

Functionalization of High-Density Polyethylene in the Molten State by Glycidyl Methacrylate Grafting

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ABSTRACT: This study concerns the melt-free radical grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE). We studied the effect of two initiators (*tert*-butyl cumyl peroxide and di-*tert*-butyl peroxide) onto HDPE. Crosslinking of polymer was observed in the presence of 0.3 wt % *tert*-butyl cumyl peroxide but not with 0.3 wt % di-*tert*-butyl peroxide. The grafting was carried out in a Brabender batch mixer at 190 °C. The grafting yield of GMA onto HDPE (determined by infrared spectrometry) is weak (<1 wt % for an initial concentration in monomer of 6 wt %). Moreover, it was noted that the degree of grafting did not vary with the concentration and the nature of peroxide used. To increase the grafting yield of GMA, we added to the HDPE/peroxide/GMA system an electron-donating monomer, such as styrene. Adding this comonomer multiplied the rate of grafted GMA 3- or 4-fold, resulting in a ratio [styrene]_i/[GMA]_i = 1 mol/mol with [GMA]_i = 6 wt %. So, the copolymerization is favored compared with the homopolymerization. This kind of copolymer presenting reactive functions is very attractive in the field of compatibilizing immiscible polymers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 581–590, 2001

Key words: high-density polyethylene; glycidyl methacrylate; styrene; melt-free radical grafting; peroxide

INTRODUCTION

The functionalization of polyolefins by radical grafting of monomers bearing carboxylic acids, anhydrides, oxazolines, or epoxides functions is an interesting way to achieve the *in situ* compatibilization of polyolefin/polyester blends. Lambla¹ and Ganzeveld and Janssen² used maleic anhydride to functionalize polyolefins. They obtained weak grafting yields despite the presence of the radical initiator. The C=C double bonding of ma-

leic anhydride is disubstituted and weakened in terms of electrons by the mesomeric effect of attraction by two carbonyl groups. The maleic anhydride does not react easily with the free radicals, and the efficiency of radical grafting onto polyolefins is limited. Ganzeveld and Janssen² have also shown that grafting yield is improved by increasing the amount of peroxide. However, the crosslinking or degradation of polyolefins limits the amount of initiator introduced and consequently the grafting yield of maleic anhydride. The solution proposed by Gaylord³ and Flat⁴ consists of introducing styrene as a comonomer. The electron transfer from donor to acceptor permits the creation of a charge transfer complex. In fa-

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voring the transfer of radical polymer to the monomers, the macroradicals are consumed more by the grafting reaction than by the parasite reactions (crosslinking, degradation). Flat⁴ has shown that the grafting yield of maleic anhydride (MA) onto polypropylene (PP) is multiplied 2- or 3-fold in the presence of styrene, with a ratio $[\text{styrene}]_f/[\text{MA}]_i = 1.2 \text{ mol/mol}$. Moffett and Dekkers⁵ grafted glycidyl methacrylate (GMA) onto ethylene propylene diene terpolymer (EPDM) in an extruder, in the presence of a radical initiator to compatibilize the polybutylene terephthalate (PBT)/EPDM blends. The yields of grafting GMA onto EPDM were 1.5, 3, and 6 wt %. The efficiency of grafting (70%) was determined by Fourier transform infrared (FTIR) spectroscopy in accordance with the method used by Galucci and Going.⁶ Liu et al.⁷ grafted various monomers in the molten state [GMA, 2-hydroxyethyl methacrylate (HEMA), *t*-butylaminoethyl methacrylate (TBAEMA), dimethylaminoethyl methacrylate (DMAEMA), and 2-isopropenyl-2-oxazoline (IPO)] onto PP to compatibilize *in situ* the PP/(arylonitrile-co-butadiene-co-acrylic acid) rubber (NBR) blends. Grafting was carried out at 180 °C in a batch mixer. The monomer, the initiator, and the homopolymer were introduced simultaneously into the batch mixer. After reaction, the samples were purified and characterized by FTIR and nuclear magnetic resonance (NMR) spectroscopy. Grafting rate did not exceed 1 wt %. The PP-*g*-GMA and PP-*g*-IPO copolymers were effective compatibilizers for PP/NBR blends. Gallucci and Going⁶ also worked on the radical melt grafting of GMA onto PP and low-density polyethylene (LDPE). The grafting was carried out in the batch mixer at 175 °C. When GMA and dicumyl peroxide (DCP) were introduced into the molten PP or LDPE, the GMA did not graft onto PP, whereas the grafting yield of GMA onto LDPE determined by FTIR was 1.9–6.7 wt %. The authors show that the grafting yield of GMA onto high-density polyethylene (HDPE) is inferior to the grafting yield of GMA onto LDPE. The differences observed between the results of Galucci and Going⁶ and Liu et al.⁷ on the grafting of GMA onto PP probably come from the type and the concentration of the peroxides used and the method of introducing these products into the batch mixer. It seems to be more efficient to introduce the polymer, monomer, and initiator together to limit the risks of evaporation of GMA and evaporation or advanced decomposition of the peroxide. These results show that the radical grafting of GMA

onto PP is more difficult than onto LDPE. The grafting yield of LDPE remains weak (<10%). Lambla et al.^{8, 9} studied the radical grafting of GMA onto PP in the molten state to compatibilize *in situ* the PP/PBT blends. They obtained a similar grafting yield (0.8%, determined by FTIR) using conditions close to those used by Liu et al.⁷ They showed that to multiply the grafting yield of GMA onto PP by a factor of 3 or 4, it is necessary to associate a comonomer such as styrene. Yao and Beatty¹⁰ synthesized polyethylene grafted GMA (PE-*g*-GMA) containing 1.2 wt % GMA. They showed that this emulsifying agent is very efficient at compatibilizing HDPE/PET blends *in situ*. More recent work by Vainio et al.^{11, 12} showed that PP/PBT blends can be compatibilized by introducing PP-*g*-oxazoline containing a maximum of 2.1% oxazoline. To synthesize this emulsifying agent, Vainio et al.^{11, 12} used the same method as the one employed in the synthesis of PP-*g*-GMA. This method is not used very often because the monomer bearing the oxazoline function is not available commercially; in contrast, GMA is available commercially.

Our study consists of radical grafting of GMA onto HDPE in the molten state and limiting the crosslinking of polymer and homopolymerization of GMA. We first studied the HDPE/initiator systems without monomer to observe the effect of the reaction of the initiator onto polymer. We then grafted GMA onto HDPE. Preliminary tests showed that GMA couldn't be grafted onto HDPE in the absence of an initiator. This result indicates that thermomechanical initiation is not powerful enough for efficient free radical initiation of grafting reactions. Consequently, we envisaged HDPE/initiator/GMA blends to carry out radical grafting of GMA onto HDPE in a batch mixer. To increase the grafting yield of GMA onto HDPE, we introduced a comonomer (electron donor), such as styrene.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) was produced by Dow, with a weight-average molecular mass of 64,000 g/mol, a number-average molecular mass of 27,000 g/mol, and a melt-flow index of 10 g/10 min (190 °C, 2.16 kg). Lotader AX8840 was a statistical copolymer of ethylene/glycidyl methacrylate (92/8 wt%), produced by Atochem. Glycidyl

methacrylate (GMA; purity, 97%) and styrene (purity, 99%) were purchased from Aldrich. *tert*-Butyl cumyl peroxy (Trigonox T, Akzo) and *di-tert*-butyl peroxy (Trigonox B, Aldrich) were used as peroxides (liquids with a purity of 98%). These two peroxides were soluble in the GMA and in the GMA/styrene mixture, and their estimated half-lifetime is close to 30 s at 190 °C. PolyGMA, synthesized by polymerization of GMA in the presence of 2,2'-azotris isobutyronitrile (AIBN) at 60 °C in tetrahydrofuran (THF), has a number-average molecular mass of 25,000 g/mol and poly-molecularity index of 5.20 (determined by gel permeation chromatography). The polystyrene used was a crystal polystyrene of type HF555, commercialized by BP Amoco group.

Grafting Procedure

Grafting in the molten state was carried out in a Rheocord Haake mixer (50 cm³). The HDPE (50 g), the monomer(s), and the peroxide were both introduced in the preheated batch mixer at 190 °C and mechanically mixed at 64 rpm for 10 min. After mixing, samples were taken from the cell and quenched into liquid nitrogen to stop further reactions. Modified HDPE samples were purified by dissolution in hot xylene and then precipitated into acetone at room temperature. Acetone permits the precipitation of GMA-modified HDPE samples, whereas the homopolymer of GMA or the nonreacted GMA are soluble. This precipitation method allows the amount of GMA grafted onto HDPE to be determined. Then, the purified copolymers were dried under vacuum at 80 °C, for 8 h. Duplication of the dissolving-precipitation procedure was conducted on the purified copolymers. FTIR measurements showed that the percentages of grafting were not altered after the second purification compared with those from a single purification. This result indicates that a single purification step is sufficient to remove nonreacted monomer and homopolymer.

Determination of Grafting Yield

The grafting yield of GMA was not determined by elementary analysis of oxygen because the obtained values reached the limit of the sensitivity of the measuring apparatus. It is not possible to carry out ultraviolet (UV) spectrometry with a solution because HDPE is only solubilized in hot aromatic solvents, such as toluene or xylene. Under such conditions, we could not differentiate

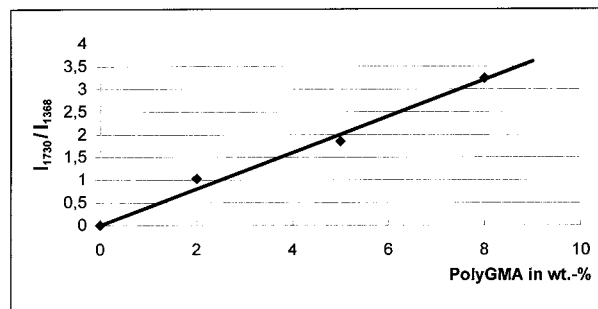


Figure 1 Calibration curve for the determination of the grafting yield of GMA by FTIR.

between absorptions of solvent and styrene. FTIR spectrometry was the most suitable method to determine the grafting yield of synthesized copolymers. The analysis was performed with a Nicolet 510P FTIR spectrometer. We used a calibration curve established with mechanical blends from HDPE and polyGMA (synthesized in our laboratory) in known proportions (2, 5, and 8 wt %). From these blends we prepared thin films (60 and 80 μ m) by compression molding at 190 °C for 2 min under a pressure of 12 MPa. We calculated the ratio I_{1730}/I_{1368} (I_{1730} , intensity corresponding to the carbonyl group of polyGMA; I_{1368} , intensity corresponding to the symmetrical deformation of methyl groups in HDPE¹³) for every sample that we reported on a graph. The results enabled us to establish the calibration curve $I_{1730}/I_{1368} = f(\% \text{ polyGMA})$; Figure 1). To determine the grafting yield of GMA in the HDPE-g-(styrene-co-GMA) purified copolymers, we calculated their ratio of intensity (I_{1730}/I_{1368} ; Figure 2) and reported these values on the calibration curve. This method can be applied because the IR absorption of free polyGMA blended with HDPE is the same as that of the grafted GMA.

To validate the method of determining the grafting yield of GMA onto HDPE, we applied it to a statistical copolymer (Lotader AX8840 commercialized by Atochem) presenting a known rate of GMA (between 7 and 8 wt %). FTIR spectroscopy was used to determine the rate of GMA present in Lotader AX8840. Samples of this statistical copolymer were pressed into thin films at 190 °C for 2 min under a pressure of 12 MPa between two Teflon sheets. To determine the quantity of GMA measured by our method, we calculated the ratio I_{1730}/I_{1368} for each sample that we reported on the calibration curve (Figure 1). We found that the statistical copolymer contained 7.5 wt % GMA. Because this result was in accordance with the

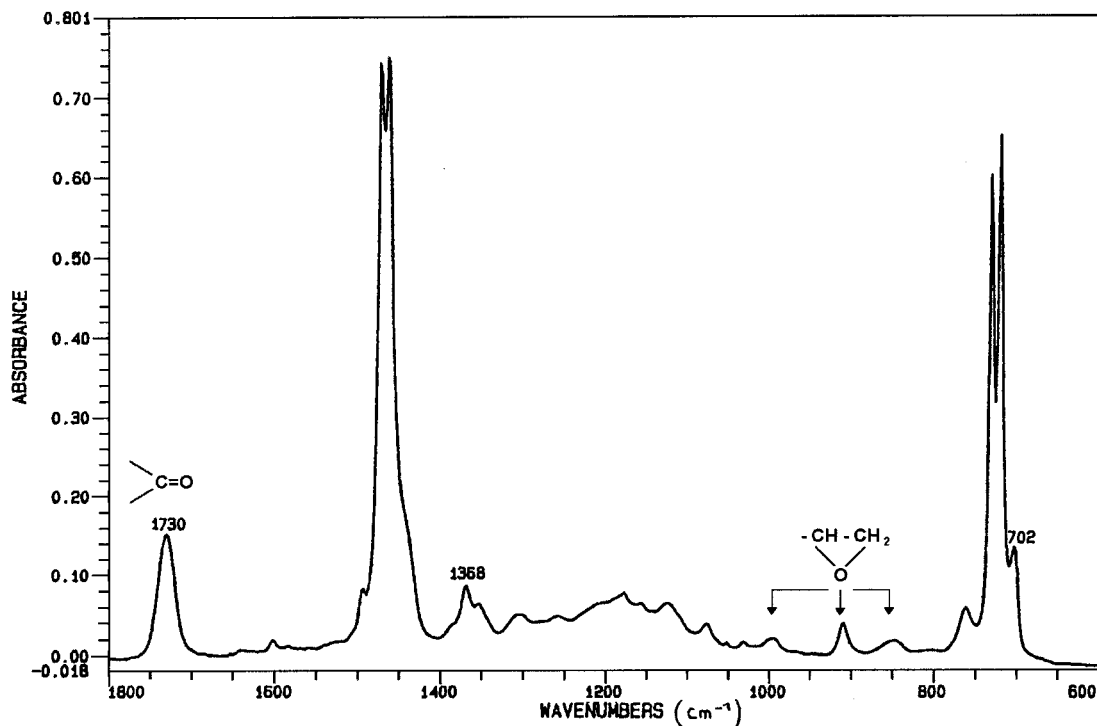


Figure 2 FTIR spectra of copolymer HDPE-g-(styrene-co-GMA).

value given by Atochem, we also used this method to determine the grafting yield of purified copolymers.

A similar method was used to measure the grafting yield of styrene onto HDPE. The calibration curve $I_{702}/I_{1368} = f(\% \text{ polystyrene})$; Figure 3) was prepared from HDPE/polystyrene mechanical blends in known proportions (2, 5, and 8 wt %). The characteristic peak of polystyrene, situated at 702 cm^{-1} (Figure 2), corresponds to the vibration of the carbon chain of polystyrene with aromatic hanging nuclei.

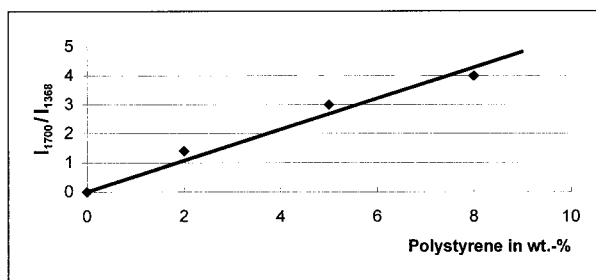


Figure 3 Calibration curve for the determination of the grafting yield of styrene by FTIR.

RESULTS AND DISCUSSION

Effects of Peroxides on HDPE

The thermal decomposition of peroxide during transformation of the polymers in a molten state generates free radicals that create reactive sites by hydrogen abstraction on the PE macromolecules, which can lead to crosslinking or degradation of the PE or the grafting of GMA onto the PE. The abstraction of the proton on the tertiary carbon sites leads to a macromolecular cleavage by the well known β -scission. The PP macromolecule is therefore more degraded than that of PE because PP contains more tertiary carbons than PE. Consequently, the macromolecular chains of the PE tend to crosslink, whereas those of the PP tend to cleave. Seadan¹⁴ and Narkis et al.¹⁵ have shown that the quantity of peroxide must not exceed 0.3 wt % of the polyolefin to avoid the crosslinking phenomena. They have also shown that it is preferable to avoid peroxides with weak polarities because they are soluble in polymer and will preferentially lead to a recombination of macroradicals rather than grafting. On the contrary, a polar peroxide will preferentially concentrate on the monomer, generating a large number of reactive sites in this monomer, thus leading to ho-

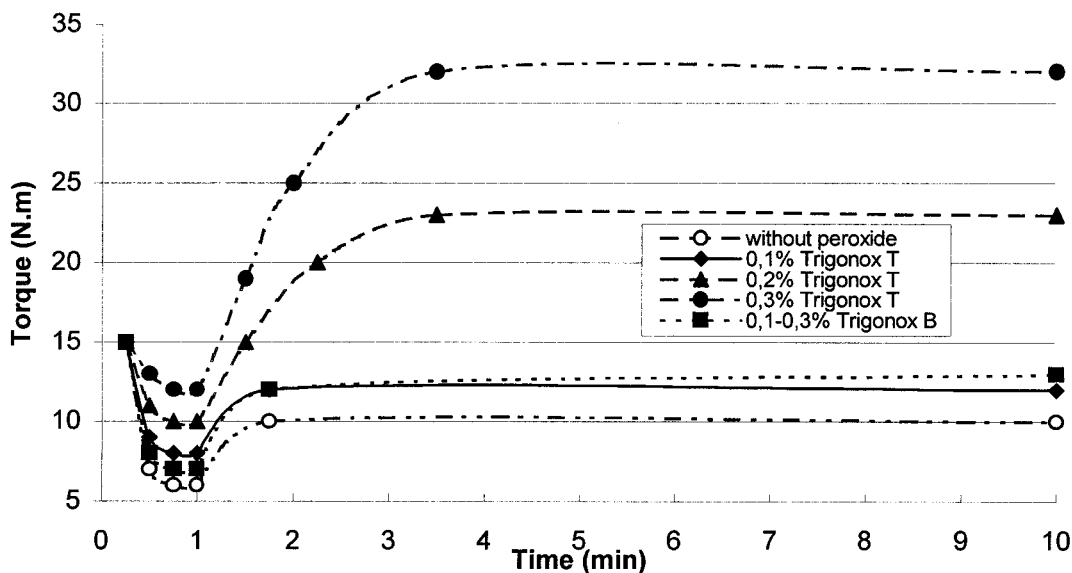


Figure 4 Evolution of the torque of HDPE/peroxide systems as a function of mixing time at 190 °C.

mopolymerization. The HDPE/peroxide systems (0.1, 0.2, and 0.3 wt %) without monomer are carried out in a batch mixer to study the reactivity of the two peroxides with the polymer. Figure 4 shows the torque variations of HDPE/peroxide (0.1, 0.2, and 0.3 wt % of Trigonox T or B) during 10 min of mixing at 190 °C. The addition of peroxide to HDPE leads to a drop in the torque at the beginning of mixing. After 1 min, the torque increases and then stabilizes after 2 or 3 min. The increase in the torque is due to the chemical reaction induced by the rapid decomposition of peroxides at 190 °C (half-lifetime near 35 s).

The efficiency of the two peroxides is very different. The quantity of Trigonox B in the HDPE scarcely modifies the torque. For 0.1, 0.2, and 0.3% Trigonox B, the curve obtained is similar to the curve obtained with 0.1% Trigonox T (Figure 4). Conversely, the quantity of Trigonox T added to HDPE changes the torque, which reaches 32 N · m for 0.3% peroxide, and this mixture presents a thick consistence. An amount of 0.3% Trigonox T crosslinks the HDPE. Trigonox T appears to be more efficient in crosslinking the HDPE than Trigonox B. The presence of gel when dissolving HDPE/Trigonox T systems in hot xylene confirms that reactions of crosslinking take place. The behavior of these two peroxides with HDPE is surprising because they possess similar half-lifetimes and molecular structures. At 190 °C, decomposition of Trigonox T leads to the formation of α -cumyloxy and *tert*-butyloxy radicals, whereas

decomposition of Trigonox B leads to two *tert*-butyloxy radicals. Kinetically, reactions of β -scission being easier ($K_b = 10^6 \text{ s}^{-1}$), the radicals obtained are given Figure 5. In principle, a radical CH_3 is more reactive with a monomer than a radical C_6H_5 , which is stabilized by resonance. Tests show that the highest levels of torque are obtained with Trigonox T. The C_6H_5 radicals appear to be more efficient than CH_3 radicals when reacting with HDPE. To check the efficiency of the C_6H_5 radical, we used peroxide containing two phenyl functions (dicumyl peroxide). HDPE and 0.3 wt % dicumyl peroxide were mixed in a preheated mixing cell at 183 °C to obtain a half-lifetime identical to Trigonox T. With these conditions, the torque is stabilized at 25 N · m. Consequently, it shows that the C_6H_5 radicals are more efficient than CH_3 radicals in crosslinking HDPE. If we refer to the dissociation energies, we note that the C_6H_5 radical possesses a potential of

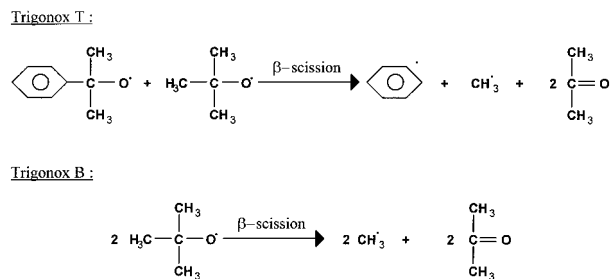
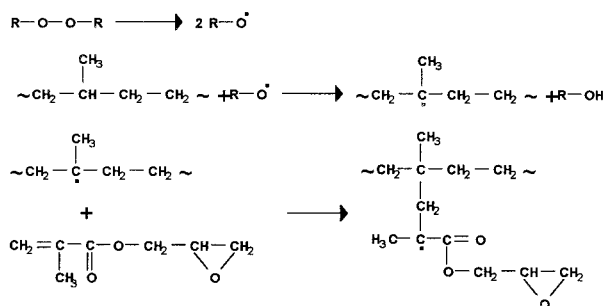
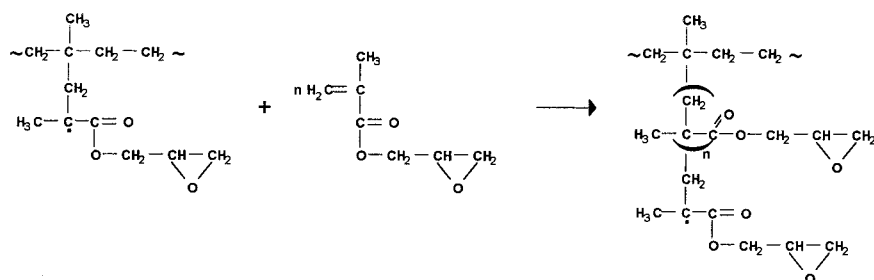
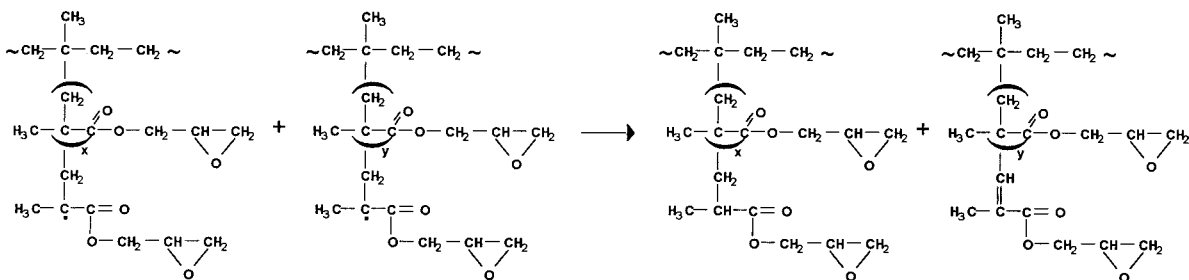
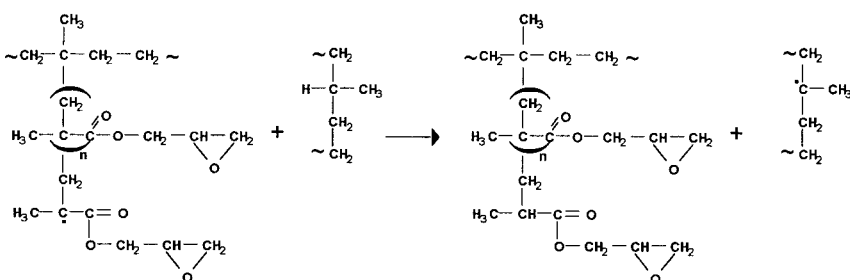


Figure 5 Radicals obtained by reactions of β -scission.

Initiation :**Propagation :****Termination by disproportionation :****Transfer :****Figure 6** Scheme of free radical grafting process.

hydrogen abstraction superior to that of CH_3 . The energy of dissociation of C_6H_5-H ($469 \text{ kJ} \cdot \text{mol}^{-1}$) being superior to that of CH_3-H ($435 \text{ kJ} \cdot \text{mol}^{-1}$), the C_6H_5 radicals will favor the production of macroradicals by hydrogen abstraction rather than the CH_3 radicals. These radicals being un-

stable, they will preferentially lead to the crosslinking of HDPE. Trigonox T at 0.3 wt % favors the crosslinking of HDPE. The increase in torque during the mixing is caused by the increase in the viscosity of the mixture. This phenomenon was not observed with Trigonox B.

Table I Grafting Yield of GMA onto HDPE^a

Ratio	[GMA] _g , wt %
HDPE/GMA	0
HDPE/0.1% Trigonox T/GMA	0.60
HDPE/0.2% Trigonox T/GMA	0.80
HDPE/0.3% Trigonox T/GMA	0.80
HDPE/0.1% Trigonox B/GMA	0.50
HDPE/0.2% Trigonox B/GMA	0.70
HDPE/0.3% Trigonox B/GMA	0.70

^a For [GMA]_i = 6 wt %.

Grafting on HDPE

The mechanism of grafting is based on the formation of free radicals released by thermal decomposition of peroxide. These radicals must generate macroradicals by hydrogen abstraction on HDPE chains. These reactive sites can be found on different places on the chain; that is, on the tertiary or secondary carbon or on a double bond depending on the polymer microstructure. The macroradicals thus formed will react with the GMA, and the propagation of the chain is quickly stopped by transfer with a polyolefin chain. However, these macroradicals, being unstable, can lead to crosslinking (preferentially for the PE) or β -scission (preferentially for the PP) rather than grafting. Aglietto et al.¹⁶ described main reactions that occur for grafting of maleate onto HDPE in the molten state. So, on the basis of these works, we propose a scheme for grafting of GMA onto HDPE (Figure 6).

Study of HDPE-g-GMA Copolymer

The FTIR spectra of purified samples show a peak at 1730 cm⁻¹ (Figure 2) and three peaks of weak intensity, typical of deformation vibrations (symmetrical and asymmetrical) of the epoxide function,¹⁷ located at 990, 908, and 850 cm⁻¹, confirming that grafting has occurred. The quantity of grafted GMA could be calculated from the ratio of the intensities of the absorbance peaks at 1730 and 1368 cm⁻¹ by using the previously established calibration curve (Figure 1). The rates of grafted GMA onto HDPE are shown in Table I: they are weak (<1%) and do not depend on the concentration and nature of the peroxide used.

It is interesting to compare our results with those of other authors. For HDPE with 0.3 wt % Trigonox T system, a strong increase in torque (32 N · m) was recorded during the mixing (Figure 4),

indicating a strong crosslinking of HDPE. Conversely, the torque of HDPE/peroxide/GMA systems is equal to 8 N · m regardless of the concentration and nature of the peroxide used. The samples obtained are then totally soluble in hot xylene, showing that crosslinking is avoided under these conditions. Therefore, the process of grafting is predominant. In polyolefin/peroxide without monomer, Sen et al.¹⁸ and Aglietto et al.¹⁹ observed a strong increase in torque and the presence of insoluble residues during the hot dissolving, thus showing the crosslinking of these systems. Conversely, they noticed that mixing polyolefin/peroxide with a monomer (dibutyl maleate or diethyl maleate) does not generate an increase in torque and that these functionalized polyolefins are soluble in hot toluene, shutting out the crosslinking of these systems. Our results are comparable to those of other authors. We can also conclude that the addition of monomer limits the crosslinking reactions to the benefit of grafting if the concentration of peroxide is weak (≤ 0.3 wt %).

Study of HDPE-g-(Styrene-co-GMA)

Previous studies^{3,4} showed that the addition of styrene as a comonomer permits a greater increase in the grafting yield of maleic anhydride because its double bond is highly activated by the formation of a charge transfer complex. To determine the ability of this comonomer to copolymerize with GMA, we took e and Q parameters (coefficients of Alfrey and Price) into account. In this method, the parameter e represents the polarity of the double bond of the monomer. A positive value indicates an electron withdrawing of the double bond (or acceptor effect). Alternating copolymerization will be obtained using e values with opposites values. For Q parameters, which give an idea of the capacity of monomers to stabilize radicals by resonance effect, best copolymerization will be obtained with monomers presenting similar values. Furthermore, copolymerization ratios r_1 and r_2 can be expressed according to e parameters as follows:

Table II Alfrey and Price Coefficients

Compound	e	Q
AM	3.69	0.86
GMA	0.20	0.96
Styrene	-0.8	1

Table III Reactivity Ratios Calculated from e and Q

Blend	r_1	r_2	$r_1 \cdot r_2$
AM/styrene	$5.48 \cdot 10^{-8}$	0.03	$1.64 \cdot 10^{-9}$
GMA/styrene	0.78	0.47	0.37

$$r_1 \cdot r_2 = e^{-(e_1 - e_2)^2}$$

So, alternating copolymerization will be perfect when e_1 and e_2 are quite different with opposite signs. Ideal cases are vinylic ether and *N*-vinylpyrrolidinone because they have opposite polarities but they possess values of Q too weak in comparison to those of GMA. Consequently, the styrene seems to be the most convenient comonomer to be associated with GMA. The values of Alfred and Price's coefficients²⁰ for maleic anhydride, GMA, and styrene are given in Table II. Starting from e and Q and Alfrey and Price's equations, we calculated the reactivity ratios (r_1 and r_2) for the maleic anhydride/styrene and GMA/styrene pairs to predict the structure of copolymers obtained (Table III). The formation of alternating copolymers is the more favored result when the two monomers have very opposite e values. In this case, the product of reactivity ratios ($r_1 \cdot r_2$) is equal to zero. Considering the reactivity ratios (r_1 and r_2) and the ($r_1 \cdot r_2$) value of maleic anhydride/styrene pair, alternating copolymers should be obtained. For this pair of monomers, Flat⁴ has shown that a charge transfer complex is a precursor to the copolymerization of maleic anhydride with styrene. This complex, with a reactivity superior to those of free monomers, therefore reacts preferentially with the growing chain. Considering the r_1 , r_2 , and $r_1 \cdot r_2$

values of the GMA/styrene pair, it seems logical that the copolymerization is favored before homopolymerization. Lambla et al.^{8,9} claim that the GMA structure does not permit one to envisage the formation of the acceptor/donor complex, but they could not prove this claim. They state that NMR and electron paramagnetic resonance analyses were carried out from room temperature to 120 °C on mixtures containing different amounts of GMA and styrene, but that the complex was not detected. The product of reactivity ratios ($r_1 \cdot r_2$) of GMA/styrene pair being different than zero, it is normal to not detect the acceptor/donor complex because the copolymers obtained should possess a statistical structure rather than an alternated structure. During our study we explored the pathway of GMA copolymerization with styrene, supposing that the free monomers participate in the propagation reaction without the formation of the acceptor/donor complex.

Study of Grafting for a Fixed Styrene/GMA Ratio

To functionalize HDPE by the GMA/styrene system in the presence of an initiator, we kept, as previously, a constant reaction time (10 min) and we used a $[\text{styrene}]_i/[\text{GMA}]_i = 1.5$ mol/mol ratio, with $[\text{GMA}]_i = 6$ wt % with regard to HDPE. The grafting of the GMA/styrene mixture at 190 °C is a rapid reaction that takes place within the first 2 or 3 min of mixing. In fact, the concentration in primary radicals coming from the decomposition of peroxides is high at the outbreak of the process because the half-lifetime of peroxides used are extremely short (30 s). The IR spectra obtained from purified samples show the presence of new peaks at 1730 cm^{-1} (grafted GMA), at 702 cm^{-1} (grafted styrene), and at 990 and 850 cm^{-1} (epoxide function). The appearance of these new peaks with regard to HDPE confirms the grafting pro-

Table IV Grafting Yield of GMA and Styrene on HDPE^a

Blend	Torque, N · m	$[\text{GMA}]_g$, wt %	$[\text{Styrene}]_g$, wt %
HDPE/GMA/styrene (without peroxide)	6	0.60	0
HDPE/0.1% Trigonox T/GMA/styrene	11	3.00	2.20
HDPE/0.2% Trigonox T/GMA/styrene	13	3.80	2.60
HDPE/0.3% Trigonox T/GMA/styrene	15	3.70	2.70
HDPE/0.1% Trigonox B/GMA/styrene	13	3.00	2.20
HDPE/0.2% Trigonox B/GMA/styrene	16	3.40	2.50
HDPE/0.3% Trigonox B/GMA/styrene	18	3.70	2.60

^a $[\text{Styrene}]_i/[\text{GMA}]_i = 1.5$ mol/mol with $[\text{GMA}]_i = 6$ wt %, 190°C, reaction time of 10 min.

Table V Effect of the Initial Concentration of Styrene on the Grafting Yield of GMA

$[\text{Styrene}]_i/[\text{GMA}]_i$ (mol/mol)	$[\text{GMA}]_i$, wt %	$[\text{Styrene}]_i$, wt %	$[\text{GMA}]_g$, wt %	$[\text{Styrene}]_g$, wt %
—	0	6.5	0	3.20
—	6	0	0.80	0
1	6	4.5	3.40	1.80
1.5	6	6.5	3.80	2.60
3	6	13.0	4.20	4.50

cess. The values of intensity ratios I_{1730}/I_{1368} and I_{702}/I_{1368} , measured on the IR spectra of purified copolymers confronted with calibration curves (Figures 1 and 3), enabled us to determine the rate of grafted GMA and styrene on the HDPE (Table IV). The increase in the grafting rate of GMA in presence of styrene (multiplied by 3 or 4) tends to confirm that the grafting follows a process of copolymerization. This process induces an increase in the viscosity and in the torque ($8 \text{ N} \cdot \text{m}$ recorded during the mixing of HDPE/peroxide/GMA systems to $18 \text{ N} \cdot \text{m}$ recorded during the mixing of the HDPE/peroxide/GMA/styrene systems. The nature of peroxides (Trigonox T or B) does not modify the rate of grafted GMA or styrene on the HDPE. For a ratio $[\text{styrene}]_i/[\text{GMA}]_i = 1.5 \text{ mol/mol}$, with $[\text{GMA}]_i = 6 \text{ wt \%}$, the increase in the peroxide concentration brings a slight increase in torque, resulting in a slight increase in the rates of grafted monomers on the HDPE. These results show that the introduction of 0.2 wt % Trigonox T is sufficient because it results in 3.8 wt % grafted GMA, which corresponds to an efficiency of grafting of $[\text{GMA}]_g/[\text{GMA}]_i$ of 63%. We did not introduce peroxide concentration superior to 0.3 wt % into the mixture because the crosslinking of polymer and the homopolymerization of monomers limit the amount of peroxide that can be used and therefore the percentage of GMA that can be grafted. We studied the effect of temperature (150, 170, and 190 °C) on the grafting yield in the following operative conditions : $[\text{styrene}]_i/[\text{GMA}]_i = 1.5 \text{ mol/mol}$, with $[\text{GMA}]_i = 6 \text{ wt \%}$ and $[\text{Trigonox B}] = 0.3 \text{ wt \%}$. It is interesting to note that the half-lifetime of Trigonox B is equal to 15 min at 150 °C, 3 min at 170 °C, and 30 s at 190 °C. Under these conditions, we observed that the temperature of mixing does not modify the rates of GMA and styrene grafted. These results are surprising because to increase the kinetic length of the chain in radical polymerization it is necessary to de-

crease the temperature. At 150 °C, we obtain rates of grafted GMA and styrene equal to 3.6 and 2.6 wt %. The half-lifetime of Trigonox B at this temperature being 15 min, the generation of primary radicals is too weak to achieve a high grafting yield during the reaction time (10 min). Moreover, the increase in HDPE viscosity with the decrease of temperature must be taken into account. Sen et al.¹⁸ observed from the HDPE functionalization by grafting of dibutyl maleate in the presence of dicumyl peroxide that the grafting yield did not change with the mixing temperature.

Effect of the Initial Concentration of Styrene on Grafting

To study the effect of the initial concentration of styrene on the grafting yield of GMA, we fixed the GMA concentration (6 wt %) and that of peroxide (0.2 wt % Trigonox T). The grafting was carried out in a batch mixer at 190 °C for 10 min. The amount of grafted GMA and styrene measured from the calibration curves (Figures 1 and 3) are given in Table V. The radical grafting of styrene alone on the HDPE is superior to that of GMA alone. Inversely, the introduction of 6 wt % of GMA and 6.5 wt % styrene increases the amount of grafted GMA (0.8–3.8 wt %) and decreases the amount of grafted styrene (3.2–2.6 wt %). These results are in agreement with those of Cartier and Hu²¹ and show that the grafting yield of GMA is improved in the presence of styrene, whereas that of styrene is altered by the presence of GMA. The increase in the amount of styrene at a fixed rate of GMA involves an increase in the amount of grafted styrene, whereas that of GMA stabilizes at ~4.2 wt %. The ratio $[\text{styrene}]_i/[\text{GMA}]_i = 3 \text{ mol/mol}$ gives a copolymer of little interest because it contains more styrene than GMA. The ratio $[\text{styrene}]_i/[\text{GMA}]_i = 1 \text{ mol/mol}$ seems to be more adjusted to our goal, which consists of syn-

thesizing a compatibilizer bearing reactive functions (epoxides) capable of reacting with the end groups of PET to compatibilize HDPE/PET blends. Taking into account the reactive ratios close to and less than 1 (0.53 and 0.44, respectively, to GMA and styrene at 60 °C²² and 0.63 and 0.34, respectively, to GMA and styrene at 65 °C²³), the copolymerization is favored with regard to the homopolymerization. Because the two monomers possess very close values of Q (0.96 for GMA and 1 for styrene), the macroradicals of HDPE should then react either with the styrene to copolymerize with GMA or with GMA to copolymerize with the styrene. The experimental results show that the copolymers obtained do not have a structure alternated because the rates of grafted GMA and styrene onto HDPE are different. The copolymers obtained also possess a statistical structure. These results are in good agreement with the theoretical predictions.

CONCLUSIONS

The mechanism of free radical grafting of GMA onto HDPE in the molten state is studied to synthesize graft copolymers able to compatibilize the HDPE/PE blends. We have shown that the grafting yield of GMA is increased when we add a comonomer, such as styrene. The degree of grafting was determined by FTIR spectrometry. The HDPE-*g*-(styrene-*co*-GMA) purified copolymer contains 3–4 wt % grafted GMA, which corresponds to a grafting efficiency of 60% compared with 13% in the absence of styrene. The copolymerization is favorable to the homopolymerization, but the grafted copolymers obtained do not possess an alternated structure but a statistical structure because the rates of grafted GMA and styrene are different. These results were foreseeable because the product of reactivity ratios ($r_1 \cdot r_2$) of GMA/styrene pair is not equal to zero.

Functionalized HDPE keeps its physical and mechanical properties, whereas its chemical properties are modified. The reactivity of a hanging group are superior to that of a group included inside a macromolecular chain,²⁴ so the low grafting yield of GMA measured could be sufficient to compatibilize *in situ* HDPE/PET blends.

ABBREVIATIONS

i initial

g grafted

co alternating copolymer

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