

Graft Polymerization of Acrylic Acid and Methacrylic Acid onto Radiation-Peroxidized Polyethylene Film in Presence of Metallic Salt and Sulfuric Acid

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ABSTRACT: Using the radiation peroxide grafting technique, a low density polyethylene film was graft copolymerized with acrylic acid and methacrylic acid in the presence of additives such as acid and metallic salts. The effect of acid and metallic salts on the grafting yield and reaction mechanisms were examined. The results showed that the inclusion of an appropriate cationic salt and acid in acrylic acid and methacrylic acid grafting solutions was extremely beneficial and led to a most unusual enhancement effect in the radiation grafting. On the other hand, inclusion of acid in the grafting solution in the absence of cationic salts led to a negative effect on the grafting reaction. It is considered that sulfuric acid accelerates the decomposition of hydroperoxides in the presence of a metallic salt such as Fe^{2+} to form radicals that can initiate a grafting reaction. Of the metallic salts for inhibiting homopolymerization, only oxidized metallic salts produced the high grafting yield of acrylic acid and methacrylic acid. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1101–1106, 1997

INTRODUCTION

Radiation-induced graft copolymerization is a well-known method for modification of the chemical and physical properties of polymer materials and has attracted considerable interest because it imparts desirable properties such as blood compatibility,¹ membrane quality, ion exchange,^{2–4} dyeability, protein adsorption,⁵ and immobilization of bioactive materials.^{6,7} The role of additives is important in radiation grafting reactions because appropriate compounds in a grafting solution can enhance the grafting yields, and the radiation dose required to achieve a particular graft percent can be lowered in the presence of suitable additives. Ódor and Geleji⁸ found that homopolymerization could be inhibited by incorporating

ferrous sulfate, while Huglin and Johnson⁹ reported that the anions have no effect on the grafting or homopolymerization. Both of these processes were suppressed by the cations in the following order of effectiveness: $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+}$. When polymer materials are subjected to ionizing radiation in the presence of oxygen or air, peroxides and hydroperoxides capable of initiating grafting reactions are generally formed. Grafting reactions using peroxides and hydroperoxides were investigated by Chapiro,¹⁰ Derai and Jendrychowska–Bonamour,¹¹ and O'Neill.¹² It is generally accepted that irradiation of polyethylene in air leads to the formation of hydroperoxides. O'Neill used only an Fe^{2+} ion as a reducing agent to decompose the hydroperoxides, thereby converting $\cdot\text{OH}$ radicals to the inactive OH^- , which can prevent an undesirable homopolymerization initiated by $\cdot\text{OH}$ radicals formed in the thermal decomposition of the hydroperoxides.¹²

In the present work, the effects of the inclusion

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Table I Effect of Various Additives on Grafting of Acrylic Acid to Polyethylene Peroxidized by Electron Beam Irradiation

Additives	Degree of Grafting (%)			Condition of Grafting Solution After Grafting Reaction
	30 kGy	50 kGy	70 kGy	
FeSO ₄ (NH ₄) ₂ SO ₄ · 6H ₂ O	191	302	357	No Gel
FeCl ₂ · 4H ₂ O	218	306	367	No Gel
FeSO ₄ · 7H ₂ O	203	337	436	No Gel
FeNH ₄ (SO ₄) ₂ · 12H ₂ O	3	4	4	No Gel
Fe ₂ (SO ₄) ₃ · xH ₂ O	4	5	5	No Gel
Cu(NO ₃) ₂ · 3H ₂ O	3	3	4	No Gel
CuCl ₂ · 2H ₂ O	1	1	1	No Gel
Ce(SO ₄) ₂ · 4H ₂ O	3	4	6	No Gel
Ca(NO ₃) ₂ · 4H ₂ O	—	—	—	Gel
Cd(NO ₃) ₂ · 4H ₂ O	—	—	—	Gel
LiNO ₃	—	—	—	Gel

Metallic salt concentration $2.5 \times 10^{-3}M$; H₂SO₄ concentration 0.2M; monomer concentration 30 vol %; reaction time 3 h; reaction temperature 70°C; FeSO₄(NH₄)₂SO₄ · 6H₂O = Mohr's salt.

of various cationic salts and acid on the radiation grafting of acrylic acid and methacrylic acid onto polyethylene film are reported. The addition of appropriate cationic salts in acidified acrylic acid and methacrylic acid grafting solutions was extremely beneficial and led to a most unusual enhancement effect in radiation grafting with specific metallic salts.

EXPERIMENTAL

Materials

Commercial low density polyethylene films of 30- μ m thickness (Hyundai Petrochemical Co., Ltd.)

Table II Effect of Metallic Salt and Sulfuric Acid on Grafting of Methacrylic Acid onto Polyethylene Irradiated to a Total Dose of 50 kGy by Electron Beam

Metallic Salt (M)	Degree of Grafting (%)			
	CuSO ₄ · 5H ₂ O		Mohr's Salt	
	No H ₂ SO ₄	0.2M H ₂ SO ₄	No H ₂ SO ₄	0.2M H ₂ SO ₄
0	432	5	432	5
5×10^{-4}	40	5	422	116
1.5×10^{-3}	39	5	353	117
2.5×10^{-3}	38	5	329	2380
5×10^{-3}	38	3	253	2303
2.5×10^{-2}	25	4	136	1640

Methacrylic acid concentration 30 vol %; reaction time 3 h; reaction temperature 70°C.

were used as a substrate for graft polymerization. Acrylic acid and methacrylic acid were supplied by Junsei Chemical Co., Ltd., and were used without further treatment. Other chemicals were reagent grade.

Irradiation

γ -Ray irradiation from ⁶⁰Co was carried out at an exposure rate of 8×10^5 rad/h in air. Electron beam irradiation was done at the conveyer speed of 5 m/min and acceleration energy of 1 MeV; absorbed dose was adjusted by varying the electric current.

Grafting Procedure

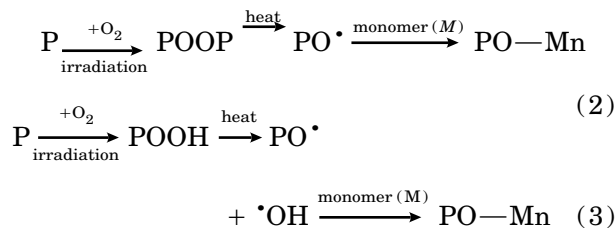
The grafting experiments were performed in a stoppered glass ampoule; the distilled water and additives were added first, followed by monomer to a total volume of 80 mL. The irradiated films were immersed in the monomer solution that was purged by bubbling nitrogen. The grafting reaction was carried out by placing the ampoules in a water bath set at a relevant temperature. After the grafting reaction, the grafted films were taken out of the monomer solution and washed with methanol and distilled water to remove the remaining homopolymer. The degree of grafting (%) was determined by the following:

$$\text{degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_g and W_o are the weights of the grafted and the ungrafted film, respectively.

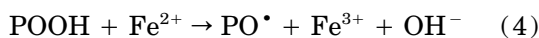
RESULTS AND DISCUSSION

Polymeric material was irradiated in air or oxygen so that macroradicals formed were converted to peroxides and hydroperoxides. This polymer can be stored at room temperature until ready for reaction with monomers. The advantage of this process was that the intermediate oxidized polymer could be kept for long periods of time before performing the final grafting reaction. When the irradiated polymer was heated in the presence of monomer, the peroxides decomposed to give $PO\cdot$ radicals that served as active sites for the grafting reaction. Chapiro¹⁰ published the fact that two different grafting procedures are possible in the peroxide grafting systems, depending on whether diperoxides or hydroperoxides can be formed in the irradiated polyethylene. Representative grafting reactions using the peroxidation technique are described as follows:



When the hydroperoxide was heated, the dissociation of the hydroperoxide led to an equal number of $PO\cdot$ and $HO\cdot$ radicals. The $HO\cdot$ radical was the direct cause of homopolymerization.

The homopolymer can be reduced by using a reducing agent as follows:



A most desirable property for a grafting system is that it be a nongelling external polymer. In an effort to prevent the gelling, Cu^{2+} , Fe^{2+} , and Fe^{3+} salts are added to the grafting solution during the simultaneous grafting reaction.

Using the radiation peroxide grafting technique in this experiment, the low density polyethylene film was graft copolymerized with acrylic acid in the presence of additives such as acid and metallic salts. The effect of acids and metallic salts on the degree of grafting was examined. Table I shows the grafting yield of low density poly-

ethylene grafted with acrylic acid in the presence of 0.2M H_2SO_4 and various metallic salts of $2.5 \times 10^{-3}M$ concentration. It was shown in this experiment that certain transition metal compounds are effective in inhibiting the homopolymerization of acrylic acid. Fe^{2+} , Fe^{3+} , Cu^{2+} , and Ce^{4+} metallic compounds were effective inhibitors of homopolymerization. The effect of Cu^{2+} and Fe^{3+} on the γ -initiated polymerization of aqueous acrylamide in acid medium was investigated by Collinson et al.,¹³ who suggested that radical termination occurs by an electron transfer process from a propagating polymer to a d orbital of the cation. Of the metallic salts used for inhibiting homopolymerization in this experiment, only metallic salts that were oxidized themselves led to high grafting yields of acrylic acid. For example, the addition of Fe^{2+} salt in the grafting solution led to high grafting yield. On the other hand, Fe^{3+} salt gave a very small grafting yield. This was explained by assuming that Fe^{2+} is oxidized to Fe^{3+} to dissociate $POOH$ into $PO\cdot + OH^-$, but Fe^{3+} cannot be oxidized to Fe^{4+} by redox systems.

Table II shows the effects of metallic salts types and sulfuric acid on the grafting of methacrylic acid onto polyethylene. The degree of grafting decreased drastically with the addition of $CuSO_4 \cdot 5H_2O$ and was reduced much more in the presence of sulfuric acid. In the case of Mohr's salts having the action of a reductant, the grafting yield of methacrylic acid declined slightly with increasing Mohr's salt concentration in the absence of sulfuric acid; however, it increased

Table III Effect of Mohr's Salt and Sulfuric Acid on Grafting of Acrylic Acid and Methacrylic Acid to Polyethylene Irradiated to Total Dose of 50 kGy by Electron Beam

Mohr's Salt (M)	Degree of Grafting (%)			
	Acrylic Acid		Methacrylic Acid	
	No H_2SO_4	0.2M H_2SO_4	No H_2SO_4	0.2M H_2SO_4
0	Gel	Gel	432	5
5×10^{-4}	7	Gel	422	116
1.5×10^{-3}	6	534	353	117
2.5×10^{-3}	4	302	329	2380
5×10^{-3}	3	157	253	2303
2.5×10^{-2}	2	44	136	1640

Monomer concentration 30 vol %; other grafting conditions are the same as in Table II.

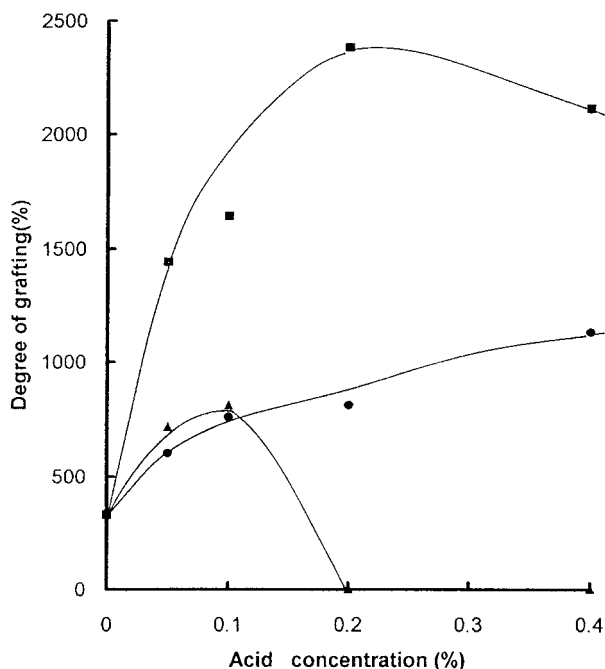
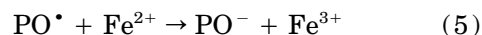


Figure 1 Effect of acid on the grafting of methacrylic acid to polyethylene irradiated to a total dose of 50 kGy by an electron beam. Mohr's salt concentration $2.5 \times 10^{-3} M$. Other grafting conditions are the same as in Table II. (■) H_2SO_4 ; (●) HCl; (▲) HNO_3 .

greatly with the addition of 0.2M sulfuric acid up to $2.5 \times 10^{-3} M$ Mohr's salt concentration. Metallic salts such as Cu^{2+} and Fe^{2+} in the absence of acid play a role in inhibiting the homopolymerization and grafting reactions. Sulfuric acid in the absence of Mohr's salt caused a negative effect on the grafting yield of methacrylic acid. From this result it was assumed that sulfuric acid accelerated the decomposition of hydroperoxide in the presence of a metallic salt such as Fe^{2+} to form radicals that can initiate the grafting reaction as shown in eq. (4). By the addition of sulfuric acid to the grafting solution, OH^- accumulated in eq. (4) can be consumed with the reaction with H^+ , which is dissociated from H_2SO_4 . Therefore, eq. (4) can progress in the presence of acid by the principle of Le Chatelier. The grafting yield was much higher in the case of Mohr's salt than that of cupric sulfate because Fe^{2+} can be transferred to Fe^{3+} by oxidation to dissociate the hydroxides. On the other hand, it is almost impossible for Cu^{2+} to be oxidized to Cu^{3+} by redox systems. This result shows that the grafting of methacrylic acid onto peroxidized polyethylene proceeds mainly through the redox system. The degree of grafting decreased with the addition of more than $5 \times$

$10^{-3} M$ Mohr's salt. Fe^{2+} played an important role in decomposing the hydroperoxides by the redox system. On the other hand, Fe^{2+} deactivated a part of the growing grafting chain radicals as follows:



This reaction led to the reduction of grafting.

It was almost impossible to graft acrylic acid onto polyethylene film without metallic salts such as Mohr's salt and $FeSO_4 \cdot 7H_2O$, regardless of the presence of acid in the grafting solution because of the formation of homopolymer (Table III). The inclusion of Mohr's salt in the grafting solution in the absence of sulfuric acid led to the low grafting yield. For example, only 4% grafting was obtained by the addition of $2.5 \times 10^{-3} M$ Mohr's salt and no addition of acid. In the grafting reaction of methacrylic acid onto polyethylene, the highest grafting yield was obtained with the addition of $2.5 \times 10^{-3} M$ Mohr's salt and 0.2M sulfuric acid. More addition of sulfuric acid led to a slight decline of the grafting yield as shown in Figure 1.

The grafting degree of methacrylic acid was much higher than that of acrylic acid. The reactivity of monomers and radicals on copolymerization is determined by the nature of the substituents

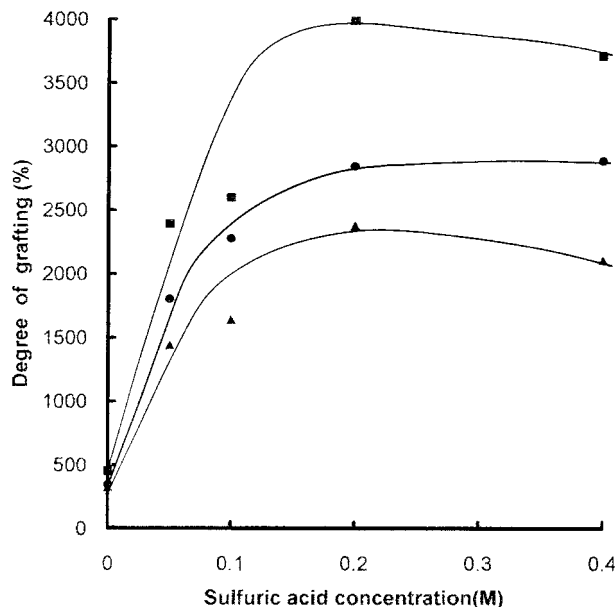


Figure 2 Effect of sulfuric acid on the grafting of methacrylic acid to polyethylene irradiated with γ ray and electron beam (EB). Grafting conditions are the same as in Figure 1. (■) 50 kGy by γ ray; (●) 70 kGy by EB; (▲) 50 kGy by EB.

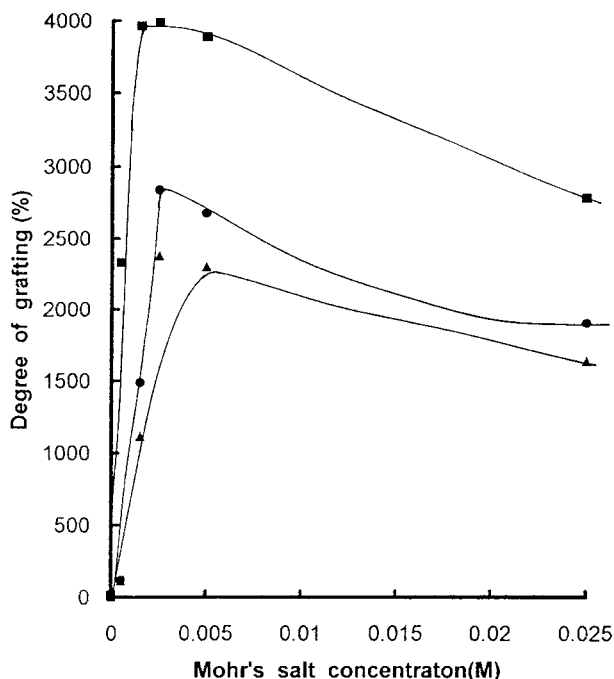


Figure 3 Effect of Mohr's salt concentration on the grafting of methacrylic acid to polyethylene; $0.2M$ H_2SO_4 concentration. Other grafting conditions are the same as in Table II. (■) 50 kGy by γ ray; (●) 70 kGy by EB; (▲) 50 kGy by EB.

on the double bond of the monomer. These substituents influence reactivity. The methyl group of methacrylic acid may activate the double bond, making the monomer more reactive than acrylic acid. It was known that energies of activation for polymerization of acrylic and methacrylic acids in salts-free solutions are 16.7 and 15.6 kcal/mol, respectively.^{14,15}

The effect of acid type on the grafting yield is shown in Figure 1. The addition of acid in the grafting system led to a great increase in grafting yield, except for the addition of more than $0.2M$ HNO_3 . The rapid decrease in grafting yield at more than $0.2M$ HNO_3 concentration can be attributed to the phenomenon that the excessive addition of HNO_3 in the grafting solution causes the segregation of methacrylic acid and water. The addition of H_2SO_4 led to a higher grafting yield compared with the addition of HCl and HNO_3 .

Figure 2 shows the effect of sulfuric acid concentration on the grafting yield of polyethylene film irradiated with a γ ray and electron beam. The addition of H_2SO_4 led to the significant increase in the grafting yield up to $0.2M$ concentration and then decreased. The grafting yield of γ -

ray irradiated polyethylene was much higher than that of electron beam irradiated polyethylene. This result can be attributed to the high peroxide concentration of γ -ray irradiated polyethylene film because the irradiation period by γ ray is much longer than that by electron beam. In this experiment, several hours were needed for γ ray irradiation, compared to a few seconds for electron beam irradiation.

Figure 3 illustrates the relation between Mohr's salt concentration and grafting percent when polyethylene films irradiated by an electron beam and γ ray were grafted with methacrylic acid. The maximum grafting yield was obtained at the condition of $2.5 \times 10^{-3}M$ Mohr's salt and $0.2M$ H_2SO_4 , regardless of the irradiation of the electron beam and γ ray.

Table IV shows the effect of reaction time and temperature on the grafting of acrylic acid and methacrylic acid to polyethylene. Reactivity of methacrylic acid was much higher than that of acrylic acid at a $70^\circ C$ reaction temperature. On the other hand, the grafting reaction of methacrylic acid at a $50^\circ C$ reaction temperature was extremely low compared with that of acrylic acid. The initial rate of grafting increased drastically at $70^\circ C$, regardless of the type of monomer. The initial grafting rate of acrylic acid at $50^\circ C$ was low, but the grafting yield continued to increase until 7 h because the peroxide decomposed slowly with increasing reaction time.

Table V shows the relation between methacrylic acid concentration and the grafting yield when Mohr's salt and $FeNH_4(SO_4)_2 \cdot 12H_2O$

Table IV Effect of Reaction Time and Reaction Temperature on Grafting of Acrylic Acid and Methacrylic Acid to Polyethylene Irradiated to Total Dose of 50 kGy by γ Ray

Reaction Time (h)	Degree of Grafting (%)			
	Acrylic Acid		Methacrylic Acid	
	$50^\circ C$	$70^\circ C$	$50^\circ C$	$70^\circ C$
1	23	516	0.4	3860
3	499	729	0.4	3987
7	594	800	0.4	4633

Mohr's salt concentration $2.5 \times 10^{-3}M$; H_2SO_4 concentration $0.2M$; monomer concentration 30 vol %.

Table V Effect of Metallic Salts and Methacrylic Acid Concentration on Grafting of Methacrylic Acid to Polyethylene Irradiated to Total Dose of 50 kGy by Electron Beam

Methacrylic Acid Concn (%)	Degree of Grafting (%)	
	Mohr's Salt + 0.2M H ₂ SO ₄	FeNH ₄ (SO ₄) ₂ · 12H ₂ O + 0.2M H ₂ SO ₄
10	1688	1.6
20	1803	1.9
30	2380	1.9
40	1828	1.6
50	1830	1.6
60	991	1.6

Grafting conditions are the same as in Table II.

were added to the grafting solution along with 0.2M sulfuric acid. The grafting yield in the case of Mohr's salt exhibited a maximum at monomer concentration of 30 vol %. The pronounced maximum in grafting yield at around 30 vol % can be partially explained by an increased rate of swelling of the grafted layer in the reaction medium of this composition.¹² The addition of FeNH₄(SO₄)₂ · 12H₂O in the grafting solution led to a grafting yield that was too low to evaluate the effect of monomer concentration, because the Fe³⁺ of FeNH₄(SO₄)₂ · 12H₂O was not oxidized to dissociate peroxides.

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