Copolymerization of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenol over a supported high-activity Ziegler–Natta catalyst

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Copolymerizations of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenol were performed at 70°C over a high-activity supported $TiCl_4/MgCl_2$ Ziegler–Natta catalyst, using $Al(C_2H_5)_3$ as cocatalyst and diphenyldimethoxysilane as external electron donor. The 4-(ω-alkenyl)-2,6-di-t-butylphenol was pretreated with a stoichiometric molar amount of triethylaluminium prior to copolymerization. After the copolymerization the protecting group was removed by converting the phenol aluminium compound to –OH functionality by HCl/ethanol treatment. The copolymerizability of 4-(ω-alkenyl)-2,6-di-t-butylphenol as a function of the number of methylene group spacers between the double bond and the phenol moiety was determined for four different spacers. The results show that the copolymerization yield as well as the phenol content of the produced copolymer increased with an increase of spacer chain length. The produced copolymers exhibited good thermo-oxidative stabilities also after a prolonged extraction with n-heptane.

(Keywords: Ziegler–Natta catalysis; propylene; copolymerization; chemically bound antioxidant; hindered phenol; stabilizer)

INTRODUCTION

The advanced Ziegler–Natta catalyst possesses the ability to replicate its morphology (shape, porosity, etc.) into the morphology of the progeny polymer particles. Hence, spherical non-dusting polymer particles with an average size of 0.2–5 mm can be produced without the expensive pelletizing step[1]. Owing to this, a polymerization process requiring no post-treatments has come closer to realization. One problem still to be solved is the introduction of the stabilizers needed in subsequent fabrication processes and during the lifetime of the polymer.

In theory, polar monomers, which are Lewis bases, can be polymerized by Ziegler–Natta catalysts, which are Lewis acids, provided that the base strength of the polar monomer is decreased or eliminated by some trick. In practice, this could be done in several ways, i.e. by increasing the steric hindrance about the heteroatom, by decreasing the electron-donating character of the heteroatom via an acid–base reaction, and fine tuning by insulating the double bond from the heteroatom by one or more methylene group spacers[2].

A serious problem as well as a limiting factor in the usefulness of various antioxidants in polymers is their physical loss through migration or diffusion with subsequent evaporation or extraction, rather than their consumption during the course of stabilization. The harmful loss of stabilizers is accentuated by the fact that antioxidants are mostly polar aromatic compounds, which are not very compatible with hydrocarbon polymers. These problems can be circumvented to some extent by the use of bulky high-molecular-weight stabilizer molecules like the well known derivatives of t-butylated phenol and pentaerythritol. Another approach is the use of oligomeric or polymeric molecules. However, the limit to this approach is that the stabilizer solubility usually decreases in the polymer when the molecular weight of the stabilizer increases.

As a result of these and other considerations, a number of research groups have started to prepare and study polymer-bound stabilizers[3]. By grafting on polypropylene (PP) antioxidant loadings of 20% in the polymer have been claimed and the resulting master batches were found to be compatible with polyolefins by conventional blending[4]. The stabilizer master batch procedure has considerable advantages in partially crystalline polymers since the stabilizer can be expected to become more concentrated in the amorphous regions of the polymer, where it is mostly needed, without affecting the crystallinity of the polymer.

Grafting and other polymer post-treatments can cause undesirable changes in the initial fine structure of the macromolecule, since the polymer is subjected to either thermal, mechanical, photochemical or other treatments. Therefore, our current view is that the stabilizer should be introduced into the polymer pellets in a more intimate way, without any post-streatments. In principle, two approaches can be considered: (1) polymerization in the presence of the stabilizer[5–9] and (2) copolymerization of an appropriate derivative of a known or new stabilizer molecule with the main olefin[10–14].

Polymerizations in the presence of various stabilizers have been successful on several occasions. Thermally

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stable olefinic polymers have been obtained by addition of monomeric or oligomeric types of stabilizers, containing in the molecule one or more sterically hindered piperidine groups, during polymerization over a supported Zeigler–Natta catalyst[5]. According to Mülhaupt even certain stabilizers such as sterically hindered amines, phenols and phosphorus (III) esters can be simultaneously or separately introduced in small quantities during polymerization of olefins without altering either polymerization activity or polymer morphology[7]. However, such approaches have the shortcomings that are associated with admixed stabilizers.

Copolymerization of the stabilizer molecule into the polymer during preparation is a most attractive approach. Using Zeigler–Natta polymerization catalysts, which are sensitive to polar monomers and additives, there exist some results according to approaches (1) or (2), and a CAS-ONLINE search displays three reports on copolymers consisting of 2,6-bis(1,1-dimethylethyl)-4-(n-alkenyl)phenols and propene[10–12].

In the registry file a search on

‘(C(16 + n)H(24 + 2n)O.C3H6)’X/MF,

$n = 0$–6, shows that the copolymers $n = 1$ and 2 are known to *Chemical Abstracts*. These copolymers were prepared by a first-generation Ziegler–Natta catalyst by polymerizing metal salts of the phenolic compound with α-olefins and converting the salt to phenolic OH groups by methanol/hydrogen chloride[10–12].

This paper reports the preparation of copolymers of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenols over a supported high-activity Ziegler–Natta catalyst.

EXPERIMENTAL

Materials

All chemicals used for the preparation of 4-(ω-alkenyl)-2,6-di-t-butylphenol were of reagent grade and obtained from Aldrich (Germany). The following chemicals were used in the copolymerization experiments. High-purity propylene (99.5%, Neste Oy, Finland), nitrogen (99.999%, Aga, Finland) and hydrogen (99.98%, Aga, Finland) were used as received without further purification. High-purity heptane (99 wt%, 0.005% CH_3OH, Merck Co., Germany) was dried over 3 Å molecular sieves and used after bubbling with nitrogen for 0.5 h. The catalytic system comprised a magnesium-chloride-supported titanium catalyst, triethylaluminium (TEA; Schering Co., Germany) as cocatalyst and diphenyldimethoxysilane (DMS; Psi Pstror Ch.Inc.) as external electron donor to control polymer tacticity (isotacticity ≈95% for polypropylene).

Preparation and characterization of 4-(ω-alkenyl)-2,6-di-t-butylphenols

A feasible pathway for the preparation of sterically hindered *para*-alkenyl phenols is to react *p*-chloromethyl-di-*o*-hindered phenol with a Grignard reagent made from an α-bromo-ω-alkene[12]. The synthetic route is illustrated in *Figure 1*.

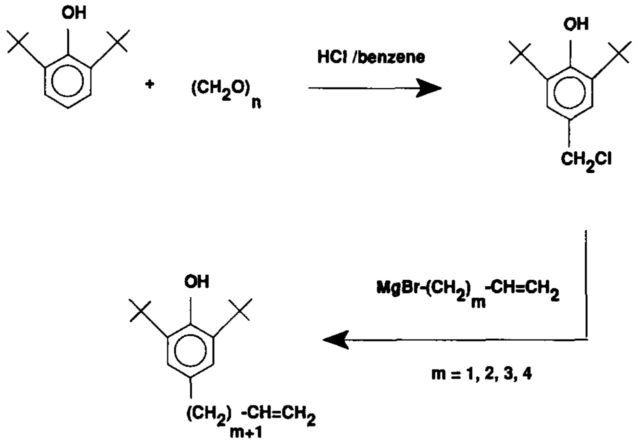

Figure 1 A synthetic route for the preparation of 4-(ω-alkenyl)-2,6-di-t-butylphenol

^1H n.m.r. spectra were recorded in $CDCl_3$ relative to tetramethylsilane (TMS) on a JEOL GX-400 spectrometer operating at 400 MHz. The splitting patterns for the ^1H n.m.r. are designated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The ^{13}C n.m.r. spectra were also recorded on the JEOL GX-400 spectrometer operating at 100 MHz; chemical shifts in the proton-decoupled spectra are reported in ppm downfield from TMS. G.c.-m.s. analyses were performed with an HP 5890 gas chromatograph (Hewlett Packard Co.) and an HP 5970 mass selective detector. The ionizing potential was 70 eV. Mass spectral peaks are given in units of mass/charge followed by relative peak intensity in parentheses.

Preparation of 4-chloromethyl-2,6-di-t-butylphenol. A 1 litre three-necked flask, equipped with a pressure-equalizing dropping funnel, a magnetic stirrer and a heating mantle, a thermometer, an anhydrous hydrogen chloride inlet and outlet connected to aqueous sodium hydroxide, was charged with 74.6 g (2.49 mol) of paraformaldehyde and 450 ml of benzene. The suspension was vigorously stirred and heated up to 55°C followed by saturation with anhydrous hydrogen chloride. The anhydrous hydrochloride was prepared by dropping concentrated hydrochloric acid into concentrated sulphuric acid. Then, 206 g (0.79 mol) of 2,6-di-t-butylphenol was dissolved in 80 ml of benzene and added dropwise to the saturated paraformaldehyde suspension at a rate of 5–10 drops per second. The addition of anhydrous hydrogen chloride was continued for an additional 8 h at the appropriate temperature. The mixture was then allowed to cool to room temperature with continued stirring, after which the product was poured into water. The organic phase was first washed with dilute HCl and then twice with water, dried over $CaCl_2$, and the benzene removed on a rotary evaporator. After evaporating, 185 g (85% yield) of 4-chloromethyl-2,6-di-t-butylphenol was obtained. Attempts to *distil* the crude product resulted in the *cleavage of HCl(g)* with the subsequent formation of 2,6-di-t-quinomethane. However, the undistilled product was pure (93% according to g.c.-m.s. analyses) enough for further reactions.

Preparation of 4-(but-3-enyl)-2,6-di-t-butylphenol. The Grignard reagent was prepared in the standard manner using 40.5 g (1.66 mol) of magnesium turnings and 199.5 g (1.66 mol) of allyl bromide in 800 ml of anhydrous ether. A solution of 300 ml anhydrous ether and 130.5 g (0.51 mol) of 4-chloromethyl-2,6-di-t-butylphenol was prepared. The solution was added dropwise to the Grignard reagent at a rate to maintain refluxing. Then, the mixture was allowed to stand for 3 h. The resulting product was poured into cold aqueous ammonium chloride solution. The phases were then separated, the ether layer was dried over magnesium sulphite and the solvent removed by a rotary evaporator. In order to obtain a very pure product, it was necessary to distil it twice. The slightly yellow product is distilled using a 15 cm column filled with 0.3 cm sections of glass tubing at 110–112°C and 1.5 mmHg to give 58 g (44% yield) of 4-(butyl-3-enyl)-2,6-di-t-butylphenol. The structure of the product was confirmed by ^1H n.m.r., ^{13}C n.m.r. and m.s. The ^1H n.m.r. (400 MHz, $CDCl_3$, TMS) spectrum showed peaks at $\delta = 1.4$ (s, $C(C\underline{H}_3)_3$, 18H), 2.3 (q, $C\underline{H}_2{-}CH{=}CH_2$, 2H), 2.6 (t, $-C\underline{H}_2-$phenol, 2H), 5.0 (s, $O\underline{H}$, 1H), 4.9–5.1 (m, $C\underline{H}_2{=}CH-$, 2H), 5.8–5.9 (m, $={C}\underline{H}-$, 1H) and 7.0 ppm (m, *m*-phenol, 1H). The ^{13}C n.m.r. ($CDCl_3$, TMS) spectrum showed peaks at $\delta = 30.3$ ($-C(\underline{C}H_3)_3$), 34.4 ($-\underline{C}(CH_3)_3$), 35.4, 36.1 ($CH_2{=}CH{-}(\underline{C}H_2)_2-$), 114.6 ($\underline{C}H_2{=}CH-$), 124.9 (*m*-phenol), 135.7 (*o*-phenol), 138.7 (*p*-phenol), 141.6 ($=\underline{C}H-$) and 151.9 ppm (OH–phenyl). The m.s. *m*/*e* (rel. int.) showed peaks at 260 (15), 219 (100), 203 (12), 161 (3), 129 (3), 91 (5) and 41 (12).

Preparation of 4-(pent-4-enyl)-2,6-di-t-butylphenol. The 4-bromo-1-butene was prepared from hexamethylphosphoramide and 1,4-dibromobutane according to the synthetic route developed by Kraus[15]. It is important to *distil* the 4-bromo-1-butene rapidly from the reaction mixture in order to *minimize diene and isomer formation.* After redistillation 133 g (46% yield) of 4-bromo-1-butene at 98–100°C and 760 mmHg was obtained. Then the Grignard reagent was prepared from 4-bromo-1-butene. To the Grignard reagent, 76.2 g (0.30 mol) of 4-chloromethyl-2,6-di-t-butylphenol was added to give 30 g (37% yield) of 4-(pent-4-enyl)-2,6-di-t-butylphenol after two distillations of 124–126°C and 1.5 mmHg. The ^1H n.m.r. (400 MHz, $CDCl_3$, TMS) spectrum showed peaks at $\delta = 1.2$–1.7 (m, allyl–$(C\underline{H}_2)-$, 2H), 1.4 (s, $C(C\underline{H}_3)_3$, 18H), 2.1 (q, $C\underline{H}_2{-}CH{=}CH_2$, 2H), 2.5 (t, $-C\underline{H}_2-$phenol, 2H), 5.0 (s, $O\underline{H}$, 1H), 4.9–5.1 (m, $C\underline{H}_2{=}CH-$, 2H), 5.8–5.9 (m, $=C\underline{H}-$, 1H) and 7.0 ppm (*m*-phenol). The ^{13}C n.m.r. ($CDCl_3$, TMS) spectrum showed peaks at $\delta = 30.5$ ($-C(\underline{C}H_3)_3$), 34.4 ($-\underline{C}(CH_3)_3$), 32.0, 33.7, 35.4 ($CH_2{=}CH{-}(\underline{C}H_2)_3-$), 114.7 ($\underline{C}H_2{=}CH-$), 125.0 (*m*-phenol), 133.3 (*p*-phenol), 135.7 (*o*-phenol), 138.7 ($=\underline{C}H-$) and 151.8 ppm (OH–phenyl). The m.s. *m*/*e* (rel. int.) showed peaks at 274 (42), 259 (100), 232 (52), 219 (45), 163 (12), 147 (9), 91 (8) and 57 (45).

Preparation of 4-(hex-5-enyl)-2,6-di-t-butylphenol. The 5-bromo-1-pentene was prepared with the same synthetic route as 4-bromo-1-butene except for using 1,5-dibromopentane instead of 1,4-dibromobutane. The yield was 123 g (45%) of 5-bromo-1-pentene. Then 69.8 g (0.27 mol) of 4-chloromethyl-2,6-di-t-butylphenol was reacted with 1-pentenyl-5-magensium bromide to give 36 g (yield 45%) of 4-(hex-5-enyl)-2,6-di-t-butylphenol after redistillation at 138–140°C and 1.5 mmHg. The ^1H n.m.r. spectrum (400 MHz, $CDCl_3$, TMS) showed peaks at $\delta = 1.2$–1.6 (m, allyl–$(C\underline{H}_2)_2-$, 4H), 1.4 (s, $-C(C\underline{H}_3)_3$, 18H), 2.1 (q, $-C\underline{H}_2{-}CH{=}CH_2$, 2H), 2.5 (t, $C\underline{H}_2-$phenol, 2H), 4.8–5.2 (m, $C\underline{H}_2{=}CH-$, 2H), 5.0 (s, $-O\underline{H}$, 1H), 5.7–5.9 (m, $=C\underline{H}-$, 1H) and 7.0 ppm (s, *m*-phenol, 1H). The ^{13}C n.m.r. spectrum showed peaks at $\delta = 28.8$ ($-\underline{C}H_2{-}CH_2{-}CH_2-$phenol), 30.37 ($-C(\underline{C}H_3)_3$), 31.5 ($-\underline{C}H_2{-}CH_2-$phenol), 33.7 ($=CH{-}\underline{C}H_2$), 34.3 ($-\underline{C}(CH_3)_3$), 35.8 ($-\underline{C}H_2-$phenol), 114.3 ($\underline{C}H_2{=}CH-$), 124.7 (*m*-phenol), 133.3 (*p*-phenol), 135.6 (*o*-phenol), 139.0 ($CH_2{=}\underline{C}H-$) and 151.7 ppm (OH–phenyl). The m.s. *m*/*e* (rel. int.) showed peaks at 288 (36), 273 (100), 232 (3), 219 (21), 161 (5), 147 (6), 91 (5) and 57 (33).

Preparation of 4-(hept-6-enyl)-2,6-di-t-butylphenol. The same method was applied as in the preparation of 4-(hex-5-enyl)-2,6-di-t-butylphenol. The first step using 680 g (2.78 mol) of 1,6-dibromohexane gave 200 g (44% yield) of 6-bromo-1-hexene and the second step gave 50 g (41% yield) of 4-(hept-6-enyl)-2,6-di-t-butylphenol at 151–153°C and 1.5 mmHg. The ^1H n.m.r. (400 MHz, $CDCl_3$, TMS) spectrum peaks at $\delta = 1.2$–1.6 (m, allyl–$(C\underline{H}_2)_3-$, 6H), 1.4 (s, $C(C\underline{H}_3)_3$, 18H), 2.1 (q, $-C\underline{H}_2{-}CH{=}CH_2$, 2H), 2.5 (t, $C\underline{H}_2-$phenol, 2H), 5.0 (s, $-O\underline{H}$, 1H), 4.9–5.0 (m, $C\underline{H}_2{=}CH-$, 2H), 5.7–5.9 (m, $=C\underline{H}-$, 1H) and 7.0 ppm (*m*-phenol). The ^{13}C n.m.r. ($CDCl_3$, TMS) spectrum showed peaks at 28.2–34.3 ($CH_2{=}CH{-}(\underline{C}H_2)_4-$), 30.5 ($-C(\underline{C}H_3)_3$), 34.4 ($-\underline{C}(CH_3)_3$), 36.0 ($-\underline{C}H_2-$phenol), 114.3 ($\underline{C}H_2{=}CH-$), 124.9 (*m*-phenol), 133.5 (*p*-phenol), 135.7 (*o*-phenol), 139.2 ($=\underline{C}H-$) and 151.4 ppm (OH–phenol). The m.s. *m*/*e* (rel. int.) showed peaks at 302 (67), 287 (100), 245 (2), 219 (33), 189 (6), 147 (9), 91 (6) and 57 (47).

Polymerizations and analysis of the produced polymers

The slurry polymerizations were conducted in a 1.0 litre or a 2.0 litre autoclave (Büchi Glass, Switzerland) equipped with a blade turbine stirrer. The stabilizer monomer, a stoichiometric molar amount of triethylaluminium and 400 ml of heptane were first injected into the autoclave under an inert atmosphere and stirred for 60 min at 70°C. The alkylaluminium and the electron donor components were then mixed in 100 ml of n-heptane under an inert atmosphere in a glove-box. After 5 min the supported Ziegler–Natta catalyst was mixed with the cocatalyst–electron donor solution in a 100 ml stainless-steel cylinder and injected into the reactor by means of nitrogen overpressure. Then the polymerization was started by introducing propylene monomer up to the desired partial pressure. Reaction temperature was controlled within ±0.3°C by a Lauda Ultra circulating water bath. Unless otherwise noted, the following conditions were kept constant for all the polymerizations:

Temperature: 70°C
Propylene partial pressure: 4 bar
TEA/DMS molar ratio: 15
Al/Ti molar ratio: 200
Stirrer speed: 500 rev min^{-1}
Polymerization time: 3 h
Catalyst load: 40 mg

Polymerizations were quenched with 400 ml of ethanol/hydrogen chloride solution and the produced polymer was filtered, dried in vacuum at 50°C and weighed to determine polymer yield. A part of the crude polymer ($\approx$0.5–1 g) was extracted in boiling n-heptane (200 ml) for 4 h. ^{13}C n.m.r. spectra of the copolymers (10% w/v in dichlorodideuteroethane) were recorded at 160°C using a JEOL GX-400 spectrometer operating at 100 MHz under proton decoupling in Fourier transform (*FT*) mode (hexamethyldisiloxane was added as internal standard). The amount of bound stabilizer was determined by u.v. analysis at the Analytical Research Laboratories of Neste Oy, Finland. The phenol group absorbs typically at 281–285 nm. Numerical values of the amount of bound stabilizer are based upon polypropylene/BHT (2,6-di-t-butyl-4-methylphenol) standards. The molecular mass distribution (*MWD*) of the copolymers was measured at 140°C with a Waters model 200 using standard polypropylene samples at the Chalmers University of Technology. 1,2,4-Trichlorobenzene was used as solvent. (Since we have no calibration curve between polypropylene and the present copolymer, M_n and M_w thus determined might be slightly incorrect). The melting point (T_m) as well as the oxidation induction temperature (*OIT*) were determined with a Perkin–Elmer model 3600 differential scanning calorimeter. D.s.c. measurements were made at a heating rate of 10°C min^{-1} starting from 50°C in a cell chamber that was purged with oxygen at 100 ml min^{-1}. The initial heating at 10°C min^{-1} resulted in an endothermic peak at $\approx$160°C, which can be attributed to the copolymer melting point. The start of the second peak, which is exothermic, is associated with the oxidation induction temperature (*OIT*). The long-term thermo-oxidative stability was studied by oven ageing at 110°C and at 130°C in an air atmosphere, with subsequent detection of oxidation products by a Perkin–Elmer 1710 Infrared Spectrometer. An increase of the absorbance peak at around 1720 cm^{-1} is due to C=O vibrations and is associated with hydrocarbon oxidation products such as acids, aldehydes and ketones. The time for the formation of the carbonyl peak was recorded.

RESULTS AND DISCUSSION

The obstacle of polymerizing polar monomers such as 4-(ω-alkenyl)-2,6-di-t-butylphenol lies in the fact that the Ziegler–Natta catalyst compounds, which are Lewis acids, have a tendency to interact with the non-bonded electron pairs on oxygen of the functional monomer, in preference to the π electrons of the olefin monomer. The resulting coordination complex between the polar group and the Ziegler–Natta initiator compounds are typically more stable than those obtained when coordination involves only the π electrons of the olefin to be inserted. Consequently, polymerization is inhibited. Therefore, it is necessary to pretreat the functional monomer with a protecting group in order to prevent catalyst poisoning during polymerization. Catalyst poisoning was verified by experimental propylene polymerization runs under standard conditions conducted in the presence of 2,6-di-t-butylphenol. As may be anticipated, even a small amount of 2,6-di-t-butylphenol was capable of deactivating most of the Ziegler–Natta polymerization sites as presented in *Table 1*. On the contrary, when the 2,6-di-t-butylphenol was pretreated with a stoichiometric amount of triethylaluminium to liberate ethane and generate alkylaluminium phenoxide[16], no severe deactivation of polymerization sites was detected.

The copolymerizations of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenol were conducted at two different concentration levels (7.5 and 15 mmol l^{-1}) of the 4-(ω-alkenyl)-2,6-di-t-butylphenol, whereas the propylene concentration was kept constant. The results of the copolymerizations are shown in *Table 2*.

Copolymers were also carried out in a similar manner except for the fact that the flow of propylene gas was stopped after approximately 5 min when the appropriate propylene concentration of 1.4 mol l^{-1} was reached. The results are presented in *Table 3*.

It is apparent from *Table 2* that, by insulating the double bond from the bulky phenol moiety by incorporation of several methylene group spacers, one can enhance the polymerization activity. The increase in the polymerization yields for spacers 4 and 5 in comparison to spacers 2 and 3 suggests that the bulky phenol moiety, when physically removed in this manner, is less likely to sterically hinder coordination and insertion of the double bond at the active site. Judging from *Table 3* it seems also that the longer methylene spacer groups of spacers 4 and 5 give copolymers with a higher phenol content than the copolymers produced with spacers 2 and 3. For the copolymers presented in *Table 3* the carbonyl peak in the i.r. spectrum did not appear within 12 days of oven ageing at 110°C, whereas unstabilized polypropylene shows a strong carbonyl peak after 6 h. Since both polymerization activity as well as the level of phenol incorporation increase with an increase of spacer group between the double bond and the phenol moiety, we decided to focus on the copolymerization of propylene with 4-(hept-6-enyl)-2,6-di-t-butylphenol.

The copolymerization of propylene and 4-(hept-6-enyl)-2,6-di-t-butylphenol was carried out by changing the concentration ratio between the monomers. The copolymer samples were extracted with boiling n-heptane, prior to u.v. measurements. The results obtained are summarized in *Table 4*.

Table 1 Results of propylene polymerizations in the presence of precomplexed (respectively unprecomplexed)2,6-di-t-butylphenol[a]

C_p[b] (mol l^{-1})	C_{st}[c] (mmol l^{-1})	Yield (kg poly. g^{-1} cat.)
1.5	–	2.4
1.5	4.0[d]	1.3
1.5	10.0[d]	0.8
1.5	10.0[e]	2.1
1.5	50.0[e]	1.6

[a] Polymerization conditions: catalyst $TiCl_4/MgCl_2$ = 40 mg (Ti content 2.6 wt%), $Al(C_2H_5)_3$ = 0.50 g, diphenyldimethoxysilane = 71.6 mg, $V_{total\,heptane}$ = 1 l, temperature = 70°C, polymerization time = 3 h

[b] C_p denotes propylene concentration

[c] C_{st} denotes the initial concentration of 2,6-di-t-butylphenol

[d] Denotes the concentration of unprecomplexed 2,6-di-t-butylphenol

[e] Denotes the concentration of precomplexed 2,6-di-t-butylphenol

Table 2 Results of copolymerizations of propylene and 4-(ω-alkenyl)2,6-di-t-butylphenol[a]

	Spacer	C_p[b] (mol l^{-1})	C_{st}[c] (mmol l^{-1})	Conc. of bound stabilizer (wt%)	Yield (kg poly. g^{-1} cat.)
		1.5	–	–	2.4
4-(But-3-enyl)-2,6-di-t-butylphenol	2	1.5	7.5	0.02	1.0
4-(But-3-enyl)-2,6-di-t-butylphenol	2	1.5	15	0.02	0.8
4-(Pent-4-enyl)-2,6-di-t-butylphenol	3	1.5	7.5	0.02	1.5
4-(Pent-4-enyl)-2,6-di-t-butylphenol	3	1.5	15	0.02	1.3
4-(Hex-5-enyl)-2,6-di-t-butylphenol	4	1.5	7.5	0.02	2.4
4-(Hex-5-enyl)-2,6-di-t-butylphenol	4	1.5	15	0.03	2.1
4-(Hept-6-enyl)-2,6-di-t-butylphenol	5	1.5	7.5	0.02	2.7
4-(Hept-6-enyl)-2,6-di-t-butylphenol	5	1.5	15	0.04	2.5

[a] Polymerization conditions: catalyst $TiCl_4/MgCl_2$ = 40 mg (Ti content 2.6 wt%), Al/Ti = 200, Al/D = 15, $V_{totalheptane}$ = 1 l, temperature = 70°C, polymerization time = 3 h

[b] C_p denotes propylene concentration

[c] C_{st} denotes the initial concentration of 4-(ω-alkenyl)-2,6-di-t-butylphenol

Table 3 Results of the batch polymerizations of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenol[a]

	Spacer	C_p[b] (mol l^{-1})	C_{st}[c] (mmol l^{-1})	Conc. of bound stabilizer (wt%)	Conversion[d] (%)	I.r.[e] (days)
4-(But-3-enyl)-2,6-di-t-butylphenol	2	1.4	30	0.06	74	12
4-(Pent-4-enyl)-2,6-di-t-butylphenol	3	1.4	30	0.12	74	12
4-(Hex-5-enyl)-2,6-di-t-butylphenol	4	1.4	20	0.16	≈100	12
4-(Hept-6-enyl)-2,6-di-t-butylphenol	5	1.4	30	0.14	90	12

[a] Polymerization conditions: catalyst $TiCl_4/MgCl_2$ = 40 mg, Al/Ti = 200, Al/D = 15, temperature = 70°C, polymerization time = 3 h

[b] C_p denotes the initial propylene concentration

[c] C_{st} denotes the initial concentration of 4-(ω-alkenyl)-2,6-di-t-butylphenol

[d] Conversion (%) = [1 – (final propylene concentration)/(initial propylene concentration)] × 100

[e] Denotes the time for the formation of the carbonyl peak by i.r. analyses for the extracted copolymer particles after oven ageing at 110°C

Table 4 Results of propylene/4-(hept-6-enyl)-2,6-di-t-butylphenol copolymerizations[a]

Sample	C_p[b] (mol l^{-1})	C_{st}[b] (mol l^{-1})	Yield (kg poly. g^{-1} cat.)	I.hep[c] (%)	Cryst.[d] (%)	M_n (10^3 g mol^{-1})	M_w (10^3 g mol^{-1})	Poly-dispersity	Conc. of bound stabilizer[e] (wt%)	I.r.[f] (days)
1	0.06	0.034	51	93	64	15 (10)[g]	340 (51)	23 (5)	1.9	5
2	0.26	0.034	90	93	55	27 (19)	189 (96)	7.0 (5)	1.0	4
3	0.50	0.034	453	92	65	44 (47)	447 (236)	9.4 (5)	0.6	1.5
4	1.28	0.034	958	92	50	58 (79)	771 (402)	13 (5)	0.3	1

[a] Copolymerization conditions: catalyst $TiCl_4/MgCl_2$ ≈ 40 mg (Ti content 2.6 wt%), total $Al(C_2H_5)$ = 2.45 g (0.50 g was used as cocatalyst), diphenyldimethoxysilane = 71.6 mg, $V_{heptane}$ = 550 ml, temperature = 70°C, polymerization time = 3 h

[b] C_p denotes propylene concentration and C_{st} the initial concentration of 4-(hept-6-enyl)-2,6-di-t-butylphenol

[c] I.hep denotes the boiling heptane insoluble fraction of the polymer

[d] Cryst. denotes the polymer crystallinity, which has been determined from d.s.c. curves, and the heat of fusion of a folded-chain polypropylene crystal has been taken[17] as 49.8 cal g^{-1}

[e] The phenol portion of the insoluble copolymer fraction in boiling n-heptane was determined by u.v. spectroscopy

[f] Denotes the time for the formation of the carbonyl peak by i.r. analyses for the extracted copolymer films (thickness ≈ 25 μm) after oven ageing at 130°C

[g] In parentheses, the molecular weights have been predicted by a kinetic model for propylene homopolymerizations[18]

Also the results of the oven ageing performed at 130°C are shown in *Table 4*. The copolymer with a high phenol content of 1 wt% showed carbonyl absorption after 4 days, whereas polypropylene without antioxidant showed carbonyl absorption already after 2 h. The results of the g.p.c. analyses are also summarized in *Table 4*. The *MWD* curves of the copolymers show a fairly unimodal shape. The M_n values are similar to those predicted by the model for polypropylene; however, the M_w as well as the polydispersities are significantly higher for the copolymers than those predicted for polypropylene by the model published elsewhere[18]. The broadening in polydispersity might be due to the fact that the alkylaluminium phenoxide may also act as a cocatalyst

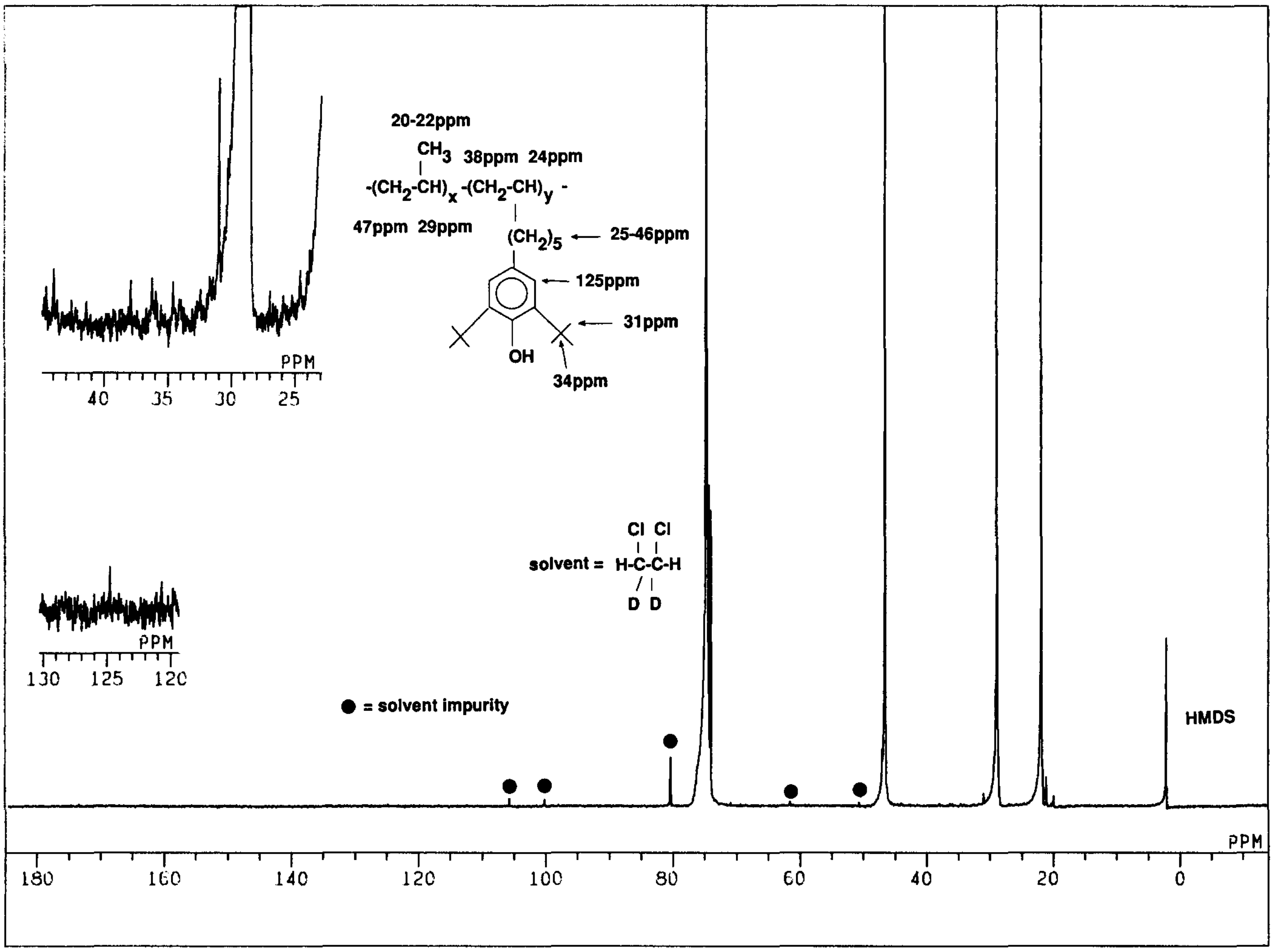

Figure 2 ^{13}C n.m.r. spectrum of the copolymer of propylene and 4-(hept-6-enyl)-2,6-di-t-butylphenol (sample 1 in *Table 4*)

Table 5 Results of copolymer fractionation with boiling n-heptane and n-octane

Sample	Extraction solvent	Insoluble fraction (wt%)	Conc. of stabilizer (wt%)
Copolymer[a]	–	100	1.75
Copolymer[a]	n-Heptane	89	0.37
Copolymer[a]	n-Octane	24.8	0.39

[a] Polymerization conditions: catalyst $TiCl_4/MgCl_2 = 59$ mg (Ti content 2.6 wt%), Al/D = 20, Al/Ti = 200, temperature = 70°C, polymerization time = 3 h. The concentration of propylene was 0.67 mol l^{-1} and the initial concentration of 4-(hept-6-enyl)-2,6-di-t-butylphenol was 0.032 mol l^{-1}

besides the triethylaluminium, and thus give rise to a multiplicity of active sites that differ in propagation rate constants (k_p). In fact, Mülhaupt observed an enhancement of propylene polymerization activity when 2,6-di-t-butylphenol-modified alkylaluminium was used as activator instead of triethylaluminium[19].

An additional copolymerization was conducted in order to evaluate the distribution of the phenol units in the copolymer. The produced copolymer was fractionated by extraction with boiling n-heptane and n-octane for 24 h in a Soxhlet-type of extractor. The results are shown in *Table 5*. Since the amount of phenol was approximately the same in both the n-heptane (0.37 wt%) and n-octane (0.39 wt%) insoluble fractions, it strongly suggests that the present copolymer has an even distribution of phenol units. The produced copolymer was mostly (75.2%) soluble in boiling n-octane, whereas according to Kawamura *et al.* only approximately 27% of isotactic polypropylene with similar molecular weight is usually soluble in boiling n-octane[20]. Judging from the differences in solubility between the copolymer and polypropyelene as well as from the even distribution of phenol units and *MWD* curves, one may conclude that the present copolymer is not a mixture of homopolymer and polypropylene, but essentially a random copolymer.

The structure of the copolymer was determined by ^{13}C n.m.r. In *Figure 2* a ^{13}C n.m.r. spectrum of the extracted copolymer sample 1 in *Table 4* is shown. The resonances at 20–22, 29 and 47 ppm are assignable to the carbons of highly isotactic polypropylene. The spectrum in *Figure 2* displays additional peaks at 38 and 24 ppm, which can be assigned to the methylene and methine carbons in the main chain that are linked by the spacer methylene carbons to the hindered phenol group. The t-butyl groups gave peaks at 31 and 34 ppm, while the resonance at 125 ppm can be attributed to the *m*-phenol carbons (the expected resonances at 135 and 153 ppm cannot be observed owing to the long relaxation times for quaternary carbons). In addition, low-intensity resonances can be observed in the region of 25 and 46 ppm, and

Table 6 Results of thermo-oxidative stability measurements of the polymers, based on d.s.c. thermograms

Sample	*OIT*[a] (°C)	T_M[b] (°C)
1[c]	180 (180)	164
2[d]	220 (246)	160
3[e]	180 (220)	168
4[f]	180 (248)	167

[a] Denotes oxidation induction temperature for the polymers after extraction with boiling n-heptane; in parentheses, the oxidation induction temperatures for the unextracted polymers

[b] T_M denotes the melting point

[c] Denotes pure polypropylene grade prepared by us

[d] Denotes the copolymer presented in *Table 2*, which contained 1 wt% of phenol

[e] Denotes a commercial polypropylene that contained several different stabilizers

[f] Denotes a pure polypropylene sample that had been admixed with 1 wt% Irganox 1010

these peaks can be assigned to the five spacer methylene carbons.

To illustrate the effectiveness of the chemically bound stabilizer, a comparison was made with two reference samples by means of a thermoanalytical technique (d.s.c.). The first reference sample was a commercial polypropylene quality containing several different stabilizers and the second sample consisted of a polypropylene that had been admixed with 1 wt% of 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, known commercially as Irganox 1010 (supplied by Ciba-Geigy). Analogous d.s.c. analyses were also performed after extracting the samples with boiling n-heptane. As expected, both the reference samples lost their stabilizer in the course of the extraction procedure, and thus exhibited an oxidation induction temperature comparable with unstabilized polypropylene. On the contrary, the oxidation induction temperature (*OIT*) for the extracted copolymer was still on the same level as the unextracted commercial reference sample. These results unambiguously suggest that the precomplexed stabilizer monomer is copolymerized with propylene over a supported high-activity Ziegler–Natta catalyst. The results from the stability measurements (*OIT*) are presented in *Table 6*.

In conclusion, the catalyst composed of $TiCl_4/MgCl_2/Al(C_2H_5)_3$/DMS was found to be effective for the production of a copolymer of propylene and 4-(ω-alkenyl)-2,6-di-t-butylphenol. The produced non-dusting and spherical copolymer particles showed outstanding thermo-oxidative stability also after a prolonged extraction with heptane.

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