

Macromolecular non-releasing additives for safer food packaging: application to ethylene/ α -olefins and propylene-based polymers

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This paper is dedicated to our young and beloved colleague, Dr. Achille Piccinini, who contributed with passion and hard work to the research presented and passed away on May 16, 2013, at the age of 29.

ABSTRACT

Some innovative solutions are proposed to the problem of the unavoidable physical migration of antioxidants from plastic films for packaging, in order to minimize the consequent undesirable effect of food contamination. In previous exploratory tests, phenolic antioxidant co-units were achieved and incorporated into polyethylene chain and now the work is extended to create new families of polymeric additives properly designed for specific materials. An effective route was designed to synthesize the functionalized comonomer, analogues of commercial 2,6-*t*-butyl-4-methoxy-phenol (BHA), containing eight methylene units as spacer between the aromatic ring and the polymerizable olefinic double bond (C8). Ethylene/1-hexene/C8 terpolymers, with 1-hexene concentration in the typical range found in commercial polyethylene grades, and propylene/C8 copolymers with microstructure similar to those of commercial packaging polypropylenes were produced. A careful ¹³C NMR study was conducted for the precise determination of the functionalized comonomer content on all terpolymer and copolymer samples. The samples melt blended with additive-free commercial LDPE and PP matrices, individually, were analyzed in terms of thermal and thermo-oxidative stability and compared with LDPE and PP films containing the traditional BHA additive analogue. The results demonstrate that, in either way, the polymeric additives exert a very positive effect on the degradation temperature of the polymeric matrices, retarding the thermo-oxidative sequence of reaction.

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Keywords: macromolecular antioxidants, blends, polyolefins, ¹³C NMR, thermogravimetric analysis (TGA)

INTRODUCTION

A serious problem, as well as a limiting factor, of the commonly used antioxidant stabilizers in polymers is their poor compatibility with the apolar polymeric matrices, being the stabilizers, usually, small polar hydroxyl and/or amino substituted aromatic compounds [1]. This leads to the physical loss of the stabilizers by migration from the polymer matrix during compounding and extrusion processes as well

as storage and final use [2, 3]. Moreover, in the case of food packaging supplies, this might cause the undesirable effect of food contamination with changes of the organoleptic properties and even some risks of allergenic phenomena.

In this framework, we have tackled an investigation to propose an innovative solution to the problem of the unavoidable physical migration of antioxidants from plastic films for packaging [4-7]. Moving from the pioneering work by Wilén and co-workers

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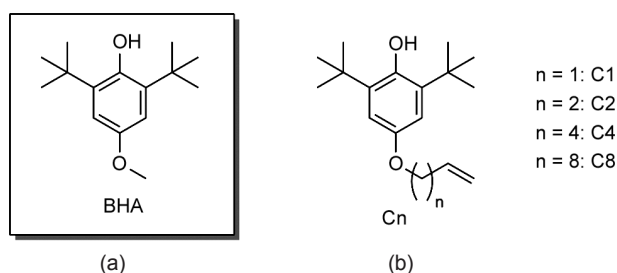


Figure 1. Structure of BHA (a) and BHA-related comonomers C_n (b)

[8,9] we designed and developed new families of macromolecular antioxidant additives bearing tuned amounts of an antioxidant functionality covalently linked to the polymeric chain. Specifically, a synthetic route to produce a series of novel comonomers analogous with 2,6-*t*-butyl-4-methoxy-phenol (a common commercial antioxidant referred also as butyl hydroxy anisole, BHA, Figure 1a) containing a different number of methylene units as spacers between the aromatic ring and the polymerizable olefinic double bond (C_n , Figure 1b) was designed and applied in detail.

Comonomers C_n were copolymerized with ethylene (Scheme 1) by using an optimized combination of proper catalyst and polymerization conditions to obtain the controlled incorporation of the antioxidant groups along the polyethylene chain, while avoiding a detrimental effect on the polymerization yield.

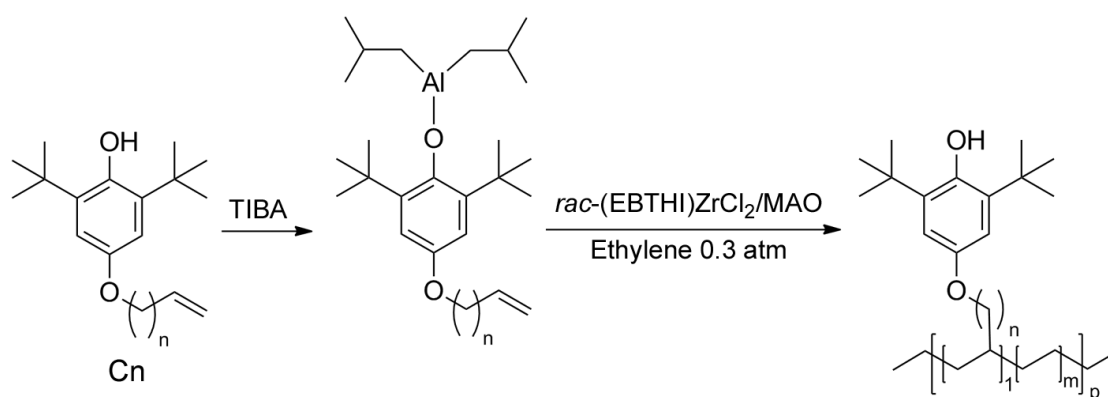
These novel polymeric additives were then used as kind of “masterbatches” in the melt-blending with commercially available polyethylene and from the ensuing blends films were prepared by compression moulding. Positively, the obtained polymeric films exhibited a stability to auto- and photo-oxidation comparable and even superior to that shown by films stabilized with similar amounts of the low molecular weight antioxidant BHA, but with reduced, if not

eliminated, risk of migration. The most satisfactory results were achieved with the comonomer bearing an eight-methylene spacer (**C8**), since it was the most easily incorporated into the polymer chain in controlled and tunable amount. Thus, comonomer **C8** was selected for the successive development of the research.

In the present work we report a compendium of the new macromolecular antioxidants containing comonomer **C8** that we have specifically formulated to be mixed with different kinds of polymeric matrices. The differentiation of the additives, according to the material they are formulated for, is expected to give a uniform distribution of the macromolecular stabilizers in the commercial polymer matrices, allowing the minimum amount of the required stabilizing additive.

In addition to a selection of the most interesting results concerning ethylene/**C8** copolymers we report also on the synthesis of novel terpolymers of ethylene with **C8** and 1-hexene (**1-H**). Indeed, the important family of polyethylenic food contact materials (although in general commercialized as “polyethylenes”) is essentially based on copolymers of ethylene with a small content (2-4 mol%) of higher α -olefins (1-butene, 1-hexene, 1-octene). We hypothesized that an ethylene/**1-H**/**C8** terpolymer, with **1-H** concentration in the typical range found in commercial polyethylene grades, should be a suitable stabilizer for these materials. Such terpolymer was expected to be more finely blended with the commercial polyethylene-based matrices and more soluble in common organic solvents than the ethylene/**C8** copolymer.

Further, polypropylene is the base of another important family of food contact materials, specifically employed for packaging of fresh vegetables and



Scheme 1. Copolymerization of comonomers C_n

fruit. Understandably, stabilizing functionalities anchored to a polypropylene chain can be efficiently dispersed in polypropylene-based food contact materials. Therefore, we developed copolymers of propylene and tunable amount of comonomer **C8**, with microstructure similar to that of the commercial polypropylenes used for packaging.

A careful ^{13}C NMR study was conducted for the precise determination of the functionalized comonomer content in all terpolymer and copolymer samples.

The prepared samples were melt blended with additive-free commercial LDPE and PP matrices, in separate batches, to obtain blends containing covalently bonded antioxidant moieties in concentration comparable to that typically used with low molecular weight antioxidants. Films obtained by compression molding of the above given blends were analyzed in terms of thermal, thermo-oxidative and photo-stability and compared with LDPE and PP films containing the traditional BHA additive analogue.

EXPERIMENTAL

Materials

All experiments and manipulations involving air-sensitive compounds were carried out under dry nitrogen atmosphere in glovebox or by using standard Schlenk line techniques. Methylaluminoxane (MAO) (10 wt% as toluene solution, Crompton) was used after removing all volatiles and drying the resulting powder at 50°C for 3 h in vacuum (0.1 mmHg). Triisobutylaluminoxane (TIBA) (Witco, toluene solution) was used as received. *rac*-(EBTHI)ZrCl₂ (**EBTHI**) was kindly provided by Basell Poliolefine Italia S.r.l. (Ferrara, Italy). Toluene was dried and distilled over sodium under nitrogen atmosphere. Nitrogen, ethylene and propylene gases were dried and deoxygenated by passage over columns of CaCl₂, molecular sieves, and BTS catalyst.

The additive-free commercial LDPE (Lupolen LP 2420F), to be used in polyethylene-based blends, was kindly supplied by Lyondelbasell Italia S.r.l. (Ferrara, Italy). Lupolen LP 2420F, a low density polyethylene (density 0.923 g cm⁻³; MFI (190°C, 2.16 kg) 0.75 g/10 min; melting temperature 111°C), contained about 1.5 mol% of 1-hexene comonomer and long

branches. For the polypropylene-based blends an additive-free polypropylene (PP) grade (R2-11-117) was kindly provided by Borealis Polyolefine GmbH (Linz, Austria) and used as matrix. PP R2-11-117 grade, an isotactic PP, had a melting temperature of 168°C. 2,6-Di-*t*-butyl-4-methoxyphenol (BHA) was purchased from Sigma Aldrich (Italy).

Alternative synthesis of functionalized phenolic comonomer **C8**

(a) *Dec-9-enyl-4-methylbenzenesulfonate*. To a solution of dec-9-en-1-ol (2.25 g, 14.4 mmol) in dry pyridine (8.5 mL) was added under nitrogen at 0-5°C *p*-toluenesulfonyl chloride (3.29 g, 17.3 mmol) in small portions. After 3 h the reaction mixture was diluted with ice-water and a 0.05 M solution of hydrochloric acid (100 mL) and then it was extracted with hexane (3 × 100 mL). The combined organic layers were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure at 30°C to afford the dec-9-enyl-4-methylbenzenesulfonate product as a colorless oil (4.35 g, 97% yield) used without further purification in the next step. ^1H NMR (400 MHz, CDCl₃, 23°C) δ 1.14-1.40 (m, 10H, 5x-CH₂ aliphatic), 1.56-1.66 (q, 2H, J = 6.7 Hz, -CH₂-CH₂-OTs), 1.96-2.05 (m, 2H, -CH₂-CH=CH₂), 2.43 (s, 3H, Me), 4.00 (t, J = 6.7 Hz, 2H, -CH₂-OTs), 4.87-5.01 (m, 2H, -CH₂=CH), 5.71-5.84 (m, 1H, -CH=CH₂), 7.30-7.36 (m, 2H, Ar), 7.74-7.80 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl₃, 23°C) δ 21.5, 25.2, 28.70, 28.73, 28.75, 28.8, 29.1, 33.6, 70.6, 114.1, 127.8, 129.7, 133.2, 139.0, 144.5. IR (cm⁻¹) 3071, 2929, 1635, 1171. MS *m/z* (relative intensity %) 173 (4), 155 (5), 91 (49), 55 (71), 41 (100)

(b) *4-Dec-9-enyloxy-2,6-di-*t*-butyl-phenyl acetate*. To a solution of 2,6-di-*t*-butyl-4-hydroxyphenyl acetate (1.46 g, 5.55 mmol) in dry DMF (25 mL) were added under nitrogen at 100°C dec-9-enyl-4-methylbenzenesulfonate (3.8 g, 12.3 mmol), potassium carbonate (3.4 g, 24.6 mmol) and potassium iodide (0.1 g, 0.62 mmol). After 60 h of stirring, the reaction mixture was diluted with diethyl ether and washed with water (3 × 50 mL) and brine (50 mL). The organic solvent was dried over anhydrous sodium sulfate, filtered and the solvent evaporated to give a crude that was purified by flash chromatography on silica gel (eluted with petroleum ether/dichloromethane: 2/1) to give 4-dec-9-enyloxy-2,6-di-*t*-butyl-phenyl acetate as a yellow liquid (1.8 g,

80 % yield). ^1H NMR (400 MHz, CDCl_3 , 23°C) δ 1.29 (s, 10H, 5x- CH_2 aliphatic), 1.33 (s, 18H, 2x-tBu), 1.77 (q, $J = 6.7$ Hz, 2H, $-\text{CH}_2-\text{CH}_2-\text{O}$), 2.00-2.09 (m, 2H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.33 (s, 3H, $-\text{OAc}$), 3.92 (t, $J = 6.7$ Hz, 2H, $-\text{CH}_2-\text{O}$), 4.90-5.04 (m, 2H, $-\text{CH}=\text{CH}_2$), 5.76-5.88 (m, 1H, $-\text{CH}=\text{CH}_2$), 6.84 (s, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , 23°C) δ 22.6, 26.1, 28.9, 29.0, 29.35, 29.39, 29.43, 31.4, 33.8, 35.5, 67.8, 112.1, 114.1, 139.2, 141.3, 143.2, 155.9, 171.6. IR (cm^{-1}) 3000, 2962, 1751, 1595, 1207. MS m/z (relative intensity %) 402 (M+, 2), 360 (53), 57 (75), 43 (100), 41(75). (c) *4-Dec-9-enoxy-2,6-di-*t*-butyl-phenol* (**C8**). To a suspension of lithium aluminium hydride (0.38 g, 10.2 mmol) in dry tetrahydrofuran (24 mL) was added at 0°C a solution of 2,6-di-*t*-butyl-4-(dec-9-enoxy) phenyl acetate (0.9 g, 3.4 mmol) in dry THF (16 mL). The reaction mixture was refluxed for 16 h, cooled at room temperature and quenched with ice and 0.01 M hydrochloric acid and extracted with diethyl ether (3 \times 50 mL). The combined organic layers were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and the product was purified by flash chromatography on silica gel (eluent petroleum ether/dichloromethane: 1/1) to give **C8** as a pale yellow oil (0.69 g, 85% yield) identical to the previous prepared samples [4,5].

Typical co- and terpolymerization procedure

The co- and terpolymerizations were performed in a round-bottom flask at 35°C under reduced (0.3 atm for ethylene and 0.5 atm for propylene) monomer gas pressure. The total volume of toluene (50 and 100 mL) was introduced into an evacuated and N_2 purged flask.

The synthesized comonomer was added with TIBA (TIBA/comonomer molar ratio = 2.0) and the solution was stirred for 2 h under N_2 pressure. Afterwards the flask was filled with MAO solution and the proper amount (2-6 μmol) of the catalyst (Al/Zr content ratio = 1500-3000). The ratio between ethylene or propylene and the comonomer was maintained with the correct proportion of N_2 and the gas in the flask. The polymerization reaction was stopped after due time through the addition of ethanol and HCl. The reaction product was stirred for several hours then filtered, washed with ethanol, and dried in vacuum.

^{13}C NMR characterization of co- and terpolymers

The amount of bound phenolic stabilizers was determined by ^{13}C NMR analysis. ^{13}C NMR spectra

of all the samples were recorded at 103°C on a Bruker Avance 400 spectrometer operating at 100.58 MHz. Conditions: 10 mm probe; 90° pulse angle; 64K data points; acquisition time 5.56 s; relaxation delay 20 s; 3-4 K transients. Proton broad-band decoupling was achieved with a 1D sequence using bi_waltz16_32 power-gated decoupling. ^{13}C DEPT NMR spectra were measured with composite pulse decoupling using the sequence $\tau_1-90^\circ-\tau_2-180^\circ, 90^\circ-\tau_2-135^\circ, 180^\circ-\tau_2$ -CPD-acquire, with delays τ_1 of 5 s, and τ_2 of 3.8 ms and 90° pulse widths of 14.3 and 28.1 μs and for ^{13}C and ^1H , respectively.

The samples (50-100 mg) were dissolved in $\text{CDCl}_2-\text{CDCl}_2$ with 1% hexamethyldisiloxane as internal chemical shift reference. Due to their low solubility, the ethylene/**C8** copolymers were stirred at 100°C for 24 h before recording their spectra. The complete signal assignment is reported in the text. Phenolic comonomer homosequences were not detected in the spectra, suggesting that the obtained products are random co- and terpolymers containing only isolated **C8** comonomer units. No detectable traces of unreacted phenolic comonomers were found in the olefinic region of the spectra.

DSC analysis of co- and terpolymers

Melting and crystallization behavior of the synthesized co- and terpolymers was analyzed by differential scanning calorimetry (DSC) using a Mettler DSC 821 $^\circ$ instrument (scanning rate $10^\circ\text{C min}^{-1}$, under N_2 atmosphere). The ethylene-based samples were treated as follows: after destroying the nascent crystallinity at 180°C , the specimens were cooled down to -100°C , and the exothermal signal associated to crystallization was recorded. A second heating was imposed to acquire information on the melting behavior. An analogous thermal treatment was imposed on propylene-based samples, though in this case the heating temperature was increased to 220°C .

Blends and films

Blends of the additive-free LDPE or PP matrices with the proper synthesized co- and terpolymers were prepared by melt blending in an internal batch mixer (Brabender W50 EHT Plasti-Corder $^\circ$). The chosen mixing conditions were 130°C , 50 rpm, 15 min for the polyethylene-based blends, and 170°C , 60 rpm, 10 min for the polypropylene-based blends; in all cases the mixing chamber was kept under N_2 overpressure.

To have 500 ppm of antioxidant moieties dispersed into the matrices, a proper amount of polymeric antioxidant was used for each blend, taking into account the specific co- or terpolymer composition. The value of 500 ppm was chosen because it was considered a typical amount of antioxidant required to stabilize polyolefinic materials. Neat LDPE and PP as well as their mixtures with 500 ppm of BHA antioxidant were treated under the same processing conditions settled for the two polyolefinic systems and used for reference purposes.

Sheets with thickness of about 400 μm were obtained from the prepared blends by compression moulding (using a P200E semi-automatic laboratory press, Collin GmbH) to ensure correct sampling and thus optimize reproducibility of the successive thermogravimetric analysis (TGA).

The compression moulding step was conducted at 160°C for the polyethylene-based samples and at 180°C for the polypropylene-based ones. About 100 μm thick films of 11 \times 11 cm^2 were analogously prepared by compression moulding and used for successive photoaging test.

TGA analysis

Thermal and thermo-oxidative stabilities of copolymers and blends were tested by TGA experiments performed, respectively, under N_2 and O_2 atmosphere using a Perkin Elmer TGA7 instrument. TGA measurements were carried out both in dynamic and isothermal conditions. In the dynamic mode, the explored temperature range was 50–700°C (heating rate 20°C min^{-1}).

Isothermal experiments were carried out by rapidly reaching 180°C for the polyethylene matrix or 220°C for the polypropylene matrix under N_2 atmosphere; after 10 min, the purge gas was switched to oxygen to start the measurements of the oxygen induction time (OIT); the instant oxygen entered the instrument furnace was referred as t_0 in the following. In order to guarantee the comparison and reproducibility of the OIT experimental results, the isothermal measurements were carried out on specimens, punched from the sheets prepared as specified above in order to have similar weight and surface area exposed to the oxygen action.

The isothermal TGA traces are the mean curves resultant from at least three different experiments carried out for each examined sample.

Photoaging test

The photoaging test was carried out on film specimens (2 \times 4 cm^2) placed horizontally onto a turntable and exposed to constant illumination produced by a 300-W Osram-Ultra VitaluxVR lamp. The lamp was placed 40 cm above the turntable with incident beam at 30°. The sample temperature, recorded by means of a data logger (Smart Reader SR04), was $70 \pm 3^\circ\text{C}$. Irradiance at sample level was measured using a portable digital photoradiometer (Delta Ohm HD2102.2) equipped with specific probes. The recorded irradiance values were $132 \pm 2 \text{ W/m}^2$ in the visible region, $11.5 \pm 0.02 \text{ W/m}^2$ in the UVA and $4.53 \pm 0.03 \text{ W/m}^2$ in the UVB region. The exposition was carried out for 48 h and during that time the films were analyzed by FTIR spectrometry (Spectrum 100, Perkin Elmer, Italy) in transmission mode (32 scans, resolution 4 cm^{-1} , wavenumber range 4000–400 cm^{-1}) to estimate the increase of the following photodegradation indexes:

- Hydroxyl index: defined as the ratio of absorbance of hydroxyl band at around 3400 cm^{-1} and the reference band at 2020 cm^{-1} .
- Carbonyl index: defined as the ratio of absorbance of carbonyl band around 1740 cm^{-1} and the reference band at 2020 cm^{-1} .

RESULTS AND DISCUSSION

Alternative synthesis of the functionalized phenolic comonomer C8

The procedure we have recently settled out for the synthesis of comonomers **C_n** requires the use of huge excesses of the proper α,ω -unsaturated alcohol [4]. Thus, while this was not particularly problematic in the case of **C1** and **C2**, because the required excess of allylic and homoallylic alcohols could be easily eliminated by distillation and both chemicals are quite cheap, the preparation of **C8** was low yielding mostly for the cumbersome purification step. Being **C8** the comonomer of choice, to prove the feasibility of our strategy for obtaining macromolecular additives destined to other polymeric materials used in food packaging, we studied a more suitable synthetic methodology for its preparation. Eventually, we developed the procedure described in Scheme 2 based on the reaction of easy available mono-acetylated hydroquinone with *o*-tosyl-dec-9-en-1-ol that affords the corresponding aryl alkyl ether in 80% yield. Reduction with LiAlH_4 of the ester group allowed

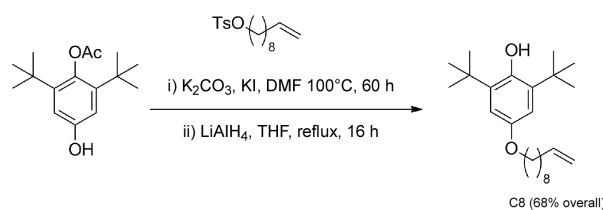
Table 1. ^{13}C NMR chemical shift assignment for phenolic comonomer **C8**

Carbon	Chemical shift (ppm)
Cf	150.47
Ce	145.82
C9	137.22
Cd	135.73
C10	112.21
Cc	109.92
C1	67.05
Cb	32.65
C8	31.59
Ca	28.55
C2	27.79
C4,C5	27.45
C7	27.09
C6	27.04
C3	24.25

the isolation of comonomer **C8** in good overall yield (68%) and, above all, avoiding the use of excess amounts of α,ω -unsaturated alcohols (Scheme 2). The ^1H -decoupled and DEPT ^{13}C NMR spectra of **C8** are presented in Figure 2. The assignments of all the detected resonances are reported in Table 1.

Ethylene/**C8** copolymerization

The copolymerization of ethylene with comonomer **C8** as well as the reference ethylene homopolymerization was conducted with methylaluminoxane (MAO) activated *rac*-(EBTHI)ZrCl₂ (**EBTHI**). This catalyst was chosen mainly because its activity has been shown to be only partially affected by the ether oxygen

**Scheme 2.** Alternative synthetic methodology for preparing comonomer **C8**

of the functionalized comonomer [4,5]. Moreover, the molecular weights produced by **EBTHI** are the lowest among those obtained with the commonly used metallocene catalysts. A relatively low molecular weight could be important to facilitate the dispersion of the functionalized polymeric additives into the matrix, thus favouring the antioxidant activity of the comonomers.

Triisobutylaluminum (TIBA) was used to prevent the catalyst deactivation: the phenol was pretreated with 2 equivalents of TIBA, in order to protect the hydroxyl group and interact with the ether oxygen [4, 5]. The polymerizations were performed at 0.3 atm of ethylene gas pressure to promote the insertion of the bulky polar comonomer with respect to ethylene. Table 2 reports the polymerization data along with the microstructural and molecular characterization of copolymers. We observed that the polyethylene yield is similar to that of all the copolymerization products, except one. Indeed, only in run 2, where the comonomer concentration was the lowest, the copolymerization yield was higher. We believe that, in this case, the well known activation effect of the hindered phenol [8] overcomes the poisoning effect of the ether oxygen.

The results show that it is possible to tune the

Table 2. Copolymerization of ethylene with **C8** catalyzed by EBTHI/MAO catalytic system^(a)

Run	C8 mmol	[C ₂ H ₄]/[C8]	Yield (g)	Activity ^(b)	C8 ^(c) mol%	C8 conversion	M _n ^(d) g/mol	M _w /M _n ^(d)
1 ^(e)	-	-	0.133	355	-	-	15500	2.1
2 ^(f)	0.40	4.45	1.045	697	0.5	45.2	n.d. ^(g)	n.d. ^(g)
3	0.66	2.61	0.698	388	1.0	33.3	11000	2.4
4	0.80	2.20	0.640	356	1.5	32.4	17000	4.0
5	1.00	1.75	0.514	286	3.0	27.1	17100	5.0

(a) Polymerization conditions: solvent = toluene, total volume = 50 mL, Al/Zr = 1500 (mol/mol), T = 35°C, P_{ethylene} = 0.3 atm, [catalyst] = 6 μmol , t_{pol} = 60 min.

(b) Activity = [(g_{pol}/mmol_{cat}h)/P].

(c) Determined by ^{13}C NMR.

(d) Determined by SEC.

(e) t_{pol} = 15 min, [catalyst] = 5 μmol .

(f) [catalyst] = 5 μmol .

(g) n.d. = not determined.

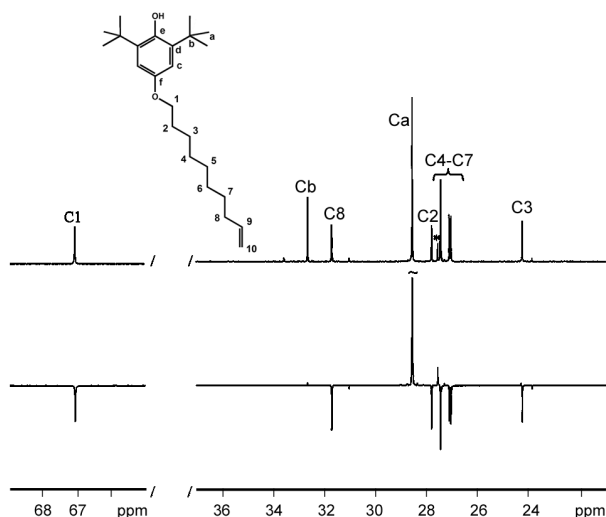


Figure 2. Aliphatic region of (a) ^1H -decoupled ^{13}C NMR and (b) DEPT spectrum of phenolic comonomer **C8**

comonomer content within the desired composition range by varying the ethylene/comonomer molar ratio (from 4.45 to 1.75) in the reaction mixture. Actually, in the following, only **C8** incorporation up to about 1 mol% was looked for since we observed that higher concentrations led to poor miscibility of the copolymer

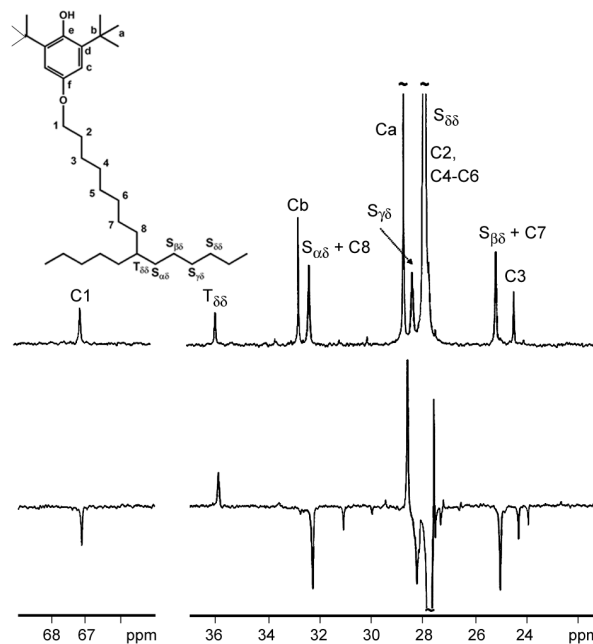


Figure 3. Aliphatic region of (a) ^1H -decoupled ^{13}C NMR and (b) DEPT spectrum of ethylene/**C8** copolymer (run 5, Table 2)

with the polyolefinic matrix.

The comonomer contents of the copolymers were determined by ^{13}C NMR analysis: the ^1H -decoupled

Table 3. ^{13}C -NMR chemical shift assignment for ethylene/**C8**, ethylene/**1-H** copolymers and ethylene/**1-H/C8** terpolymer

Carbon	E/ C8 copolymer	E/ 1-H copolymer	E/ 1-H/C8 terpolymer
	Chemical shift (ppm)	Chemical shift (ppm)	Chemical shift (ppm)
Cf	150.47	-	150.47
Ce	145.82	-	145.82
Cd	135.73	-	135.73
Cc	109.92	-	109.92
C1	67.05	-	67.05
T _{δδ}	35.87	35.81	35.81(E 1-HE triad), 35.85(E C8E triad)
Cb	32.65	-	32.65
S _{αδ}	32.23	32.23	32.23
C8	32.23	-	32.23
4B4	-	31.85	31.85
Ca	28.58	-	28.58
S _{γδ}	28.25	28.25	28.25
S _{δδ}	27.73	27.73	27.73
C2, C4-C6	27.73	-	27.73
3B4	-	27.26	27.26
S _{βδ}	25.02	25.00	25.00
C7	25.02	-	25.00
C3	24.32	-	24.32
2B4	-	21.18	21.18
1B4	-	12.08	12.08

Table 4. Terpolymerization of ethylene with **1-H** and **C8** catalyzed by **EBTHI/MAO** catalytic system ^(a)

Run	C8 (mmol)	[C ₂ H ₄]/ [C8]	[C ₂ H ₄]/ [1-H]	Yield (g)	Activity ^(b)	1-H mol% ^(c)	1-H conver.	C8 mol% ^(c)	C8 conver.	M _w ^(d) g/mol	M _w /M _n ^(d)
6 ^(e)	-	-	4.31	0.776	2070	4.12	48.7	-	-	24600	1.94
7	0.5	6.95	4.31	0.837	558	1.21	21.9	1.27	42.3	109900	3.12
8	0.25	13.90	2.16	1.293	862	3.01	40.7	0.75	61.4	160200	3.17

(a) Polymerization conditions: solvent = toluene, total volume = 100 mL,

Al/Zr = 1500 (mol/mol), T = 35°C, P_{ethylene} = 0.3 atm, [catalyst] = 5 μ mol, t_{pol} = 60 min.(b) Activity = [(g_{pol}/mmol_{cat}·h)/P].(c) Determined by ¹³C-NMR.

(d) Determined by SEC.

(e) t_{pol} = 15 min.

and DEPT spectra are presented in Figure 3.

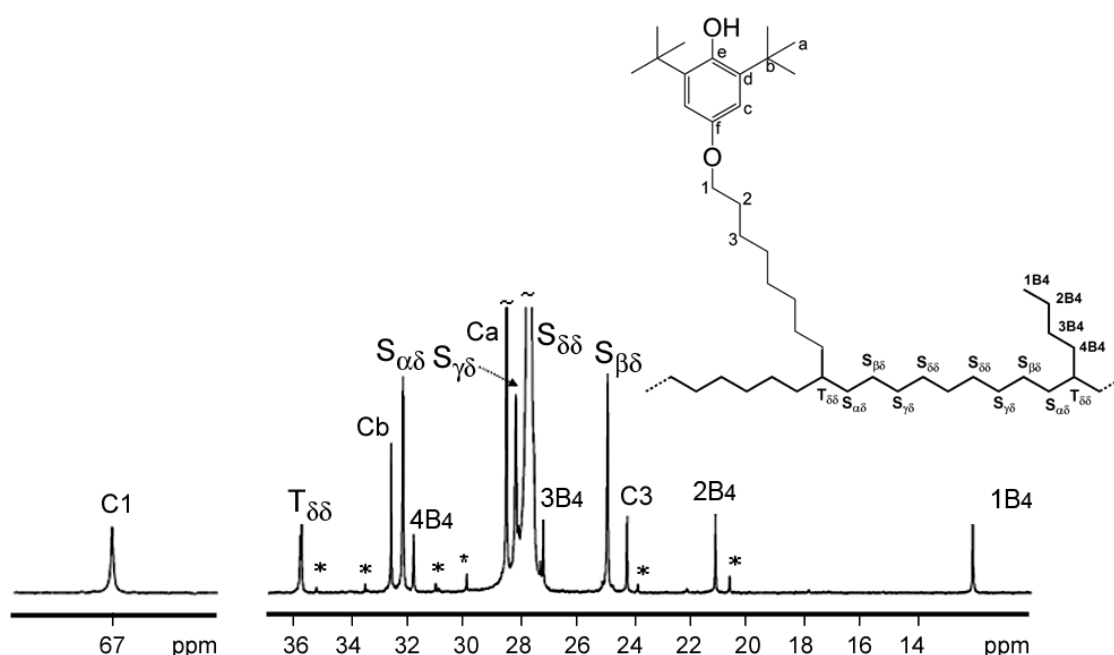
The ¹³C NMR assignment of the copolymers was mainly performed by comparison with the spectrum of the phenolic comonomer (Figure 2), which is particularly useful to assign the signals of C2 and of C4-C6 methylenes, undetectable in the spectra of copolymers due to the overlap with the most intense resonance of polyethylene (CH₂)_n carbons. On the basis of data from literature regarding copolymers of ethylene with higher α -olefins, namely 1-hexene [10-12] and 1-octene [13-15] the signals of the carbons of the main chain S _{$\alpha\delta$} , S _{$\beta\delta$} , S _{$\gamma\delta$} , and T _{$\delta\delta$} , diagnosed as inserted comonomer, were easily assigned. No detectable traces of unreacted phenolic comonomers were found in the olefinic region of the spectra. All the resonance assignments are reported in Table 3.

The signals of methylenes C1 and C3 are found the most suitable for exact evaluation of **C8** comonomer content.

Ethylene/1-hexene/C8 terpolymerization

The terpolymerizations of ethylene with 1-hexene (**1-H**) and **C8**, as well as the reference copolymerization of ethylene with **1-H**, were conducted with MAO-activated **EBTHI**. The polymerization conditions and the procedure adopted to protect the oxygen atoms of the comonomer in order to prevent catalyst deactivation are the same as described in the previous section. The polymerization data along with the microstructural and molecular characterization of the polymers are presented in Table 4.

First of all, a few copolymerizations of ethylene with

**Figure 4.** Aliphatic region of ¹³C NMR spectrum of ethylene/**1-H**/**C8** terpolymer (run 7, Table 4)

1-H have been carried out to settle the copolymerization conditions suitable to obtain 3-4 mol% incorporation of **1-H**. The settled conditions are those of run 6. $[C_2H_4]/[C8]$ ratio equal to 6.95 was possibly chosen to obtain **C8** incorporation of 0.5~1 mol% (run 2, Table 2).

The chosen $[C_2H_4]/[C8]$ and $[C_2H_4]/[1-H]$ feed molar ratios gave unexpected results in the terpolymerization (run 7): with respect to the above given reference copolymerizations, where the 1-hexene content decreases and, surprisingly, the **C8** content shows an about three-fold increase. To obtain the desired results a lower amount of **C8** was used (run 8). We considered such result quite advantageous since it allowed for notable saving of the synthesized comonomer. We account for this phenomenon with the consideration that the presence of comonomer **1-H** solubilizes the chain segment bound to the catalytic complex, thus favouring an easier access of the bulky **C8** comonomer to the active centre.

The comonomer contents of the co- and terpolymers were determined by ^{13}C NMR analysis: the spectrum of the terpolymer at higher comonomer content (run 7,

Table 4) is presented in Figure 4.

The ^{13}C NMR assignment of the terpolymers was performed by comparison with the spectrum of the phenolic comonomer **C8** (Figure 2 and Table 1) and with the spectra of the corresponding copolymers, namely ethylene/**1-H** (run 6 in Table 4), and ethylene/**C8** copolymer (Figure 3 and Table 3). All the resonance assignments are reported in Table 3.

Propylene/**C8** copolymerization

The copolymerizations of **C8** with propylene (P) were conducted in the presence of the same MAO activated **EBTHI** catalyst, chosen on the basis of the same considerations reported in the previous sections. Moreover, **EBTHI** as being prevalently an isospecific catalyst, allowed polypropylene copolymers with isotactic microstructure being obtained similar to that of commercial “polypropylene” grades. The same concepts of the ethylene-based copolymerizations were applied in propylene-based copolymerizations: reduced propylene gas pressure (0.5 atm) was adopted to favour the bulky comonomer insertion. The

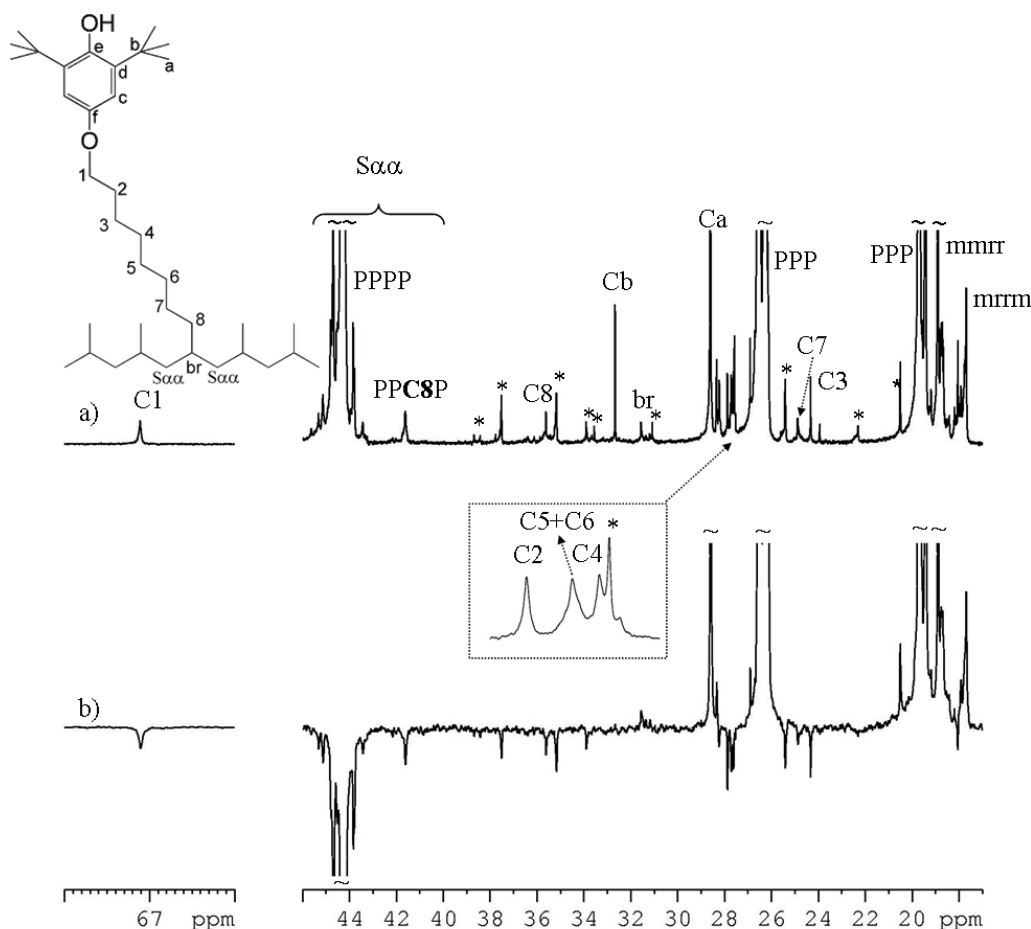


Figure 5. Aliphatic region of (a) 1H -decoupled ^{13}C NMR and (b) DEPT-135 spectrum of run 12 in Table 3

Table 5. Copolymerization of propylene with **C8** catalyzed by **EBTHI/MAO** catalytic system^(a)

Run	C8 mmol	[C ₃ H ₆]/[C8]	Yield (g)	Activity ^(b)	C8 ^(c) mol%	C8 conversion	M _n ^(d) g/mol	M _w /M _n ^(d)
9 ^(e)	-	-	0.617	2468	-	-	5700	1.64
10	0.24	389.5	0.910	910	0.27	23	3500	1.71
11 ^(f)	0.36	259.7	1.061	848	0.58	39	3900	1.79
12	0.48	186.9	0.662	662	1.09	33	4500	2.14

(a) Polymerization conditions: solvent = toluene, total volume = 100 mL, Al/Zr = 3000 (mol/mol), $t_{\text{pol}} = 60$ min, $T = 35^{\circ}\text{C}$, $P_{\text{propylene}} = 0.5$ atm, [catalyst] = 2 μmol .

(b) Activity = [(g_{pol}/mmol_{cat}·h)/P].

(c) Determined by ¹³C-NMR.

(d) Determined by SEC.

(e) $t_{\text{pol}} = 15$ min.

(f) [catalyst] = 5 μmol , $t_{\text{pol}} = 30$ min.

polymerization data along with the microstructural and molecular characterization of the copolymers are presented in Table 5.

In a typical copolymerization of **C8** with ethylene, the [C₂H₄]/[**C8**] ratio in the polymerization mixture required a **C8** content of about 1 mol% is 2.61 (run 3, Table 2), whereas the [C₃H₆]/[**C8**] ratio required to obtain the same **C8** content in the propylene-based copolymer was 186.9 (run 4, Table 2). This is to say that **C8** must have been about 70 times more reactive in copolymerization with propylene than with ethylene. Propylene is likely less competitive with **C8** in coordinating on the active site than the smaller ethylene. However, in our opinion, the solubility of

the polypropylene chain linked to the active site and as a consequence the easier accessibility of **C8** to the polymerization centre is the prevalent factor of the higher reactivity.

The comonomer content of the copolymers was determined by ¹³C NMR analysis: the ¹³C NMR spectrum of the copolymer of run 12 in Table 5 is shown in Figure 5 together with the corresponding DEPT-135 spectrum.

The ¹³C NMR assignments were mainly performed (i) by comparison with the spectrum of the phenolic comonomer (Figure 2 and Table 1), (ii) by comparison with the spectrum of the corresponding ethylene/**C8** copolymer (Figure 3 and Table 3), and (iii) according to literature, in particular, data regarding propylene/1-decene copolymers [16] allowed us to easily assign the C7, C8 methylenes of the branch and the resonances that are diagnosed as inserted comonomer, namely, the tertiary carbon (br) and the centered $\alpha\alpha$ methylene of the PPC8P sequence. The DEPT experiment was of great help in confirming the above assignments. The numerous signals starred in the spectrum of Figure 5a are assigned to a variety of chain-end groups and branches [17] that may be attributed to low propylene pressure adopted in the copolymerization. The complete absence of the signal of **C8C8** homodiad in the S _{$\alpha\alpha$} methylene region confirms that the obtained copolymers contain only isolated comonomer units. No detectable traces of unreacted phenolic comonomers can be found in the spectra of all the copolymers. Beside the resonance of methylene C1, the centered $\alpha\alpha$ methylene of the PPC8P sequence is the most suitable for more precise evaluation of **C8** comonomer content. All the resonance assignments are collected in Table 6.

The thermal behavior of co- and terpolymers

Table 6. ¹³C-NMR chemical shift assignments for propylene/**C8** copolymers

Carbon	Chemical shift (ppm)
Cf	150.12
Ce	145.18
Cd	135.76
Cc	109.96
C1	67.03
S _{$\alpha\alpha$} (PPPP)	44.12
S _{$\alpha\alpha$} (PPC8P)	41.59
C8	33.84-33.64
Cb	32.65
br	31.54
Ca	28.58
C2	27.87
C5+C6	27.69
C4	27.55
PPP	26.56
C7	24.85
C3	24.30
PPP <i>mmmm</i>	19.67
PPP <i>mmmr</i>	19.40
PPP <i>mmrr</i>	18.88
PPP <i>mrrm</i>	17.66

Table 7. Thermal properties of E/C8 and E/1-H copolymers, E/1-H/C8 terpolymers and P/C8 copolymers. The reference data for polyethylene and polypropylene are reported for comparison

Run	E mol%	P mol%	1-H mol%	C8 mol%	T _c ^(a) (° C)	ΔH _c ^(a) (J g ⁻¹)	T _m ^(b) (° C)	ΔH _m ^(b) (J g ⁻¹)
1	100	-	-	-	112	-219	141	222
2	99.5	-	-	0.5	111	-175	131	176
3	99.0	-	-	1.0	107	-162	130	168
4	98.5	-	-	1.5	101	-130	125	139
5	97.0	-	-	3.0	91	-94	109	101
6	95.88	-	4.12	-	87	-122	98	125
7	-	-	1.21	1.27	103	-138	117	138
8	-	-	3.01	0.75	100	-121	115	121
9	-	100	-	-	94	-86	136	95
10	-	-	-	0.27	81	-63	107	74
11	-	-	-	0.58	69	-49	94	60
12	-	-	-	1.09	54	-41	81	47

(a) Determined by DSC on cooling.

(b) Determined by DSC on second heating.

listed in Table 2, 4 and 5 as well as those of the reference polyethylene (**1**) and polypropylene (**9**) homopolymers, was investigated by DSC analysis. Crystallization and melting temperatures (T_c and T_m) and the related enthalpy (ΔH_c and ΔH_m) values are reported in Table 7.

As expected, starting from the reference homopolymers on increasing the comonomer content, a progressive decrease in crystallization temperatures and related enthalpy values is observed upon cooling the specimens from the molten state at a rate of -10°C min⁻¹. A similar trend is observed for the melting temperatures and related enthalpies recorded on heating the samples immediately after the cooling run.

Blends and films

Ethylene-based co- and terpolymers were melt blended in an internal batch mixer with an additive-free commercial LDPE matrix, whereas for propylene-based copolymers an additive-free polypropylene (PP) grade was used as matrix. As detailed in the experimental section, each polymeric antioxidant was added to the proper polyolefin matrix taking into account its composition in order to have a final content of 500 ppm antioxidant functionalities in the resultant blend. Neat LDPE and PP matrices as well as their mixtures with 500 ppm of the BHA antioxidant were treated under the processing conditions chosen for each of the two different systems and used for comparison purposes. Indeed, 500 ppm is a typical amount of commercial low molecular weight antioxidant added in industry to stabilize such kinds of polyolefinic

materials.

Mixing conditions (temperature, rotor speed and residence time) were chosen in order to optimize the dispersion of the macromolecular additives into the polyolefin matrices meanwhile reducing, as much as possible, the oxidative and thermo-mechanical stresses experienced by the polymeric melt. Moreover, the blends were prepared under N₂ overpressure in order to minimize oxidation phenomena, which can occur during the residence time in the mixing chamber.

It is worth noticing that by mixing copolymer samples **4** and **5** with the LDPE matrix the resultant blends consisted of two macroscopically distinct phases, thus indicating that the LDPE matrix and the copolymeric additive became increasingly incompatible when **C8** concentration was relatively high. This phenomenon was not observed in the explored composition range for the blends prepared with the terpolymer as well as the PP-based blends.

TGA analysis

Thermal and thermo-oxidative stability of the LDPE- and PP-based blends containing the synthesized polymeric additives was investigated by TGA measurements, carried out in dynamic mode under nitrogen and oxygen atmospheres.

Under N₂ atmosphere, within each series of investigated samples, the additive-free matrix and its blends with 500 ppm of commercial BHA antioxidant or the proper amount of polymeric antioxidants (as specified in the Experimental) exhibit no remarkable differences in the degradation behavior. Indeed, the

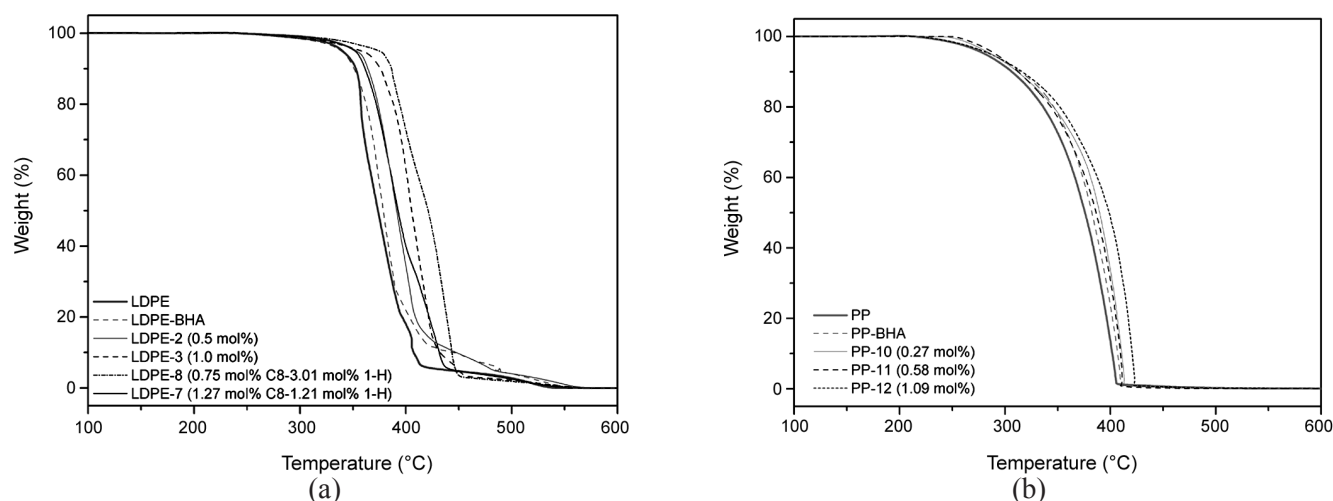


Figure 6. Dynamic TGA curves under O_2 (heating rate $20^\circ C\ min^{-1}$) of (a) LDPE blends and (b) PP blends containing the macromolecular antioxidants. Neat LDPE and PP matrices as well as the matrices containing 500 ppm BHA are also reported for comparison

temperature of the maximum degradation rate was around $512^\circ C$ for the LDPE-based samples and around $492^\circ C$ for the PP-based ones.

Analogous dynamic TGA experiments were also carried out in oxidative atmosphere constituted by pure oxygen. As shown in Figure 6, for all the blends containing the polymeric antioxidants, the degradation process took place at temperatures higher than those observed not only for the neat reference matrices but for the blends containing the traditional BHA antioxidant as well.

In particular, for the LDPE-based blends, as clearly evident from Figure 6a, T_{D25} and T_{D50} values (temperatures at which the sample weight loss is equal to 25 and 50%) are shifted, respectively, at temperatures 12 - $35^\circ C$ and 15 - $45^\circ C$, higher than those observed for neat LDPE and BHA-additive containing samples. From a closer inspection of the TGA curves of Figure 6a, one can observe that between the two copolymeric additives the one containing 1 mol% of **C8** appears to be more effective in protecting the LDPE matrix from thermo-oxidation with respect to the copolymer containing 0.5 mol% of comonomer. Whereas, between the two terpolymeric antioxidants, the higher efficiency towards thermo-oxidation is attained using the additive with 0.75 mol% of **C8** and 3.0 mol % of **1-H**. Thus, this latter finding suggests that the presence of a lower amount of phenolic **C8** pendant moieties together with a higher amount of **1-H** co-units favors a better dispersion of the macromolecular additive in the LDPE matrix.

As for the PP blends, as shown in Figure 6b, the T_{D25} and T_{D50} values are higher of about 8 - $15^\circ C$

and 12 - $25^\circ C$, respectively, compared to the similar temperatures observed for neat PP and its blend with BHA. This result appears quite interesting, also taking into account the intrinsic lower thermo-oxidative stability of polypropylene with respect to polyethylene.

Isothermal TGA experiments were also carried out in pure oxygen atmosphere for all the produced blends. In Figure 7 the resultant isothermal curves are reported for LDPE-(a) and PP-(b) based blends. In both cases the behaviors of neat LDPE and PP matrices as well as their mixtures with 500 ppm of BHA antioxidant are shown for comparison purposes. In Table 8 the measured OIT values are presented.

In Figure 7a it is possible to appreciate that the synthesized terpolymeric additives show a similar behaviour in protecting the LDPE matrix and they

Table 8. Oxygen induction time data of neat LDPE and PP matrices, their blends with BHA and polymeric antioxidants

Samples	1-H mol% ^(a)	C8 mol% ^(a)	OIT (min) ^(b)	OIT (min) ^(c)
LDPE	-	-	2.7	-
LDPE-BHA	-	-	2.9	-
LDPE-2	-	0.5	3.2	-
LDPE-3	-	1.0	4.9	-
LDPE-7	1.21	1.27	3.7	-
LDPE-8	0.75	3.01	4.2	-
PP	-	-	-	1.2
PP-BHA	-	-	-	1.2
PP-10	-	0.27	-	3.1
PP-11	-	0.58	-	3.5
PP-12	-	1.09	-	1.2

(a) Determined by ^{13}C -NMR.

(b) OIT measured at $180^\circ C$.

(c) OIT measured at $220^\circ C$.

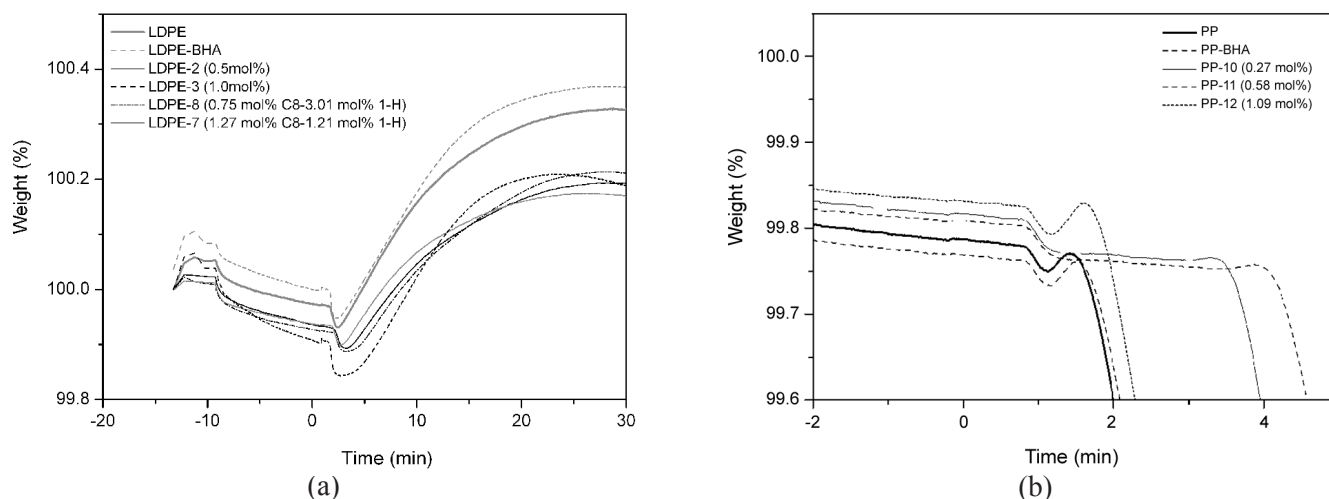


Figure 7. Isothermal TGA curves under O_2 at: (a) 180°C for LDPE blends containing the macromolecular antioxidants, (b) 220°C for PP blends containing the macromolecular antioxidants. Neat LDPE and PP matrices as well as their blends containing 500 ppm BHA are reported for comparison.

are both more effective with respect to commercial BHA antioxidant, which instead leads to an OIT value comparable to that of the neat LDPE matrix. The blend containing the copolymeric additive with 1 mol % of **C8** content (run 3) exhibits the highest antioxidant protection among all the investigated polyethylene-based additives.

As for the PP-based blends, the three containing the polymeric additives consisting of propylene/**C8** copolymers exhibit a higher thermo-oxidative stability with respect to neat PP and its blend with BHA. The best performance is here offered by the copolymer with 0.58 mol % concentration of **C8**. The poor result observed with the blend containing PP-12 shows that, with this family of macromolecular additives, a phenolic comonomer concentration higher than 1 mol% does not allow for an optimal dispersion in the matrix.

It is worth noticing that the gathered results demonstrate, in any case, the very positive effect the polymeric additives have on the degradation onset of the polyolefinic matrix, retarding the thermo-oxidative sequence of reaction. The fact that neat matrices and BHA-containing matrices have similar overall degradative behavior can be ascribed by the loss of low molecular weight additive, that can occur during preparation of the film specimen by compression moulding and/or during the TGA heating run by diffusion of BHA toward the specimen surface and its subsequent evaporation. This assumption was also verified by Tocháček, who measured significant weight losses of different stabilizers in polypropylene sample added with commercial non-polymeric antioxidants

during their exposure at elevated temperatures due to their volatilization [18].

Photoaging test

The effect of UV-visible light was evaluated on films from PP-based blends containing the synthesized polymeric additives when exposed to air, that is in the presence of 21% of oxygen. Although the short exposure, the lighting led to some modifications in the FTIR spectra of the PP-based films (Figure 8).

In particular, it can be seen that there are bands in two regions of the spectrum that have changed-time. In the 3600-3100 cm^{-1} range a wide peak appeared due to hydrogen-bonded hydroperoxides, while a band in the range between 1850 and 1600 cm^{-1} was attributed to the carbonyl group stretching. It is well known that the formation of the carbonyl group is very useful to follow the polypropylene degradation. Polypropylene,

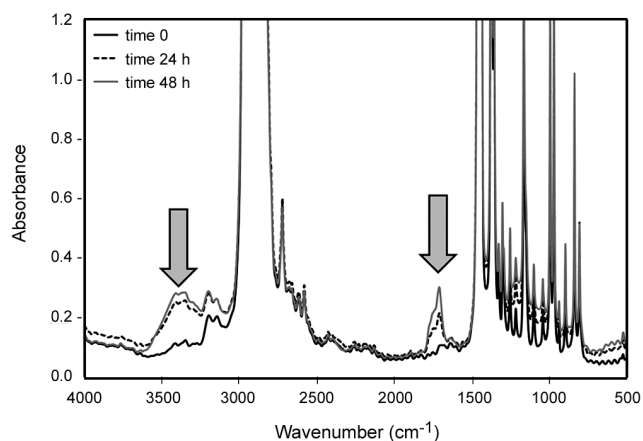


Figure 8. Particular of the spectrum of the PP-based film containing the polymeric additive of run 12 during photoaging

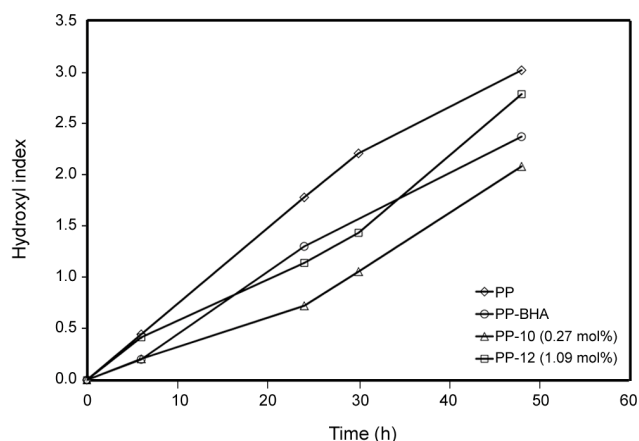


Figure 9. Hydroxyl and carbonyl index evolution during exposition

in fact, is very sensitive to photo-oxidation: during exposure it becomes more brittle and its color changes rapidly. The rising of the background around 1300-700 cm^{-1} is attributed to the absorption of degraded polypropylene products which are difficult to be analyzed [19-20].

In Figure 9 the evolution of hydroxyl and carbonyl indexes is shown for the tested PP-based films. The increase of hydroxyl index was linear over time while the carbonyl index changed slowly during the first hours, especially when the additive was present. The sample with the additive containing 1.09% of **C8** (run 12) showed a behavior similar to BHA-containing PP. Between the two new additives it seemed that the copolymer with comonomer concentration of 0.27 mol% (run 10) was the most efficient against photo-degradation of the PP matrix.

CONCLUSION

A novel and more efficient route was designed for the synthesis of a functionalized comonomer analogous to commercial 2,6-*t*-butyl-4-methoxyphenol (BHA) antioxidant containing eight methylene units as spacer between the aromatic ring and the polymerizable olefinic double bond (**C8**).

Starting from previous results concerning ethylene/**C8** copolymers, we prepared a few samples of ethylene/1-hexene/**C8** terpolymer with 1-hexene concentration in the typical range found in commercial polyethylene grades. Such terpolymers are specifically designed to protect the important family of polyethylene-based food contact materials that are known to essentially consist of copolymers

of ethylene with a small content of a higher α -olefin.

A small series of copolymers of propylene with controlled amount of comonomer **C8** were prepared as well, aimed to stabilize the likewise important family of propylene-based food contact materials, commonly employed for packaging of fresh vegetables and fruit.

A carefully and exhaustive ^{13}C NMR structural determination was carried out to quantify the comonomer content in the co- and terpolymers: such analysis allowed us to identify all the produced copolymer compositions as random co- and terpolymers with isolated **C8** comonomer unit and to exclude the presence of unreacted comonomer.

With respect to the starting ethylene/**C8** copolymers, the novel terpolymers and polypropylene copolymers clearly present a few advantages:

- (i) All the samples are well soluble in common organic solvents and are consequently more easily characterizable by NMR and SEC compared to ethylene/**C8** copolymers.
- (ii) Even more interestingly, the solubility of the terpolymer and polypropylene growing chain linked to the active sites make them more accessible for the bulky **C8** comonomer. A more advantageous comonomer conversion is thus obtained, accompanied by a noticeable saving of the precious synthesized comonomer.

The suitability of these new polymeric stabilizers designed for commercial polymeric materials is demonstrated by the positive improvement of the thermal and thermo-oxidative stability of their blends with LDPE- and PP-matrices. Indeed, for all the blends containing the synthesized polymeric antioxidants the degradation process takes place at temperatures higher than those observed not only for the neat reference matrices but for the blends containing the traditional BHA antioxidant as well. This implies that, the usual practice of overloading plastics with antioxidants to prevent their loss during processing can be avoided, or at least reduced, by following the proposed approach, since the polymeric additives cannot, in principle, be released from the polymer matrix.

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BOSs): design and preparation of lasting polyolefin films with no risk of food contamination and degradation". The authors warmly thank Mr. Giulio Zannoni who expertly performed all the NMR spectra and Mr. Daniele Piovani for helpful contribution to SEC analysis.

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