High Density Polyethylene-*g*-Maleic Anhydride Preparation in Presence of Electron Donors

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Synopsis

The reaction of molten HDPE with MAH at 215 and 250°C using di-*t*-amyl peroxide and *t*-butyl cumyl peroxide as catalysts yielded HDPE-*g*-MAH accompanied by crosslinked polymer. The formation of the latter, increased by the presence of MAH and insoluble in refluxing xylene, was prevented by the presence of electron donor additives, i.e., dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), and tri(nonylphenyl)phosphite (TNPP). A charge containing 0.0625–0.125% catalyst, 5% MAH and 0.5% additive, all based on HDPE and added to the molten HDPE in four portions, resulted in gel-free polymer with an MAH content of 0.7–1.7%. HDPE-*g*-MAH with the least color was obtained with TNPP, followed by DMAC and DMSO. Notwithstanding the absence of gel in the HDPE-*g*-MAH prepared from HDPE with a melt flow of 17 g/10 min, the carboxylated HDPE had a melt flow of 0.0–1 g/10 min, indicative of an increase in the molecular weight of the product. This is attributed to a coupling reaction between MAH radicals appended to the HDPE backbone (HDPE–MAH ·) and HDPE radicals formed as a result of hydrogen abstraction from HDPE by radicals from the catalyst and/or excited MAH.

INTRODUCTION

The reaction of a polyolefin in the melt with maleic anhydride (MAH), in the presence of a free radical precursor, results in the appendage of individual MAH units onto the polyolefin backbone, accompanied by crosslinking and/or chain scission. Crosslinking is the predominant side reaction in the case of low density polyethylene (LDPE),[1,2] while the presence of propylene units as in polypropylene results in extensive degradation.[3] The reaction of ethylene–propylene copolymer rubber with MAH yields a maleated product, accompanied by both crosslinking and scission.[4]

The presence of electron donor compounds, i.e., compounds which contain nitrogen, phosphorous, or sulfur atoms, and inhibit the homopolymerization of MAH but not that of methyl methacrylate, prevent the crosslinking and/or degradation which normally accompanies MAH grafting on molten polymers.[5,6]

The present investigation was undertaken to study the peroxide-catalyzed preparation of high density polyethylene HDPE-*g*-MAH and the effect of electron donor compounds on the crosslinking which accompanies the carboxylation, i.e. appendage of MAH.

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EXPERIMENTAL

Materials

HDPE GERS 1613NT containing a small amount of butene-1 and having a density of 0.951 g/mL and a melt index of 17 (ASTM D1238, Condition E) was used as received in powder form (Polyolefins Division, Union Carbide Corp.). Maleic anhydride (MAH) was purified by recrystallization from chloroform. The free radical catalysts di-*t*-amyl peroxide (DtAP) (95% active, Aztec Chemicals Co.) and *t*-butyl cumyl peroxide (tBCP) (90% active Lupersol 801, Lucidol Division, Pennwalt Corp.) were used as received. The additives *N*,*N*-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), and tri(nonylphenyl and dinonylphenyl)phosphite (TNPP) (Polygard, Chemical Group, Uniroyal Inc.) were used as received.

HDPE–MAH Grafting Reactions

Reactions were carried out at 215 or 250°C at 100 rpm in a Brabender Plasticorder. The mixing chamber was heated to a temperature of about 15–20°C higher than the desired reaction temperature under a nitrogen atmosphere. The addition of 39 g powdered HDPE decreased the temperature of the chamber and its contents below the desired reaction temperature. The HDPE was heated for about 5 min until it was completely molten and the reaction temperature was reached. The flow of nitrogen into the mixing chamber was stopped. A mixture of MAH, catalyst, additive, and 1 g HDPE, the latter added to convert the paste into a powder, was added in four equal portions at 2-min intervals. The contents of the mixing chamber were mixed for an additional 2 min after the last addition and then removed from the chamber.

The torque was continuously recorded during the mixing and note was taken of the torque reading after the molten polymer was fluxed and again just prior to opening the chamber. The difference in torque (torque change = final − initial readings) was an indication of the absence or presence of crosslinked polymer and/or an increase in the polymer molecular weight. Torque change values of less than 80 generally indicated the absence of gel or crosslinked polymer.

Melt Index

The melt flow (g/10 min) of the HDPE-*g*-MAH was determined in a Tinius-Olsen melt indexer at 190°C under a load of 2.160 kg (ASTM D1238, Condition E). Due to the presence of unreacted MAH, the melt index values obtained from the crude polymer taken from the mixing chamber of the Plasticorder and used without further purification were about 0.5–1.5 units higher than those obtained from the polymer from which unreacted MAH had been removed. The latter was obtained by compression molding 5–10 mil film from the crude polymer, at 290–300°F using a press cycle of 10 min under 3000 psig, followed by 2 min under 40,000 psig. The film was suspended in a water bath maintained at 95–100°C for 6–8 h to hydrolyze the unreacted MAH and remove it as the water-soluble maleic acid. The film was wiped dry

with a paper towel, rinsed with acetone, and dried in a vacuum overnight at room temperature. The film was cut into small pieces for determination of the melt index.

Gel Content of HDPE-*g*-MAH (Xylene-Insoluble Fraction)

The gel content of the crude polymer from the Plasticorder was determined by heating about 5 g of crude polymer in 250 mL of refluxing xylene (about 130°C) for 4 h. The hot solution or suspension was filtered through several layers of cheese cloth. About 1 L of cold acetone was added to the filtrate to precipitate the xylene-soluble, acetone-insoluble polymer. The latter was collected on filter paper by vacuum filtration, washed with acetone, and dried in a forced air oven at 75–80°C overnight. The cheese cloth containing the xylene-insoluble, gel polymer, was dried in an air oven at 75–80°C overnight and, after subtracting the weight of the cheese cloth, yielded the gel content of the polymer.

MAH Content of Xylene-Soluble HDPE-*g*-MAH

The MAH content of the xylene-soluble polymer was calculated from the acid number. The latter was obtained by heating about 1 g of polymer for 1.5 h in 150 mL of 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 color was back-titrated to a yellow end point by the addition of 0.05*N* isopropanolic HCl to the hot solution. The KOH solution was standardized against a solution of potassium hydrogen phthalate.

The acid number and MAH content were calculated as follows:

$$\text{acid number (mg KOH/g)} = \frac{\text{mL KOH} \times N \text{ KOH} \times 56.1}{\text{g polymer}}$$

$$\text{MAH (\%)} = \frac{\text{acid number} \times 98}{2 \times 561}$$

RESULTS AND DISCUSSION

The reaction of MAH with molten HDPE (MI 17 g/10 min) was carried out in the presence of a free radical precursor and an electron donor compound. The reactions were conducted at 215 and 250°C, where the free radical catalysts DtAP and tBCP had extremely short half-lives in the range of 0.4–120 s. The mixture of MAH, free radical catalyst, and electron donor additive was in the form of a paste. However, the addition of a small amount of HDPE powder converted the paste to a powder which could be added in four equal portions at 2 min intervals to the molten HDPE in the chamber of a Brabender Plasticorder.

The crude HDPE–MAH reaction product was extracted in refluxing xylene to separate the crosslinked gel fraction from the xylene-soluble HDPE-*g*-MAH. The latter was recovered by precipitation with acetone. In some cases about

TABLE I
HDPE–MAH Reaction in Presence of DtAP at 215°C[a]

DtAP (g)	Additive (g)	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	HDPE-*g*-MAH Insoluble (%)	HDPE-*g*-MAH Soluble MAH (%)
0.05[b]	None	20	4.1	1.9	0
0.05	None	140	0.0	44.0	2.85
	DMAC 0.2	70	0.0	5.4	1.18
	0.4	10	1.2	0	0.67
	DMSO 0.2	60	0.05	1.2	1.38
	0.4	30	0.35	5.3	1.05
0.025	None	80	0.0	11.4	1.82
	DMAC 0.2	50	0.11	0	1.10
	DMSO 0.2	30	0.50	0	1.05
	TNPP 0.2	25	1.63	0	0.78

[a] Reactants 40 g HDPE, 2 g MAH, 4-shot addition mode.
[b] HDPE (MI 17) mixed at 215°C in absence of MAH.

5% gel content was indicated by xylene extraction, although the small increase in torque reading indicated the absence of gel. The apparent gel was a presumably high molecular weight polymer which did not readily dissolve in the refluxing xylene during the extraction period.

The formation of high molecular weight polymer during the HDPE–MAH reaction was indicated by the reduction of the melt index of water-extracted, monomer-free unfractionated polymer from 17 to 0 g/10 min, although xylene extraction demonstrated the absence of insoluble, crosslinked polymer.

HDPE–MAH Reaction in Presence of DtAP

The reaction of HDPE with 0.125% DtAP based on HDPE at 215°C in the absence of MAH and an additive resulted in the formation of 1.9% xylene-insoluble material and a decrease in the melt index from 17 to 4.1 g/10 min.

In the presence of 5% MAH based on HDPE and the absence of an additive, the insoluble fraction increased to 44% and the melt index decreased to 0.0 g/10 min. The xylene-soluble fraction had a 2.85% MAH content. Reduction of the DtAP concentration to 0.0625% in the presence of 5% MAH and the absence of an additive reduced the insoluble fraction to 11.4% while the melt index was unchanged at 0.0 g/10 min. The MAH content of the xylene-soluble fraction was reduced to 1.82% (Table I).

The presence of an additive such as DMAC, DMSO, or TNPP, at a concentration of 10% based on MAH, reduced the gel content to 5% or less at DtAP concentrations of 0.0625 or 0.125% in the presence of 5% MAH. The melt index was increased from 0.0 g/10 min but remained below 2 g/10 min, while the MAH content of the xylene-soluble fraction was reduced to about 0.7–1.1%.

The reaction of HDPE with 5% MAH at 250°C in the presence of 0.0625 or 0.125% DtAP and an additive (10% based on MAH) resulted in the formation of HDPE-*g*-MAH with little or no gel content and a xylene-soluble fraction with an MAH content of 0.72 to 1.68%. Despite the absence of crosslinked polymer, the melt index remained at about 1 g/10 min or less (Table II).

TABLE II
HDPE–MAH Reaction in Presence of DtAP at 250°C[a]

DtAP (g)	Additive (g)	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	HDPE-*g*-MAH Insoluble (%)	HDPE-*g*-MAH Soluble MAH (%)
0.05	DMAC 0.2	5	0.0	0	0.72
	DMSO 0.2	20	0.0	1.5	1.68
0.025	DMAC 0.2	0	1.15	0	0.78
	DMSO 0.2	20	0.30	0	0.96
	TNPP 0.2	20	0.0	1.6	1.51

[a] Reactants 40 g HDPE (MI 17), 2 g MAH, 4-shot addition.

TABLE III
HDPE-*g*-MAH with 0–5% Gel Prepared with DtAP[a]

DtAP (g)	Temp (°C)	MAH (g)	Additive (g)	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	HDPE-*g*-MAH Soluble MAH (%)	HDPE-*g*-MAH Gel (%)
0.05	215	2.0	DMAC 0.2	70	0.0	1.18	5.4
			DMSO 0.2	60	0.05	1.38	1.2
	250	2.0	DMAC 0.2	5	0.0	0.72	0
			DMSO 0.2	20	0.0	1.68	1.5
0.025	215	2.0	DMAC 0.2	50	0.11	1.10	0
			DMSO 0.2	30	0.50	1.05	0
			TNPP 0.2	25	1.63	0.78	0
	250	2.0	DMAC 0.2	0	1.15	0.78	0
			DMSO 0.2	20	0.3	0.96	0
			TNPP 0.2	20	0.0	1.51	1.6

[a] Charge 40 g HDPE (MI 17).

Compositions which yielded HDPE-*g*-MAH with 0–5% gel in the presence of DtAP are summarized in Table III.

HDPE–MAH Reaction in Presence of tBCP

The reaction of HDPE with 0.125% tBCP based on HDPE at 215°C in the absence of MAH and an additive yielded a gel-free polymer with a melt index of 2.3 g/10 min.

The presence of 5% MAH based on HDPE increased the gel fraction to 38.6% and the melt index decreased to 0.0 g/10 min. The xylene-soluble fraction had a 2.48% MAH content. When the tBCP concentration was reduced to 0.0625% in the presence of 5% MAH and the absence of an additive at 215°C, the xylene-insoluble fraction was reduced to 17.1% while the melt index remained at 0.0 g/10 min. The MAH content of the soluble fraction was reduced to 1.92% (Table IV).

The presence of additives, i.e., DMAC, DMSO and TNPP, at a concentration of 10% based on MAH, resulted in the preparation of gel-free polymer in the presence of 5% MAH at tBCP concentrations of 0.0625 or 0.125% at 215°C.

TABLE IV
HDPE–MAH Reaction in Presence of tBCP at 215°C[a]

tBCP (g)	Additive (g)	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	Insoluble (%)	Soluble MAH (%)
0.05[b]	None	50	2.3	0	0
0.05	None	115	0.0	38.6	2.48
	DMAC 0.2	50	0.0	0	1.46
	DMSO 0.2	50	0.0	0	1.10
	TNPP 0.2	60	0.11	0	1.15
0.025	None	95	0.0	17.1	1.92
	DMSO 0.2	70	0.0	0	1.44
	0.3	0	0.82	0	0.75
	0.4	20	0.62	0	0.93

[a] Reactants 40 g HDPE, 2 g MAH, 4-shot addition mode.
[b] HDPE (MI 17) mixed at 215°C in absence of MAH.

The melt index was essentially unchanged while the MAH content of the soluble fraction ranged from 1.1 to 1.46%. When the concentration of additive, e.g., DMSO, was increased to 15–20% based on MAH at a tBCP concentration of 0.0625%, the melt index increased but remained below 1 g/10 min while the MAH content of the soluble fraction decreased below 1% (Table IV).

A decrease in the MAH concentration to 2.5% in the presence of 0.125% tBCP and the absence of an additive at 215°C resulted in a reduction of the xylene-insoluble fraction to 32.7% and a decrease in the MAH content of the soluble fraction to 1.4%, while the melt index was unchanged at 0.0 g/10 min. The presence of 10% DMSO based on MAH reduced the gel content to 19.8% while the presence of 10% TNPP based on MAH gave gel-free polymer. In both cases, the melt index was 0.0 g/10 min while the MAH content of the soluble fraction was essentially unchanged at 1.4%. When the TNPP concentration was increased to 20 and 25% based on MAH, the gel-free polymer had an MAH content of less than 1% while the melt index increased but remained below 1 g/10 min (Table V).

Compositions which yielded HDPE-*g*-MAH with 0–5% gel in the presence of tBCP are summarized in Table VI.

The HDPE–MAH reactions detailed in Tables I–VI were carried out by the addition of a mixture of MAH, catalyst, and additive to the molten HDPE in four equal portions at 2 min intervals. As shown in Table VII, when the addition of the mixture of reactants was carried out in one or two portions while, maintaining the total reaction time at 10 min, the MAH content of the gel-free polymer was essentially unchanged at about 1% while the melt index increased to 3 g/10 min.

General

As summarized in Tables III and VI, the various electron donor compounds at a concentration of 10% based on MAH generally resulted in a gel-free

TABLE V
HDPE–MAH Reaction in Presence of tBCP at 215°C[a]

tBCP (g)	Additive (g)	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	HDPE-*g*-MAH Insoluble (%)	HDPE-*g*-MAH Soluble MAH (%)
0.05[b]	None	50	2.3	0	0
0.05	None	80	0.0	32.7	1.40
	DMSO 0.1	80	0.0	19.8	1.35
	TNPP 0.1	70	0.0	0	1.37
	0.2	40	0.75	0	0.99
	0.25	40	0.56	0	0.79
0.025	DMSO 0.2	30	0.75	0	0.84

[a]Reactants 40 g HDPE, 1 g MAH, 4-shot addition mode.
[b]HDPE (MI 17) mixed at 215°C in absence of MAH.

TABLE VI
HDPE-*g*-MAH with 0–5% Gel Prepared with tBCP[a]

tBCP (g)	Temp (°C)	MAH (g)	Additive (g)	Torque change (m g)	MI (g/10 min)	Soluble MAH (%)	Gel (%)
0.05	215	2.0	DMAC 0.2	50	0.0	1.46	0
			DMSO 0.2	50	0.0	1.10	0
			TNPP 0.2	60	0.11	1.15	0
		1.0	TNPP 0.2	40	0.75	0.99	0
0.025	215	2.0	DMSO 0.2	70	0.0	1.44	0
		1.0	DMSO 0.2	30	0.75	0.84	0
	250	2.0	DMSO 0.2	40	0.0	1.60	0

[a]Charge 40 g HDPE (MI 17).

TABLE VII
HDPE–MAH Reaction in Presence of tECP at 215°C[a]

Addition shots[b]	Torque change (m g)	HDPE-*g*-MAH MI (g/10 min)	HDPE-*g*-MAH Insoluble (%)	HDPE-*g*-MAH Soluble MAH (%)
4	60	0.11	0	1.15
2	20	0.11	1.4	1.24
1	0	3.33	0	1.07

[a]Reactants 40 g HDPE (MI 17), 2 g MAH, 0.05 g tBCP, 0.2 g TNPP.
[b]Addition modes: 39 g HDPE charged into mixing chamber and mixed at 215°C until fluxing (5 min), then MAH–tBCP–TNPP mixture (containing 1 g HDPE) added as follows: *1-shot:* 100% added to fluxing HDPE, followed by 10 min mixing; *2-shot:* 50% added to fluxing HDPE, followed by 5 min mixing, then remaining 50% added, followed by 5 min mixing; *4-shot:* 25% added to fluxing HDPE at 2-min intervals, followed by 2 min mixing.

polymer with the following range of MAH contents:

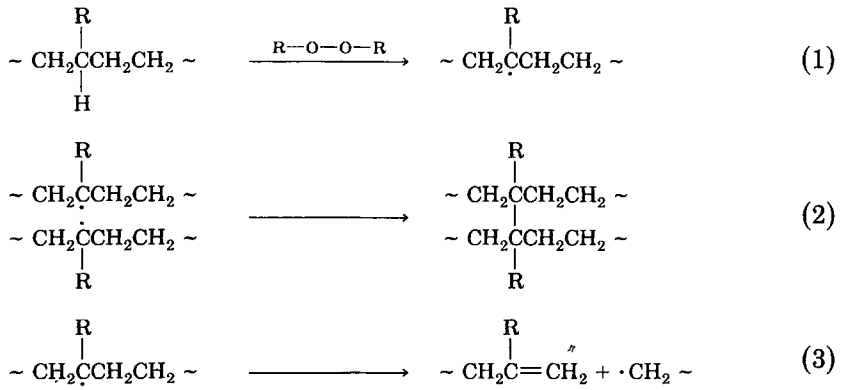
Additive	% MAH in HDPE-*g*-MAH
DMSO	1.0–1.7
TNPP	0.8–1.5
DMAC	0.7–1.2

However, HDPE-*g*-MAH with the best color was obtained with TNPP, followed by DMAC and DMSO.

Notwithstanding the 0–5% gel content of the HDPE-*g*-MAH prepared by reaction of HDPE (MI 17 g/10 min) with MAH in the presence of electron donor compounds, the melt index was generally in the range of 0.0–1.6 g/10 min, with most of the readings below 0.5 g/10 min. The low melt index values may be attributed to an increase in the molecular weight of the reaction product.

Mechanism

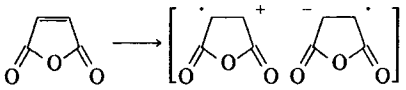
The crosslinking and/or scission of a polymer in the presence of free radicals generated from peroxide decomposition is a result of hydrogen abstraction which forms radical sites on the polymer. The macroradicals either undergo crosslinking through coupling or scission as a result of disproportionation.



The course of the reaction is determined by the polymer structure. Thus, polyethylenes generally undergo crosslinking while polypropylene generally undergoes scission. Both reactions actually occur but the indicated route is the dominant mode. HDPE is particularly prone to crosslinking, presumably due to the proximity of the linear chains in the melt. Although the preferred site for radical formation is the tertiary carbon at a branch point, the secondary carbons also participate in radical formation.

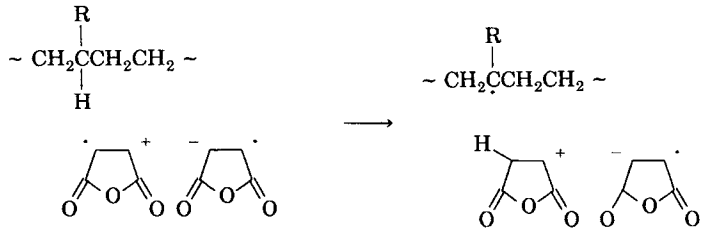
The presence of MAH in the polymer–peroxide reaction mixture results in increased crosslinking or scission, as compared with that noted in the absence of MAH. The increased crosslinking in HDPE is clearly shown in Tables I and IV. This presumed increase in the precursor polymer radicals has been attributed to the presence of excited MAH, i.e., an excimer which is generated when a peroxide which is present undergoes rapid decomposition and exhibits chemically induced dynamic nuclear polarization (CIDNP). Presumably the

triplets which are present during CIDNP interact with ground state MAH to form the MAH excimer[7]:

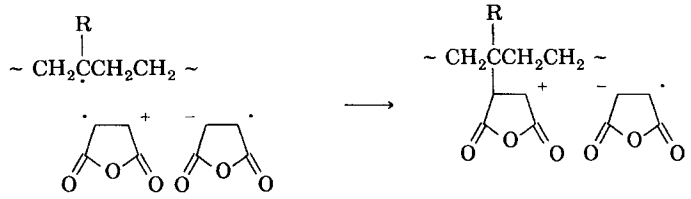


(4)

The excimer is a hydrogen abstracting species and, therefore, by reaction with a polymer, promotes the formation of polymer macroradicals [eq. (5)], which undergo crosslinking and/or disproportionation or add excimer [eq. (6)]. The excimer also adds to the polymer macroradicals generated as a result of abstraction from the polymer by the radicals generated from peroxide decomposition:

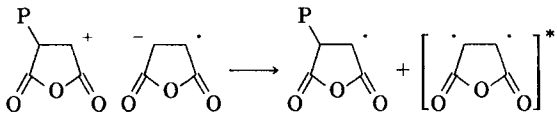


(5)



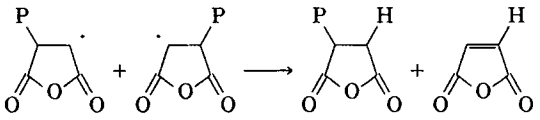
(6)

The terminal cation formed by the addition of the MAH excimer to the polymer radical [eq. (6)] may then take an electron from the MAH anion-radical, i.e., intramolecular electron transfer, and generates a terminal radical and an "activated" monomer:



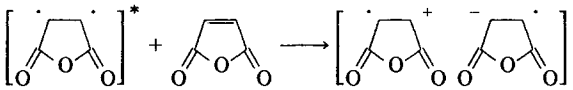
(7)

The terminal radical terminates by disproportionation:



(8)

The "activated" monomer donates an electron to MAH to generate excimer:



(9)

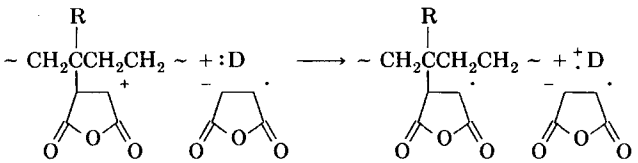
Thus, a relatively low concentration of peroxide undergoing rapid decomposition leads to a high concentration of excimers, which are responsible for the

generation of polymer macroradicals. The latter undergo crosslinking and/or disproportionation as well as the appendage of MAH units through the appendage of the excimer.

A reduction in excimer concentration should decrease both crosslinking and/or degradation as well as the appendage of MAH units. The addition of antioxidants, radical traps, inhibitors, or quenchers will certainly prevent excimer formation by interaction with the catalyst or the species generated as the catalyst undergoes decomposition. However, the resultant large decrease or even total inhibition of the appendage of MAH units would be overkill.

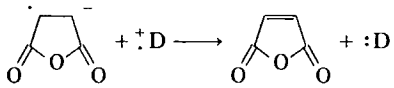
Certain electron donating compounds which have little or no effect on radical polymerization, e.g., the polymerization of acrylic monomers in the presence of a peroxide, do prevent MAH homopolymerization. This suggests that they do not interact with the species generated from the catalyst excessively and therefore should not prevent excimer formation. However, since they prevent MAH homopolymerization, they apparently interfere with the propagation step.[5,6]

These compounds are effective in decreasing the extent of crosslinking and/or degradation, while still permitting the appendage of MAH units, when they are present during the reaction of MAH with a polyolefin in the presence of a peroxide.[5] The effective compounds include nitrogen, phosphorous, and sulfur compounds, which are electron donors and presumably donate an electron to the MAH cation resulting from excimer addition to the polymer radical:



(10)

The donor cation radical accepts an electron from the MAH anion radical to regenerate the donor compound and MAH:



(11)

Thus, due to the conversion of the terminal cation to a terminal radical, the generation of "activated" monomer and excimer, as shown in eqs. (7) and (9), respectively, is prevented and crosslinking and/or degradation are minimized. The MAH-containing polymer formed in the presence of the electron donor additive contains individual MAH units, as it did when formed in the absence of the additive.

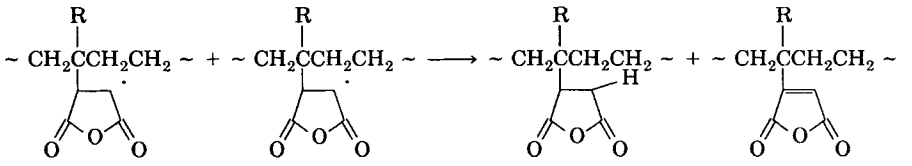
Although radicals are generated on the polymer in the presence of peroxides and undergo crosslinking in the absence of MAH, the presence of MAH results in an increase in crosslinking, presumably due to the formation of even more polymer radicals. Crosslinking in the presence of MAH may be attributed to the following reactions:

$$P\cdot + P\cdot \longrightarrow P - P \tag{12}$$

$$P - MAH\cdot + P - MAH\cdot \longrightarrow P - MAH - MAH - P \tag{13}$$

$$P - MAH\cdot + P\cdot \longrightarrow P - MAH - P \tag{14}$$

However, since MAH is a strong electron acceptor, MAH radicals would be expected to undergo disproportionation [eq. (15)] rather than coupling:



(15)

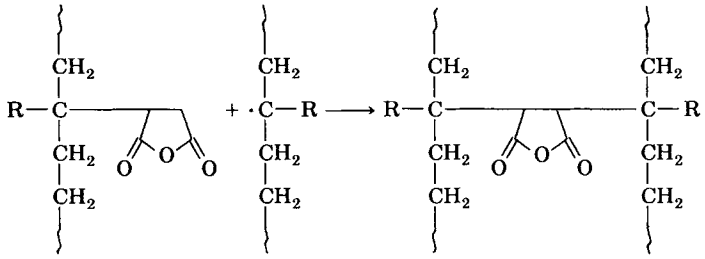
Therefore, the PMAH· coupling reaction [eq. (13)] cannot play a significant role in crosslinking.

It has previously been shown that the electron donor additives have no effect on the crosslinking of polyethylene[1,2] and the degradation of polypropylene[3] which occur in the absence of MAH. Although the crosslinking reaction is not prevented by the presence of the electron donor additive in the absence of MAH, it is prevented by the presence of the additive in the presence of MAH. Therefore, the polymer radical coupling reaction [eq. (12)] cannot play a role in crosslinking in the presence of MAH.

It is reasonable to assume that when MAH and peroxide are present, the MAH excimer adds to the polymer radicals. The resultant P—MAH$^+$ $^-$MAH [eq. (6)] is converted to P—MAH· by intramolecular electron transfer [eq. (7)] and crosslinking results from the coupling of the polymer radical P· and the P—MAH· [eq. (14)].

When the electron donor additive is present, the P—MAH$^+$ $^-$MAH is converted to P—MAH· by electron donation [eq. (10)]. This becomes the dominant reaction forming P—MAH· and in the absence of "activated" monomer [eq. (7)] the excimer formation [eq. (9)] is reduced. The resultant reduced P—MAH· concentration leads to a reduction in P—MAH· coupling with P· [eq. (14)] and minimizes or eliminates the crosslinking reaction.

Crosslinking requires the formation of at least two linkages between two polymer chains. Reduction in the number of linkages reduces the extent of crosslinking. However, polymer chains joined by one linkage are not crosslinked but have a higher molecular weight than the original chains.



(16)

This is consistent with the low melt index values of the gel-free HDPE-*g*-MAH formed in the presence of the additives.

While the coupling of P—MAH· and P· radicals [eq. (16)] leads to the presence of saturated MAH units in the HDPE-*g*-MAH, the infrared spectrum (Fig. 1) shows a triple peak in the carbonyl region. This triple peak is also present in the spectra of the unsaturated citraconic anhydride (methyl-

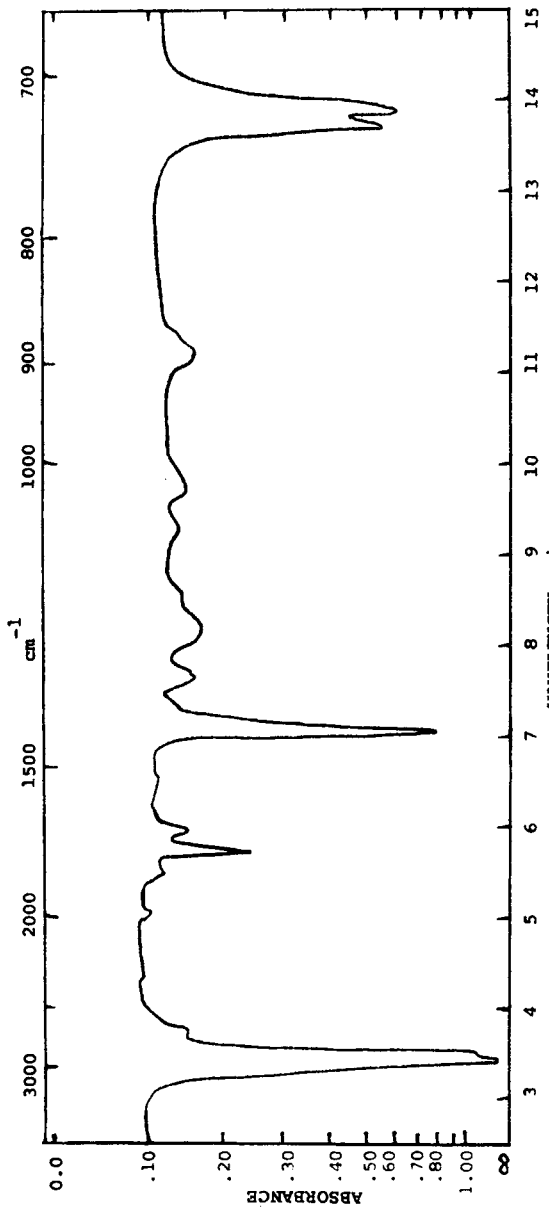


Fig. 1. Infrared spectrum of HDPE-*g*-MAH.

maleic anhydride), 2,3-dimethylmaleic anhydride and 3,4,5,6-tetrahydrophthalic anhydride,[8] and is attributed to the presence of unsaturated MAH units. The latter, arising from disproportionation [eq. (15)] have also been noted in the spectra of LDPE-*g*-MAH[1] and PP-*g*-MAH.[3]

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