

Melt Grafting of 10-Undecenoic Acid onto Linear Low Density Polyethylene

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ABSTRACT: The melt grafting of 10-undecenoic acid (UA) onto a linear low-density polyethylene (LLDPE) was studied. The grafting reaction was performed in a thermoplastic mixer and 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane was used as initiator. The concentration of UA and peroxide ranged from 1 to 4% (w/w) and 0.025 to 0.1% (w/w), respectively. Evidence of the grafting of UA as well as its extent was determined by FTIR. Experimental results showed that the amount of UA grafted increases with both the UA and initiator concentrations. However, the greatest efficiency of grafting was found at the lowest concentration of UA investigated. The grafting efficiency ranged from 8 to 40%. The dynamic linear viscoelastic properties of the original polymer and the grafted materials were evaluated at different frequencies at 160°C using a dynamic rotational rheometer. The modification process affected the melt elasticity and viscosity of the LLDPE. When the original polymer was modified only with peroxide both properties in-

creased with respect to those of the original material. However, when UA was grafted onto LLDPE, the resulting polymers displayed values of elastic moduli and viscosity lower than those of the polymer modified with peroxide. Moreover, when a concentration of 4% of UA was used, the values of those properties were even lower than those corresponding to the original LLDPE. These observations combined with the data obtained from the GPC results suggest that scission reactions may be favored by the presence on UA. In contrast with previous observations, the thermal properties measured by DSC were only slightly altered. The fusion temperature of the modified polymers was slightly lower than that corresponding to the original polymer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2303–2311, 2004

Key words: linear low-density polyethylene (LLDPE); modification; functionalization of polymers; reactive processing; rheological properties

INTRODUCTION

The chemical modification of polyethylene is a matter of both academic and commercial interest because it yields new materials with enhanced or new specific properties. In general, the aim of this modification is to alter the chemical properties of the polymer, mainly its polarity.^{1–4} The grafting of polar groups onto the non-polar chains of the polymer is one of the procedures most commonly used. The grafted polyethylenes are used in several different applications. For example, they are commonly used as chemical coupling agents and as compatibilizers for blends and fillers.^{2,3}

The free-radical grafting in the melt involves the reaction between the polymer and a vinyl-containing monomer, which is able to become grafted onto the molecular chain in the presence of free radicals that

are usually generated from the thermal decomposition of an added peroxide.⁴ A great variety of polar monomers have been used for grafting onto polyethylene with the aim of obtaining single-monomer grafts or short-length grafts. Among the most commonly used monomers we may mention acrylic acids and esters,⁵ maleic anhydride,⁶ unsaturated carboxylic acids derivatives, and vinyl silanes.^{7,8} All the monomers are relatively small molecules containing a vinyl group and differing in their functional groups.

In this work we explored the use of 10-undecenoic acid (UA) as a polar monomer for grafting onto linear low-density polyethylene (LLDPE) using 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DBPH) as a free-radical initiator. UA has recently been used to modify ANS terpolymer in solution⁹ and polypropylene in the melt¹⁰ as well as copolymerized with ethylene using metallocene-based catalysts.¹ In spite of this, to our knowledge a long-chain carboxylic acid has not yet been used for modifying polyethylene in the melt.

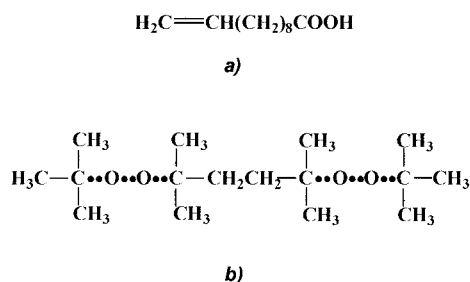
The modification of the LLDPE was performed in the melt using a thermoplastic mixer. The molecular structure of the polymers was studied using a combination of gel permeation chromatography–multiangle laser light scattering (GPC–MALLS) and FTIR tech-

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Scheme 1 Chemical structures of (a) 10-undecenoic acid and (b) 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane.

niques. The influence of the monomer and initiator concentration on the amount of UA grafted and the grafting efficiency was studied. Thermal and melt properties of the modified polymers were measured and analyzed in terms of the concentration of both UA and initiator.

EXPERIMENTAL

Materials

The LLDPE was provided by Polisor-PBB S.A. of Argentina as a powder without additives. The polymer has a weight-average molecular weight (M_w) of 65,000 and a polydispersity index (M_w/M_n) of 2.1, which were determined by GPC-MALLS following standard procedures.

The initiator used was DBPH, kindly provided by Akzo-Nobel Química S.A. of Argentina. The peroxide was used in a diluted solution of hexane (5.165 g DBPH/L of solution).

10-Undecenoic acid (UA) ($M_w = 184.28$ g/mol) was provided by Fluka Chemie AG (Buchs, Switzerland) and used as received. UA is a white solid, which melts at 23–25°C, and is soluble in many organic solvents, such as hexane and ethanol.¹¹ The chemical structures of UA and DBPH are shown in **Scheme 1**.

Melt grafting procedure

UA, LLDPE, and an aliquot of DBPH solution were put into contact by pouring them into a beaker in such a proportion to give the desired concentration of each substance after evaporation of hexane. The concentrations of UA studied in this work were 1, 2, and 4% (w/w), whereas those corresponding to DBPH were 0.025, 0.05, and 0.1% (w/w). The concentration was based in 100 g of LLDPE.

The grafting reactions were carried out in the 50-cm³ mixing chamber of a Brabender plastograph equipment (Brabender Instruments, South Hackensack, NJ). The reaction temperature was set at 180°C and the screw speed rotation was 20 rpm. The peroxide had a half-life of 1 min at 180°C according to the

information supplied by the manufacturer.¹² The variation of the torque with time was followed for each reactive mixture. A time period of 20 min was necessary to ensure a complete reaction. A constant value of the measured torque was taken as indication of the end of the modification reaction.

Characterization of materials

When the reaction period was completed, the unreacted initiator and its decomposition products together with the free UA and other byproducts of the reaction were separated from the modified polymer following two different washing procedures.

In one of these procedures, the modified polymer was purified by dissolving it in xylene at 130°C (0.1% polymer solution) and then pouring this solution into cold methanol. Then, the obtained precipitate was separated and repeatedly washed with methanol and acetone.

The second procedure consisted of dissolving the polymer in hot xylene as before, and then allowing the solution to cool to room temperature to promote the crystallization of the polymer. After that, the polymer was filtered and repetitively washed with methanol and acetone.

All the purified materials were dried in vacuum for 48 h before their analysis. The chemical and physical characterization of the materials did not revealed noticeable differences between the substances obtained following the two procedures of purification. From now on we will use the designation LLDPE-g-UA to identify the purified material from that obtained from mixer, which is called "crude."

The evidence of grafting was determined by FTIR. Films of about 0.10 ± 0.01 mm in thickness were prepared by melt pressing the materials at 150°C. The FTIR spectra were recorded from these films using a Nicolet FTIR 520 spectrometer (Nicolet Analytical Instruments, Madison, WI) in the wavenumber range from 600 to 4000 cm⁻¹. The presence of grafted monomer was determined by analyzing the absorption bands at about 1712 cm⁻¹. These bands are typically assigned to stretching of >C=O groups from carboxylic acids.¹³

We also used titration techniques to quantify the amount of grafted UA following the method suggested in the literature.^{9,10,14} This method has been shown to be effective in determining the amount of carboxylic groups that were incorporated into the molecular structure of various polymers undergoing grafting of UA.^{9,10} In our case, it was found such a large scatter in the titration data values rendered them useless. Uncertainty in the determination of the end point was the main cause of such scatter in the results. This may be attributed, at least in part, to the low

amount of UA grafted to the LLDPE as will be shown below.

The molecular weight distribution of the polymers was determined by combining size-exclusion chromatography (GPC) and light-scattering (MALLS) techniques. A Waters 150-C ALP/GPC chromatograph (Waters Chromatography Division/Millipore, Milford, MA), equipped with a set of 10 μm PLGel columns from Polymer Labs (Amherst, MA) with nominal porous sizes of 10^6 , 10^3 , and 500 \AA , was used connected in line to a Wyatt multiangle laser light scattering system (Wyatt Technology, Santa Barbara, CA). The solvent was 1,2,4-trichlorobenzene at 140°C .

A differential scanning calorimeter (Perkin-Elmer Pyris 1; Perkin Elmer Cetus Instruments, Norwalk, CT) was used to study the fusion behavior of LLDPE and LLDPE-g-UA. The instrument was calibrated with an indium standard. A nitrogen purge was used in all the determinations. Each sample was melted in the calorimeter at 150°C at $10^\circ\text{C}/\text{min}$, and then cooled to 30°C at the fastest cooling rate permissible by the calorimeter. This procedure ensured the same thermal history for all the samples. After this treatment, the endotherm of fusion was recorded between 30 and 150°C at a heating rate of $10^\circ\text{C}/\text{min}$. The melting peak and the area of the endotherm were determined to give the temperature (T_f) and the enthalpy (ΔH_f) of fusion.

The rheological characterization was performed in small-amplitude oscillatory shear-flow tests. A rotational rheometer from Rheometrics RDA-II (Poole, UK) was used for this purpose in the parallel-plate mode. Samples of the LLDPE and LLDPE-g-UA were molded into discs of 25 ± 0.01 mm diameter and about 1 mm thickness using a thermostated hydraulic press set at 150°C . The discs were then used to examine the dynamic properties of the melt. The dynamic elastic modulus [$G'(\omega)$] and the dynamic viscosity [$\eta'(\omega)$] were determined in the linear viscoelastic range of strain at 160°C and at frequencies (ω) ranging from 0.1 to 500 s^{-1} . The tests were performed under nitrogen atmosphere to avoid degradation of the polymer.

RESULTS AND DISCUSSION

Behavior of reactive mixtures

The chemical modification of LLDPE using different concentrations of UA and DBPH was carried out in the molten state as described in the experimental section. Figure 1 shows the evolution of torque with time for a selected set of reactive mixtures. The curves correspond to the original material and those modified with 0.1% of DBPH and concentrations of UA ranging from 1 to 4%. The variation in the values of the torque may be considered as a measure of the variation of the

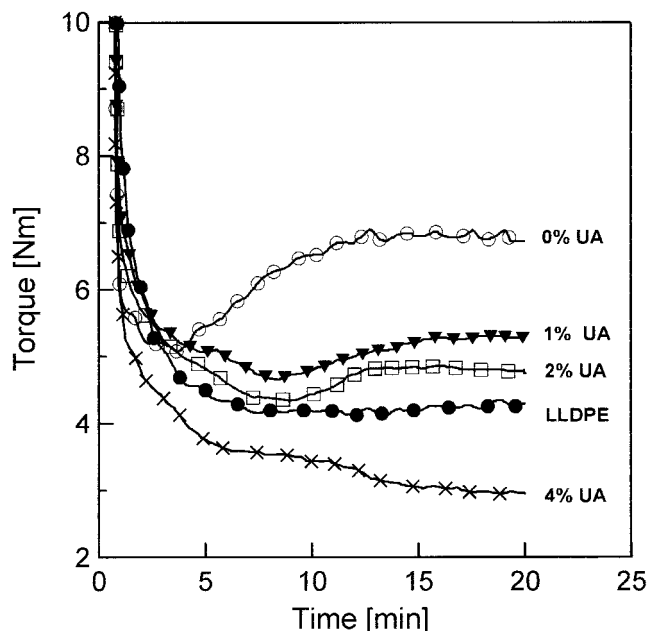


Figure 1 Torque–time dependency for original LLDPE and selected reactive mixtures modified with 0.1% (w/w) DBPH and different amounts of UA. (UA concentrations are indicated beside curves in the graph.)

melt viscosity of the medium with the reaction time. In all the curves, it is observed that the torque initially decays as a result of melting of the LLDPE. After about 5 min in the mixer the original polymer reached a constant torque value of about 4.3 Nm. The constancy in the value of the torque indicates that the molecular structure of LLDPE did not undergo noticeable alterations during the processing time of the experiments.

When peroxide was added to the polyethylene, the torque increased gradually after the melting of the material. After about 16 min of reactive blending, the torque leveled off to a value of 6 Nm, which is larger than that corresponding to the LLDPE. This can be associated with an increase in the melt viscosity as a consequence of a molecular weight increment produced by the peroxide attack to the LLDPE. The organic peroxide underwent thermal decomposition at the reaction temperature producing oxyradicals, which in turn attacked the molecules of polyethylene forming macroradicals.¹⁵ Then, the macroradicals may follow combination and scission reactions. In the particular case of polyethylene the first one is the reaction that prevailed. This phenomenon produced an increase in the molecular weight of the polymer and the melt properties were affected accordingly.^{16–18}

Table I presents the final torque values measured after modifying the LLDPE with different concentrations of UA and peroxide. It may be observed that the final torque of the modified LLDPE increases with the concentration of DPBH. Figure 1 shows that, when UA

TABLE I
Values of the Final Torque Measured for Original and Modified LLDPE

DBPH % (w/w) ^a	AU % (w/w) ^a	Final torque (Nm)
—	—	4.3
0.025	—	4.2
	1	3.9
	2	3.2
0.050	4	3.0
	—	4.9
	1	4.1
0.100	2	3.2
	4	2.8
	—	6.6
	1	5.2
	2	4.4
	4	2.9

^a Basis: 100 g of LLDPE.

was added to the reactive mixture, the final torque reaches lower values than those corresponding to the LLDPE/DBPH mixtures.

The values of the final torque decreased with increasing concentrations of UA. A qualitatively similar behavior was observed for the other peroxide concentrations, as can be inferred from the data presented in Table I. This can be explained by a combination of at least two factors, one of which may be the plasticizing phenomenon that is produced by the acid, and the other the scavenging of free radicals by UA. These two factors may be operative during the reactive processing.

The first factor reduces the viscosity of the media so that the torque needed for mixing decreases with the UA concentration. The second may diminish the amount of free radicals available for the production of chain links. The UA may react with either the oxyradical or the macroradical to produce the graft or secondary products, as for example oligomeric UA. These reactions are the possible path that may follow vinyl-containing monomers and in particular long-chain carboxylic acid, like UA, during the modification of polyolefins and copolymers.^{9,19}

FTIR characterization

The crude material obtained from the mixer was washed to eliminate byproducts in the manner described above in the experimental section. The polymers were then characterized in terms of their molecular structure. FTIR spectroscopy was used to confirm the grafting of UA onto LLDPE. Figure 2 shows three FTIR spectra in the 2000–600 cm^{-1} zone corresponding to the original LLDPE, the crude material modified with 4% AU and 1% of initiator before washing, and the LLDPE-g-UA obtained after purification of the

crude material. To allow a clear distinction of the differences between the three spectra, they were shifted slightly along the absorbency axis.

The spectra corresponding to the crude material display two absorption bands that can be attributed to the presence of UA. The band at 1710 cm^{-1} is attributed to the carbonyl absorption ($\nu > \text{C}=\text{O}$) from the carboxyl group ($-\text{COOH}$) and the other band at 910 cm^{-1} corresponds to the carbon double bond ($\nu -\text{C}=\text{C}$) of the vinyl group.¹³ These two bands are not observed in the spectra of LLDPE. After washing the crude material, the intensity of the carbonyl band noticeably decreased, whereas the vinyl absorption band cannot be detected. This result indicates that the washing process removed the unreacted UA.

A representative set of FTIR spectra in the 2000–600 cm^{-1} zone is shown in Figure 3 for LLDPE and selected samples of the LLDPE-g-UA. It can be seen that the spectra of the LLDPE-g-UA polymer are very similar to that of the original LLDPE over the whole range of wavenumbers. In the case of LLDPE-g-UA polymers, the band centered at 1712 cm^{-1} that corresponds to carbonyl absorption is clearly distinguished. In addition, another band can be identified at 1590 cm^{-1} , with a relatively lower intensity than that of the 1712 cm^{-1} band. This last band is not present in the pure LLDPE and can be attributed to asymmetrical stretching of the carboxylate ion ($-\text{COO}^-$).²⁰ These results indicate that a fraction of the UA was converted to salt either before or after it was grafted. This chemical group may result from the reaction of the $-\text{COOH}$ group with metallic species from catalyst residue or from the parts of the mixer equipment.²¹

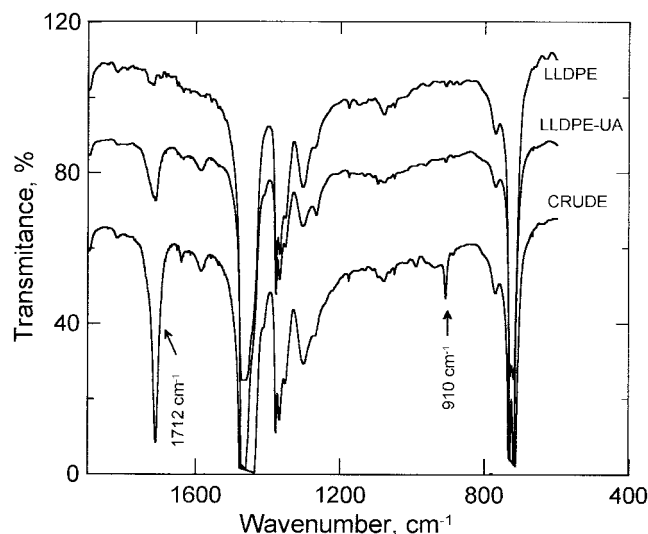


Figure 2 FTIR spectra in the 2000–600 cm^{-1} zone of original LLDPE, crude material, and LLDPE-g-UA polymers. The legend beside each curve identifies the material. The concentration of UA and initiator was 4 and 0.1%, respectively.

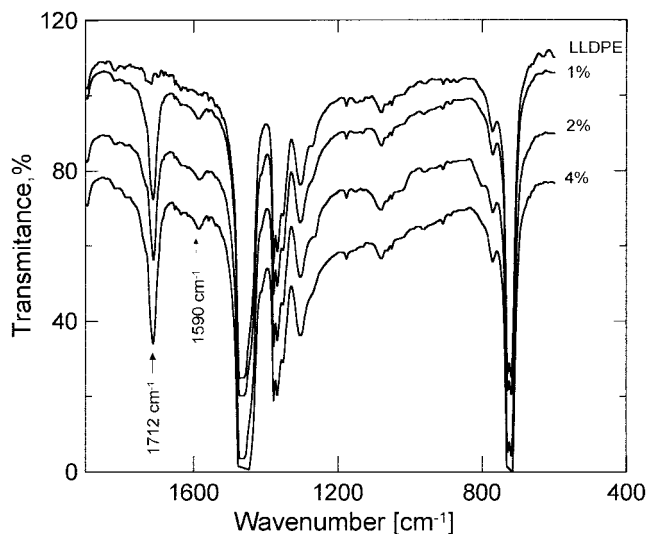


Figure 3 FTIR spectra in the 2000–600 cm^{-1} zone of original LLDPE and LLDPE-g-UA polymers. The legend beside each curve identifies the original LLDPE resin and the different UA concentrations used in the initial reactive mixtures. All LLDPE-g-UA polymers were obtained using 0.1% (w/w) of initiator.

Table II shows the absorbency of the 1712 cm^{-1} band normalized by the thickness of the film for both the crude material and the LLDPE-g-UA. The FTIR results indicate that the intensity of the 1712 cm^{-1} band does not change very much with the concentration of UA when a comparison is made between the LLDPE-g-UA polymers obtained using the same amount of peroxide. This means that the amount of UA incorporated onto LLDPE seems to be independent of the UA concentration.

Table II includes an index (I_g) that may be considered just as indicative of a grafting efficiency of UA onto LLDPE. The index is expressed as a percentage, and it was obtained from the relationship between the normalized intensity of the 1712 cm^{-1} band corre-

sponding to the LLDPE-g-UA polymer and that of the crude material.

As we pointed out in the experimental section, we found a large scattering in the values of the titration methods used to determine the amount of grafted UA. Because of this, the parameter I_g was used to estimate the grafting degree of UA (GD). These values are shown in the last column of Table II and they were calculated according to the initial amount of UA in the reactive mixture. However, it is necessary to take into account that a small quantity of the monomer may be lost during the mixing process and manipulation of material for preparing films. Consequently, the actual concentration of UA at the moment of recording the spectra was not known accurately. Therefore, the calculated amounts of grafted UA presented in Table II could be overestimated because the actual concentration of UA in the crude material may be lower than that used to prepare the reactive blending. Nevertheless, the data in that table suggest that the fraction of incorporated monomer depends slightly on the UA concentration. For a given UA concentration, a somewhat larger amount of UA is incorporated into the LLDPE chains when the concentration of peroxide increases. Thus, an increase of DPBH concentration enhances grafting of UA onto LLDPE.

The results presented here do not coincide with those of other studies that use carboxyl acid derivatives of lower molecular weight.^{4,22} In these studies, the percentage of grafting followed an increasing trend with the monomer concentration. However, a qualitative agreement exists with respect to the effect of the initiator. In general, in the range of peroxide concentration used here, it was observed that the amount of monomer incorporated into the polymer increases with the concentration of peroxide.²³ However, the grafting efficiency observed in the present study is much lower than that reported by other in-

TABLE II
Absorbency of the 1712 cm^{-1} Band Normalized with the Film Thickness, Extension of Grafting (I_g), and Grafting Degree (GD)

DBPH % (w/w)	AU % (w/w)	A_{1712}/mm		I_g (%)	GD ^a
		Crude	LLDPE-g-UA		
0.025	1	2.2 ± 0.3	0.6 ± 0.1	~27	~0.29
	2	4.6 ± 0.5	0.7 ± 0.1	~15	~0.32
	4	8.2 ± 1.7	0.7 ± 0.1	~8	~0.32
0.050	1	2.4 ± 0.3	0.9 ± 0.1	~36	~0.36
	2	3.6 ± 0.8	0.9 ± 0.1	~24	~0.48
	4	9.0 ± 0.8	0.9 ± 0.1	~10	~0.36
0.100	1	2.1 ± 0.2	0.9 ± 0.1	~41	~0.41
	2	3.8 ± 0.6	1.1 ± 0.1	~29	~0.58
	4	8.1 ± 0.3	1.1 ± 0.1	~14	~0.56

^a Grafted UA (in grams) per 100 g LLDPE (estimated from I_g and the initial amount of UA in the reactive mixture).

TABLE III
Temperature (T_f) and enthalpy (ΔH_f) of Fusion for Some of the Modified Materials and Original LLDPE

DBPH % (w/w)	AU % (w/w)	T_f (°C)	ΔH_f (J/g)	UA (mol %) ^a
—	—	127	137	—
0.025	1	125	137	0.04
	4	125	138	0.05
0.100	1	124	135	0.06
	4	125	135	0.08

^a Data expressed as mol of UA/100 mol ethylene calculated from the values of GD.

investigators (~ 90%) in the modification of polyethylene with a short-chain carboxylic monomer.¹⁹

Thermal characterization

All the polymers showed a fusion range that spreads over a wide range of temperatures, as is typically observed in compositionally nonuniform ethylene copolymer. Table III shows the values of melting temperatures (T_f) obtained from the endothermic peak, and enthalpies of fusion (ΔH_f) of some selected samples from this study. The thermal properties of the LLDPE are equivalent to a compositionally nonuniform ethylene-1-butene copolymer having a content of butene of about 1.2 mol %.²⁴ The experimental results of the grafted materials indicate that the thermal properties do not undergo a significant change with respect to the original LLDPE. It is well known that the heat of fusion and the melting point of polyethylene are reduced when structural irregularities or pendant groups are randomly introduced along crystallizable segments of the polymer molecules. The degree to which those properties are reduced depends on the number of these pendant groups.^{24,25}

For LLDPE-g-UA polymers, the values of DG or I_g obtained from FTIR can be used to roughly estimate the amount of new branching points introduced into the LLDPE chains, assuming that molecules of UA are randomly incorporated one by one into the molecular chains. Data values in the last column of Table III indicate that the amount of new branches incorporated may be between 0.04 to 0.08 mol %. Such increases in the number of branches would produce a decrease in the melting temperature of about 2–3°C in ethylene-1-butene copolymer.²⁵ Therefore, the slight decreases in the melting point observed in the LLDPE-g-UA polymers can be attributed to the small amount of UA incorporated. On the other hand, the insensibility observed in the values of heat of fusion may be associated with the experimental difficulty in determination of the area under the endothermic peak when estimating the enthalpy of fusion. All the polymers showed a fusion range that spreads over a wide range

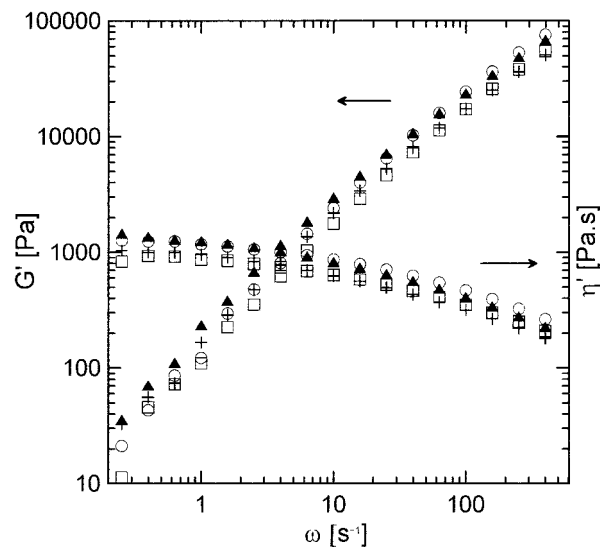


Figure 4 Dynamic elastic modulus $G'(\omega)$ and viscosity $\eta'(\omega)$ measured at 160°C for original LLDPE and LLDPE-g-UA modified with 0.025% (w/w) DBPH. Symbols: (○) LLDPE; (▲) 0% UA; (+) 1% UA; (□) 4% UA.

of temperatures, making it quite difficult to define precisely the limits of the endotherm of fusion.

Rheological characterization

Samples of the modified polymers and LLDPE were tested in dynamic shear flow at low strain to determine their melt properties. Figures 4 and 5, respectively, show the evolution of $G'(\omega)$ and $\eta'(\omega)$ with

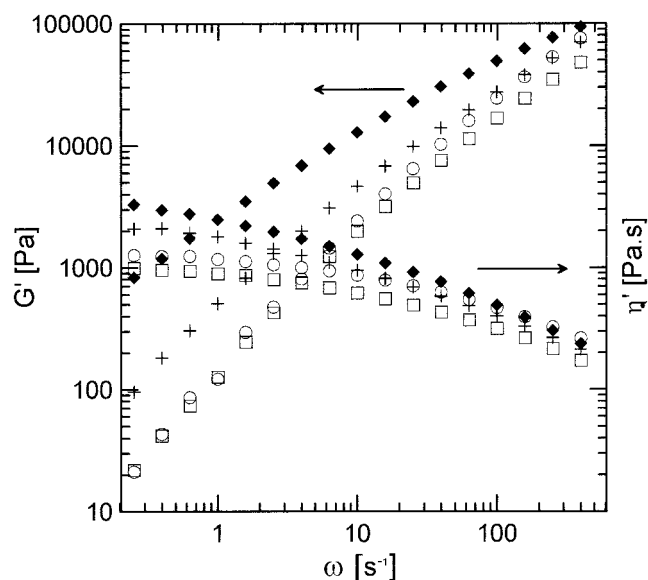


Figure 5 Dynamic elastic modulus $G'(\omega)$ and viscosity $\eta'(\omega)$ measured at 160°C for original LLDPE and LLDPE-g-UA modified with 0.1% (w/w) DBPH. Symbols: (○) LLDPE; (◆) 0% UA; (+) 1% UA; (□) 4% UA.

frequency for the original LLDPE and selected LLDPE-g-UA samples obtained using 0.025 and 0.1% of DBPH. These samples were selected as representative examples of the rheological behavior observed in all the studied materials.

The main differences between the samples appear at the low-frequency range. The values $G'(\omega)$ and $\eta'(\omega)$ of the polymer modified with peroxide are higher than those corresponding to the original PE at low frequencies. An increment in peroxide concentration produces an increase in the value of the properties at a given frequency. This phenomenon is attributed to the molecular weight increment as a consequence of the predominance of chain-linking reactions. When the peroxide concentration increases the molecular weight increases, and so do values of the melt properties. Other investigators have observed a similar effect of the peroxide on the melt properties when they studied the chemical modification of polyethylene with organic peroxides.^{26–29}

In the case of the LLDPE-g-UA, the values of $G'(\omega)$ and $\eta'(\omega)$ were reduced with respect to those values corresponding to the LLDPE modified with peroxide. The effect became even more substantial as the concentration of UA in the mixture increased. This finding is opposite to the results observed when polyethylene was modified with other monomers. It was previously reported that crosslinking reactions are favored using monomers such as acrylic acid or ester derivatives and maleic anhydride. Moreover, an enhancement in crosslinking occurs with respect to the one that is produced by the peroxide.^{4,19}

A plausible explanation is that the crosslinking, which accompanies the modification of the polyethylene, is reduced or eliminated in the presence of UA. Moreover, it may favor chain scission that produces a material with viscosity and elasticity lower than those of the original polyethylene. To prove this, we evaluated the change in the molecular weight of some of the modified polymers. In Figure 6 the GPC-MALLS results are presented for some selected samples. Comparing the curve of the original polyethylene with those corresponding to the modified polymers, it may be observed that there is a slight shift of the molecular weight distribution toward lower molecular weights, in particular on the high molecular weight side of the distribution. This result, which agrees with the rheological data, indicates that a scission or degradation process may have occurred during the modification carried out to obtain these samples.

Hypothetical reaction scheme

Scheme 2 summarizes the reactions considered possibly dominant in the conditions examined in this work that will be discussed below. This hypothetical reaction mechanism for UA grafting onto LLDPE in the

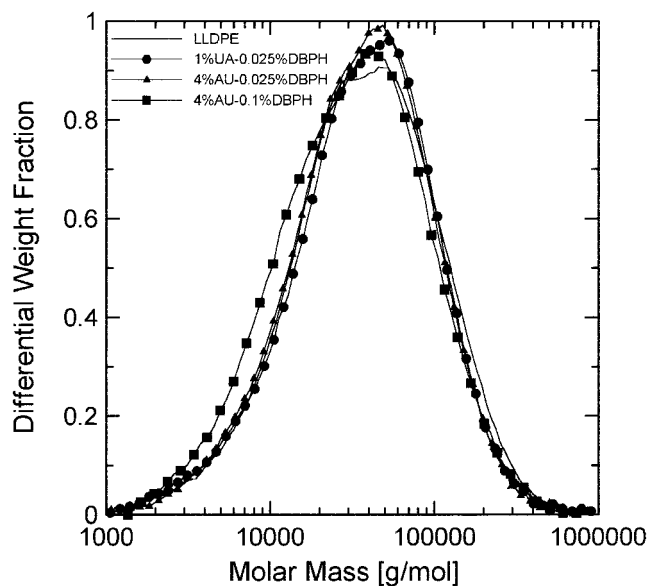


Figure 6 Molecular weight distribution of LLDPE and LLDPE-g-UA polymers obtained using the concentration of initiator and UA indicated in the legend.

melt using DBPH as initiator is simple, although it could partially explain some of the experimental results already reported.

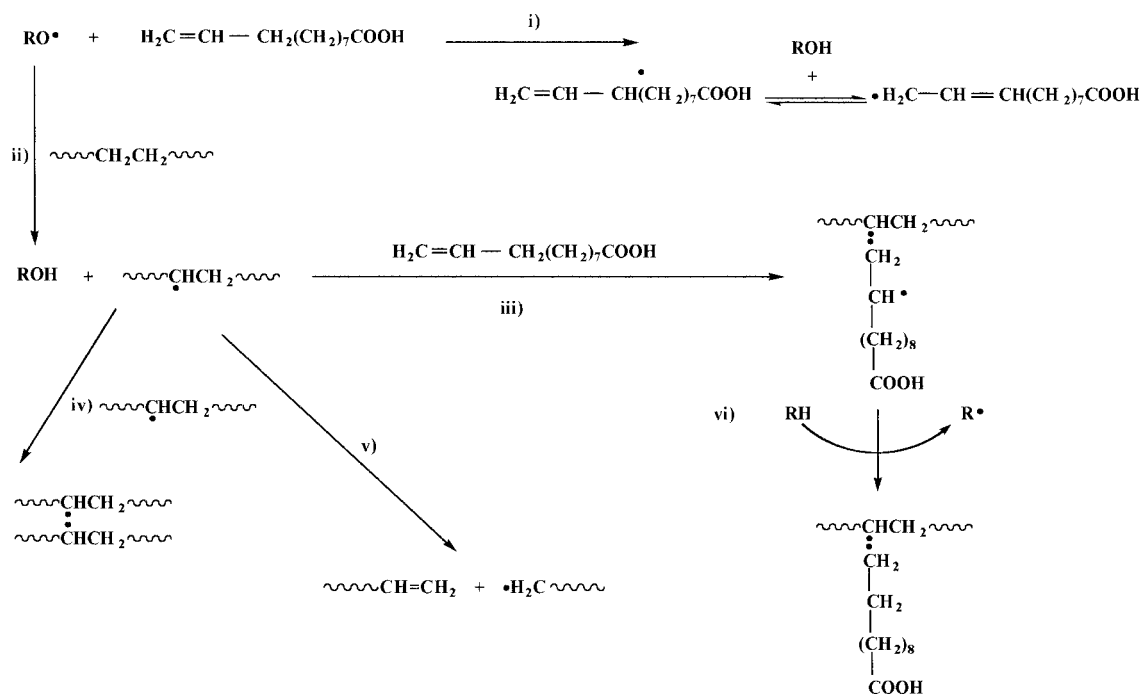
The first step of the process involves the homolytic scission of DBPH that produces oxyradicals. The oxyradicals generated can react either with UA (reaction i in **Scheme 2**) or with LLDPE chains (reaction ii).

Although both reactions are possible, we assume that the attack on UA is more likely because the hydrogen abstraction from the allylic position is extremely facile because of the weakness of the allylic C—H bonds.³⁰ The allylic radicals so generated are quite stable³¹ and they undergo termination by reaction with each other or, more likely, with propagating radicals.³² The consequences of this process are obvious: it diminishes the concentration of oxyradicals and polymer chains remain unaffected.

On the other hand, the attack by oxyradicals on polymer chains induces new radicals onto LLDPE chains (reaction ii). The reaction between UA and macroradicals can occur in two different ways: by transferring the radical activity or by effective grafting (reaction iii).

Once grafting occurs, the grafted macroradical could transfer its radical activity to any chemical species present in the media (reaction vi), although we conjecture that transfer to UA is more likely because of the generation of stable allylic radicals. Therefore, the overall effect of this process is a new consumption of reactive radicals.

Coupling reactions occur when macroradicals react with others radical species (reaction iv). As the literature suggests, crosslinking occurs by coupling reac-



Scheme 2 Hypothetical reaction mechanism for UA grafting onto LLDPE.

tions between macroradicals. In our experimental conditions, however, we suppose that this last reaction may occur with a low probability. On the contrary, we surmise that macroradicals may undergo β -scission instead of crosslinking reactions (reaction v).

A plausible explanation for this could be the presence of UA in the reaction media. If we assume that UA promotes side reactions (such as chain transfer), then the process could favor β -scission over crosslinking. The effect can be thought of as a degradative chain process,^{32,33} and it seems to be important when high UA concentrations are used.

CONCLUSIONS

10-Undecenoic acid (UA) was successfully grafted onto molten LLDPE using 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane as initiator. FTIR analysis of grafted polymers showed that the grafting efficiency increases with the concentration of initiator. On the other hand, for a given initiator concentration, the grafting efficiency seems to be independent of UA concentration.

Thermal properties such as fusion enthalpy (ΔH_f) and melting temperature (T_f) of grafted polymers were similar to those of the original LLDPE resin. The melting temperature showed a slight trend to decrease with the incorporation of UA into the polyethylene. These results suggest that the thermal properties are not affected to a great extent because of the low amount of grafted UA.

The modification process affects the melt elasticity and viscosity of the LLDPE. When the original polymer was modified only with peroxide both properties increased with respect to those of the original material. However, when undecenoic acid was grafted to LLDPE, the resulting polymers displayed values of elastic moduli and viscosity lower than those of the polymer modified with peroxide. Moreover, when a concentration of 4% of UA was used, the values of those properties were even lower than those corresponding to the original LLDPE. These observations combined with the data obtained from the GPC suggest that chain-scission reactions may be promoted by the presence of undecenoic acid.

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