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Polar Activation in Copolymerization of Propylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over a Racemic [1,1′-(Dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium Dichloride/Methylalumoxane Catalyst System

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ABSTRACT: Copolymers of propylene and the polar monomer 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol were obtained with racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]-zirconium dichloride and methylalumoxane activator. The copolymers contained from 1.3 to 5.5 wt % of phenolic units and exhibited high thermooxidative stability even after prolonged extraction with a mixture of refluxing (50:50) 2-propanol/cyclohexane. The initial polymerization rate, compared to that of homopolymerization of propylene, increased up to almost 6 times when the sterically hindered phenolic stabilizer monomer was added. A similar increase in activity was recorded when 2,6-di-*tert*-butylphenol was added during propylene polymerization. The activity enhancement was attributed to the ability of the phenolic stabilizer to function as a large weakly coordinating anion, which stabilizes the cationic polymerization center. The degree of microtacticity of the copolymer, isotactic triad mm > 0.96, was similar to that of isotactic polypropylene prepared by the same catalyst system. The dominating insertion mechanism was 1,2 addition with very low amounts of 1,3-addition irregularities. The produced copolymers exhibited lower melting points and crystallinities than polypropylene obtained under similar conditions. According to gel permeation chromatography, the copolymers had a narrow molecular weight distribution ranging from 1.9 to 2.1, which is close to those values characteristic for polymers produced by single-site catalysts.

Introduction

Stabilization of polypropylene is usually accomplished by melt blending with a stabilizer (or a combination of stabilizers).[1] In this way a heterophase polymer/stabilizer system is formed, which may be best described as a physical dispersion of a low molecular weight stabilizer in a polymer matrix. The vast majority of commercial stabilizer compounds have very different chemical structures from that of the nonpolar host polyolefin. For this reason, the compatibility of various conventional stabilizers with polyolefins is poor, leading to migration of admixed stabilizers across a boundary from polypropylene into neighboring matter such as fillers, air, water, or soil or into the human environment. Thus, even if the stabilizer has good intrinsic characteristics, the physical loss of admixed stabilizers by migration to high-energy surfaces of various fillers, blooming, leaching, volatilization, and the like, may reduce the lifetime of the polymer article to that of unstabilized polypropylene. Hence, it can be stated that two factors are responsible for the effectiveness of stabilizers: the intrinsic stabilizer behavior and the permanence of the stabilizer in the polymer matrix. In demanding applications, as in under the hood components in the automobile industry' in the carpet and textile industries, where the polypropylene fibers are exposed to extractive conditions during detergent washing and dry cleaning processes, and in various composite applications, satisfactory polymer performance and durability can frequently be obtained only when the antioxidant is completely immobilized. Lately numerous patents as well as several publications have appeared which claim that chemically bound stabilizers are outperforming conventional admixed antioxidants.[2] In addition, reprocessing of thermoplastics which have been subjected to industrial and/or domestic environments require nonvolatile stabilizers in order to make recycled plastics mechanically viable in numerous applications.

As a result of these and other considerations, we started to prepare and copolymerize various stabilizers with propylene over both heterogeneous and homogeneous Ziegler–Natta catalysts. Furthermore, we have investigated the feasibility of such novel copolymers in certain composite[3] and medical-grade applications.[4] Heterogeneous Ziegler–Natta catalysts, which are sensitive to polar stabilizer monomers, were used in some copolymerizations of propylene with stabilizers such as 4-(ω-alkenyl)-2,6-di-*tert*-butylphenol,[5] 4-hex-5-enyl-2,2,6,6-tetramethylpiperidine,[6] and 4-(ω-alkenyl)-*N*,*N*-dimethylaniline.[7]

To the best of our knowledge, there have been no reports in the literature where stabilizers have been copolymerized with propylene by homogeneous catalysts based on group IV metallocene/methylalumoxane systems. However, some protected polar monomers have been copolymerized with propylene using metallocene catalysts. The polar monomer *p*-*tert*-butoxystyrene, where the polar moiety is separated from the double bond, was polymerized over metallocene/MAO in good yield, but attempts to use isobutyl vinyl ether failed.[8] Catalysts derived from the reaction of dimethylbis(pentamethylcyclopentadienyl)-zirconium activated with tris(pentafluorophenyl)borane or [*N*,*N*-dimethylanilinium]$^+$[tris(pentafluorophenyl)-borane] can polymerize the functionalized diene 4-(trimethylsiloxy)-1,6-heptadiene and the polar monomers 5-(*tert*-butyldimethylsiloxy)-1-pentene and 5-(*N*,*N*-diisopropylamino)-1-pentene.[9] The incorporation of methylmethacrylate units with organolanthanide[10] catalyst and zirconocene cations[11] has also been reported.

This paper describes the copolymerization of 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol with propylene by racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride using methylalumoxane as the activator. During this study it became

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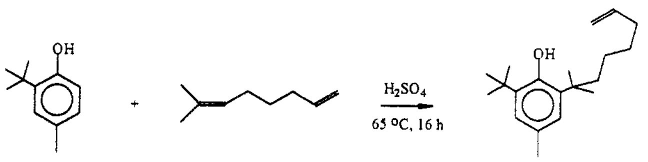
Scheme 1. A Convenient Method for the Preparation of 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol



clear that besides the production of the copolymer with high thermooxidative stability, the addition of the phenolic stabilizer also led to a dramatic increase in the polymerization rate.

Experimental Section

Materials. All chemicals used for the preparation of 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol and racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride were of reagent grade and obtained from Aldrich. The racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride was prepared essentially according to the published method by Welborn.[12] The following chemicals were used in the copolymerization experiments. High purity propylene (99.5%, Neste Oy, Finland) and nitrogen (99.9999%, AGA, Finland) was used as received without further purification. High purity toluene was refluxed over CaH_2 and subsequently distilled under argon atmosphere. Methylalumoxane (MAO 29.3% w/w toluene solution, Al total 13.1% w/w, Al as TMA 3.50% w/w, supplied by Witco) was used as received.

Synthesis of 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol. The synthetic route to 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol is illustrated in Scheme 1. A 250-mL two-necked flask, equipped with an effective reflux condenser and a dropping funnel, was charged with 55 g (0.34 mol) of 2-*tert*-butyl-4-methylphenol and 78 g (0.63 mol) of 7-methyl-1,6-octadiene. Then, 2.4 g of 98% sulfuric acid was added dropwise over a period of 5 min into the stirred reaction mixture. After 16 h at 65 °C the brown mixture was allowed to cool to room temperature with still continued stirring, after which the product was poured into a solution of 50 g of potassium hydroxide in 60 g of water and 140 g of methanol (according to G. Stillson et al.[13] 2,6-di-*tert*-butyl-4-methylphenol is insoluble in aqueous alkali of any strength), followed by the addition of *n*-hexane. The phases, which separate slowly were isolated and the organic layer was washed twice with water. The crude product, obtained after evaporation of the organic solvent and the excess 7-methyl-1,6-octadiene, contained 83% of 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol as determined by gas chromatography. After two distillations at 135 °C and 0.5 mmHg 64 g (65%) of the title compound was isolated as a pale yellow oil with the following spectral data. (Caution: The title compound should be distilled rather rapidly in order to avoid dealkylation). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 1.1 (m, $-CH_2$-CH_2-allyl, 2H), 1.3 (t, $-C(CH_3)_2CH_2-$, 2H), 1.38 (s, *m*-phenol, 1H), 1.41 (s, *m*-phenol, 1H), 1.7–1.8 (m, $-CH_2$-allyl, 2H), 2.0 (q, $—CH_2CH=$, 2H), 2.3 (s, phenol-CH_3, 3H), 4.9–5.0 (m, $CH_2=CH—$, 2H), 5.0 (s, $-OH$, 1H), 5.7–5.9 (m, $—CH=$, 1H), 6.9 (s, *m*-phenol, 1H) and 7.0 (s, *m*-phenol, 1H). ^{13}C NMR: 21.4 (phenol-CH_3), 24.8 ($CH_2CH_2CH_2CH=$), 29.3 ($-C(CH_3)_2CH_2-$), 29.6 ($—CH_2CH_2CH=$), 30.4 ($-C(CH_3)_3$), 33.6 ($—CH_2CH=CH_2$), 34.2 ($-C(CH_3)_3)_3$), 37.8 (phenol-$C(CH_3)_2CH_2-$), 41.6 ($-C(CH_3)_2$-CH_2-), 114.2 ($CH_2=CH—$), 125.5 and 126.7 (*m*-phenol), 128.2 (*p*-phenol), 134.2 and 135.6 (*o*-phenol), 139.1 ($CH_2=CH—$) and 151.6 ppm (HO-phenol). MS *m/e* (rel intensity): 288 (11), 243 (1), 205 (100), 177 (6), 145 (6), 105 (4), 91 (4), 57 (15), and 41 (15).

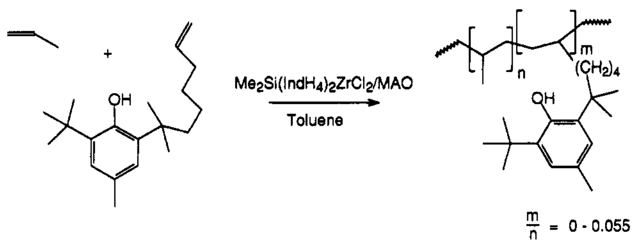
Polymerization Procedure. The sampling of the catalyst, activator, and phenolic monomer were carried out under nitrogen in a MBROWN glovebox containing <2 ppm oxygen and <5 ppm water. The reaction temperature was controlled within ±0.3 °C by a Lauda Ultra circulating ethanol bath. The slurry polymerizations were carried out in a 0.5-L jacketed glass autoclave (Büchi Glass, Switzerland) equipped with a blade turbine stirrer. The dry glass autoclave was evacuated and backflushed with nitrogen. This procedure was repeated several times. Then 200 mL of freshly distilled toluene was injected into the autoclave by means of nitrogen overpressure. Half of the methylalumoxane/toluene solution to be used was added to the reactor and stirred for 5 min in order to reduce any impurities in the reactor. In a parallel procedure the *ansa*-metallocene (1.1 × 10^{-2} mmol) was dissolved in the remaining half of the MAO/toluene solution quantity and preactivated for 5 min by standing at room temperature. The catalyst/activator mixture was then charged into the reactor. The prepolymerization was started by introducing propylene monomer ($P_{\mathrm{propylene}}$ = 1.4 bars). After 5 min the appropriate quantity of phenolic stabilizer diluted in 15 mL of toluene was flushed into the reactor by means of gaseous propylene until the propylene partial pressure reached 2 bars. The polymerization rate was determined as the rate of propylene consumption by keeping such a flow rate of propylene which maintained the 2 bar partial pressure of propylene throughout the polymerization. (Consumption of propylene as a function of time is monitored by having the propylene bottle on a scale.) After 60 min the polymerizations were quenched by rapidly venting the propylene and adding 100 mL of methanol. The produced polyolefin was filtered and the catalyst residues were removed by treatment with 1% methanol/HCl solution. Then the polyolefin was washed twice with ethanol, dried in vacuum at 50 °C, and weighed to determine the polymerization yield. The copolymers were extracted with refluxing 2-propanol/cyclohexane[14] for 24 h in a soxhlet apparatus prior to the determination of the amount of bound phenolic stabilizer and thermooxidative studies. A control experiment was carried out to show the efficiency of the extraction procedure, i.e. a control sample consisting of polypropylene containing 1.5 wt % of admixed Irganox 1076 (Irganox 1076 = octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxylphenyl)propionate, supplied by CIBA) was extracted for 24 h, whereby the stabilizer was completely removed from the polymer.

Polymer Characterization. The amount of bound phenolic stabilizer was determined by UV analyses and the numerical values are based upon polypropylene/Irganox 1076 standards. UV–visible spectra were obtained with a Schimadzu UV-240 spectrometer. Spectra were recorded between 220 and 350 nm. The phenolic stabilizer and Irganox 1076 exhibited a strong absorbance in this region at 280 nm with identical extinction coefficients: all measurements were monitored at this wavelength. Melting and crystallization thermograms were recorded with a Perkin-Elmer DSC IV system by raising the temperature from 50 to 200 °C at a rate of 10 °C/min. Nitrogen was used as the sweeping gas. The results of the second scan are reported to eliminate differences in sample history. The crystallinity was determined from the DSC curves using 49.8 cal/g[15] as the heat of fusion. The thermooxidative stability of the extracted copolymer films, thickness approximately 70–100 μm, was studied by oven aging at 110 °C in air, with subsequent detection of oxidation products by a Perkin-Elmer 1710 infrared spectrometer. The increase of the absorbance peak at 1720 cm^{-1} is associated with hydrocarbon oxidation products such as acids, aldehydes, and ketones.[16] The time for the formation of the carbonyl peak was recorded. The ^{13}C NMR analyses were carried out on a Jeol 400-MHz spectrophotometer at 110 °C. Polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2. The GPC chromatograms were obtained with a Waters high-temperature GPC device equipped with three TOSOH mixed-bed columns with an exclusion limit for polystyrene of 4 × 10^8 using 1,2,4-trichlorobenzene as solvent at a flow rate of 1.0 cm^3/min.

Results and Discussion

Synthetic Approaches to Polymerizable Sterically Hindered Phenolic Stabilizers. In order to prepare copolymers of propylene with various stabilizers over heterogeneous and soluble Ziegler–Natta catalysts, we have studied several synthetic routes to produce sterically hindered ω-alkenylphenols on a large scale. In theory the more closely the functionally substituted monomer resembles an α-olefin, the greater is the potential for it to polymerize at the same centers that are active for simple nonpolar olefins.[17]

Scheme 2. Copolymerization of Propylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol



Therefore, in the design of polymerizable sterically hindered phenolic stabilizers some prerequisites have to be fulfilled. First, there should be sufficient steric encumbrance about the heteroatom, second the double bond should be located in the alkenyl chain end, and third the terminal double bond should be insulated from the phenolic moiety by several methylene group spacers. Physically separated from the double bond, the functional group is less likely to sterically or electronically hinder the coordination and insertion of the double bond at the active site, particularly when heterogeneous Ziegler–Natta catalysts are employed. Flexible and efficient large-scale synthetic routes to this class of stabilizer compounds have not been developed previously. Shavanov et al.[18] described a preparative method for the production of 4-(ω-alkenyl)-2,6-di-*tert*-butylphenols. In general, this technique involves the alkylation of 2,6-di-*tert*-butylphenol with ω-haloalkenes in the presence of a base and a phase-transfer catalyst in an alcoholic medium such as butanol or cyclohexanol at 80–100 °C. Our attempts to prepare 4-hex-5-enyl-2,6-di-*tert*-butylphenol according to the base route gave rather low yields (<40%) accompanied with the formation of considerable amounts of the corresponding alkenyl aryl ether. Another method for the preparation of 4-(ω-alkenyl)-2,6-di-*tert*-butylphenol is a two-step reaction,[5a] starting with the preparation of 4-(chloromethyl)-2,6-di-*tert*-butylphenol by reacting 2,6-di-*tert*-butylphenol with a combination of paraformaldehyde and hydrogen chloride. The disadvantage of this reaction is that the strongly carcinogenic dichloromethyl ether is formed in considerable amounts as a byproduct in the first step and that the chloromethylated phenol easily undergoes cleavage of HCl(g) with the subsequent formation of 2,6-di-*tert*-quinomethane during distillation. In the second step the chloromethylated phenol is reacted with a large excess of Grignard reagent prepared from ω-bromoalkene and magnesium to give the desired product in good yield based on the phenol. The above described procedures were not attractive from a preparative point of view because of restrictions on the starting materials employed, multistep syntheses, generation of toxic byproducts, and/or low yield. For these reasons we developed a simple procedure to ω-alkenylphenols that fulfill the prerequisites cited above. The 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol was prepared from 2-*tert*-butyl-4-methylphenol and 7-methyl-1,6-octadiene via Friedel–Crafts alkylation in one step and in good isolated yield (65%). The reaction pathway is outlined in Scheme 1.

Results of the Copolymerizations. Copolymerizations of propylene and 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol, Scheme 2, were carried out by changing the Al/Zr ratio while keeping all the other parameters constant and the results of these copolymerizations together with propylene polymerizations are graphically shown in Figure 1. The polymerization activity for the homopolymerization of propylene was more or less independent of the Al/Zr ratios used, whereas for the copolymerizations the highest polymerization activity was recorded for an Al/Zr ratio of 3000. Therefore, all further copolymerizations were carried out by using an Al/Zr ratio of 3000. Next copolymerizations were carried out by changing the concentration of the phenolic monomer while keeping all other parameters constant, and the results are summarized in Table 1.

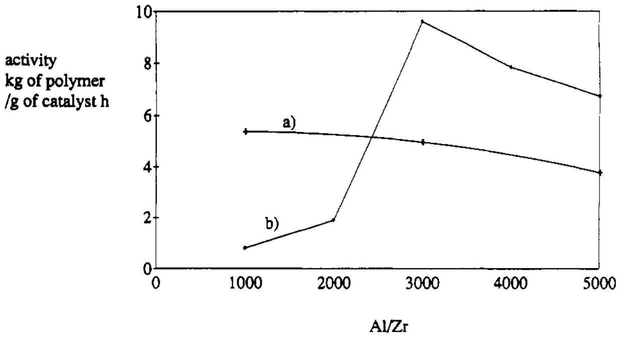


Figure 1. Activities for the polymerization of propylene and copolymerization of propylene and 2-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol (0.0344 mol/L) at different Al/Zr ratios using racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO keeping the concentration of the Zr-compound constant at 0.044 × 10^{-3} mol/L. Polymerization conditions: T = 20°C, T_p = 60 min, $V_{toluene}$ = 250 mL, and $P_{propylene}$ = 2 bars. Line a shows propylene homopolymerizations. Line b shows copolymerization of 2-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol and propylene. The phenolic stabilizer was added after 5 min of propylene polymerization.

The polymerization activity (Table 1) was markedly higher at Al/phenol molar ratios >4.4. The low activity at low Al/phenol ratios may be attributed to rapid catalyst deactivation in the absence of an excess of free MAO or TMA. The molecular weights of the copolymers increased with increasing phenol concentration and at the highest initial phenol concentration the molecular weight of the produced copolymer is similar to that of polypropylene prepared under similar conditions. The molecular weight distributions of the copolymers lie in a narrow range of values between 1.9 and 2.1 which are close to those values characteristic of polymerizations over single site catalysts.[19] When compared with the homopolymer the crystallinities and melting points of the copolymers are lower. This may be due to the fact that the large phenol groups cannot completely be expelled from the crystalline phase whereby both the crystallinity and melting point are reduced. According to Chung et al.,[20] who prepared hexenol/propylene copolymers the degree of depression of melting point and crystallinity compared to polypropylene depends mainly on the sequences of hexenol repsective propylene units. The functional copolymer prepared by Chung et al. had approximately the same degree of crystallinity as polypropylene. The preservation of crystallinity was attributed to a unique blocky microstructure which offered enough consecutive sequences of propylene units in the polymer backbone to form a crystalline phase. Apparently, the produced 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol/propylene copolymer does not have such a blocky microstructure. Besides, a propylene/stabilizer copolymer with a blocky microstructure, contrary to the prepared copolymer, would presumably exhibit a low thermooxidative stability. Therefore, it is more likely that the prepared copolymer has an random microstructure with evenly distributed phenolic units.

At lower polymerization temperatures the molecular weight increases, the molecular weight distribution remains almost constant, the melting point increases from 126 to

Table 1. Results of the Copolymerization of Propylene and 6-*tert*-Butyl-2-(1,1-dimethylhep-6-enyl)-4-methylphenol[a]

entry	C_{phenol},[b] mol/L	Al/phenol, mol ratio	activity, kg of polym/g of cat. h	M_n, g/mol	P_d[c]	cryst,[d] %	melting point, °C	conc of bound stabilizer,[e] wt %
1	0		5.0	28 000	1.9	43	146	0
2	0.0172	7.4	12.6	10 000	2.1	29	130	1.3
3	0.0264	5.2	12.3	10 000	2.1	30	126	2.5
4	0.0344	4.4	9.6	14 000	2.1	33	128	3.8
5	0.0472	3.0	1.5	35 000	1.9	33	138	5.5

[a] Polymerization conditions: catalyst racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride, cocatalyst MAO, Al/Zr = 3000, $P_{\text{propylene}}$ = 2 bars, polymerization time 60 min, T = 20 °C, and V_{toluene} = 250 mL. The appropriate amount of phenolic stabilizer monomer was added after 5 min of propylene polymerization. [b] C_{phenol} denotes the concentration of 6-*tert*-butyl-2-(1,1-dimethylhep-6-enyl)-4-methylphenol. [c] P_d denotes molecular weight distribution. [d] Cryst denotes the polymer crystallinity, which was determined from DSC curves, and the heat of fusion of a folded-chain polypropylene crystal has been taken as 49.8 cal/g. [e] The amount of bound phenolic stabilizer was determined by UV spectroscopy after extracting the copolymers for 24 h with a mixture of refluxing (50:50) 2-propanol/cyclohexane.

Table 2. Effect of Polymerization Temperature on Molecular Weight and Catalyst Activity[a]

entry	C_{phenol}, mol/L	T, °C	activity, kg of polym/g of cat. h	M_n, g/mol	M_w, g/mol	P_d	T_m, °C	conc of bound stabilizer, wt %
1	0	20	5.0	28 000	52 000	1.9	146	0
3	0.0264	20	12.3	10 000	21 000	2.1	126	2.5
6	0.0264	0	0.7	64 000	121 000	1.9	146	2.5
7	0.0264	−20	0.03	132 000	249 000	1.9	150	n.d.[b]

[a] Polymerization conditions: Al/Zr = 3000, $C_{\text{propylene}}$ = 1.5 mol/L, V_{toluene} = 250 mL, and polymerization time = 60 min. The phenolic stabilizer was added after 5 min of propylene polymerization. [b] The amount of bound phenolic units were not determined due to insufficient amount of copolymer to perform UV analysis.

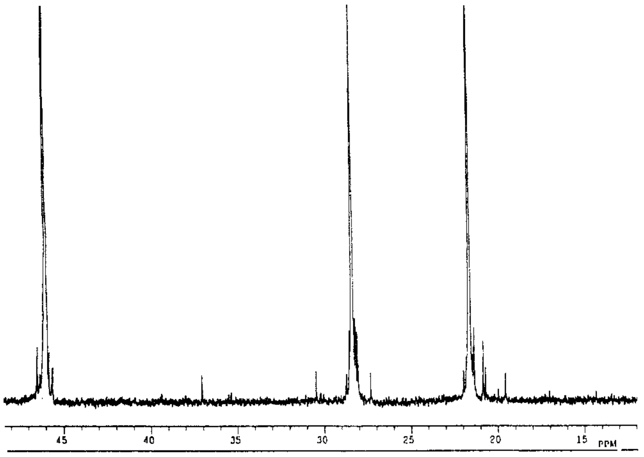


Figure 2. ^{13}C NMR spectrum of polypropylene (entry 1, solvent 1,1,2,2-tetrachloroethane-d_2).

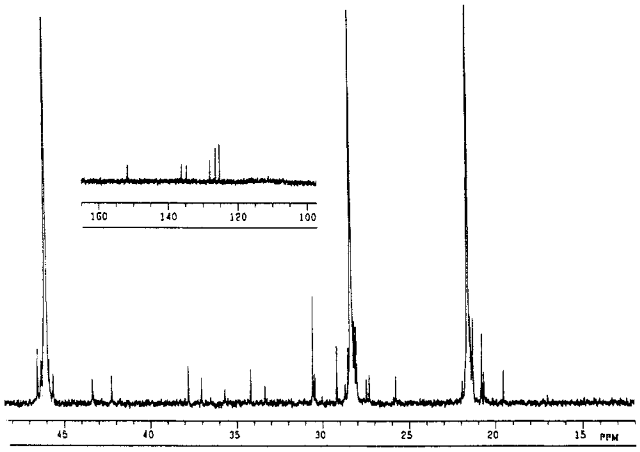


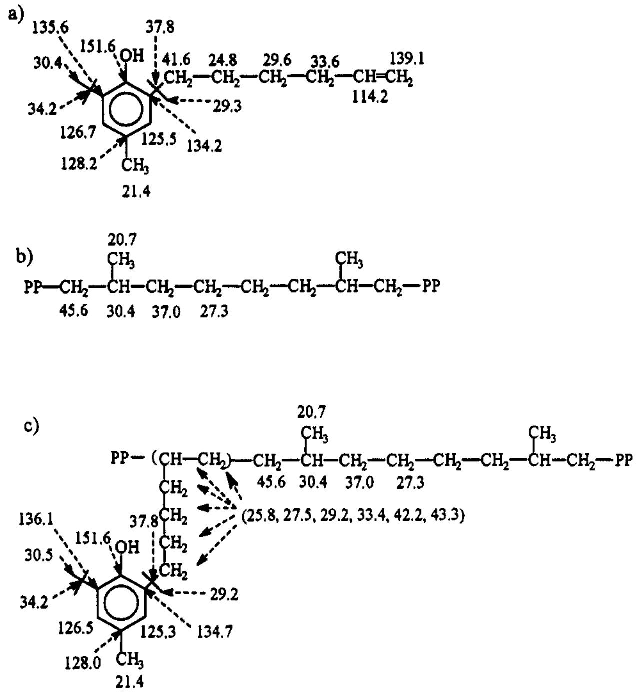
Figure 3. ^{13}C NMR spectrum of copolymer (entry 5, solvent 1,1,2,2-tetrachloroethane-d_2).

150 °C, and the polymerization acitivity decreases as shown for polymerization temperatures, T_p, from 20 to −20 °C in Table 2. The results presented in Tables 1 and 2 suggest that the copolymer melting point depends mainly on the phenol concentration in the copolymer as well as on the molecular weight of the copolymer.

The ^{13}C NMR spectra of the copolymer and polypropylene have been amplified in order to see all minor resonances, as shown in Figures 2 and 3, respectively. The chemical shift data for the phenolic monomer, copolymer, and polypropylene are shown in Scheme 3. The overall stereoregularity of the polymers can be evaluated from the relative areas of the resonances of the methyl stereochemical triads. The stereochemical triad composition of the copolymer, expressed as fractions of isotactic mm = 96.2, heterotactic mr = 3.1, and syndiotactic rr = 0.7 triads, is similar to that of the polypropylene, mm = 96.9, rr = 2.2 and rr = 0.9, prepared by the same catalyst system. Since 2rr/mr is "close" to 1,[21] the triad composition suggest that the propagation step is mainly enantiomorphic site controlled. On the basis of ^{13}C NMR spectra the propylene insertion proceeds dominantly via 1,2 additions with much lower amounts of 1,3 additions. No traces of 2,1 additions[22] can be detected in our ^{13}C NMR spectra. The chain-end structures of the polymers, which could have given an insight into initiation, chain-transfer, and termination reactions, are not visible in the ^{13}C NMR spectra. The absence of double-bond resonances (the phenolic monomer exhibits strong double-bond resonances at 139 and 114 ppm) in the ^{13}C NMR spectra of the copolymer and the shifts in the spacer carbons ($-(CH_2)_4-$) in comparison with the phenolic monomer unambiguously suggest that the phenolic stabilizer monomer is copolymerized with propylene over the racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system. The FT-IR spectra of the extracted copolymer (entry 5) and polypropylene prepared by the same catalyst (entry 1) are shown in Figure 4. The spectrum of the copolymer displays additional peaks at the following frequencies: 3640 (strong hindered phenol O–H stretching), 1600–1670 (weak Ar stretching), 1230 (medium OH bending), 860 (medium Ar wagging), 770 and 730 cm^{-1} (medium and weak $-(CH_2)_4-$rocking). Otherwise all characteristic vibrational bands from C–C and C–H in the saturated polymer backbones are similar, with no detectable peaks at 3070, 1640, and 910 cm^{-1}, that would indicate the presence of vinyl groups.

Kinetic Profiles of Homo- and Copolymerizations. The polymerization rates, taken as R_p = kilograms of

Scheme 3.[a] ^{13}C NMR Shift Data for (a) 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol, (b) Polypropylene (Entry 1), and (c) Copolymer (Entry 5)



[a] PP denotes an isotactic polypropylene chain.

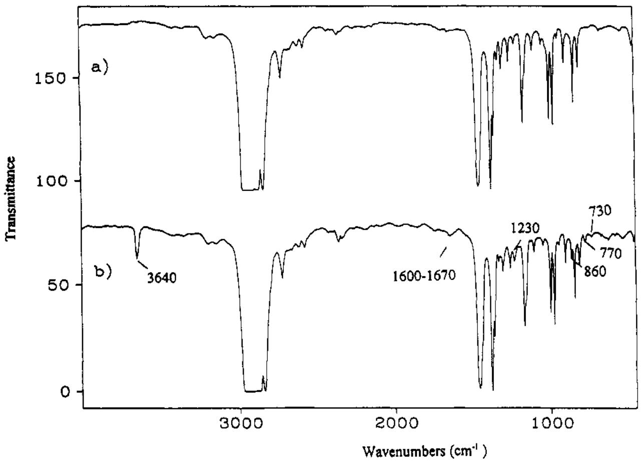


Figure 4. (a) The FTIR spectrum of polypropylene (entry 1) and (b) the FTIR spectrum of copolymer (entry 5).

polymer/(grams of catalyst × hours), of homo- and copolymer formations are directly related to the feed rate of propylene to the semibatch reactor operated at constant pressure and temperature. The kinetic profiles for the polymerizations after adding the phenolic monomer prior to the introduction of metallocene catalyst and after 5, 20, and 40 min of propylene polymerizations are graphically plotted in Figure 5. The homopolymerization of propylene exhibited a steady-state type of kinetic curve, whereas the copolymerization kinetic curve showed an initial rapid increase in polymerization rate followed by a decay type of kinetic behavior. The decrease in catalytic activity during copolymerization can rationally be explained by the fact that the concentration of the phenolic stabilizer available to complex with the active catalyst site decreases as a function of polymerization time; approximately 60% of the initially charged monomer is incorporated into the copolymer within 20 min. The observed 5-fold increase in the initial polymerization rate upon addition of the polar 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol is unprecedented in the chemical literature.

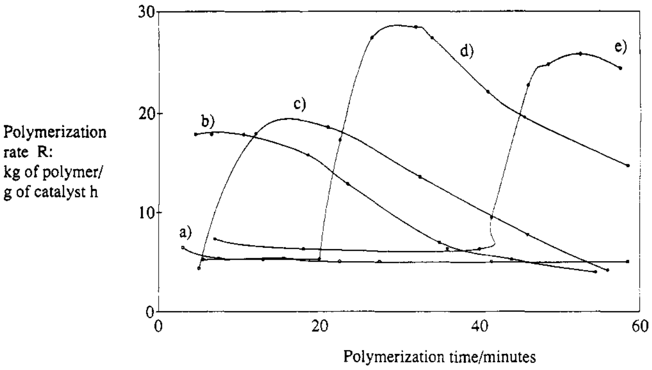


Figure 5. The "instantaneous" rate profiles for the polymerization of propylene and copolymerization of propylene and 2-*tert*-butyl-2-(1,1-dimethylhept-6-enyl-4-methylphenol adding the comonomer at different times using racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO as catalyst. Polymerization conditions: Al/Zr = 3000, T = 20 °C, $P_{\text{propylene}}$ = 2 bars, and V_{toluene} = 250 mL. Line a shows polymerization of propylene (entry 1). Line b shows when the phenolic stabilizer (final concentration 0.0344 mol/L) was first precomplexed with MAO for 75 min prior to the addition of the metallocene catalyst. The unprecomplexed phenolic monomer (final concentration 0.0344 mol/L) was added after (c) 5 (entry 4), (d) 20 and (e) 40 min of propylene polymerization.

However, Srinivasa Reddy et al.[23] observed a very small but definite enhancement of the initial rate of ethylene polymerization when $AlMe(BHT)_2$ (BHT = 2,6-di-*tert*-butyl-*p*-cresol) was used as a second cocatalyst in conjunction with the Cp_2ZrCl_2/TMA (Cp = cyclopentadienyl, TMA = trimethylaluminum) catalyst system. No specific reason for the activity enhancement upon the addition of $AlMe(BHT)_2$ was given and the catalyst productivities for both of the above-mentioned catalyst systems were far inferior to that of Cp_2ZrCl_2/MAO catalyst system. The formation and composition of products formed between sterically hindered phenols (2,6-di-*tert*-butyl-*p*-cresol, BHT) and substituted alkylaluminum compounds were reported by Shreve et al.,[24] and for TMA the observed species were Al_2Me_6, Al_2Me_5BHT, $AlMe_2BHT$, and $AlMeBHT_2$. The MAO solution used in the present study contained 26.7% of residual TMA, therefore it is likely that AlMe(phenolic monomer)$_2$ and $AlMe_2$(phenolic monomer) were formed. These sterically hindered aryloxides may also function as cocatalysts besides MAO and TMA. Resconi et al.[25] proposed that the actual cocatalyst in the metallocene/MAO system is actually TMA itself, with MAO acting as a soluble carrier–activator of the ion pair formed upon the reaction of the metallocene with TMA.

A question that still awaits a satisfactory answer is the precise structural nature of the catalyst–cocatalyst interaction. Consensus appears to be developing that in these systems the active catalysts are the electronically 14 electron d^0 (or d^0f^n) metallocene alkyl compounds which together with MAO are presumed to be ion pairs $[Cp_2MR]^{+-}$[aluminate] (Cp = dicyclopentadienyl, M = metal, and R = alkyl).[26,27] Recently an isolable and crystallographicaly characterizable, highly active "cation-like" zirconocene polymerization catalyst was reported[28] and later Chien et al.[29] reported that the free racemic [ethylenebis(indenyl)] methylzirconium cation isospecifically polymerized propylene. The cation was even more active than the racemic [ethylene-1,2-bis(1-indenyl)]-zirconium dichloride/MAO catalyst system. An unprecedented behavior in Ziegler–Natta catalysis was found since the activity increased with decreasing polymerization temperature. The effect of different counterions on the metallocene polymerization of propylene have shown that

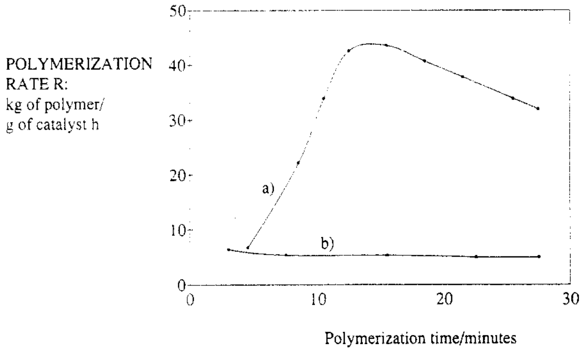


Figure 6. Comparison of the "instantaneous" rate profiles in the polymerization of propylene with and without phenol using racemic [1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system. Polymerization conditions: Al/Zr = 3000, T = 20 °C, $P_{\text{propylene}}$ = 2 bars, and V_{toluene} = 250 mL. Line a shows the addition of 2,6-di-*tert*-butylphenol (0.0344 mol/L) after 5 min of propylene polymerization. Line b shows homopolymerization of propylene (entry 1).

the sterically demanding, noncoordinating $[B(C_6F_5)_4]^-$ gave the best activity and highest molecular weight.[30] Assuming that the generally accepted structure of the "cation-like" active center presented above is correct, a likely hypothesis of the role of the phenolic monomer on the active center is that, the phenolic monomer functions as a large weakly coordinating anion which stabilizes the cationic polymerization center. Another possibility is that the phenol removes TMA from the vicinity of the polymerization centers. Then the strongly methylating TMA cannot compete with the coordinating monomers for the active centers. This is in accordance with the recent findings by Tritto et al.,[31] who studied the role of "free" TMA in MAO solutions on the polymerization activity of the group 4 metallocene–MAO-based catalytic systems. Tritto et al. proposed contrary to previous hypothesis that MAO, and not the "free" TMA, is the actual cocatalyst in metallocene–MAO-based catalytic systems. In addition, Tritto claimed that only MAO gives a complex with a metallocene catalyst that have characteristics close to active cation-like species outlined previously, whereas a TMA-activated metallocene catalyst shows hardly any polymerization activity.

There is, of course, the obvious concern that the activity enhancement is, in fact, due to some synergistic copolymerization effect as reported for the polymerization of ethylene and 1-hexene.[32] In order to eliminate this possibility a polymerization of propylene in the presence of 2,6-di-*tert*-butylphenol was carried out, and the result is graphically plotted in Figure 6. The addition of 2,6-di-*tert*-butylphenol (0.0344 mol/L) after 5 min of propylene polymerization caused a similar increase in the initial polymerization rate of propylene. This result also supports the above presented hypothesis of the role of the phenolic monomer on the active center. The polymerization rate of propylene increased by almost 8 times after a short build-up period and the polymerization was agitation limited after only 30 min. The observed slight decrease in polymerization rate after the build-up period may be attributed to mass transfer limitations at such high polymerization rates and/or the rapidly precipitating polypropylene that decrease the amount of the sterically hindered phenol.

The major differences between copolymerizing propylene and sterically hindered phenolic stabilizers over a metallocene catalyst compared to employing a supported heterogeneous catalyst ($TiCl_4/MgCl_2/Al(C_2H_5)_3$/diphenyldimethoxysilane) are that higher incorporation yields of phenolic units are obtained as well as an enhancement in the polymerization rate is observed when using the metallocene catalyst. Other advantages of using metallocene catalyst are that there is no broadening of molecular weight distribution and that the phenolic monomer does not have to be precomplexed with a stoichiometric molar amount of triethylaluminum prior to copolymerization as in the case when heterogeneous Ziegler–Natta catalyst are employed.[5c]

Table 3. Results of the Thermooxidative Stability Studies of the Extracted Copolymers by FTIR after Oven Aging at 110 °C in Air

entry	conc of bound stabilizer, wt %	M_n,[c] g/mol	P_d[d]	time for the formation of the carbonyl peak, h
a[a]		28 000	1.9	6
b	3.7 (80%)[b]	20 000	2.1	700
c	3.8 (85%)	14 000	2.1	600
d	3.1 (94%)	14 000	2.5	700
e	2.8 (62%)	10 000	2.5	400

[a] These polymers were prepared according to procedures a–e in Figure 5, i.e. polymer a was prepared according to procedure a etc. [b] The number in parentheses denotes the conversion of the phenolic monomer to copolymer; i.e. (%) = [(copolymerized phenolic monomer/initially charged phenolic monomer into the reactor) × 100%]. [c] The number average molar mass was obtained before the extraction.[d] The polydispersity index was measured before the extraction.

Stability Studies. The thermooxidative stability of the copolymer was determined by oven aging at 110 °C in an air atmosphere in combination with FTIR analyses. The copolymers were extracted prior to oven aging with refluxing 2-propanol/cyclohexane for 24 h in a soxhlet apparatus in order to extract residual monomers. For the copolymers presented in Table 3 the carbonyl peak appeared after 400–700 h of oven aging at 110 °C, whereas unstabilized polypropylene showed a strong carbonyl peak after 6 h.

Conclusions

We have shown that isotactic narrow molecular weight distribution copolymers of propylene and 6-*tert*-butyl-2-(1,1-dimethyl-hept-6-enyl)-4-methylphenol over a racemic [1,1′-(dimethyl-silylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system can be obtained in high yields. The produced copolymer had high thermooxidative stability, and the addition of the phenolic stabilizer led to a significant enhancement of polymerization rate. The increase in polymerization activity was attributed to the ability of the phenolic monomer to stabilize the cationic polymerization center. Since the molecular weight distribution of the copolymers is close to 2, it may be concluded that the "stabilized" active sites are uniform in chemical structure. However, the precise mechanism of the interaction between the phenolic monomer and the polymerization center, and also of the reaction between MAO (and/or TMA) and the phenolic monomer, are not totally clear at present.

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