The rate of grafting decreased with increasing time of storing polyethylene because of the decay of trapped radicals. The effects of storage conditions on the grafting activity was reasonably interpreted by assuming that grafting is predominantly controlled by both concentration of trapped radicals and monomer diffusibility in the polymer matrix. Mohr's salt was found to depress the homopolymerization of acrylic acid without marked change of grafting rate. The rate of grafting was increased by the addition of ethylene dichloride due to the increase in monomer diffusion.

INTRODUCTION

In the radiation grafting of acrylic acid onto polyethylene film, the effects of various factors on the grafting have been studied in detail and the results have been kinetically analyzed in the previous paper.¹

In this system, the grafting is largely governed by the diffusibility of monomer through the substrate as well as by the other factors, such as preirradiation dose, monomer concentration, and grafting temperature. We have discussed the grafting mechanism to suggest that the grafting begins on the surface of film and then proceeds successively into its inner part with the gradual diffusion of monomer through the grafted layer.

From the practical viewpoint of this grafting system, there are some other important factors influencing significantly the graft reaction and the properties of products.

The present paper deals with the effects of preirradiation atmosphere, storage of the film after irradiation, and additives such as Mohr's salt and ethylene dichloride on the grafting.

EXPERIMENTAL

Materials

Polyethylene film, acrylic acid, and Mohr's salt were the same as mentioned in the previous paper.¹

Ethylene dichloride and xylene were reagent grade (Kishida Chemicals Co., Ltd.) and used without further purification.

Irradiation and Grafting Procedures

Unless otherwise indicated, the preirradiation and grafting were carried out according to the previously outlined procedure.¹

Gel Measurement

Gel fraction of the irradiated film was determined by the extraction using xylene. The film was extracted in boiling xylene containing 0.5 wt % hydroquinone for 16 h. Hydroquinone was used to prevent oxidative degradation of polyethylene during extraction. The resulting sample was dried and weighed.

Swelling Measurement

The swelling of the film was determined gravimetrically. The film was immersed in a swelling solvent at 25°C for a given time and then weighed immediately after the solvent remaining on the surface was wiped off with filter paper.

RESULTS AND DISCUSSION

Air during Irradiation

In the preirradiation grafting, the effect of oxygen during irradiation is one of the important factors controlling the grafting as well as the other conditions such as preirradiation dose, grafting temperature, monomer concentration and so on. Figure 1 shows the effects of irradiation atmosphere on the rate and final percent grafting for the polyethylene films. The grafting was found to be enhanced by the preirradiation in air.

When polyethylene is irradiated in air, free radicals formed in the amorphous regions and a part of the radicals formed in the crystalline regions, i.e., the radicals which migrate to the surface of the crystalline phase, may react with oxygen to form peroxides such as diperoxides ($R-O-O-R$) and hydroperoxides ($R-O-O-H$), which can initiate graft reaction in the presence of monomer only at an elevated temperature. Thermal dissociation of the peroxides is not so remarkable at room temperature. Generally, the grafting on radiation-peroxidized polymers should be carried out at an elevated temperature more than 40–50°C.² Therefore, in this grafting, the contribution of thermally decomposed peroxides seems to be low because the grafting was carried out at room temperature.

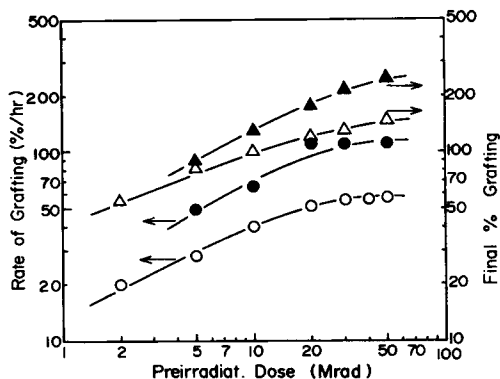


Fig. 1. Logarithmic plots of rate and final % grafting vs. preirradiation dose. Monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C; film thickness, 25 μ m, preirradiat. atmosphere: (O, Δ) in N₂; (●, \blacktriangle) in air.

The higher yields of grafting in air might be interpreted by the presence of Mohr's salt (redox system). It can be expected that in the presence of Fe²⁺ diperoxides and hydroperoxides may decompose even at a lower temperature to form radicals which can initiate the grafting.³ Also, the dissociation of hydroperoxides leads to the formation of HO· radicals besides RO· radicals. The HO· can initiate homopolymerization of vinyl monomers. In the presence of Fe²⁺, however, HO· radicals will be converted into OH⁻ ions, which are no longer capable of initiating homopolymerization. Consequently, the grafting efficiency will be expected to become higher. In this grafting, however, it is very doubtful that diperoxides and hydroperoxides are formed during the irradiation in air and their amounts are sufficient to enhance the reaction, since the irradiation of the films were carried out at a high dose rate (ca. 1×10^5 rad/s) for a short period of time using an electron beam accelerator. In order to form the peroxides, oxygen must diffuse to radical sites on the polymer chains. During a very short period of irradiation, oxygen scarcely diffuses into polyethylene film.

As will be described later, the grafting did not proceed even in the presence of Fe²⁺ for the films irradiated by electron beams or γ -rays from Co-60 and maintained in air for 10 days. In these two cases, most radicals should be converted into the peroxides during the irradiation or storage.

Therefore, the higher graft yield for the films irradiated in air than in nitrogen may be interpreted by assuming that monomer can diffuse easier in the polymer preirradiated in air than that done in nitrogen. As shown in Figure 2, the gel fraction of the polyethylenes irradiated in nitrogen is markedly larger than that of polyethylene irradiated in air. The film irradiated in air was also found to have the higher rate and equilibrium value of swelling than those for the film irradiated in nitrogen, as shown in Figure 3. These results mean that crosslinking of polymer chains occurs hardly in air but does in nitrogen, and consequently the diffusibility of monomer into polymer matrix may be higher in the polyethylene irradiated in air.

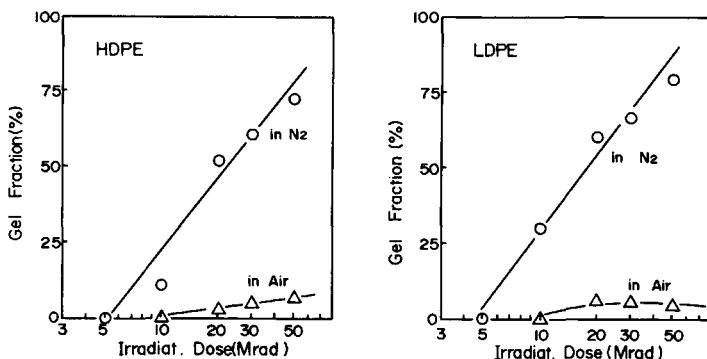


Fig. 2. Effect of irradiation dose on gel fraction of polyethylene irradiated in N_2 and in air. Irradiat. temp, room temp; film thickness, $25 \mu m$.

Storage after Preirradiation

It is well known that the grafting activity decreases with the storage of the irradiated polymer because of the decay of radicals; the higher the temperature, the larger the decreasing rate. The storage temperature and time dependencies of the grafting activity for the polyethylene-acrylic acid system have been investigated from the viewpoint of practical application.

The films were stored at various storage conditions for a certain period of time immediately after being irradiated in nitrogen before the graft polymerization. Figure 4 shows the graft-yield-time curves for the films stored at $22^\circ C$. The rate of grafting was found to decrease markedly with storage time. For a short storage time, however, the final percent grafting scarcely change.

Figure 5 shows the relationships of the rates of grafting as a function of storage time at the various temperatures. It is seen that the rate of grafting decreases gradually with time even at a lower temperature, and the decrement increases with storage temperature.

The plots of final percent grafting against storage time at various temperatures are shown in Figure 6. At a storage temperature ranging from -24 to $5^\circ C$, the final percent grafting of HDPE, at first, decreases slightly with time and, then, remains constant throughout the duration of storage. On the other hand, the final percent grafting for LDPE was found to behave similarly to that of HDPE only at the initial stage of storage and then to decrease with increasing temper-

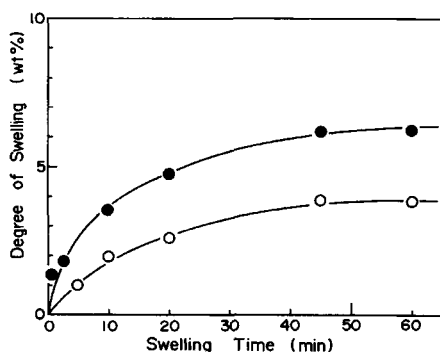


Fig. 3. Degree of swelling vs. swelling time for polyethylene irradiated in N_2 and in air. Polyethylene, $25 \mu m$ HDPE; irradiat. dose, 30 Mrad; swelling agent, xylene; swelling temp, $25^\circ C$.

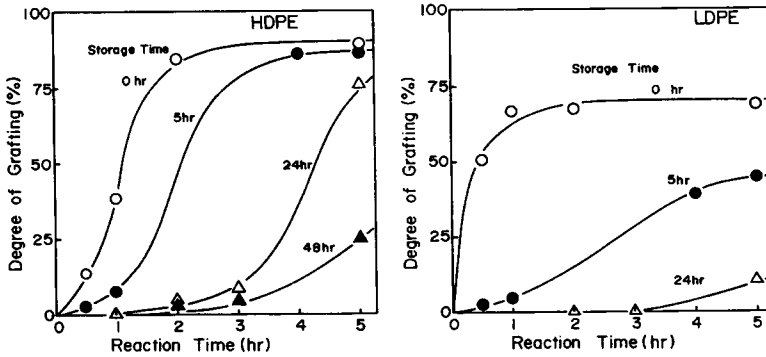


Fig. 4. Grafting curves for polyethylenes stored at 22°C for various storage times. Film thickness, 25 μm ; preirradiat. dose, 10 Mrad; monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C.

ature and time except at -24°C . By comparing these results for HDPE and LDPE, it is concluded that the grafting activity of HDPE remains during its higher crystallinity, i.e., the higher the crystallinity, the longer the lifetime of free radicals.

As mentioned above, the grafting activity is largely dependent on the con-

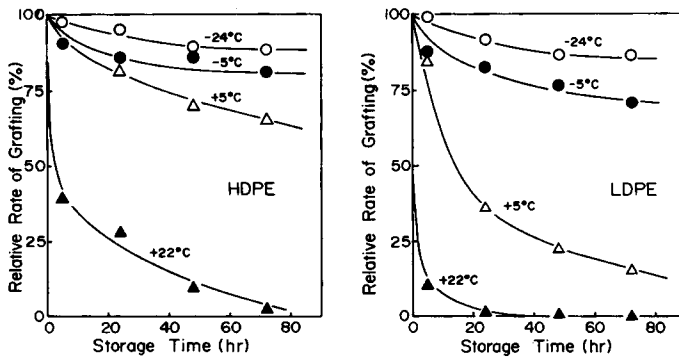


Fig. 5. Relationship between grafting rate and storage time at various storage temperatures. Film thickness, 25 μm ; preirradiat. dose, 10 Mrad; storage atmosphere, in N_2 ; monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C.

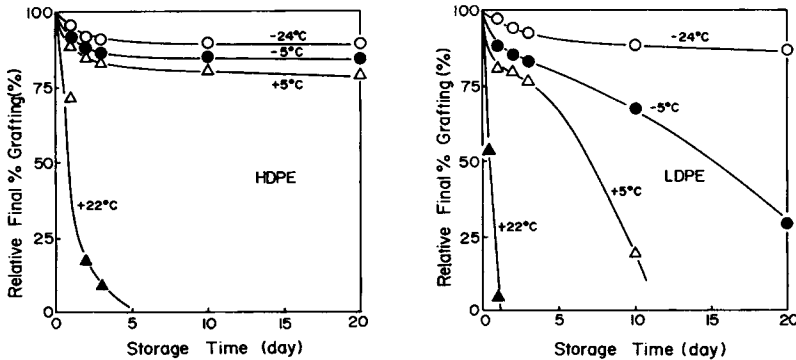


Fig. 6. Relationship between final % grafting and storage time at various storage temperatures. Experimental conditions are the same as in Figure 5.

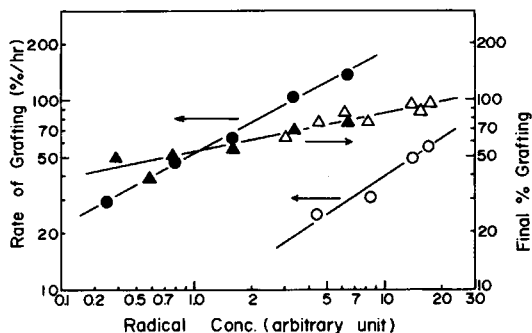


Fig. 7. Logarithmic plots of rate and final % grafting vs. radical concentration for polyethylene stored under various storage conditions. Monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C; polyethylene: (○, △) 25 μ m HDPE; (●, ▲) 25 μ m LDPE.

centration of free radicals which decrease on the storage. The rate and final percent grafting for the film stored under the various storage conditions are plotted as a function of total concentration of trapped radicals determined by ESR, as shown in Figure 7. For both LDPE and HDPE, the rate of grafting is linearly proportional to the radical concentration. As discussed already in the previous paper,¹ the larger rate of grafting for LDPE than that for HDPE may be attributable to both a higher concentration of radicals at the surface of crystallites and a higher diffusion rate of monomer into polyethylene film, since LDPE has smaller crystallite sizes and lower crystallinity than those of HDPE. For the final percent grafting, however, there is no significant difference between LDPE and HDPE. In both cases, they increase with radical concentration. These results are consistent with those obtained at various preirradiation doses,¹ i.e., it is suggested that the effects of storage conditions on the grafting activity can be reasonably interpreted by assuming that the grafting is predominantly controlled by both concentration of trapped radicals and monomer diffusibility in the polymer matrix.

Mohr's Salt

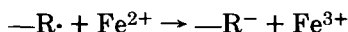
In the preirradiation method, homopolymerization does not take place so largely as it does in the direct method in which the monomer is exposed to the ionizing radiation and easily forms its homopolymer. In the preirradiation method, monomer can homopolymerize by the active sites formed by chain transfer reaction of growing polymer radicals and/or by dissociation of peroxides. In the grafting of the peroxidized polymer, the addition of redox system can prevent the formation of homopolymer. The thermal dissociation of hydroperoxide (ROOH) forms HO· radicals which can initiate homopolymerization. In the presence of Fe²⁺ (redox system), however, this initiation would be avoided by the following mechanism:



In this grafting system (polyethylene-acrylic acid), the formation of peroxides such as ROOH and ROOR seems to be relatively low, because the irradiation was carried out under nitrogen atmosphere and at a high dose rate. However, it was observed that acrylic acid homopolymerizes easily to give a very viscous reaction

medium without any radical inhibitors, and that addition of Mohr's salt to the monomer solution is effective for depressing the homopolymerization. In this case, acrylic acid may be homopolymerized by the active sites which are formed by the chain transfer of growing polymer radicals to monomer or water. In the presence of Fe^{2+} , the resulted active sites, such as monomer radicals and HO-radicals, may be deactivated, and consequently homopolymerization will be suppressed.

On the other hand, Fe^{2+} may also influence the propagation. A part of the growing chain radicals may be deactivated. In fact, it was found that the grafting is lowered by the addition of small amount of Mohr's salt. Figure 8 shows the relationship between the final percent grafting and concentration of Mohr's salt. The grafting decreases rapidly with increasing Mohr's salt, particularly in the lower range of the concentration. Beyond 2.5%, the value remains almost constant, because of the precipitation of Mohr's salt in the reaction medium. This result suggests that a part of growing chain radicals is deactivated as follows:



This reaction results in the reduction of the grafting as well as inhibitions of homopolymerization. Since the concentration of Mohr's salt is much lower in polyethylene matrix than in monomer solution, the reduction of the grafting is not remarkable in comparison with that of homopolymerization.

Ethylene Dichloride

As revealed above, this grafting is largely dependent on the diffusibility of acrylic acid into polymer matrix. The addition of some organic solvents which have a stronger affinity for polyethylene than water may enhance the graft reaction.

The effects of ethylene dichloride on this grafting have been investigated. In Figure 9 is shown the graft-yield-time curves at various concentrations of ethylene dichloride. Although the final percent grafting was not affected, the rate of grafting was found to increase with ethylene dichloride.

From the temperature dependency of grafting rate, it was found that addition

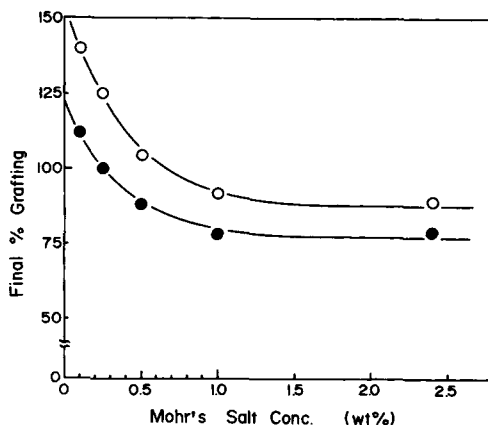


Fig. 8. Relationship between final % grafting and Mohr's salt concentration. Preirradiat. dose, 30 Mrad; monomer concn, 50 wt %; (○) 25 μm HDPE; (●) 25 μm LDPE.

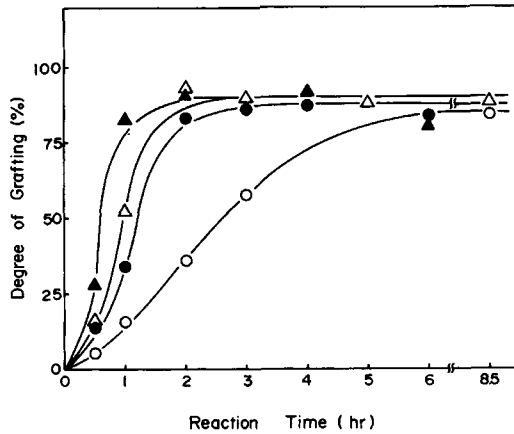


Fig. 9. Grafting curves at various concentrations of ethylene dichloride. Preirradiat. dose, 10 Mrad; grafting temp, 25°C; composition of monomer solution (acrylic acid:ethylene dichloride:water) (○) 50:0:50; (●) 47.5:2.5:50; (△) 45:5:50; (▲) 40:10:50; polyethylene, 25 μ m HDPE.

of ethylene dichloride reduces the apparent activation energy of grafting. By the addition of 2.5% ethylene dichloride, 17.2 and 9.0 kcal/mol were obtained as the apparent activation energies for HDPE and LDPE, respectively. These values are much lower than those (27.3 and 19.6 kcal/mol)¹ obtained in the absence of ethylene dichloride.

These results suggest that the diffusion of acrylic acid into polyethylene film is increased by ethylene dichloride to enhance the graft reaction. Figure 10 shows the swelling behavior of the acrylic-acid-grafted films in the reaction medium with and without ethylene dichloride. It is seen that both the rate and equilibrium value of swelling are higher in the presence of ethylene dichloride than

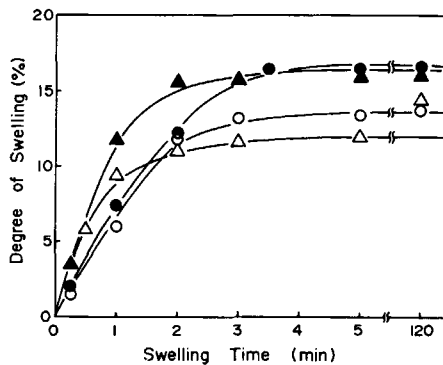


Fig. 10. Swelling curves for the acrylic acid-grafted polyethylene. Swelling temp, 25°C.

Symbol	Polyethylene	Degree of grafting (%)	Swelling agent (wt %)		
			Acrylic acid	Ethylene dichloride	Water
○	25 μ m HDPE	67	25	0	75
●	25 μ m HDPE	67	25	2.5	72.5
△	25 μ m LDPE	59	25	0	75
▲	25 μ m LDPE	59	25	2.5	72.5

in the absence. This result is one of the strong supports for the above conclusion.

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