Ethylene/Hindered Phenol Substituted Norbornene Copolymers: Synthesis and NMR Structural Determination

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ABSTRACT: A new family of ethylene-based copolymers with controlled amounts of a norbornene comonomer (N_{ArOH}) bearing a stabilizing antioxidant functionality (2,6-di-*tert*-butyl phenol) was prepared. Due to unavoidable *exo*/*endo* equilibrium operative in N_{ArOH} comonomer, a complete and detailed NMR assignment of the structure of the prepared ethylene/N_{ArOH} copolymers was carried out for the determination of the *exo*/*endo* ratio inside the polymer. These novel functionalized comonomers can be considered suitable starting material for preparing ethylene-based copolymers, with tunable comonomer content, as non-releasing macromolecular antioxidant additives for specific application in safe food and/or drug packaging © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: antioxidants; ethylene/norbornene copolymerization; macromolecular additives; metallocene catalysts; NMR; packaging

INTRODUCTION Any polymer used for food packaging application is neither durable nor processable without antioxidant additives that inhibit or retard degradation.[1,2] Unfortunately, most of the commonly used additives are low molecular weight compounds, more polar than the polyolefin matrices, and consequently they are extractable to some extent into the food due to diffusion and volatility. In the last few years, we carried out a research aimed to propose innovative solutions to the unavoidable physical migration of low molecular antioxidant additives from plastic films used in food or drug packaging.[3–5] Within the frame of such research, the most satisfactory results arose studying new macromolecular antioxidant additives bearing tunable amounts of a selected antioxidant functionality. Specifically, a synthetic route to produce a series of novel comonomers **A–D** bearing a highly efficient phenolic antioxidant unit and different methylene spacers between the aromatic ring and the polymerizable olefinic double bond was devised (Fig. 1).

Comonomers **A–D** were copolymerized with ethylene (E) to obtain copolymers, with a controlled incorporation of the antioxidant group along the polyethylene chain (Fig. 1), which represent a new family of non-releasing macromolecular antioxidant additives to be used as "masterbatches" in blends with commercial polyolefins, for specific application in safe food and/or drug packaging. The crucial point of this approach is to devise feasible synthetic routes for the preparation of comonomers bearing the antioxidant functionality and an easily polymerizable double bond. Norbornene (N) is proved to be an extremely effective monomer in polymerization with metallocene-based catalysts.[6,7] Moreover, literature reports several examples of copolymerizations of ethylene with functionalized norbornene derivatives.[8–13] These amorphous copolymers are strong, stiff, highly transparent materials with very high moisture barrier as well as interesting electrical proprieties that allows their use primarily in applications requiring glass-like clarity. Thus we focused our efforts on the synthesis of a norbornene comonomer (N_{ArOH}) bearing, in *exo* and/or *endo*-position, a hindered phenol (2,6-di-*tert*-butyl-phenol) as a pendant stabilizing substituent. The copolymerizations were then designed to achieve the controlled insertion of the comonomer up to about 2% mol: indeed with higher comonomer concentrations, we have experienced a poor miscibility of the functionalized copolymers with the polyolefinic matrix.[5] In general, *exo*-isomers of substituted norbornene are reported to be more reactive than the *endo*-isomers in the polymerization reaction.[14–16] Therefore, this article discusses stereodefined synthesis of N_{ArOH} comonomer as well as the role of such stereochemistry on the formation of the corresponding ethylene copolymers.

For this purpose, a careful NMR study was conducted on the comonomer and on the prepared copolymers for the

Additional Supporting Information may be found in the online version of this article.

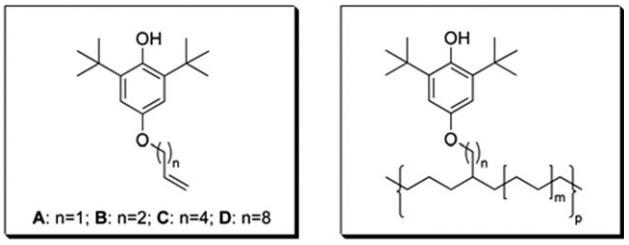


FIGURE 1 Comonomers (**A–D**) and copolymers previously prepared that inspired the present study.

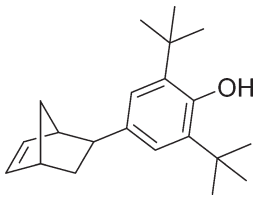
determination of the *exo*/*endo* ratio. Mono- and multidimensional NMR data were either found in the literature for ethylene/norbornene (E/N) or ethylene/functionalized norbornene copolymers[6–13,17–24] or registered on E/N copolymers appositely prepared. The next sections illustrate how NMR data were utilized to achieve the complete assignment of the structure of these new antioxidant pending comonomers and copolymers.

EXPERIMENTAL

Synthesis

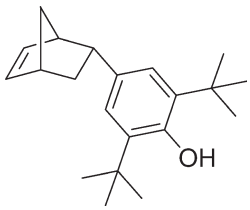
All the reactions were monitored by thin layer chromatography (TLC) on commercially available precoated plates (silica gel 60 F 254) and the products were visualized with acid vanillin solution. Silica gel 60, 230–400 mesh, was used for column chromatography. Unless otherwise noted, ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini 200, Varian Gemini 300, and with a Varian Mercury Plus 400 in $CDCl_3$ solutions. Residual $CHCl_3$ was used as reference at 7.26 and 77.00 ppm. Infrared spectra (IR) were recorded on a FTIR Infrared Spectrometer 1600 Perkin Elmer in KBr pellets or in $CDCl_3$ solutions using a CaF_2 cell. Adsorptions are reported in cm^{-1}. Mass spectra were measured with a Shimadzu QP5050, by FAB (*m*-nitrobenzyl alcohol as matrix) or by electron spray ionization (ESI) using JEOL MS station JMS700. All commercially compounds were used as received, unless otherwise stated and without further purifications.

(exo)-2,6-Di-tert-butyl-4-(bicyclo[2.2.1]hept-5-en-2-yl) phenol (exo-1)



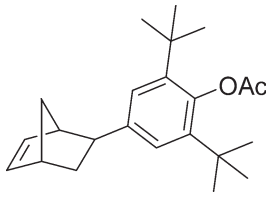
A Schlenck tube was charged with 4-bromo-2,6-di-*tert*-butylphenol (1.27 g, 4.47 mmol) and triphenylphosphine (118 mg, 0.45 mmol) then was evacuated and refilled with nitrogen three times, dry dimethylformamide (DMF) (7 mL) and bicycle[2.2.1]hepta-2,5-diene (norbornadiene) (2.5 mL, 23 mmol) were added through the rubber stopper via a syringe and stirred to dissolve the solid. Palladium acetate (49 mg, 0.22 mmol) was added followed by ammonium formate (1.15 g, 18.32 mmol) and the reaction mixture was stirred at 90°C overnight. The mixture was cooled to room temperature, diluted with dichloromethane (DCM) (200 mL), washed with 0.1M hydrochloric acid (150 mL) and water (3× 150 mL), the organic layer was dried over Na_2SO_4 filtered and concentrated in vacuum. The crude product was purified by flash chromatography on silica gel using 15:1 petroleum ether:DCM as eluent to give the title compound as a colorless oil in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.40–1.44 (m, 1H, H_7), 1.46 (s, 18H, H_f), 1.57–1.63 (m, 2H, H_6, H_7), 1.71–1.76 (m, 1H, H_6), 2.64 (dd, $J = 8.2$, 5.0 Hz, 1H, H_5), 2.84 (bs, 1H, H_4), 2.96 (bs, 1H, H_1), 5.04 (s, 1H, OH), 6.15 (dd, $J = 5.6$, 2.8 Hz, 1H, H_2), 6.26 (dd, $J = 5.6$, 2.8 Hz, 1H, H_3), 7.09 (s, 2H, H_b); ^{13}C NMR (100 MHz $CDCl_3$, δ): 30.4 ($6C_f$), 33.6 (C_6), 34.4 ($2C_e$), 42.2 (C_1), 43.7 (C_4), 45.8 (C_7), 48.7 (C_5), 124.1 ($2C_b$), 135.5 ($2C_c$), 136.4 (C_a), 137.1 (C_2), 137.5 (C_3), 151.6 (C_d); IR (KBr): $\nu = 3639$, 3156, 2957, 1659, 1460.35 cm^{-1}; MS (*m/z* (%)): 298 (2) [M^+], 232 (100), 217 (78), 57 (41). Anal. calcd for $C_{21}H_{30}O$: C 84.51, H 10.13; found: C 84.44, H 10.50.

(endo)-2,6-Di-tert-butyl-4-(bicyclo[2.2.1]hept-5-en-2-yl)phenol (endo-1)



Isolated by flash chromatography after partial RDA/DA equilibration. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.17–1.26 (m, 1H, H_6), 1.33–1.57 (m, 2H, $2H_7$), 1.42 (s, 18H, H_f), 2.14–2.26 (m, 1H, H_6), 2.92 (bs, 1H, H_1), 3.02 (bs, 1H, H_4), 3.24–3.33 (m, 1H, H_5), 4.99 (s, 1H, OH), 5.89 (dd, $J = 5.8$, 2.8 Hz, 1H, H_3), 6.26 (dd, $J = 5.8$, 2.8 Hz, 1H, H_2), 6.95 (s, 2H, H_b); IR (KBr): $\nu = 3639$, 3156, 2957, 1659, 1460.35 cm^{-1}; MS (*m/z* (%)): 298 (2) [M^+], 232 (100), 217 (78), 57, (41). Anal. Calcd for $C_{21}H_{30}O$: C 84.51, H 10.13; found: C 84.44, H 10.50.

(exo)-4-(Bicyclo[2.2.1]hept-5-en-2-yl)-2,6-di-tert-butylphenyl acetate (exo-2)



A Schlenck tube was charged with 4-bromo-2,6-di-*tert*-butylphenyl acetate (1.50 g, 4.58 mmol) and triphenylphosphine (118 mg, 0.45 mmol) then was evacuated and refilled with nitrogen three times, DMF dry (7 mL) and bicycle[2.2.1]-hepta-2,5-diene (norbornadiene) (2.5 mL, 23 mmol) were added through the rubber stopper via a syringe and stirred to dissolve the solid. Palladium acetate (49 mg, 0.22 mmol)

and ammonium formate (1.13 g, 17.88 mmol) were added in sequence and the reaction mixture stirred at 90°C overnight. Then, it was cooled to room temperature, diluted with DCM (200 mL), washed with 0.1M hydrochloric acid (150 mL) and water (3× 150 mL), the organic layer was dried over Na_2SO_4 filtered and concentrate *in vacuo*. The crude product was purified by flash chromatography on silica gel using 2:1 petroleum ether:DCM as eluent to give the title compound as colorless oil in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.350 (s, 9H, H_f), 1.352 (s, 9H, H_f), 1.40–1.44 (m, 1H, H_7), 1.57–1.63 (m, 2H, H_6, H_7), 1.71–1.76 (m, 1H, H_6), 2.34 (s, 3H), 2.67 (dd, J = 8.6, 4.6 Hz, 1H, H_5), 2.88 (bs, 1H, H_1), 2.97 (bs, 1H, H_4), 6.15 (dd, J = 5.6 2.8 Hz, 1H, H_2), 6.26 (dd, J = 5.6 2.8 Hz, 1H, H_3), 7.209 (s, 1H, H_b), 7.210 (s, 1H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 22.7 (1C), 31.5 (6C_f), 33.6 (1C_6), 35.4 (2C_e), 42.2 (1C_1), 43.8 (1C_4), 45.8 (1C_7), 48.3 (1C_5), 125.5 (1C_b), 125.6 (1C_b), 137.3 (1C_2), 137.4 (1C_3), 141.66 (1C_c), 141.68 (1C_c), 142.4 (1C_a), 145.6 (1C_d), 171.2 (1C).

(exo)-2,6-Di-tert-butyl-4-(bicyclo[2.2.1]hept-5-en-2-yl) phenol (exo-1)

Lithium aluminum hydride (0.557 g, 14.66 mmol) was suspended in tetrahydrofurane (THF) (50 mL) under a nitrogen atmosphere at 0°C. A solution of the *exo*-***2*** (1.634 g, 4.79 mmol) in THF (50 ml) was added to the suspension and the mixture was refluxed for 16 h. A solution 0.1M of hydrochloric acid (200 mL) was added to the reaction mixture under ice cooling and extracted with DCM (3× 150 mL), the combined organic layers were dried over Na_2SO_4 filtered and concentrated in vacuum to afford *exo*-**1** as a colorless oil in 98% of yield.

X-Ray Analysis

(*exo*)-4-(bicyclo[2.2.1]Hept-5-en-2-yl)-2,6-di-*tert*-butylphenyl acetate (*exo*-**2**): $C_{23}H_{32}O_2$, M = 340.49, Monoclinic, space group *P21/c*, a = 9.821(1), b = 17.719(1), c = 12.742(1) Å, β = 111.41(1)°, V = 2064.3(3) Å^3, Z = 4, D_c = 1.096 mg/m^3, μ = 0.68 mm^{-1}, F(000) = 744, experiment T = 293 K. 13,203 reflections were collected with a 4.31< θ < 29.34 range; 4850 were independent; the parameters were 226 and the final R index was 0.0935 for reflections having $I>2\sigma I$. The non-hydrogen atoms were refined anisotropically. Aromatic, methylic, methylenic, and methynic hydrogens were assigned in calculated positions, all of them were refined as isotropic.

X-ray analysis was carried out with a Goniometer Oxford Diffraction KM4 Xcalibur2. Graphite-monochromated Mo/Kα radiation (40 mA/−40 kV) and a KM4 CCD/SAPPHIRE detector were used for cell parameter determination and data collection. The integrated intensities, measured using the ω scan mode, were corrected for Lorentz and polarization effects.[25] The substantial redundancy in data allows empirical absorption corrections (SADABS[26]) to be applied using multiple measurements of symmetry-equivalent reflections. The structure was solved by direct methods of SIR2004[27] and refined using the full-matrix least squares on F^2 provided by SHELXL97.[28]

The X-ray CIF file for this structure has been deposited at the Cambridge Crystallographic Data Center with the deposition number *CCDC 857071*. Copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (e-mail: deposit@ccdc.cam.ac.uk; internet://www.ccdc.cam.ac.uk).

Copolymerization

All experiments and manipulations involving air-sensitive compounds were carried out under a dry nitrogen atmosphere in a glovebox apparatus or 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, in solution of toluene) was used as received. *rac*-Et(Ind)$_2$ZrCl_2 was kindly provided by Basell Poliolefine Italia S.r.l. Toluene was dried and distilled from sodium under nitrogen atmosphere. Nitrogen and ethylene gases were dried and deoxygenated by passage over columns of $CaCl_2$, molecular sieves, and BTS catalysts.

Typical Copolymerization Procedure

The copolymerizations were performed in a round-bottom flask at 25°C and 0.5 atm of ethylene gas pressure. The total volume of toluene (100 mL) was introduced into the evacuated and N_2 purged flask. The synthesized comonomer was added with TIBA (ratio between TIBA and comonomer = 1.2) and the solution was stirred for 2 h under N_2 pressure. Afterward the flask was filled with 6 mmol of MAO solution, 2 μmol of the catalyst (ratio between Al and Zr = 3000), and ethylene at 0.5 atm pressure (ratio between ethylene and the comonomer = 6.67), maintained with the correct proportion of N_2 and ethylene gas in the flask. The copolymerization was stopped after 30 min, through the addition of ethanol and 37% hydrochloric acid. The reaction product was stirred for several hours then filtered, washed with ethanol, and dried in vacuum.

Reduction of Copolymer E/N_{ArOAc}

In a flat-bottom PE syringe, equipped with sintered Teflon filters, copolymer E/N_{ArOAc} (41 mg, loading 1.36% mol) was pre-swelled in dry THF (1 mL) for 6 h, then $LiAlH_4$ (38 mg) was added and the suspension was swelled at room temperature overnight. The reaction mixture was purred into ice and 0.1M aqueous solution of hydrochloric acid and filtered through the syringe which was equipped with Teflon tubing and valves to wash under suction with THF, EtOAc, DCM (3× 20 mL each). The resulting copolymer was dried under vacuum over KOH pellets. We verify the formation of the required copolymer E/N_{ArOH} by comparison of the corresponding FTIR spectra (see Supporting Information).

NMR Analysis

^{13}C NMR spectra of comonomer was recorded in $CDCl_2CDCl_2$ at 28°C and 103°C on a Bruker Avance 400 spectrometer operating at 100.58 MHz, internal chemical shift reference: 1% hexamethyldisiloxane. Conditions: acquisition time 1.80 s; relaxation delay 16 s. All the copolymers were recorded in $CDCl_2CDCl_2$ at 103°C. Conditions: 10 mm probe; 90° pulse angle; 64 K 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 τ_1-90°-τ_2-180°, 90°-τ_2-135°, 180°-τ_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 ^{1}H, respectively.

Two dimensional NMR parameters: 90° pulse widths for ^{1}H and ^{13}C were 6.95 and 13.90 μs respectively; relaxation delay, 1.2 s; gradient heteronuclear single quantum coherence (gHSQC) experiments were carried out with a delay of 1.67 ms corresponding to a $^{1}J_{CH} = 150$ Hz, for the creation of antiphase magnetization. Data were zero filled and weighted with a shifted sinebell function before Fourier transformation.

gHMBC experiments, with a two-fold low pass J-filter, to suppress one-bond correlations, were carried out with a delay of 100 ms for the evolution of long-range coupling and delays corresponding to $^{1}J_{CH}$ values of 130 and 160 Hz, for the creation of the antiphase magnetization.

On the basis of the proposed assignments, the N_{ArOH} content in the produced copolymers was calculated by the following equations:

$$N_{ArOH}\ (\text{mol\%}) = \frac{[N_{ArOH}]}{[N_{ArOH}] + [E]} \times 100$$

$$N_{ArOH}\ (\text{mol\%}) = \frac{\bar{I}_{NArOH}}{\bar{I}_{NArOH} + \bar{I}_{E}} \times 100 \quad (1)$$

$$\bar{I}N_{ArOH} = \frac{1}{21}\left[\sum_{n=1}^{21}(I_{nx} + I_{nn})\right] \quad (2)$$

where I_{nx} indicates the area of the signal of the carbon n of the *exo* isomer and I_{nn} the area of the signal of carbon n of the *endo* isomer.

In particular:

$$\bar{I}N_{ArOH} = (I_{7x} + I_{7n}) \quad (3)$$

For the above equation, the signals of the *exo–endo* pair of C_7 methylene carbon are chosen as being the only ones not overlapped with other signals.

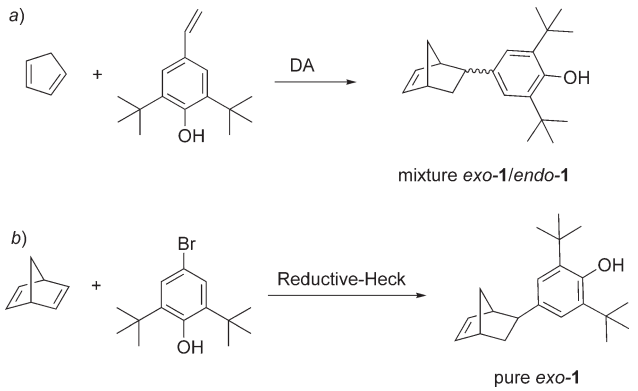
$$\bar{I}_{E} = \frac{1}{2} I_{E} \quad (4)$$

where I_E is the total area of methylene peaks, from 28.12 to 27.40 ppm. Due to the overlap of $S_{\alpha\delta}$, $S_{\gamma\delta}$, and γB_1, the intensities of such peaks can be separated using the following expression that involves the correlation between integrated peak areas of signals of sequences linked by stoichiometric relationships ($\beta B_1 = \gamma B_1$):

$S_{\alpha\delta} + S_{\gamma\delta}$ = area of the peak at 28.12 ppm—area corresponding to βB_1 peak at 25.18 ppm.

Molecular Analysis

Molecular mass and molecular mass distributions were determined by using a GPCV2000 system from Waters, equipped with a differential refractometer. The column set was composed of three mixed TSK-Gel GMHxl-XT columns from Tosohaas (mobile phase *o*-dichlorobenzene; temperature 145.8°C; flow rate 0.8 mL/min; injection volume 300 mL). Universal calibration with polystyrene standards was used.



SCHEME 1 Alternative available access to comonomer N_{ArOH} **1**.

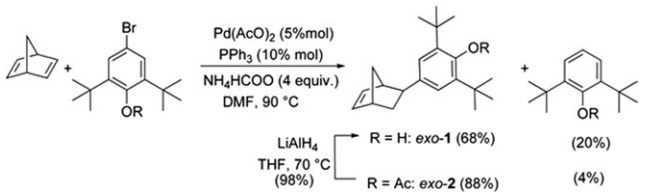
RESULTS AND DISCUSSION

Synthesis of 2,6-Di-*t*-butyl-phenol-norbornene comonomers

We focused the synthetic efforts to the preparation of (*exo*)-2,6-di-*tert*-butyl-4-(bicyclo[2.2.1]hept-5-en-2-yl)phenol, indicated as *exo*-**1** thereafter, since it bears a 2,6-di-*tert*-butyl substituted phenol that ensures an high antioxidant protection and it possesses the correct *exo* geometry for an efficient participation to polymerization.[14–16] Indeed, *exo*-**1** was inspired to BHT (butylated hydroxy toluene, i.e., 2,6-di-*tert*-butyl-4-methylphenol) an antioxidant additive world-widely used, for the protection of, *inter alia*, plastic materials toward oxidative damage.

The synthesis of *exo*-**1** can be envisaged either via a Diels–Alder (DA) reaction of cyclopentadiene with the proper styrene (Scheme 1, path a) or via a reductive Heck cross-coupling of norbornadiene with 2,6-di-*tert*-butyl-4-bromophenol (Scheme 1, path b). While a mixture of *exo*-**1** and *endo*-**1** is expected using a DA procedure, literature data[29,30] support the use of a reductive Heck reaction for achieving the complete control of the *exo* stereochemistry of norbornadiene arylation (Scheme 1).

Commercially available 2,6-di-*tert*-butyl-4-bromophenol was reacted in DMF at 90°C with an excess of norbornadiene in the presence $Pd(AcO)_2$ and PPh_3 (5% and 10% mol, respectively), using 4 equiv. of ammonium formate as reducing agent (Scheme 2). After 24 h, we observed the complete reaction of the starting bromide and the formation of the adduct *exo*-**1** (*vide infra*) as the sole isomer, regrettably, contaminated by a significant amount (≈ 20%) of 2,6-di-*tert*-butylphenol, formed as the result of a competitive reductive de-bromination. This process, not reported in the case of unsubstituted 4-halophenols,[29,30] is particularly critical since



SCHEME 2 Reductive-Heck preparation of *exo*-**1** and *exo*-**2**.

the two products are very difficult to separate. Considering the high nucleophilicity of the aromatic ring as one of the possible reasons of the observed de-bromination, the procedure was repeated under the same reaction condition but with the *O*-acetylated 2,6-di-*tert*-butyl-4-bromophenol as starting material. Positively, the corresponding *O*-acetylated norbornene adduct **2** (N_{ArOAc}) was obtained in good yields, with only trace amounts ($\approx$ 4%) of the corresponding debrominated derivative, yet again as single *exo* diastereoisomer (Scheme 2).

Lithium aluminum hydride reduction of the acetyl group of *exo*-**2** and silica gel column chromatography allowed the isolation of *exo*-**1** as pure compound (*vide infra*). The *exo* geometry of N_{ArOH} and N_{ArOAc} was demonstrated by comparison of their spectroscopic data with those of similar derivatives available in the literature.[31] Moreover, it was possible to obtain suitable crystals of *O*-acetylated *exo*-**2** to run a X-ray analysis which definitely demonstrated the *exo* geometry of compounds deriving from the reductive Heck reaction (Fig. 2).

Interestingly, we were able to point out how compound *exo*-**1** was not stereostabile on standing, since variable amount of the *endo*-**1** isomer, along with other minor by-products, are formed keeping *exo*-**1** either in solution or as pure compound. Such behavior was not observed in *exo*-**2** that was configurationally stable for months. Most likely, this phenomenon is caused by a retro Diels–Alder (RDA)/DA process that occurs from both free phenolic isomeric derivatives *exo*-**1** and *endo*-**1** and foresees the formation of cyclopendadiene and 2,6-di-*tert*-butyl-4-vinylphenol as reactive intermediates (Schemes 3 and 1a).

Literature data on the peculiar electronic characteristics, and consequential attitude to RDA processes, of norbornene-based cycloadducts,[32] as well as the well-known anionic RDA acceleration,[33,34] which in this case can be effective only on phenolic compounds **1** but not on ester **2**, corroborate our hypothesis. Indeed, comonomer *exo*-**1**, obtained as single stereoisomer by reduction of the corresponding acetylated

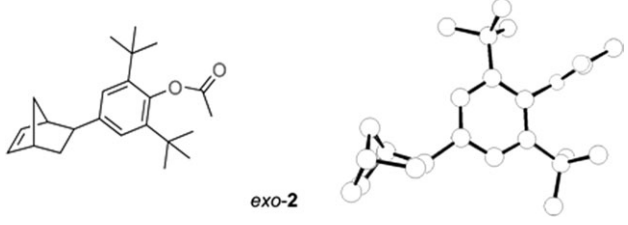
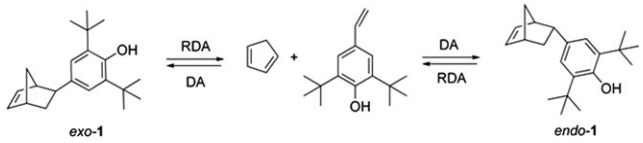


FIGURE 2 X-ray structure of *exo*-**2** (N_{ArOAc}).



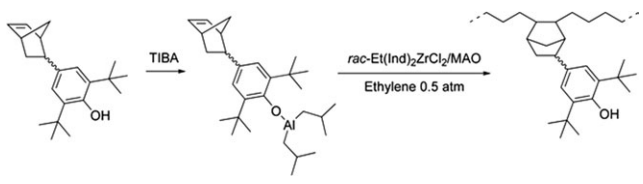
SCHEME 3 RDA/DA mediated stereolability of *exo*-**1**.

derivative *exo*-**2** as described in Scheme 2, undergoes an unavoidable isomerization that, depending on the storage period and conditions, causes the formation of variable amounts of the *endo*-**1** stereoisomer. As a matter of fact, the copolymerizations described in the next section were carried out using two different samples of comonomer **1**, namely a 1.1/1 and a 6/1 mixture of *exo*/*endo* isomers respectively as verified registering the ^{1}H NMR just before to run the copolymerization. Once the double bond of *exo*-**1** (or *endo*-**1**) has participated to the polymerization, the RDA process is no more allowed, hence, in the final copolymers the [2.2.1] bicyclic system results stereochemically and structurally very stable.

Ethylene/2,6-Di-*t*-butyl-phenol-norbornene copolymerizations

The copolymerization of ethylene with 2,6-di-*t*-butyl-phenol-norbornene (N_{ArOH}) with the homogeneous MAO-activated *rac*-Et(Ind)$_2$ZrCl$_2$ (**EI**) catalyst was investigated. **EI** was chosen because it is able to incorporate bulky comonomers, specifically norbornene (N), in ethylene-based copolymers. Triisobutylaluminum (TIBA) was used to protect the hydroxyl of N_{ArOH} in order to prevent the catalyst deactivation. The copolymerization reactions were performed at 0.5 atm of ethylene gas pressure: the reduced pressure was chosen to promote the insertion of the bulky polar comonomer with respect to ethylene. Polymerization times were chosen since to avoid the complete comonomer conversion to prevent the formation of polyethylene chains. The protected hindered phenol does not act as a poison for metallocene complex and, under the proper polymerization conditions, could positively affect the polymerization activity.[35–38] The copolymerization procedure is sketched in Scheme 4.

The two N_{ArOH} isomeric mixtures (1.1/1 and 6/1) were pre-treated in toluene solution for 2 h with 1.2 equiv of TIBA. An ethylene/norbornene (E/N) copolymer was also prepared, under the same conditions, as a model. In order to obtain a copolymer containing exclusively an *exo* comonomer, the copolymerization of ethylene was carried out with *exo*-**2** (N_{ArOAc}). In this case N_{ArOAc} was pre-treated with 2.2 equiv of TIBA to "protect" both oxygens of the carboxylic group. In spite of the protection, a noticeable catalyst deactivation was



SCHEME 4 Ethylene/N_{ArOH} copolymerization procedure.

TABLE 1 Ethylene/N_{ArOH} and Ethylene/N_{ArOAc} Copolymerizations With rac-[$Et(Ind)_2ZrCl_2$]/MAO: Analytical Results[a]

	Comonomer [mmol-exo/endo)]	PE (Atm)	[E]/[com]	Yield (mg)	Activity (gpol/$mmol_{cat}\cdot h\cdot P_E$)	Incorporated Comonomer[b] [mol%—(*exo*/*endo*)]	Conversion (wt %)	M_w[c] ($\times 10^3$)	M_w/M_n[c]
(Run 1) N[d]	1	1	13.34	547	1,642	1.98	36.9	322	2.2
(Run 2) NArOH	1–(1.1/1)	0.5	6.67	470	1,880	0.43–(3/2)	7.0	418	3.0
(Run 3) NArOH	2–(1.1/1)	0.5	3.35	450	1,800	1.20–(3/2)	8.6	n.d.	n.d.
(Run 4) NArOH	0.5–(6/1)	0.5	13.34	390	1,560	0.78	20.1	n.d.	n.d.
(Run 5) NArOAc[e]	1 (>99/1)	0.5	6.67	230	184	1.36–(>99/1)[f]	9.7	314	9.8

[a] Polymerization conditions: solvent = toluene, total volume = 100 mL, [com]/[TIBA] = 1:1.2, t_{pol} = 15 min, [catalyst] = 2 μmol, [MAO]/[Zr] = 3,000 (mol/mol), $T = 30°C$.
[b] Determined by ^{13}C NMR.
[c] M_n and M_w/M_n determined by SEC.
[d] t_{pol} = 10 min.
[e] [com]/[TIBA] = 1:2.2, [catalyst] = 5 μmol, [MAO]/[Zr] = 2000 (mol/mol), t_{pol} = 30 min.
[f] Determined by ^{13}C NMR after reduction.

observed when the polymerization conditions adopted for N_{ArOH} were applied to N_{ArOAc} and negligible amounts of copolymer were produced. Different polymerization conditions (specifically, higher amount of catalyst and increased polymerization time) were required to achieve acceptable yield of copolymer. Eventually, the copolymer obtained with E/N_{ArOAc} was reduced with $LiAlH_4$, as described in the Experimental Section, since to obtain the free ArOH group and hence a pure *exo*-E/N_{ArOH} copolymer. The copolymerization results are summarized in Table 1.

NMR Structural Determination of Comonomer and E/N_{ArOH} Copolymers

Figure 3 shows the C indexing and the NMR spectrum of the 6/1 *exo/endo* sample of comonomer **1** (Fig. 3).

The aromatic region of the spectrum was assigned by comparison with literature data regarding a different comonomer bearing the same phenolic substituent.[3–5] A DEPT 135 experiment was acquired to discriminate methyl and methine groups. The use of HSQC and HMBC NMR techniques helped for the distinction between C_2 and C_3 olefinic carbons, as being three bond correlated to the H_6 methylene and H_5 methine protons, respectively. C_4, C_1, and C_7 are thus assigned (see Supporting Information). The NMR experiments commonly conducted at 28°C were repeated at 103°C to facilitate the comparison with the spectra of the ethylene base copolymers that are soluble only at high temperature. The complete peak assignment is available as Supporting Information.

The general structure and carbon indexing of an E/N_{ArOH} copolymer chain is sketched in Figure 4. For the backbone methylene carbons (S) the two Greek subscripts indicate the distances from the neighboring methines. The carbons related to the *exo* and *endo* isomers are designated by subscripts *x* and *n* respectively.

For the ^{13}C NMR assignment of E/N_{ArOH} structure the copolymer containing 1.20% mol of comonomer (Table 1, Run 3) was used. The complete ^{13}C NMR spectrum is presented in Figure 5. In the expanded aromatic region the signals of the carbons of the 2,6-di-*t*-butyl-phenolic substituent (C_a–C_d) of both the *exo* and *endo* isomers were assigned by comparison with the spectrum of the comonomer (see previous section). No traces of further olefinic species are detectable in this region.

In Figure 5(a, b), the expanded aliphatic region from 24 to 48 ppm of the spectrum of Figure 4 is shown along with the corresponding region of the spectrum of the E/N copolymer

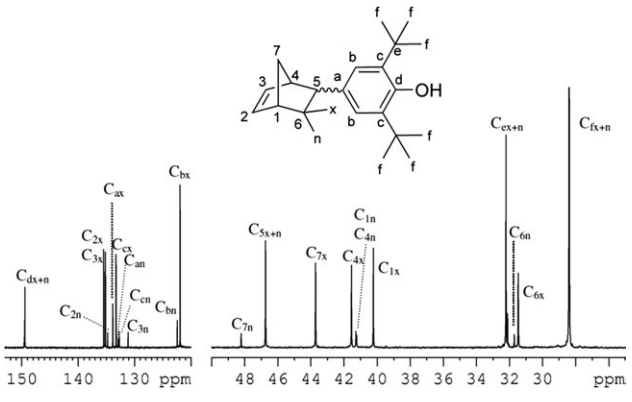


FIGURE 3 Carbon indexing and ^{13}C NMR spectrum of a sample of a 6/1 *exo/endo*-**1** mixture.

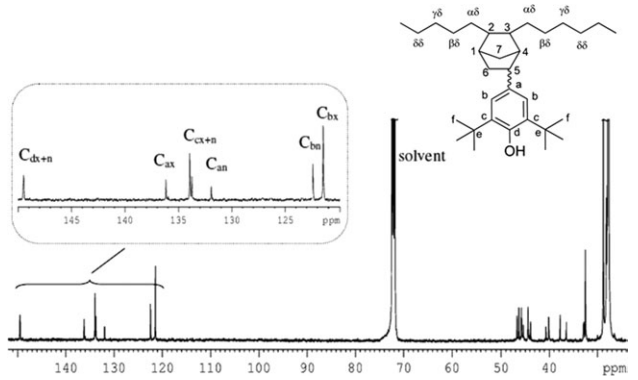


FIGURE 4 Carbon indexing in E/N_{ArOH} copolymer and ^{13}C NMR spectrum of the E/N_{ArOH} copolymer (1.20 mol % of comonomer) and assignments of the aromatic region.

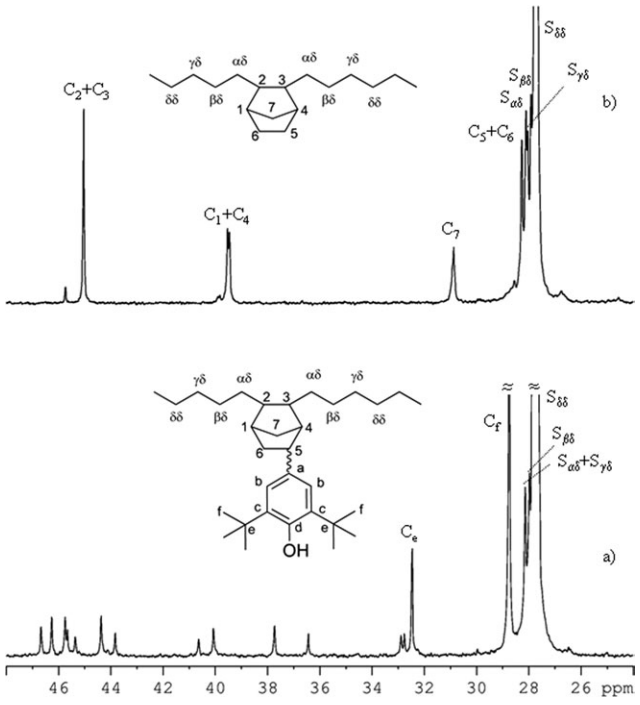


FIGURE 5 ^{13}C NMR spectrum of a model ethylene/N copolymer (a) and expanded aliphatic regions of the spectrum of Figure 4 (b).

(Table 1, Run 1). By comparing the two spectra, the well detected signals between 28.12 and 27.93 ppm could be safely assigned to the $\alpha\delta$, $\gamma\delta$, and $\beta\delta$ methylene carbons of the chain.[6,17] The presence of these signals is diagnostic of the occurred insertion of the comonomer into the chain, an evidence boosted by the absence of any trace of unreacted comonomer in the olefinic region of the spectra.

In Figure 6 (a, b) the expanded aliphatic region from 30 to 48 ppm of the spectrum of Figure 4 is shown along with the corresponding region of the spectrum of the pure *exo*-copolymer prepared reducing the E/N_{ArOAc} copolymer. The comparison of the two patterns allowed for the complete distinction between the chemical shifts of the *endo* and *exo* inserted comonomer forms.

By comparison with the assignment of C_2 and C_3 methine in ethylene/hydroxyl norbornene copolymers,[18] we assigned the signals at 45.75 and 44.37 ppm to C_{2x} and $C_{3x,}$ respectively, and the signals at 45.66 and 43.83 ppm, of equal intensity, to the corresponding C_{2n} and C_{3n}.

In the DEPT spectrum, two CH_2 signals are detected at 37.73 and 32.76 ppm, respectively, while the former can be assigned to C_{7x} on the basis of data reported in literature,[39] the latter is not as easily attributed. According to literature, we hypothesized that the 6x and 6n methylenes are likely overlapped by the intense signals of C_f carbon atom belonging to the *tert*-butyl group at 28.80 ppm.[18] The three methine carbons $C_{1x,}$ $C_{5x,}$ and C_{4x} were assigned with the help of the $^1H–^{13}C$ bidimensional heteronuclear NMR techniques (Fig. 7). Considering that in the HMBC spectrum the

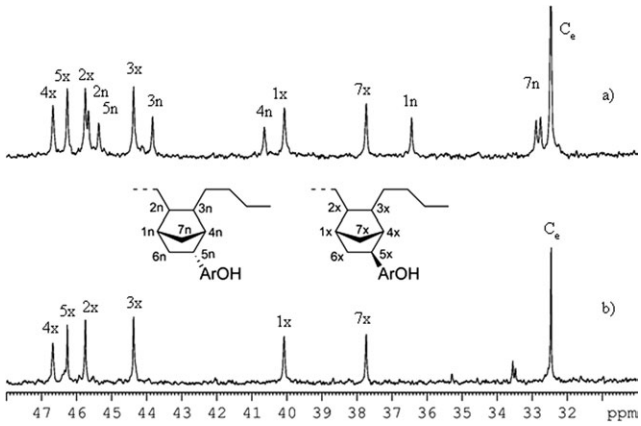


FIGURE 6 Expanded aliphatic regions of the spectrum of Figure 4 (a) and of the copolymer containing the pure *exo*-**1** comonomer (b).

low field cross-peaks arise only from $H_b(C_b)$ long-terms connectivities, these resonances were considered as a starting point for the other resonances assignments, as it follows. H_b proton (7.5 ppm) correlates with the aromatic carbons C_d (149.45 ppm), C_a (136.18 ppm), C_c (133.95 ppm), and C_e (32.46 ppm). Noticeably, it correlates with C_{5x} that consequently was safely assigned at 46.27 ppm. To discriminate between C_{1x} and $C_{4x,}$ we took advantage of the specific correlation of $H_4(C_4)$ with the C_a carbon.

The bidimensional technique also permitted to check most of the above described assignments. Signals of comonomer

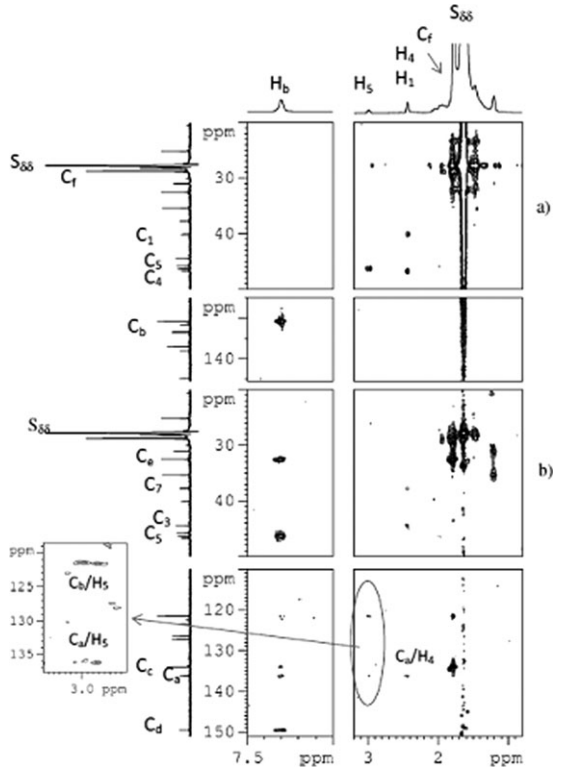


FIGURE 7 HSQC (a) and HMBC (b) spectra of Run 3 in Table 2.

TABLE 2 ^{13}C NMR Chemical Shift Assignments for E/N_{ArOH} and for E/N Copolymers

Carbon	Isomer	E/N_{ArOH} Chemical Shift (ppm)	E/N[a] Chemical Shift (ppm)
C_d	exo	149.45	
	endo	149.49	
C_a	exo	136.18	
	endo	131.92	
C_c	exo	133.95	
	endo	133.75	
C_b	exo	121.46	
	endo	122.44	
C_3	exo	44.37	45.03
	endo	43.83	
C_5	exo	46.27	28.33
	endo	45.39	
C_2	exo	45.75	45.03
	endo	45.66	
C_4	exo	46.67	39.50
	endo	40.64	
C_1	exo	40.07	39.50
	endo	36.44	
C_7	exo	37.73	30.90
	endo	32.88	
αB_1		35.28	
C_e	exo	32.46	
	endo	32.33	
C_6	exo	28.80	28.33
	endo	28.80	
C_f	exo	28.73	
	endo	28.73	
$S_{\alpha\delta}+S_{\gamma\delta}+\gamma B_1$		28.12	28.07–28.12
$S_{\beta\delta}$		27.93	27.95
$S_{\delta\delta}$		27.73	27.73
βB_1		25.18	
$1B_1$		17.93	

[a] Ref. [17]

homosequences were not detectable, suggesting that the obtained products are random copolymers containing only isolated comonomer units. A list of complete peak assignment is shown in Table 2.

DISCUSSION

Using a reductive Heck coupling of norbornadiene and an acetylated 4-bromophenol it is possible to obtain a new antioxidant bearing comonomer N_{ArOH} that, in its free phenolic form, is not stereostabile. Two *exo*/*endo* mixtures of derivative **1** were tested as potential new comonomer for the preparation of macromolecular antioxidant additives by copolymerization with ethylene. Polymerizations were accrued out using MAO-activated *rac*-Et(Ind)$_2$ZrCl$_2$ as catalyst and protecting the polar function of comonomers with TIBA. In comparison to N, the TIBA protected N_{ArOH} showed an obviously lower incorporation rate into the polymer chain. This result was expected due to high steric demand of the TIBA protected comonomer. A sensible difference in incorporation was also observed among the 6/1 and 1.1/1 comonomer samples. The results reported in Table 1 showed that *exo*-enriched comonomer (6/1) is markedly more reactive than the 1.1/1 sample. As a consequence, the former allows a higher comonomer conversion ($\approx$ 20%). Both copolymers resulted enriched in the more reactive *exo* form with respect to the starting comonomer, confirming the general preferential insertion of the *exo* isomer in the growing chain. However, despite such selectivity, because of the stereochemical and structural instability of the comonomer, the presence of a variable amount of the *endo* form in the copolymers appears unavoidable. Actually, the whole antioxidant effect of macromolecular additive will be directly related to the amount of the inserted comonomer independently on its *exo*/*endo* ratio. In this regard, the present study will be particularly useful for future applications of these additives since it establishes a relationship between the amount of comonomer insertion as function of the *exo*/*endo* ratio of the comonomer used. The copolymerization of the pure *exo*-**2** comonomer, followed by reduction of the ester group, allowed the preparation of a copolymer containing the pure *exo* form and a comonomer content about three times higher than that obtained in Run 2 with the same comonomer molar fraction. However, the low polymerization activity deriving from the partial poisoning of the catalyst discourages the use of such procedure. In this context, our aim was mainly to obtain copolymers suitable for microstructural investigation as a mandatory requisite for future studies on the effectiveness of this new family of polymeric additives in protecting the polyolefin matrix.

CONCLUSIONS

A norbornene comonomer bearing an antioxidant hindered phenol was prepared and, using a metallocene catalyst, reacted with ethylene to give new copolymers with variable amounts of the stabilizing unit. A carefully and exhaustive NMR structural determination was carried out to quantify the *exo*/*endo* ratio on comonomer and copolymers and to study its effect in the rate of polymerization. The results obtained allowed to establish the suitable condition for the preparation and NMR characterization of E/N_{ArOH} copolymers to be used as "masterbatches" in blends with commercial polyolefins, for specific application in safe food and/or drug packaging. A forthcoming paper will illustrate more in detail the production of polymeric films, using these macromolecular additives and the properties that make them suitable for food packaging. Specifically, the follow-up paper will examine the studied films' effectiveness in terms of thermal, thermo-oxidative, photo-stability, and no releasing character compared with those of low density polyethylene (LDPE) films containing traditional antioxidant additives.

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