

Grafting of Maleic Anhydride on Polyethylene in a Homogeneous Medium in the Presence of Radical Initiators

Mousa Ghaemy*, Solaiman Roohina

Department of Chemistry, University of Mazandaran, Babolsar-47415
P.O. Box : 311, I.R. Iran

Received 30 October 2001; accepted 22 September 2002

ABSTRACT

Functionalization of polyethylene has been performed by means of homogeneous grafting reactions of maleic anhydride initiated by free radicals. Benzoyl peroxide, azobisisobutyronitrile, and dicumylperoxide have been used as free radical sources and their efficiency has been compared. The effects of the solvent, time and temperature of the reaction, and concentration of monomer on the percentage of grafting have been investigated. A comparison of the effectiveness of the nature of initiator, solvent, atmosphere and monomer concentration showed that polyethylene macroradicals are formed mainly through the chain transfer reactions. This mechanism of reaction was also confirmed by the influence of the nature of polymer and monomer concentration. Side groups of maleic anhydride and side chains of poly(maleic anhydride) are formed by addition of polyethylene macroradicals to the double bond of maleic anhydride molecule and by a combination of polyethylene macroradicals with those of poly(maleic anhydride).

Iranian Polymer Journal, 12 (1), 2003, 21-29

Key Words:

polyethylene;
grafting;
functionalization;
maleic anhydride.

INTRODUCTION

Functionalization of polyolefins can be accomplished by grafting unsaturated molecules bearing functional groups through a radical reaction initiated by organic peroxides [1].

Polyolefins modified by the introduction of polar groups in their

backbones have been prepared in order to improve the physicochemical properties of the parent polymers and to promote adhesion, dyeability, cross-linking, or other chemical modifications. They have also been used as starting materials to prepare

(*)To whom correspondence should be addressed.
E-mail: ghaemy@umz.ac.ir

graft copolymers either by initiating the polymerization of a different monomer on the functional groups or by binding chains of a different polymer having reactive end groups. Block and graft copolymers have been extensively used in blends of two immiscible homopolymers to improve the interfacial adhesion between the two phases [2].

The heterogeneous reaction, i.e. molten maleic anhydride is insoluble in aliphatic hydrocarbons including molten polyolefins, resulted in the appendage of maleic anhydride (MAH) units onto the polyethylene backbone and was accompanied by the cross-linking of the polyethylene. Since cross-linking occurred to a greater extent in the presence of MAH than its absence, it was proposed that intermediates in the homopolymerization of MAH were responsible for the increased cross-linking.

The presence of nitrogen, phosphorous- and sulphur-containing organic electron donors which inhibit the homopolymerization of MAH in the reaction mixture prevented the cross-linking of polyethylene and yielded soluble polyethylene with appendaged MAH units [3,4]. The heterogeneous radical catalyzed graft copolymerization of MAH onto LDPE film suspended in acetic anhydride at 80-110°C yielded cross-linked MAH-containing LDPE film [5]. The reaction of molten isotactic polypropylene (IPP) with MAH in the presence of a free radical catalyst, in a Barbender plasticorder or in an extruder resulted in extensive degradation and a significant decrease in the intrinsic viscosity of the IPP [6]. The degradation was presumably decreased to some extent when the reaction was conducted in xylene solution. Functionalization of an amorphous ethylene-propylene copolymer (EPM) has been performed by means of homogeneous grafting reaction of unsaturated dicarboxylic anhydrides initiated by free radicals [7].

Grafting dicarboxylic anhydrides such as MAH onto high density polyethylene (HDPE) in the presence of various comonomers using a twin-screw extruder was also studied by White and co-workers [8]. It was indicated that ethylenically unsaturated cyclic dicarboxylic anhydrides show much less tendency to being grafted onto polyethylene than does MAH, especially if a long aliphatic chain is attached to unsaturation.

The present investigation was undertaken to study the possibility and the extent of grafting of MAH onto HDPE and LDPE in a homogeneous reaction using boiling xylene as solvent under free radical conditions.

The experiments were carried out to study the influence of parameters such as: time, temperature, MAH concentration, type of free radical initiators, their concentrations and solvent, on the percentage of grafting.

EXPERIMENTAL

Materials

HDPE with a melt flow index (MFI) of 17.75 and a density of $d=0.952$ was received from Iranian Petrochemical Complex. To remove substances added during manufacturing, HDPE pellets were dissolved in boiling xylene and then precipitated in methanol while the solution was still hot. MAH was purified by recrystallization from chloroform. The free radical catalyst benzoyl peroxide (97%, Fluka) (BP) was purified by dissolving in chloroform and then recrystallized in methanol.

Azobisisobutyronitrile (AIBN) and dicumyl peroxide (DCP) (99% and 97%, respectively, Fluka) were used as received. Solvents such as *o*-, *m*-, and *p*-xylene, 1,2-dichlorobenzene, methanol, DMF and *t*-butyl benzene (Fluka) were used as received.

HDPE-MAH Grafting Reactions

Reactions were carried out in a flask equipped with a nitrogen inlet, thermometer, reflux condenser. PE dissolves in xylenes, 1,2-dichlorobenzene, and *t*-butyl benzene at the boiling points of the solvents. The reaction flask containing certain amount of PE in xylene was heated (in an oil bath) to dissolve the polymer. When the dissolution was complete, certain amount of maleic anhydride and initiator were added to the mixture. The time of addition of MAH and initiator was recorded as the starting time of the reaction. After reaching the desired time, the reaction was stopped and the polymeric product was precipitated in acetone, repeatedly washed with acetone to remove unreacted MAH and finally it was filtered and dried in a vacuum oven at 50°C to a constant weight. To remove all the unreacted MAH, the precipitated polymer was dissolved in xylene at 134°C and refluxed for 4 h and it was then again precipitated in acetone, washed and finally dried in a vacuum oven. In case when there is some cross-linked polymer, the reaction product would not be dissolved completely in boiling xylene. In this case, the hot suspension was filtered to remove the gel and acetone was added to the filtrate to precipitate the

xylylene-soluble, acetone-insoluble polymer. The latter was collected on filter paper by vacuum filtration, washed with acetone, and dried in a vacuum oven at 50°C. The filter paper containing the xylylene-insoluble, gel polymer was dried in a vacuum at about 80°C overnight and, after subtracting the weight of the filter paper, the yield of the gel content of the polymer was obtained.

Evaluation of Grafting Degree

The amount of the grafted anhydride in HDPE-g-MAH was determined by titrating the acid groups after complete hydrolysis of the anhydride groups [8]. The acid groups were obtained by heating 1 g of polymer in 150 mL refluxing water-saturated xylene. The hot solution was titrated immediately with 0.05 N ethanolic KOH using three to four drops of 1% thymol blue in DMF as indicator. A 0.5-1.0 mL excess of KOH solution was added and the deep blue colour was back-titrated to a yellow end point by the addition of 0.05 N isopropanolic HCl to the hot solution. The acid number and grafted MAH content were determined as follows:

Acid number (mg KOH / g polymer) =

$$\frac{\text{mL KOH} \times \text{N KOH} \times 56.1}{\text{polymer(g)}}$$

Therefore,
$$\text{MAH (\%)} = \frac{\text{Acid no.} \times 98}{2 \times 56.1}$$

IR Measurements

The IR spectra were obtained with a Perkin-Elmer 276 IR spectrophotometer.

RESULTS AND DISCUSSION

In order to insert randomly single functional groups onto polyethylene chains, maleic anhydride may be considered appropriate unsaturated molecule. Polyethylene with over 10% grafting of MAH is brown, similar to poly(maleic anhydride). The grafted polymer is soluble in hot xylene, poly(maleic anhydride) is soluble in acetone, and the cross-linked PE is insoluble in both solvents.

The comparison of the infra-red spectra of the original HDPE and MAH-g-HDPE films, Figures 1 and 2,

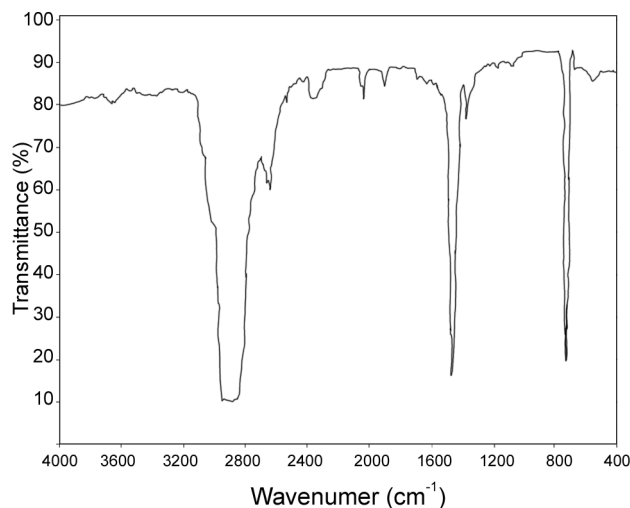


Figure 1. Infrared spectrum of the pure HDPE.

confirm the presence of maleic anhydride units on polyethylene backbones. In comparison with the infrared spectrum of pure polyethylene, that of the graft copolymer shows very strong bands at 1779 and 1859 1/cm which are characteristics of cyclic anhydrides. The band at 1221 1/cm corresponds to C-O stretching vibrations in the cyclic anhydride.

Influence of Oxygen on the Degree of Functionalization

The percentage of grafting of MAH onto HDPE in air is to some extent higher than in nitrogen atmosphere, Table 1. The grafting reactions in air or in nitrogen were carried out in the presence of free radicals formed by thermal decomposition of benzoyl peroxide.

The oxidation of polyethylene in the presence of air at high temperatures which leads to the formation of polymeric hydroperoxides and oxyradicals can be the cause for the higher percentages of grafting.

Table 1. Effect of oxygen on the grafting yield of MAH with PE in xylene; 0.5 g BP and 8 g MAH in 100 g solvent, 2.5 g HDPE, at 110°C.

Time (min)	Grafting in air (%)	Grafting in nitrogen (%)
30	7	7
60	11	9.5
90	17.5	15.5
120	22	19.8

Table 2. Effect of MAH concentration on grafting degree of 2.5 g PE, 0.5 g BP in 100 g solvent, at 110°C for 60 min.

MAH Concentration (%)	Grafting* (%)
4	5.5
6	7.5
8	11
10	13.5
12	15.2

(*) Percentage of grafting was calculated on the basis of the initial amount of MAH.

Influence of MAH Concentration on the Degree of Functionalization

The influence of monomer concentration on grafting degree is shown in Table 2. As it was said in the experimental section, the MAH content in the xylene soluble polymer was determined by titration. The percentage of grafting increases as the concentration of MAH in the reaction mixture is increased. This result also indicates that as the concentration of MAH increases the possibility of formation of cross-linked polymer and poly(maleic anhydride) increases. This result is consistent with the findings of Gaylor and coworkers [4] who worked on grafting of MAH on HDPE at melting stage.

Influence of the Various Free Radical Initiators on the Degree of Functionalization

The grafting reaction of MAH onto HDPE chains were carried out using three types of free radical initiators: Azobisisobutyronitrile (AIBN), benzoyl peroxide (BP), and dicumyl peroxide (DCP).

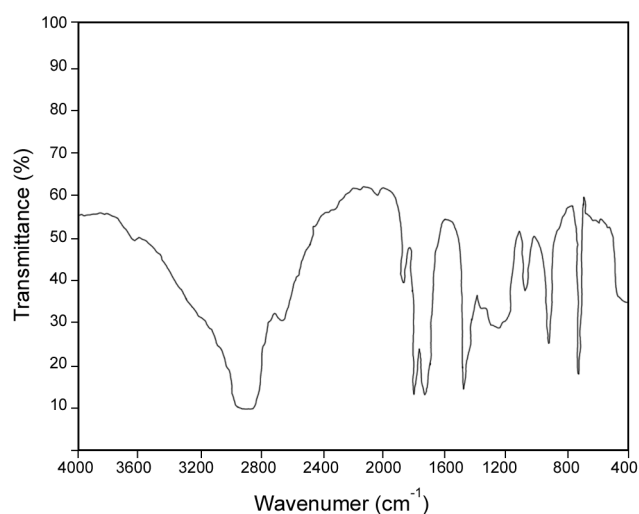


Figure 2. Infra-red spectrum of the grafted PE (MA-g-HDPE).

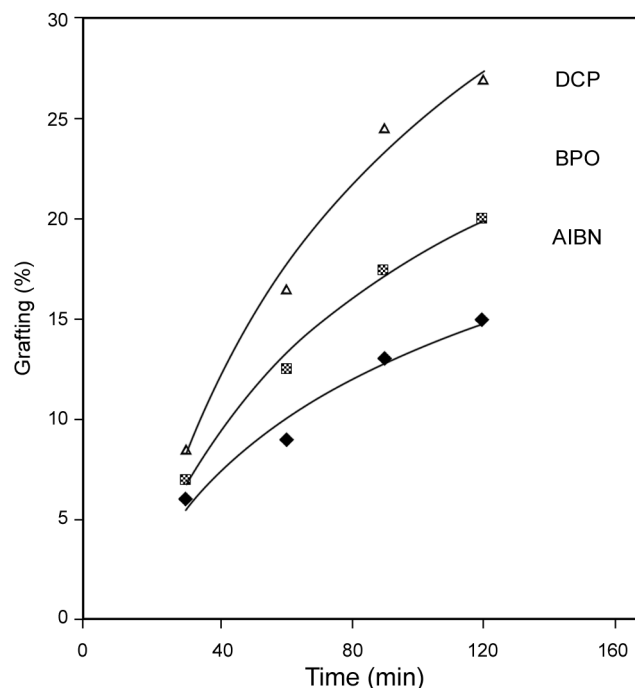
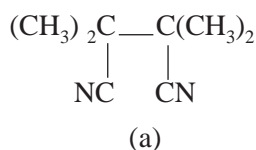


Figure 3. Infra-red of the various free radical initiators on the percentage of grafting. Temperature, 110°C; MAH concentration, 10%; initiators concentration, 0.5 g/100 g of solvent; HDPE, 2 g.

and dicumyl peroxide (DCP). Studies were conducted for 10% MAH in xylene with 2.0 g HDPE and 0.5 g initiator (equivalent to 0.00206 mol BP, 0.00315 mol AIBN and 0.00185 mol DCP) per 100 g solvent at 110°C. The results in Figure 3 show that the grafting yield in the presence of DCP was at the highest and in the presence of AIBN at the lowest level. At 110°C, the half life for AIBN is less than 7 min, for BP is about 18 min, and for DCP is almost 12 h [10]. This can explain for the better efficiency of DCP. The shorter half life initiator generates more radicals at a certain time, and thus more termination reaction by recombination of radical species can take place. In addition to this, due to structural nature of AIBN more chain transfer to initiator can take place than BP or DCP. Chain transfer to initiator molecule can terminate active polymer chain and thus reduce degree of functionalization. Recombination of initiator radicals can, in the case of BP and DCP produce the initial molecules which can again undergo thermal decomposition, but in the case of AIBN produces stable molecules. AIBN molecules produce N_2 molecules and isocyanopropyl radicals during thermal decomposition. Recombination of two radicals produces stable molecule of (a). These can explain the lowest yield of grafting of MAH onto

HDPE in presence of AIBN.



Influence of Time of Reaction on the Degree of Functionalization

The time dependence of the grafting reaction is presented in Figure 4. After an initial sharp increase of the percentage of grafting, the curve becomes parallel to the time axis. This result shows that 3.6 g MAH from the initial amount of 10 g is grafted on PE chains after 10 h, the rest is consumed in different ways: unreacted, homopolymerized, and by cross-linking.

Influence of Reaction Temperature on the Degree of Functionalization

The effect of temperature on the efficiency of grafting MAH onto PE chains was studied at temperatures 50 to 140°C in the presence of AIBN, BP, and DCP initiators. The obtained results are shown in Figure 5. The experiments were carried out for 3 g HDPE, 0.5 g initiator, and 12 g MAH in 100 g solvent for 3 h. The highest yield for AIBN was obtained around 80°C, for BP around 110°C, and for DCP at the boiling temperature of xylene.

Influence of Initiator Concentration on the Degree of Functionalization

Studies of the influence of the benzoyl peroxide concentration were conducted under oxygen and nitrogen

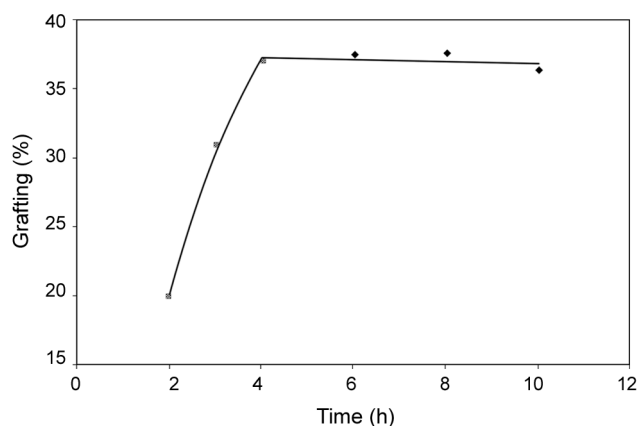


Figure 4. Percentage of grafting vs. time of reaction. Temperature, 110°C; MAH concentration, 10%; benzoyl peroxide concentration, 0.5 g / 100 g of solvent; HDPE, 2 g.

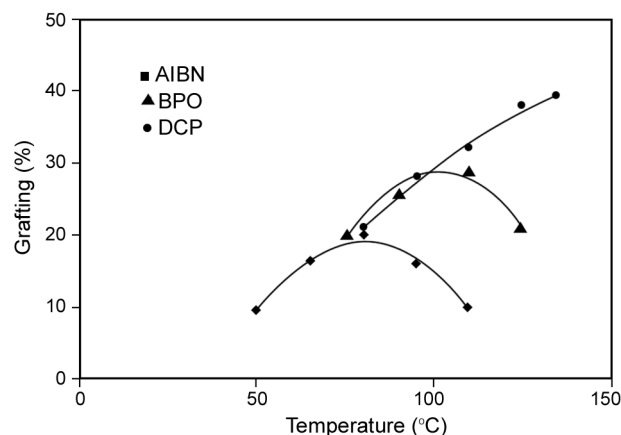


Figure 5. Percentage of grafting vs. temperature for various free initiators. Time, 3 h; MAH concentration, 10%; initiators concentration, 0.5 g / 100 g of solvent; HDPE, 2 g.

atmosphere at 110°C in xylene. The obtained results, Figure 6, show that the highest yield of grafting was obtained for 1 g of BP in a homogeneous reaction at 110°C. This is in contrary for heterogeneous reaction where it was reported 0.05 g BP at 110°C [5]. The increase of the percentage of grafting in the first section of the curves can be due to the increase of the rate of chain transfer reactions and formation of macroradicals, the increase of rate of homopolymerization of MAH and formation of side chains, and also the oxidation of polyethylene which is more pronounced in the presence of oxygen. The percentage of grafting depends not only on the quantity of side chains but also on their molecular weight, which undoubtedly decreases with increasing initiator concentration. Beyond a certain point this caused a decrease in the percentage of grafting. At the same time reactions which are compet-

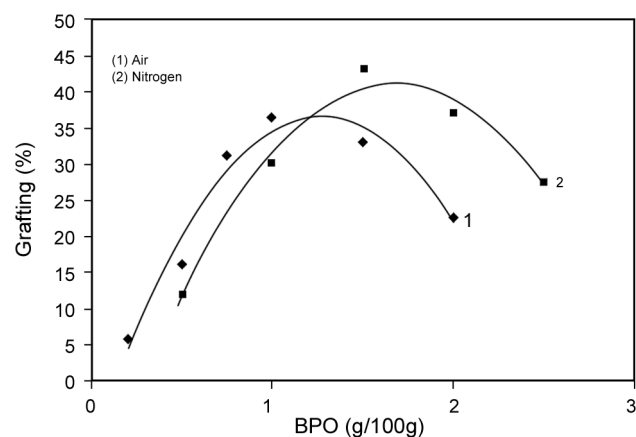


Figure 6. Percentage of grafting vs. benzoyl peroxide concentration: (1) in air, (2) in nitrogen. Temperature, 110°C; time, 3 h; MAH concentration, 10%; HDPE, 2 g.

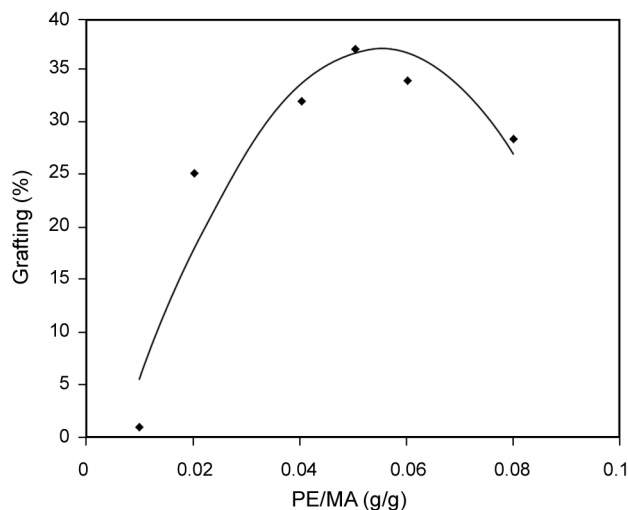


Figure 7. Percentage of grafting vs. ratio of PE/MAH. Temperature, 110°C; time, 3 h.; MAH concentration, 16%; benzoyl peroxide concentration, 0.75 g / 100 g of solvent.

itive to grafting, such as combination and disproportionation of macroradicals, take place in solution. When the concentration of poly(maleic anhydride) macroradicals increases, the rate of their combination and disproportionation increases faster than the rate of their combination with polyethylene macroradicals. These two factors are responsible for the decrease in the percentage of grafting.

Influence of the Amount of HDPE on the Degree of Functionalization

The influence of polymer concentration on the percentage of grafting in the presence of air was studied. In these experiments, the concentrations of initiator and MAH monomer were kept constant (0.75 g BP and 16 g MAH per 100 g solvent) at 110°C for 3 h. As it is noticed in Figure 7, the percentage of grafting shows a maximum which describes the fact that grafting reactions take place through chain transfer reactions. As the concentration of polymer is increased the possibility of chain transfer reactions between polymer chains and various radicals increases and thus more macroradicals are formed. The maximum appears when the weight ratio of PE/MAH in solvent is about 0.05. The percentage of grafting starts to decrease when the weight ratio of PE/MAH reaches 0.06. This can be due to increase in viscosity, which formation of more macroradicals in the viscous medium can bring about their combination. Therefore, termination through combination of

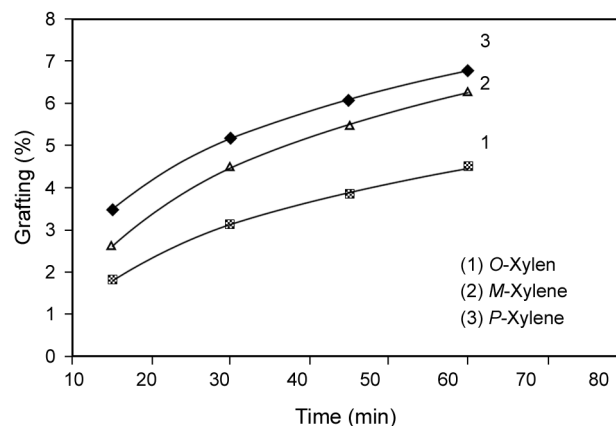


Figure 8. Influence of the percentage of grafting. Temperature, boiling points of the solvents; MAH concentration, 2%; HDPE, 2 g; benzoyl peroxide concentration 0.1 g / 100 g of solvent.

radicals increases and percentage of grafting decreases. Faster combination of macroradicals not only decreases the quantity of side chains but it also decreases their molecular weight which both influence the increase in the percentage of grafting.

Influence of Solvent on the Degree of Functionalization

By taking into account the free radical mechanism of the functionalization process, we have also investigated the influence of the nature of solvent on the grafting reaction in a homogeneous system. It has been suggested [11] that alkylbenzenes in the presence of free radicals may give rise to Ar-CH-R radicals. These radicals can also contribute in the free radical reactions and will have influence on the degree of grafting. The results given in Figure 8, show that the percentage of grafting in xylenes as solvent follows as :

$$p\text{-xylene} > m\text{-xylene} > o\text{-xylene}$$

Benzylic radicals, Ar-CH₂, which form from hydrogen atom abstraction of xylene molecules by chain transfer reactions can add to unsaturation of MAH or abstract hydrogen atom from polymer chain among other reactions which are able to take place.

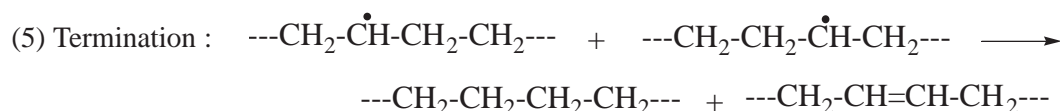
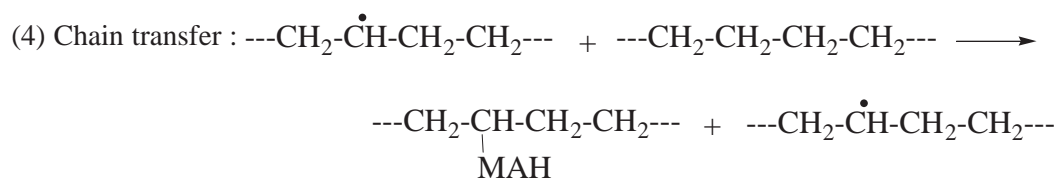
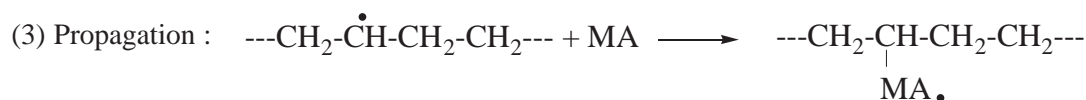
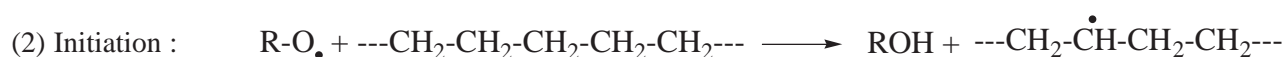
Macroradicals can also add to unsaturation of MAH and the resultant radicals can abstract hydrogen atom from solvent molecules or combine with a benzylic radical. These reactions can take place with *p*-xylene easier than *m*- or *o*-xylenes. By using solvents

such as chlorobenzene and *t*-butyl benzene which are without benzylic hydrogen, somehowless grafted polymer was obtained. It is also worth remarking that for reaction time of 1 h using *p*-xylene as solvent, no gel was formed while using chlorobenzene or *t*-butyl benzene as solvent, gel (cross-linked polymer) was formed which was insoluble in hot xylene. Therefore, in the presence of small amount of MAH, where cross-

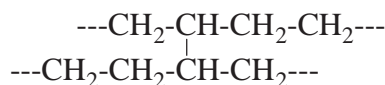
linking is the dominant process, xylenes as solvent prevent cross-linking due to chain transfer reactions to solvent molecules.

Mechanism of Grafting

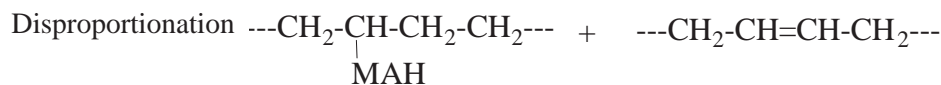
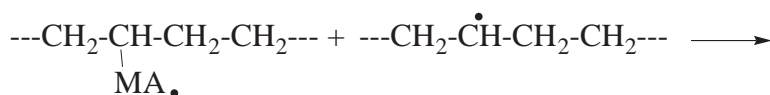
The grafting mechanism of maleic anhydride onto polyethylene backbone with peroxide initiation would involve following steps:



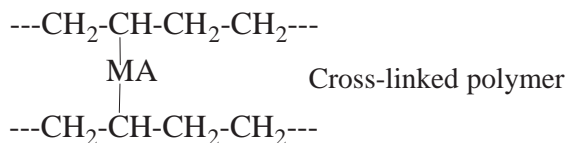
Disproportionation



Cross-linked polymer



and



During the heating of polyethylene in a solution of maleic anhydride with radical initiators in air, the formation of macroradicals of polyethylene may be due to two reactions: (1) chain transfer from radicals formed by decomposition of the initiator or from growing chains of poly(maleic anhydride) or (2) decomposition of peroxide and hydroperoxide groups formed during the oxidation of polyethylene.

Macroradicals of polyethylene formed in these reactions can initiate the polymerization of maleic anhydride or combine with the growing chains of poly(maleic anhydride). Both reactions may, of course, occur simultaneously.

To determine which mechanism corresponds with reality more closely, the reactions in air and in nitrogen atmospheres were compared. Clearly the percentage of grafting is to some extent higher in the presence of oxygen, but in the presence of free radical initiator is not a decisive agent. The reaction in nitrogen was studied for concentration of BP of 0.5 g/100 g of solution, and the percentage of grafting reached almost 20% after 120 min compared with 22% grafting in the presence of air and under the same conditions.

A comparison of results obtained when grafting was conducted with BP and with AIBN indicates that grafting is mainly based on a chain transfer reaction to polyethylene. In grafting via the chain transfer reaction AIBN is less active than BP. In our work, we also found that the percentage of grafting obtained with BP is much higher than with AIBN.

A comparison of results also obtained when grafting was conducted in *p*-xylene and in chlorobenzene as solvent indicates that homogeneous grafting reaction is mainly based on chain transfer reactions. In grafting via the chain transfer reaction xylenes are much more active than chlorobenzene and thus, more PE macroradicals are formed through chain transfer with benzylic radicals. Thus, polyethylene macroradicals are formed mainly through the chain transfer reaction with radicals which result from thermal decomposition of the initiators. In the above scheme, HDPE macroradicals were generated by hydrogen abstraction from HDPE chain promoted by the primary free radicals, RO \cdot , arising from thermal decomposition of initiator. New macroradicals are formed by the addition of PE macroradicals to the double bond of MAH. This latter reaction is favoured by the strong electron attracting properties of the double bond of MAH as it is the cause for the formation of alternating copolymer. The fate of

PE macroradicals can be found by successive addition of unsaturated molecules (MAH) on them. This can lead to the formation of a homopolymer of MAH grafted to HDPE chain which may be considered to be unlikely on the basis of its steric hindrance and, consequently, no formation of a real graft copolymer should occur.

The interdependence of the percentage of grafting and monomer concentration showed that the initial increase is due to an increase of the rate of homopolymerization which form the growing chains of poly(maleic anhydride) and their subsequent bimolecular termination reactions with polyethylene macroradicals. Thus, the rate of combination of both kinds of macroradicals rises, and the percentage of grafting increases as well. But with a further rise in the concentration of poly(maleic anhydride) macroradicals, due to increase in monomer concentration, their mutual combination outweighs their combination with polyethylene macroradicals. Further increase in monomer concentration can probably increase cross-linking of PE chains through maleic anhydride side chains. Thus, formation of more xylene insoluble polymer increases as the concentration of MAH increases.

It is much more difficult to decide whether the formation of the graft copolymer is due to the initiation of polymerization by the PE macroradicals or to their combination with the growing chains of poly(maleic anhydride).

CONCLUSION

These studies proved that the homogeneous insertion of an unsaturated molecule such as maleic anhydride onto polyethylene backbone in the presence of free radical initiator can be easily accomplished. These investigations can probably suggest that a combination of polyethylene macroradicals with the maleic anhydride molecules and with the growing poly(maleic anhydride) chains are responsible for the formation of side chains.

Comparisons of grafting in air and in nitrogen and of grafting in the presence of benzoyl peroxide and AIBN, indicate that polyethylene macroradicals are formed mainly from chain transfer reactions by free radicals which are generated from thermal decomposition of organic initiators. The formation of side groups and side chains is mainly due to addition of polyethylene macroradicals to the double bond of maleic anhy-

dride molecules and also the combination of polyethylene macroradicals with those of poly(maleic anhydride). Investigations on the influence of efficiency of the initiators and their concentrations, monomer concentration, nature of the solvent, temperature and reaction time on the percentage of grafting confirmed the mechanism of grafting.

The change of all factors which influence both reactions conditioning grafting (chain transfer reactions and addition of polyethylene macroradicals to maleic anhydride) leads to the appearance of maxima in the dependence of the percentage of grafting on these factors. This is related to the occurrence of reactions competitive to grafting in the described system.

REFERENCES

1. Minoura Y., Ueda M., Minozuma S., and Oba M., "Role of reaction time in batch process modification of atactic polypropylene by maleic anhydride in melt" ; *J. Appl. Polym. Sci.*, **13**, 1625-1634 (1969).
2. Ide F., and Hasegawa A., "Studies on polymer blend of nylon 6 and polypropylene or nylon 6 and polystyrene using the reaction of polymer" ; *J. Appl. Polym. Sci.*, **18**, 963-968 (1974).
3. Gaylord N.G. and Mehta R., "Peroxide-catalyzed grafting of maleic anhydride on to molten polyethylene in the presence of polar organic compounds"; *J. Polym. Sci., Part A, Polym. Chem.*, **26**, 1189-1198 (1988).
4. Gaylord N.G., Mehta R., Kumar V., and Tazi M., "High density polyethylene-g-maleic anhydride preparation in presence of electron donors"; *J. Appl. Polym. Sci.*, **38**, 359-371 (1989).
5. Gabara W. and Porejko S., "Grafting of maleic anhydride on polyethylene. I-Mechanism of grafting in a heterogeneous medium in the presence of radical initiators"; *J. Polym. Sci., Part A-1*, **5**, 1547-1562 (1967).
6. Gaylord N. G. and Mishra M. K. "Non-degradative reaction of maleic anhydride and molten polypropylene in the presence of peroxides"; *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 23-30 (1983).
7. De Vitos G., Lanzetta N., Maglio G., Malinoconico M., Musto P., and Palumbo R., "Functionalization of an amorphous ethylene propylene copolymer by free radical initiated grafting of unsaturated molecules"; *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1335-1347 (1984).
8. Gaylord N., G., Mehta M., and Mehta R. "Degradation and cross-linking of ethylene-propylene copolymer rubber on reaction with maleic anhydride and / or peroxides"; *J. Appl. Polym. Sci.*, **33**, 2549-2558 (1987).
9. Samay G., Nagy T., and White J. L., "Grafting of maleic anhydride and comonomers onto polyethylene"; *J. Appl. Polym. Sci.*, **56**, 1423-1433 (1995).
10. Carry M., Curos A., Flu T.A., "The radical grafting of styrene onto polyethylene intensive mixer"; *J. Appl. Polym. Sci.*, **69**, 1307-1317 (1998).
11. Shechter H., and Barker H., "Addition reactions of arylalkanes and maleic anhydride occurring by chain processes"; *J. Org. Chem.*, **21**, 1473-1477 (1956).