Macromolecular Non-Releasing Additives for Commercial Polyolefins

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Summary: Four comonomers bearing a highly efficient phenolic antioxidant unit and different distance between the antioxidant moiety and the double bond have been prepared and tested in co-polymerization with ethylene by means of three selected metallocene based catalysts. The possibility to obtain a masterbach suitable for melt blending with commercial polyolefins has been evaluated by modifying: i) the structure of the functionalized comonomer, ii) the kind of catalyst, iii) the polymerization conditions. The pair *rac*-[Me_2Si-(2-Me-4,5-BenzInd)$_2$]$ZrCl_2$ catalyst and comonomer with the longest spacer (8 methylene units) allowed the highest comonomer incorporation, while with *rac*-(EBTHI)$ZrCl_2$ catalyst the highest polymerization activity was observed. TGA analysis has been carried out on some of the copolymers in order to investigate the influence of type and amount of the comonomer on their thermal stability and to test the efficiency of the antioxidant group both in nitrogen and oxygen atmosphere.

Keywords: antioxidant additive; copolymerisation; functionalized comonomer; metallocene; polyolefins

Introduction

Due to their peculiar sealing properties, their low cost and low reactivity, polyolefins are the plastics most frequently used as food contact materials. The disadvantages with polyolefins are in that they are products quite sensitive to oxidation and require to be stabilized by melt blending with an antioxidant additive to inhibit or retard degradation.[1] The vast majority of commercial antioxidants are low molecular weight derivatives of sterically hindered monohydroxy phenols.

In Scheme 1 some examples of commercial antioxidants containing the 2,6-di-*t*-butylphenol units, including Butyl Hydroxyl Toluene (BHT) and Butyl Hydroxyl Anisole (BHA), are shown.

Since their chemical structure is quite different from that of the non polar polymer matrix, two problems can be envisaged: i) the poor compatibility or solubility of the antioxidants into the polyolefin matrix, which can induce aggregation of the stabilizers and hence a heterogeneous distribution; ii) the mobility and volatility of the antioxidants, that can lead to their physical loss by migration or diffusion from the polyolefin matrix.

Numerous efforts have been made to solve the problems due to migration as well as to volatility and extraibility of stabilizers by chemically linking the antioxidant additives to the polymeric matrix.[2] Since the early seventies a series of patents reports on the copolymerization of derivatives of BHT bearing the polymerizable double bond with olefins under Ziegler-Natta-type catalyst conditions.[3] The copolymerization of propylene with stabilizing

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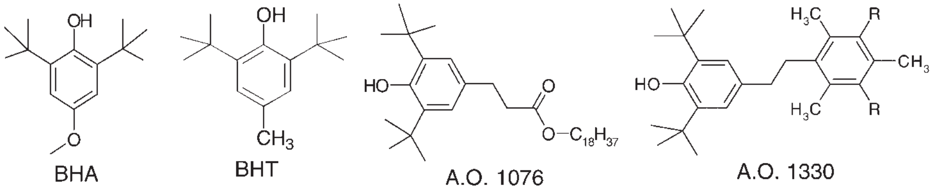


Scheme 1.

comonomers, such as 4-(ω-alkenyl)-2,6-di-*t*-butylphenol, with different number of methylene units as spacer between the double bond and the phenol moiety, was conducted by using a supported highly active Ziegler-Natta catalyst.[3] However the poor incorporation of bulky comonomers with traditional heterogeneous Ziegler-Natta catalytic systems and the decrease of catalytic activity due to catalyst poisoning by the polar comonomer were detrimental to the application of such polymerization processes.

More recently, Wilén and co-workers succeeded in the achievement of good yields of copolymers with high thermooxidative stability by copolymerizing ethylene and propylene with the comonomer moiety [6-*t*-butyl-2-(1,1-dimethylhept-6-enyl-9,4-methylphenol)] over a number of different metallocene catalysts.[4] A limitation to the applicability of such an interesting process relies in the fact that most commercial polyolefin materials are still produced with traditional heterogeneous catalysts, only capable to incorporate linear conventional comonomers.

This consideration was at the origin of the present work, whose aim is to develop copolymers at tuned content of a comonomer bearing an antioxidant group to be employed as macromolecular additives for commercial polyolefin products. This idea appears appealing for the wide range of possibility offered by metallocene catalysis, and for the opportunity to use the low cost polyolefins commercially available added with the novel macromolecular antioxidants.

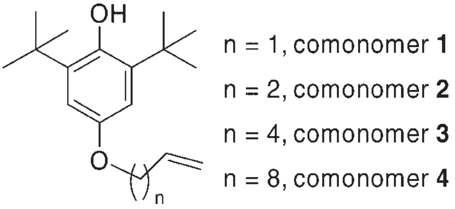
In this paper, the first results of a research aimed at obtaining polymeric antioxidant additives, to be used as masterbatch in the melt blending with commercial polyolefin materials are presented. The strategy consists in finding the optimized combination of: i) structure of the functionalized comonomer, i) kind of catalyst, iii) polymerization conditions, to obtain the incorporation of considerable amounts of an efficient antioxidant group along the polyethylene chain, while avoiding a too detrimental effect on polymerization yield.

Results and Discussion

Choice of the Stabilizing Comonomers

In all the previous works only comonomers derived from Butyl Hydroxyl Toluene (BHT) have been used since they are known as polymerization activity enhancers, due to the ability of the phenolic monomer to stabilize the cationic polymerization center.[5] Nevertheless we have decided to explore the copolymerization of ethylene with comonomers derived from BHA, for the reason that BHA shows a higher antioxidant activity compared with BHT. Indeed, the measured O–H BDE (Bond Dissociation Enthalpy) for BHT and BHA are 81 and 78 kcal/mol,[6] while their k_{inh} in the auto-oxidation of hydrocarbons (like styrene) are 1×10^4 and 3×10^5 mol^{-1}s^{-1}, respectively.[7,8] This ensures a much better ability in scavenging radical species of BHA than BHT, and hence a superior ability in protecting the polyolefin materials from oxidation.

Four novel comonomers bearing the same antioxidant group, with different distance between the antioxidant moiety and the double bond, have been synthesized, namely 4-allyloxy-2,6-di-*t*-butylphenol (**1**), 4-but-3-enyloxy-2,6-di-*t*-butylphenol



Scheme 2.

(**2**), 4-hexa-9-enyloxy-2,6-di-*t*-butylphenol (**3**) and 4-dec-9-enyloxy-2,6-di-*t*-butylphenol (**4**) (Scheme 2).

Copolymerization of Ethylene with Phenolic Comonomers

The research of the optimized polymerization conditions was conducted by using the phenol BHA, to verify if and to what extent the methoxy group could act as a catalyst poison. *rac*-(EBTHI)$ZrCl_2$ (**a** in Figure 1) was first chosen among the possible metallocene complexes, being a classical well known catalyst with good capability of inserting bulky comonomers.

To maintain controlled and reproducible the polymerization conditions, "*dried*" MAO, characterized by a low content of free TMA, was used as a cocatalyst. Triisobutylaluminium (TIBA) was used to prevent the catalyst deactivation: the phenol was pretreated with 2 equivalents of TIBA, in order to protect the hydroxy group and interact with the ether oxygen.[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 1 reports the polymerization results along with the microstructural and molecular characterization of copolymers.

The results show that, under our conditions, the presence of BHA does not

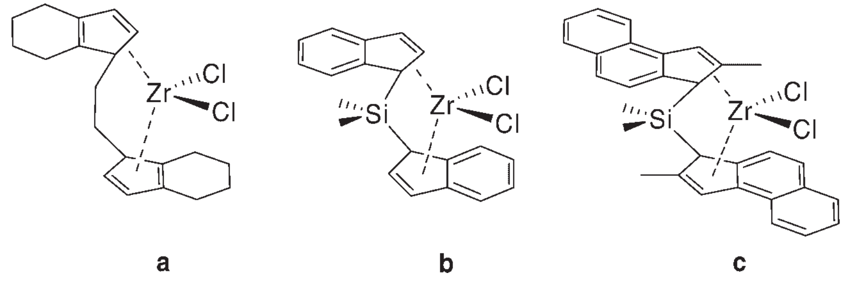


Figure 1.
(a) *rac*-(EBTHI)$ZrCl_2$, (b) *rac*-[$Me_2Si(Ind)_2$]$ZrCl_2$ and (c) *rac*-[Me_2Si-(2-Me-4,5-BenzInd)$_2$]$ZrCl_2$.

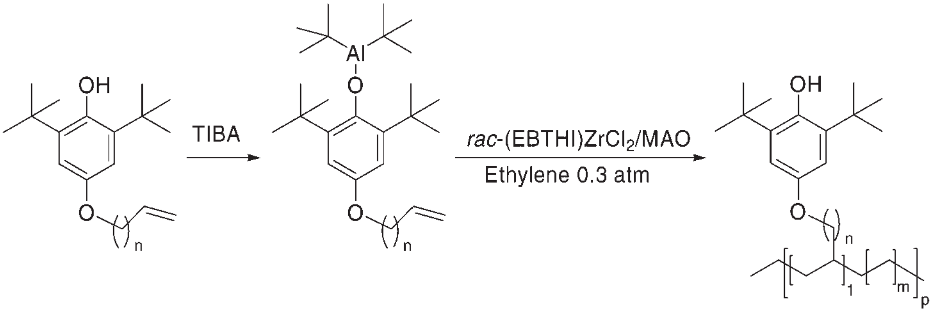
Table 1.
Copolymerization between ethylene and comonomers **1–4** catalyzed by *rac*-(EBTHI)$ZrCl_2$ and MAO as catalytic system[a].

Comonomer	Bound monomer (mol %)	Bound monomer (wt %)	Conversion (%)	Yield (mg)	Activity [(g_{pol}/$mmol_{cat}$*h)/P]	M_w	M_w/M_n
–	–	–	–	133	355[b]	15500	2.1
–	–	–	–	124	331[c]	13900	3.3
1	1	8.6	10.1	305	407	21000	2.8
2	0.2	2.2	0.7	93	124	15200	2.5
3	0.5	5.7	5.2	278	371	26000	2.8
4	3	28.5	26.4	315	413	13500	4.4

[a] Polymerization conditions: solvent = toluene, total volume = 50 mL, catalyst = 5 μmol, Al/Zr = 1500 (mol/mol), t_{pol} = 30 min, T = 35 °C, P ethylene = 0.3 atm, comonomer = 1 mmol, TIBA/comonomer = 2 (mol/mol), [ethylene]/[monomer] = 1.75;

[b] t_{pol} = 15 min; no TIBA;

[c] BHA (2,6-di- t-butyl-4-metoxy-phenol) = 1 mmol, t_{pol} = 15 min.



Scheme 3.

sensibly affect the catalyst activity. The procedure adopted for copolymerization with comonomers **1–4** containing polar groups analogous to BHA was the same as described for BHA (Scheme 3). The copolymerization times (30 minutes) were fixed to obtain a sufficiently low comonomer conversion, in order to prevent the formation of polyethylene chains and to ensure a relatively uniform comonomer distribution.

The results show that the phenolic comonomers influenced the activity of the catalyst in different ways. Comonomers **1** and **4**, with one and eight methylene spacers, gave quite good and similar activities, followed by comonomer **3**. The lowest activity was observed for the comonomer **2** with a two methylene spacer.

The comonomer contents were determined by ^{13}C NMR. The assignment of the chemical shifts of the copolymers is described in Ref.[9] As an example, the ^{13}C NMR spectrum of a copolymer containing comonomer **4** is shown in Figure 2. With comonomer **1** the good activity is accompanied by a relatively low comonomer content. Likely, due to the fact that the distance between the double bond and the functional group is short, the bulky phenol

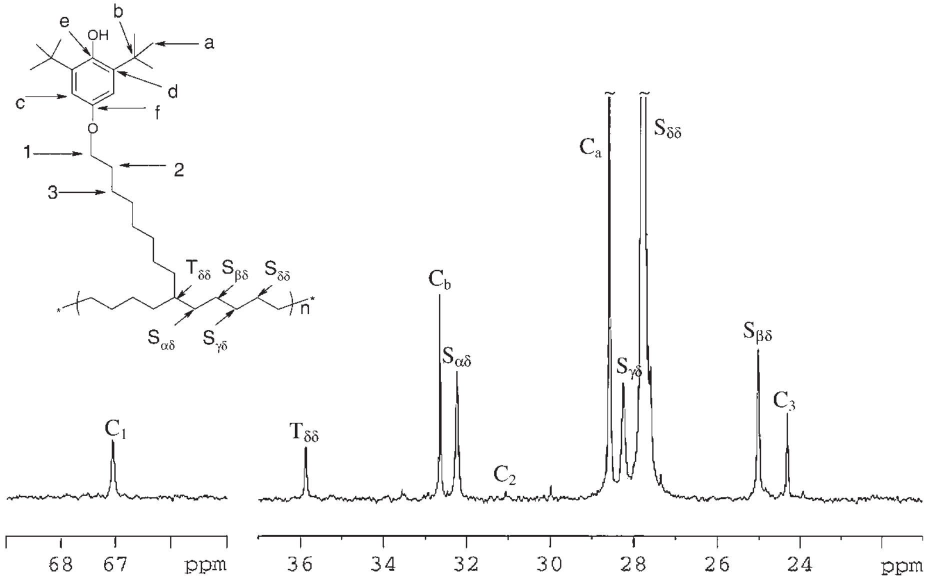
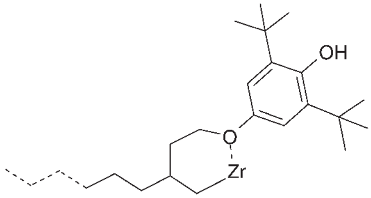


Figure 2.
^{13}C NMR spectrum of ethylene/comonomer 4 copolymer.



Scheme 4.

shields the double bond and reduces its incorporation capacity. Comonomer **4** gives the best compromise between polymerization activity and comonomer content. For what concern the behavior of comonomer **2**, we observed the lowest activity and the lowest comonomer incorporation. Our hypothesis is that, after a comonomer insertion, an intramolecular species is formed in which the ether oxygen atom is coordinated to zirconium. Actually, a six membered ring is generally energetically favored and relatively stable. This species could be a "dormant" or an inactive site from which a chain propagation can not easily occur (Scheme 4).

The behavior of comonomer **3** is the less easy to be accounted for; the yield obtained was indeed reasonable, thus indicating that the ether oxygen does not sensibly inactivate the catalytic site, but, surprisingly, the comonomer content is relatively low.

Copolymerizations with Different Metallocene Catalysts

The copolymerization behaviour of comonomer **4** was also studied in the presence of metallocene catalysts **b** and **c** (see Figure 1) under the polymerization conditions described in the previous section. The results are shown in Table 2, along with the microstructural and molecular characterization.

Differently from what observed with catalyst **a**, with both catalyst **b** and **c** a decrease in catalyst's activity occurs with respect to the homopolymerization. Looking at Table 2 we also observe that, among the three catalysts studied, *rac*-[Me_2Si-(2-Me-4,5-BenzInd)$_2$]$ZrCl_2$ (**c**) gives the highest comonomer incorporation (more than 50% by weight) and, as expected, the highest value of molecular weight. It is worth noting that with all the three catalysts the molecular weight distribution of the copolymers noticeably increases with respect to that of the corresponding homopolymers.

Thermal Stability

The thermal stability of all the copolymers was investigated by thermal gravimetric analysis, TGA, both under nitrogen and oxygen atmosphere, using a heating rate of 20 °C/min. A sample of polyethylene homopolymer prepared under the same polymerization conditions, without any antioxidant added, was used as a reference. The results obtained under nitrogen indicate that, as expected, the stability of the copolymers decreases on increasing comonomer content independently of the type of comonomer, and it is lower than that of the reference homopolymer. TGA curves of some selected samples are reported in Figure 3a.

Table 2.
Copolymerization of ethylene with comonomer **4** catalyzed by different metallocene based catalysts[a].

Catalyst	Bound comonomer (mol %)	Bound comonomer (wt %)	Conversion (%)	Yield (mg)	Activity [(g_{pol}/$mmol_{cat}$*h)/P]	M_n	M_w/M_n
b	–	–	–	177	335[b]	35800	2.2
b	3.0	28.5	31.5	399	213	24000	3.1
c	–	–	–	146	389[b]	63000	3.3
c	8.0	52.8	41.8	428	285	36400	3.9

[a] Polymerization conditions: solvent = toluene, total volume = 50 mL, catalyst = 6 μmol, Al/Zr = 1500 (mol/mol), t_{pol} = 30 min, T = 35 °C, P ethylene = 0.3 atm, comonomer = 1 mmol, TIBA/comonomer = 2 (mol/mol), [ethylene]/[monomer] = 1.75;

[b] t_{pol} = 15 min, catalyst = 5 μmol, no TIBA.

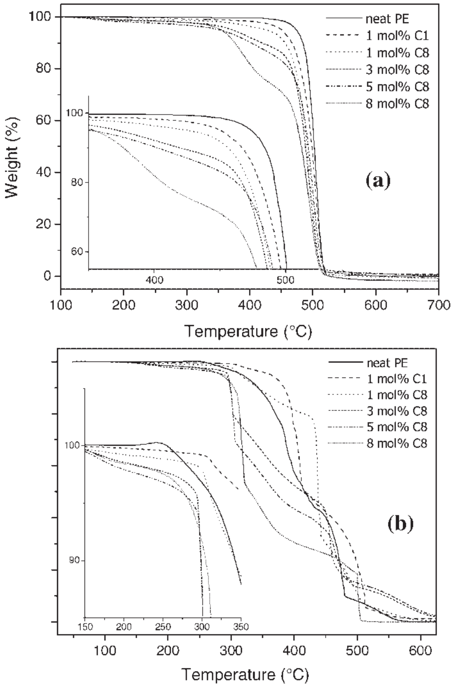


Figure 3.
TGA traces of selected samples: (a) under nitrogen; (b) under oxygen.

Under oxygen atmosphere, the beneficial effect on the copolymer stability is clearly evident at lower comonomer content (up to 1 mol%): indeed, as compared to the homopolymer, which is the only one showing oxygen uptake, the degradation takes place at higher temperature independently of the length of the spacer (Figure 3b). Nevertheless, the shortest spacer seems to be more effective. The degradation profile becomes rather complex on increasing comonomer content.

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