Macromolecules

Volume 29, Number 27 December 30, 1996

Copolymerization of Ethylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over Three Different Metallocene−Alumoxane Catalyst Systems

Carl-Eric Wilén, Hendrik Luttikhedde, Thomas Hjertberg,[†] and Jan H. Näsman*

Àbo Akademi University, Department of Polymer Technology, Porthansg. 3−5, SF-20500 Finland, and Chalmers University of Technology, Department of Polymer Technology, S-412 96 Göteborg, Sweden

Received June 6, 1996; Revised Manuscript Received October 15, 1996[⊗]

ABSTRACT: Copolymers of ethylene and the polar monomer 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol were synthesized using three different homogeneous metallocene−methylalumoxane catalyst systems, i.e. *rac*-[1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride ($Me_2Si(IndH_4)_2ZrCl_2$)/methylalumoxane (MAO), *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride ($Et(IndH_4)_2$-$ZrCl_2$)/MAO, and dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2)/MAO. The initial polymerization rate, compared to that of ethylene homopolymerization, increased up to almost 3 times when the sterically hindered phenolic stabilizer was added during ethylene polymerization over one of the two chiral bridged metallocene catalysts. In contrast, the addition of the phenolic monomer during ethylene polymerization over the achiral Cp_2ZrCl_2 catalyst did not result in an appreciable change in polymerization activity. The dissimilarity in polymerization rate behavior of chiral versus achiral metallocene catalysts may be attributed to differences in the gap aperture between the π-ligands of the catalyst and to sterical and electronic factors. The level of comonomer incorporation was also found to be different with copolymers produced over chiral versus achiral metallocene catalyst. The comonomer content was 2−3 times lower for the copolymers produced over the achiral Cp_2ZrCl_2 catalyst compared to the copolymers prepared over either of the two chiral catalysts under similar conditions at low temperatures. As expected, the melting points and crystallinities of copolymers decreased with increasing phenol content. According to ^{13}C NMR studies, the chemical shifts of the copolymer's methylene and methine backbone carbons correspond to those observed for random ethylene/1-octene copolymer with isolated hexyl branches. Thus, the produced copolymers are random copolymers, which contain isolated phenolic long chain branches. No detectable traces of phenolic homopolymer or blockcopolymer fragments were found by ^{13}C NMR. The thermo-oxidative stability of the copolymers prepared was high even after prolonged extraction with a mixture of refluxing (50:50) 2-propanol/cyclohexane; the oxidation induction time at 200 °C ranged from 18 to 72 min for the copolymers whereas unstabilized polyethylene exhibited an oxidation induction time of only 1 min, as determined by differential scanning calorimetry (DSC). The numerical values of the ratio of weight-to-number average molecular weights of the copolymers were below 3 and thus characteristic of polymers produced by single-site catalysts. Furthermore, the copolymer molecular weights were similar to those of polyethylene prepared under similar conditions.

Introduction

Polyolefins are prone to degradation and/or cross-linking at nearly all stages of their life cycle, i.e. during production, storage, processing, and end use. The degradation is detrimental to polyolefins performance in terms of melt flow, color stability, and retention of physical properties. Therefore, in many cases various stabilizers must be added to polyolefins to retard or inhibit degradation.[1] Effective stabilizing additives should, apart from having a suitable chemical structure for proper functioning, also have the ability to physically remain in the polyolefin throughout their life cycle. From the physicochemical point of view chemically bound stabilizers offer advantages over conventional admixed stabilizers, since chemically bound stabilizers cannot be physically lost due to migration, volatilization, or extraction. Although there has been academic re-

---

* Author to whom correspondence should be sent.

[†] Chalmers University of Technology.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

S0024-9297(96)00830-3 CCC: $12.00

search on polymer-bound stabilizers for a long time, the intensity has not been overwhelming.[2] However, an increasing number of groups have started research in this field.[3] The activities have mainly been concentrated on grafting functionalized antioxidants (e.g. acryloyl, methacryloyl) onto the polymer backbone by using photoreactive stabilizers[4] or with the help of coupling agents and/or peroxide.[5] The method of reactive grafting using peroxides is normally associated with some problems, i.e. part of the stabilizer is consumed by the peroxide during grafting, the bulk polyolefin may undergo cross-linking and/or degradation and only a low level of binding is obtained as a result of major side reactions (homopolymerization) of the antioxidant during processing.[6] The second method of tethering stabilizers onto the polyolefin backbone using photoreactive hindered amine light stabilizers (HALS) photografted at the polymer surface is very interesting, although this approach is limited to polyolefin products used in outdoor applications.

We have investigated an alternative method for attaching stabilizers onto the polyolefin, i.e. the copolymerization of stabilizers with α-olefins over metallocene catalysts. In a recent paper we reported the copolymerization of propylene and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over a *rac*-$Me_2Si(IndH_4)ZrCl_2$/MAO catalytic.[7] The sterically hindered phenolic monomer was most useful both as a polar activator and as an effective monomer to copolymerize with propylene over the *ansa*-metallocene catalyst. This paper describes the copolymerization of 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol and ethylene over three different metallocene/MAO catalyst systems. The addition of the phenolic monomer enhanced the polymerization rate of ethylene over either of the two bridged metallocene catalysts whereas it was invariant when the unbridged Cp_2ZrCl_2 catalyst was used. The properties of the produced copolymer were also examined.

Experimental Section

Materials. 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 as described previously.[6] The *rac*-[1,1′-(dimethylsilanylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride and *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride were prepared essentially according to the literature,[8,9] whereas Cp_2ZrCl_2 was purchased from Aldrich. The following chemicals were used in the copolymerization experiments: high-purity ethylene (99.5%, Neste Oy), nitrogen (99.9999%, AGA), high-purity toluene (refluxed over sodium and subsequently distilled under argon atmosphere prior to use), and methylalumoxane (MAO, 29.3% w/w toluene solution; Al total 13.1%w/w; Al as TMA, 3.50% w/w; supplied by Witco and used as received).

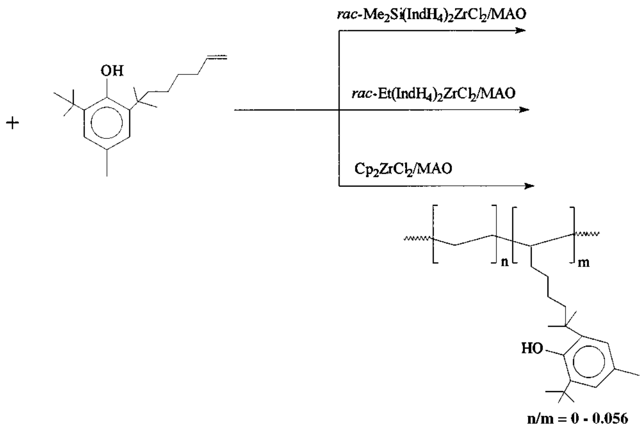
Polymerization Procedure. The sampling of the catalyst, activator, and phenolic monomer was carried out under nitrogen in a MBROWN glovebox containing <2 ppm oxygen and < 5 ppm water. The reaction temperature was controlled within ±0.3 °C by a Lauda Ultra circulating water bath. The slurry polymerizations were carried out in a 0.5 L jacketed glass autoclave (Büchi Glass) equipped with a blade turbine stirrer. The dry glass autoclave was evacuated and backflushed with nitrogen. This procedure was repeated several times. Then 330 mL of freshly distilled toluene was injected into the autoclave by using 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 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. Then the catalyst/activator mixture was charged into the reactor. The prepolymerization was started by introducing ethylene monomer ($P_{\text{ethylene}} = 1.4$ bar). After 5 min the appropriate quantity of phenolic stabilizer diluted in 15 mL of toluene was flushed into the reactor by means of gaseous ethylene until the ethylene partial pressure reached 1.6 bar. The polymerization rate was determined as the rate of ethylene consumption keeping a flow rate of ethylene to maintain a 1.6 bar partial pressure of ethylene throughout the polymerization. After 20 or 40 min the polymerizations were quenched by rapidly venting the ethylene and adding 100 mL of methanol. The catalyst residues of the produced polyolefin were removed by treatment with 1 L of ethanol containing 40 mL of 10% HCl solution and subsequent filteration. Then the polyolefin was washed twice with ethanol, dried in vacuum, and weighed to determine the polymerization yield. The copolymers were extracted with refluxing 2-propanol/cyclohexane[10] for 24 h in a Soxhlet apparatus prior to the determination of the amount of bound phenolic stabilizer and thermo-oxidative studies.

Polymer Characterization. The amount of bound phenolic stabilizer was determined by UV analyses, and the numerical values are based upon polypropylene/Irganox 1076 standard films, which had an thickness of ≈70 μm. 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 exhibit a strong absorbance in this region at 280 nm with identical extinction coefficients, and all measurements were carried out at this wavelength. Melting and crystallization thermograms were recorded with a Perkin-Elmer DSC IV system by raising the temperature from 35 to 180 °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 66 cal/g as the heat of fusion.[11] The oxidation induction time was determined from data recorded during isothermal test using differential scanning calorimetry (DSC) in accordance with ASTM method D3895. The DSC was calibrated with an indium standard ($T_{\text{fus}} = 156.6$ °C). A sample (≈6 mg) was placed in an aluminium pan and heated at 10 °C/min to the test temperature, i.e. 200 °C. Once the temperature had equilibrated (after approx. 2 min), the run was commenced, by shifting the test gas from nitrogen to a constant oxygen flow rate of 30 mL/min. The oxidation time was determined by extrapolating the exotherm associated with the beginning of oxidation to the baseline of the trace. The molecular mass distribution was determined with a Waters 150 CV, equipped with an on-line viscometer and a refractive index (RI) detector, at 135 °C with 1,2,4-tricholorbenzene (TCB) as solvent. The size exclusion chromatography (SEC) apparatus was also coupled with a Wyatt Dawn F multi angle laser light scattering detector (MALLS). Sample (2 g/L) were dissolved over night in TCB at 135 °C, 200 μL was injected. The equipment was calibrated by narrow polystyrene standards, from 20 000 000 to 450 g/mol, according to the principle of universal calibration. Besides using the calibration curve, the molecular mass was also calculated from the light scattering signal. The results were evaluated using the software from Waters and Wyatt.

Results and Discussion

Copolymerizations of ethylene and 6-*tert*-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol (Scheme 1), were carried out with three different metallocene catalyst systems, namely *rac*-[1,1-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO, *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO, and dicyclopentadienylzirconium dichloride/MAO in toluene at 20 °C. The kinetic profiles of the homo- and copolymerizations are graphically plotted in Figures 1−3. The homopolymerization of ethylene over the two bridged metallocene catalysts exhibited essentially a steady-state type of kinetic curve,

Scheme 1. Copolymerization of Ethylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over Three Different Metallocene/MAO Catalysts Systems



whereas the copolymerization over the two bridged metallocene catalysts showed a kinetic curve with a definite enhancement of the initial polymerization rate upon comonomer addition followed by a decay type of kinetic profile. The initial increase in the polymerization rate is attributed to the polar monomer which may raise the amount of active sites or increase the propagation rate constant due to the following reasons. (1) The phenol removes the "free" trimethylaluminium (TMA) from the vicinity of the polymerization sites by forming sterically hindered aryl oxides ($AlMe(PH)_2$ and $AlMe_2(PH)$; PH = 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenoxide).[12] Then the strongly methylating TMA cannot interact with the active site. This assumption is in agreement with the findings by Tritto and coworkers,[13] who claim that MAO is a better alkylating agent than the "free" TMA and it has a greater capacity for producing and stabilizing cation-like complexes. (2) The formed sterically hindered aryl oxides may also function as cocatalysts besides MAO and TMA. A similar indication have recently been published by Soga et. al.,[14] who noticed that polyethylene was obtained in high yields over a range of metallocene catalyst systems composed of a mixture of a metallocene compound [e.g. Cp_2ZrCl_2 and $Et(IndH_4)_2ZrCl_2$] and $Si(CH_3)_3OH$ using trialkylaluminium as cocatalyst. The Lewis base modified metallocene catalysts exhibited much higher polymerization activities than the corresponding unmodified catalysts also with the use of MAO as cocatalyst. (3) The polar phenolic monomer simply increases the dielectric constant of the medium. It is known, that the addition of polar solvents like CH_2Cl_2 to the polymerization medium (toluene) enhances the activity of metallocene catalysts.[15]

By contrast, the addition of the phenolic monomer after 5 min during ethylene polymerization over the unbridged Cp_2ZrCl_2 had only a negligible impact on the initial kinetic curve, whereas the rate of decay seems moderately faster. The initial ethylene consumption during copolymerization over the Me_2Si-bridged metallocene catalyst is almost 3 times higher compared to the value for the homopolymerization of ethylene over the same catalyst under similar reaction conditions (see Figure 2). The ethylene-bridged catalyst shows a similar behavior except that the magnitude of the increase of catalyst productivity is smaller and the rate of decay is faster. The slight difference in kinetic behavior between the bridged catalyst is attributed to the difference in the space volume between the aromatic ligands available for catalysis, indicating that a narrow angle (Me_2Si-bridge) is energetically more favorable than a wider angle (ethylene bridge) in this type of copolymerization. The unbridged Cp_2ZrCl_2 catalyst shows a comparable activity for both homo- and copolymerization under these reaction conditions. The dissimilarity in polymerization rate behavior of bridged versus unbridged metallocene catalysts may arise from the differences in the gap aperture between the π-ligands of the catalysts and/or from steric and electronic conditions at the catalytic center. The level of comonomer incorporation was also found to be different with copolymers produced over bridged versus unbridged metallocene catalysts, i.e. the comonomer content was 2−3 times lower for the copolymers produced over the unbridged Cp_2ZrCl_2 catalyst system compared to the copolymers prepared over either of the two stereospecific catalysts at 20 °C in toluene, as shown in Table 1. Since Cp_2ZrCl_2-based catalyst shows a kinetic decay curve both in homopolymerization and copolymerization unlike the bridged catalysts, a substantial amount of homopolymer is produced in 5 min prior to the addition of phenolic comonomer. Thus the produced copolymer over the Cp_2ZrCl_2 catalyst contains a substantial amount of homopolymer which was produced during the initial 5 min of polymerization. This circumstance is partially responsible for the fact that the comonomer incorporation level appears to be so low for the copolymers produced over the unbridged metallocene catalyst. However, this circumstance can not alone account for the fact that the difference of comonomer concentration is 2 or 3 times lower for copolymers prepared over the unbridged catalyst in comparison to the copolymers prepared over either of the two bridged catalysts.

The relatively low phenol content of copolymers prepared over the aspecific Cp_2ZrCl_2 catalyst is presumably due to the fact that the Cp_2ZrCl_2 catalyst is a poor polymerization catalyst for prochiral monomers, as reported by Kaminsky and co-workers.[16] As expected, the copolymers melting points and crystallinities decreased with increasing phenol content, i.e. with the increasing density of side chains. Each copolymer (e.g. entries 4, 6, and 10) with similar density of side chains shows similar crystallinities and melting points, with negligible influence of the catalyst used to prepare the copolymer. Interestingly and contrary to the previously published copolymerization of propylene and 6-*tert*-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol over the *rac*-[1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system, the overall ethylene copolymerization activities were not influenced by the variation of Al/phenol molar ratio between 1.2 and 4.8, whereas during the propylene copolymerization the catalyst activity was markedly reduced at Al/phenol molar ratios <4.4 under similar reaction conditions. Furthermore, the activity enhancement was more profound during propylene (5-fold increase) than ethylene (2−3-fold increase) copolymerizations upon phenol comomomer addition. These results indicate that ethylene coordination and insertion into the catalytically active zirconium site compared to propylene coordination and insertion is less sensitive to polar monomer/catalyst site (donor/acceptor) interactions occurring at the active zirconium site.

All the homo- and copolymers produced by these three catalyst systems, at 20 °C, are quite high molecular weight polymers, as suggested by their low solubilities. On the basis of a report in the literature, viscosity-

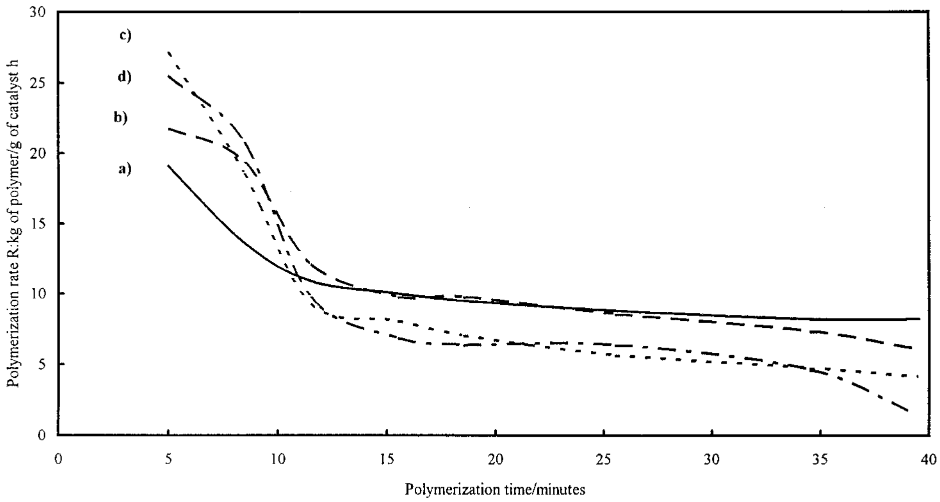


Figure 1. The "instantaneous" rate profiles for the polymerization of ethylene and copolymerization of ethylene and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over Cp_2ZrCl_2/MAO catalyst system adding the phenolic comonomer after 5 min of ethylene polymerization. Line a shows polymerization of ethylene (entry 1), and lines b (entry 2), c (entry 3), and d (entry 4) show the kinetic curves of copolymerizations using different Al/phenol mole ratios.

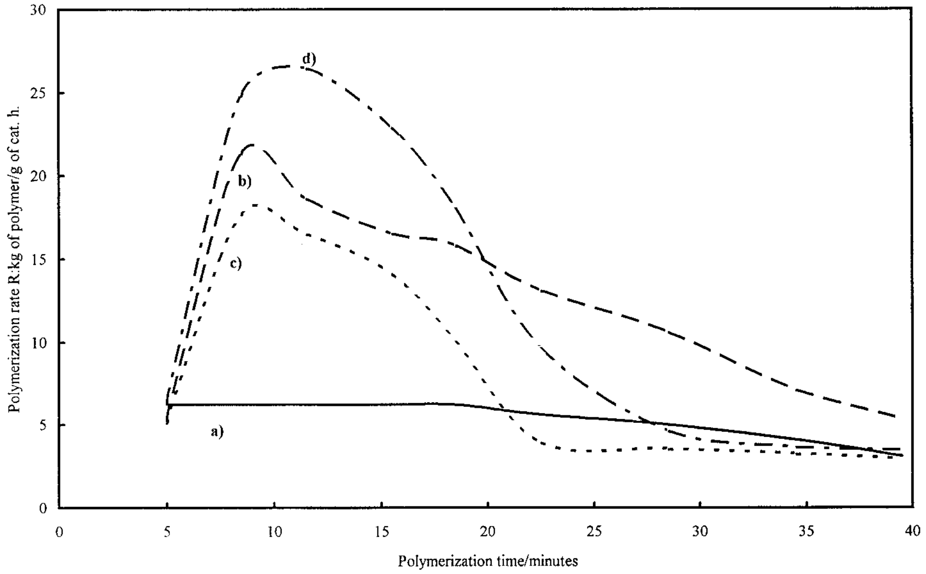


Figure 2. The "instantaneous" rate profiles for the polymerization of ethylene and copolymerization of ethylene and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over *rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO catalyst system adding the phenolic comonomer after 5 min of ethylene polymerization. Line a shows polymerization of ethylene (entry 5), and lines b (entry 6), c (entry 7), and d (entry 8) show the kinetic curves of copolymerizations using different Al/phenol mole ratios.

average molecular weight (M_η) are probably higher than 350 000.[17] In order to obtain polymers with lower molecular weights, polymerizations were conducted at 80 °C, and the complete list of molecular weight information of homo- and copolymers is summarized in Table 2. In fact, as seen in Table 2, all homo- and copolymer pairs have fairly similar molecular weights and molecular weight distributions. Thus, the overall molecular weight is not determined by the presence of phenolic comonomer. It is noteworthy that at high polymerization temperatures, i.e. 80 °C, the active sites become more sensitive to donor/acceptor interactions compared to the situation where copolymerizations are conducted at 20 °C. In fact, as shown in entry 14, at an initial mole ratio of Al/phenol = 2.2, the active polymerization sites are poisoned at 80 °C, whereas at low polymerization temperatures, entries 2, 3, and 4, the catalyst efficiency is independent of the Al/phenol ratio between 1.2 and 4.8. In order to avoid catalyst poisoning at 80 °C, further copolymerizations were conducted at a higher Al/phenol molar ratio of $\approx$10. The data presented in Tables 1 and 2 also seems to indicate that at high polymerization temperatures, i.e. 80 °C, a relatively higher portion of 6-*tert*-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol is incorporated into the copolymer compared to copolymerizations conducted at 20 °C.

A typical ^{13}C NMR spectrum of the extracted copolymer is shown in Figure 4. The observed resonances at 27.4, 30.7, and 34.6 for the methylene and 38.3 for the methine backbone carbons correspond to those reported for ethylene/1-octene copolymers with isolated hexyl branches.[18] (The ethylene/1-octene copolymer serves as a good reference polymer for identifying resonances in polyethylenes associated with isolated long chain branching.) Thus, the ^{13}C NMR spectra suggest that the prepared copolymer is in fact a random copolymer, which contains isolated phenolic long chain branches. No detectable traces of phenolic homopolymer or block copolymer fragments can be found in the ^{13}C NMR spectrum. The dominating end groups in the copolymer for which the ^{13}C NMR spectrum is presented in Figure

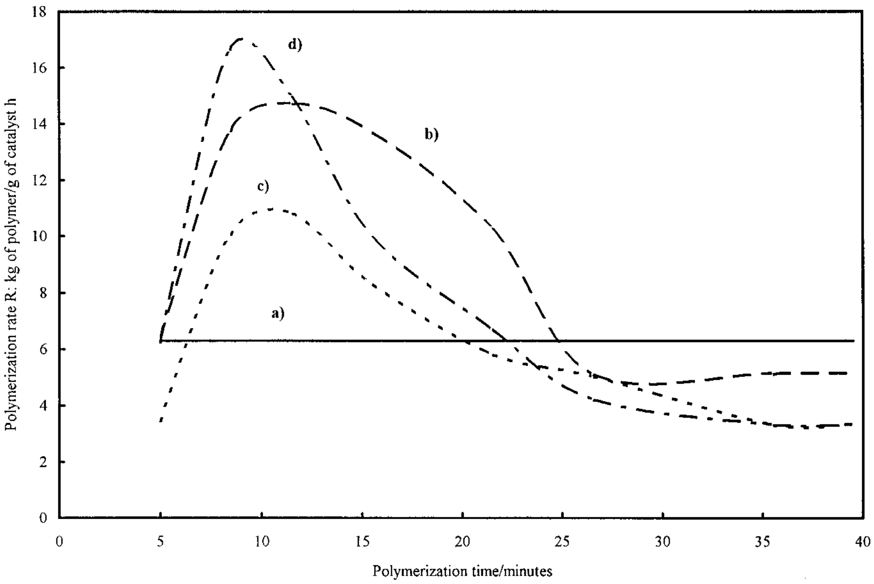


Figure 3. The "instantaneous" rate profiles for the polymerization of ethylene and copolymerization of ethylene and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over *rac*-$Et_2(IndH_4)_2ZrCl_2$/MAO catalyst system adding the phenolic comonomer after 5 min of ethylene polymerization. Line a shows polymerization of ethylene (entry 9), and lines b (entry 10), c (entry 11), and d (entry 12) show the kinetic curves of copolymerization using different Al/phenol mole ratios.

Table 1. Results of the Copolymerization of Ethylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol over Various Metallocene Catalysts at 20 °C[a]

entry	catalyst system	C_{phenol},[b] mol/L	Al/phenol, mol ratio	activity, kg of polymer/g of cat. h	melting point, °C	cryst,[c] %	concn of bound stabilizer,[d] wt %
1	Cp_2ZrCl_2/MAO	0		11.3	135	44.2	0
2	Cp_2ZrCl_2/MAO	0.017	4.8	11.4	131.6	43.6	0.67
3	Cp_2ZrCl_2/MAO	0.037	2.2	11.8	130.9	42.9	1.6
4	Cp_2ZrCl_2/MAO	0.058	1.4	10.7	130.8	38.0	2.7
5	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0		5.7	134	43.5	0
6	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0.017	4.3	10.1	126.5	38.3	2.9
7	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0.037	1.8	8.4	123.3	32.2	5.5
8	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0.058	1.2	10.8	118.2	33.5	5.4
9	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0		6.5	136.1	45.1	0
10	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0.017	4.7	8.7	130.5	37.8	2.6
11	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0.037	2.1	6.3	122.7	33.4	4.8
12	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0.058	1.3	7.5	121.8	32.9	6.7

[a] Polymerization conditions: Al/Zr = 3000, $P_{ethylene}$ = 1.6 bar, polymerization time 40 min, and $V_{toluene}$ = 330 mL. The appropriate amount of the phenolic stabilizer was added after 5 min of ethylene polymerization. [b] C_{phenol} denotes the concentration of 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol. [c] Cryst denotes the polymer crystallinity, which was determined from DSC curves, and the heat of fusion of a folded-chain polyethylene crystal has been taken as 66.6 cal/g.[11] [d] The amount of bound phenolic stabilizer was determined by UV spectroscopy after extracting the copolymers for 24 h with a mixture of refluxing 2-propanol/cyclohexane (50:50).

Table 2. The results of Copolymerization of Ethylene and 6-*tert*-Butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol at 80 °C[a]

entry	catalyst system	C_{phenol}, mol/L	Al/phenol, mol ratio	activity, kg of polymer/g of cat. h	M_n, g/mol	P_d[b]	melting point, °C	cryst, %	concn of bound stabilizer, wt %
13	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0		14	27 900	2.0	134.1	71.5	0
14	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0.037	2.2		no copolymer was obtained[c]				
15	*rac*-$Me_2Si(IndH_4)_2ZrCl_2$/MAO	0.01	8.8[d]	22.5	28 300	2.2	130.5	61.1	2.8
16	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0		14.2	32 300	2.3	134.0	67.3	0
17	*rac*-$Et(IndH_4)_2ZrCl_2$/MAO	0.01	10.7[d]	22.5	22 400	2.4	128.8	58.0	2.8
18	Cp_2ZrCl_2/MAO	0		31.8	23 700	2.5	132.9	68.4	0
19	Cp_2ZrCl_2/MAO	0.01	11.7[d]	24	20 200	2.4	131.8	61.1	2.5

[a] Polymerization conditions: Al/Zr = 3000, $P_{ethylene}$ = 1.6 bar, polymerization time 20 min, and $V_{toluene}$ = 330 mL. The appropriate amount of the phenolic stabilizer was mixed with half the MAO amount for 5 min prior to the addition of metallocene/MAO catalyst system. [b] P_d denotes molecular weight distribution. [c] The appropriate amount of the stabilizer was added after 5 min of ethylene polymerization whereby polymerization ceased at a Al/phenol ratio = 2.2. [d] Therefore, the subsequent copolymerizations were conducted at a lower Al/phenol ratio of ≈10, in addition the phenolic monomer was added prior to the metallocene catalyst.

4 are methyl groups resulting from hydrogen transfer with a minor portion of vinyl groups resulting from β-H-elimination (The copolymer has been prepared in the presence of hydrogen as chain transfer agent). Furthermore, the absence of double bond resonances in the ^{13}C NMR spectra of the copolymer and the shifts at the spacer carbons ($-(CH_2)_4-$) in comparison with the phenolic monomer unambiguously suggest that the phenolic monomer is copolymerized with ethylene over the metallocene catalysts.

The FT-IR spectra of the extracted copolymer and polyethylene are depicted in Figure 5. The spectrum of the copolymer displays additional peaks at the following frequencies: 3640 (strong hindered phenol

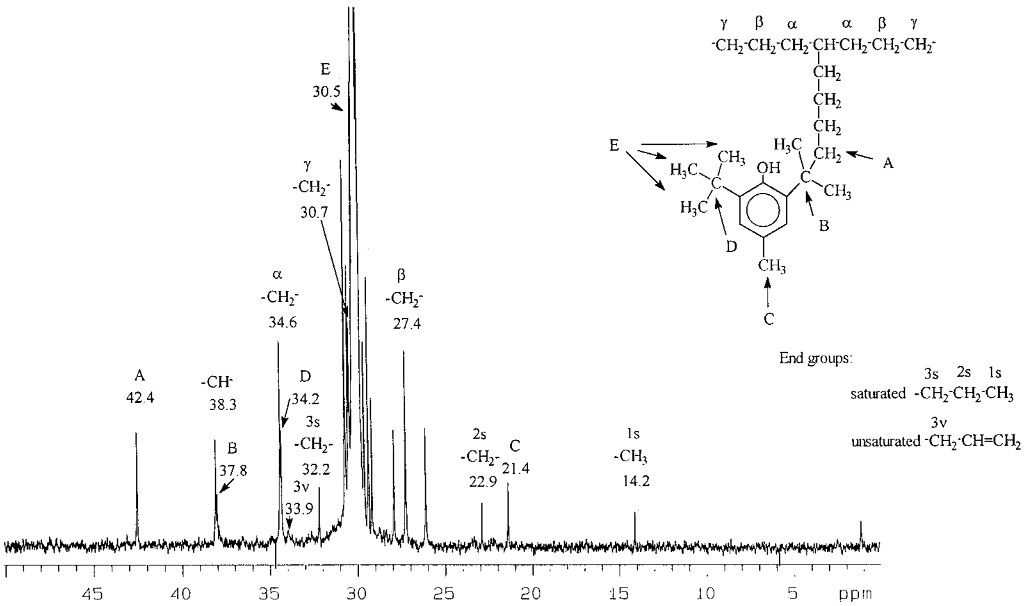


Figure 4. ^{13}C NMR spectrum of copolymer (polymerization conditions: $P_{\text{ethylene}} = 1.6$ bars, $P_{\text{hydrogen}} = 0.04$ bar, $T = 20$ °C, Al/Zr = 3000, and *rac*-$(CH_3)_2Si(IndH_4)_2ZrCl_2$/MAO catalyst system).

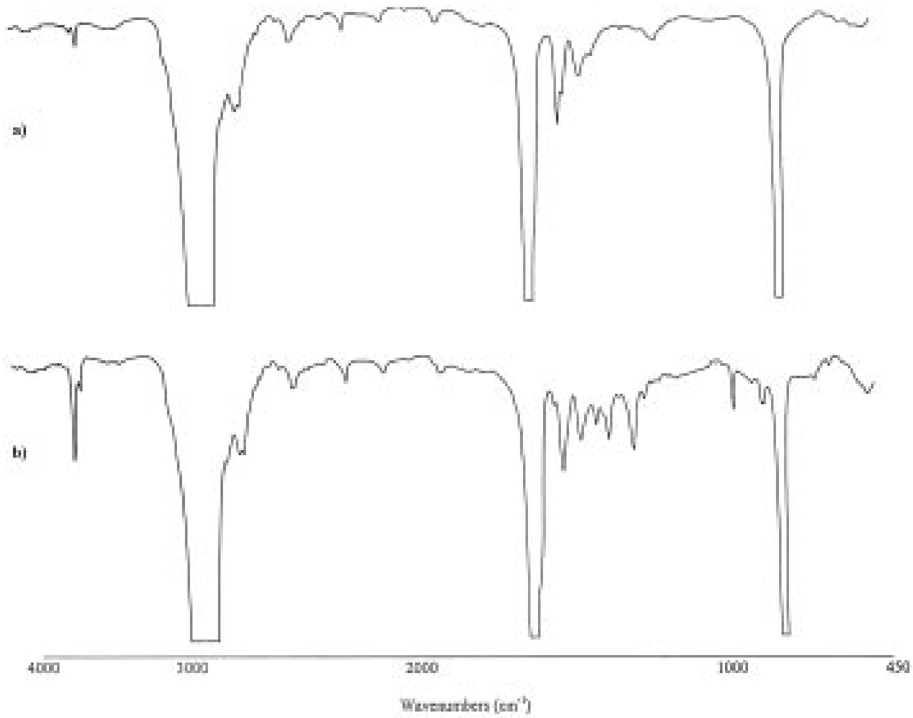


Figure 5. (a) The FTIR spectrum of polyethylene (entry 5) and (b) the FTIR spectrum of copolymer (entry 7).

O−H stretching), 1600−1670 (weak Ar stretching), 1230 and 1160 (medium OH bending), 860 (medium Ar wagging), and 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 backbone are similar, with no detectable peaks at 3070, 1640, and 910 cm^{-1} that would indicate the presence of vinyl groups.

Stability Studies

The copolymers were extracted prior to stability studies with refluxing 2-propanol/cyclohexane for 24 h in a Soxhlet appartus in order to extract any residual comonomer. The oxidation induction times were determined by DSC measurements and the results are shown in Table 3, i.e. the oxidation time was determined by extrapolating the exoterm associated with beginning of oxidation to the baseline of the trace. The oxidation induction times for the copolymers range from 18 to 72 min, depending on the phenol concentration, whereas

Table 3. Results of the Thermo-Oxidative Stability Studies of the Extracted Copolymers by Thermal Analysis

entry[a]	concn of bound stabilizer,[b] %	oxidation induction time at 200 °C, min
1	0	1
2	0.7	18
6	2.9	48
7	5.5	72

[a] See Table 1. [b] The copolymers were extracted prior to DSC measurements with refluxing 2-propanol/cyclohexane for 24 h in a soxhlet appartus.

the unstabilized polyethylene exhibits an abrupt departure from the baseline signal after only 1 min. Thus, the chemically bound phenolic units are effective in delaying polymer oxidation by virtue of their high radical trapping ability. At the test temperature, 200 °C, the polymer is in the melt state and the segmental mobility is rather high compared to normal end-use conditions. In the latter case, segments of the main chain are included in the crystalline structure, which drastically reduce the mobility of the noncrystalline part between crystalline segments. In addition, the lower temperature implies a lower segmental mobility also in the amorphous segments where the phenol moieties are found. For long-term stability, it is therefore essential to test the efficiency of these copolymers at temperatures below 100 °C.

Conclusion

In this paper, we have shown an effective route to prepare novel random copolymers of ethylene and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol, which had good thermo-oxidative stability using three different metallocene catalyst systems, i.e. *rac*-[1,1′-(dimethylsilylene)bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO, *rac*-[ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO, and dicyclopentadienylzirconium dichloride/MAO. In general, the bridged catalysts are much more effective than the unbridged catalyst in the incorporation of the phenolic monomer into the polyethylene structure, presumably because the unbridged Cp_2ZrCl_2/MAO catalyst system is a poor catalyst for prochiral monomers. Four possible explantions for the increase in polymerization rate over chiral metallocene catalysts upon phenol addition are presented.

However, the data presently available do not allow us to give a precise mechanism of the interaction between the phenolic monomer and the active catalyst site, and also of the reaction between MAO (and/or TMA) and the phenolic monomer. Further work is in progress to examine the role of MAO (and/or TMA) by conducting additional copolymerizations over these metallocene catalysts by using different activators such as $[(C_6H_5)_3C^+][B(C_6F_5)_4^-]$, $B(C_6F_5)_3$, sterically hindered aryl oxides and MAO.

Acknowledgment. The authors are grateful to the Technology Development Center (TEKES) for financial support. The referees are also thanked for valuable comments.

References and Notes

(1) (a) Al-Malika, S. Effects of Antioxidants and Stabilization. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds. (Eaastwood, G. C., Ledwith, A., Russo, S., Sigwalt, P., volume Eds.); Pergamon Press: New York, 1989; Vol. 6, pp 539−576. (b) Roscoe, J. P.; Gardner, P. S. *Tappi J.* **1990**, *September*, 117.

(2) (a) Patton, T. L; Horeczy, J. T.; Bown, D. E. U. S. Patent 3 477 991, 1961. (b) Tadao, I.; Juntaro, S.; Yamaguchi, I. D. E. Patent 1 947 590, 1970. (c) Kuczkowski, J. A.; Gillick J. G. *Rubber Chem. Technol.* **1984**, *57*, 621. (d) Al-Malika, S. *Chemtech* **1990**, June, 366. (e) Wilén, C-E.; Auer, M.; Näsman, J. H. *Polymer* **1992**, *33*, 5049. (f) Wilén, C-E.; Auer, M.; Näsman, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *114*, 9679. (g) Al-Malaika, S.; Ibrahim, A. Q.; Rao, M. J.; Scott, G. *J. Appl. Polym. Sci.* **1992**, *44*, 1287. (h) Bertiolini, G.; Lanzini, L.; Marchese, L.; Roggero, A.; Lezzi, A.; Costanzi, S. *J. Polym. Sci. Chem. Ed.* **1994**, *32*, 961. (i) Ekman, K. B.; Ekholm, L. G.; Näsman, J. H. Preparation of a novel HALS-polypropylene stabilizer. *J. Appl. Polym. Sci.*, in press.

(3) Macro IUPAC conference in Prague, Czechoslovakia, 1992, and at the ACS symposium in Chicago, August 1993.

(4) Ligner, G.; Avar, L. New technologies to tie down UV light stabilizers in polyolefins. Proceedings of the Meeting of the American Chemical Society, Division of Polymer Chemistry, Chicago, IL, August 1993; p 160.

(5) Al-Malaika, S. Effect of processing on antioxidant transformation and approaches to deal with problems of their migration. Proceedings of the Meeting of the American Chemical Society, Divison of Polymer Chemistry, Chicago, IL, August 1993; p 172, and references therein.

(6) Munteanu, D. *Developments in Polymer Stabilization-8*; Scott. G., Ed., App. Sci. Pub.: London, 1987; Chapter 5.

(7) Wilén, C-E.; Näsman, J. H. *Macromolecules* **1994**, *27*, 4051.

(8) Welborn, H. C. EP Patent 0 344 887 A2, 1989.

(9) Wild, F. R. W. P; Zsolani, L.; Huttner, G.; Brinzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(10) Nielsen, R. C. Extraction and quantification of polyolefin additives. IUPAC International Symposium, POLYMER 91, Australia, 1991; p 571.

(11) Chung, T. C, Lu, L. H.; Li, C. H. *Macromolecules* **1994**, *27*, 7533.

(12) Shreve, A. P.; Mulhaupt, R; Fultz, W.; Calabrese, J; Robbind, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

(13) Tritto, I; Li, S.; Sacchi, M. C.; Zannoni, G. *Macromolecules* **1993**, *26*, 7111

(14) Soga, K; Kim, H. J.; Shiono, T. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 765.

(15) Eisch, J. J; Caldwell, K. R.; Werner, S.; Kruger, C. *Organometallics* **1991**, *10*, 3417.

(16) Kaminsky, W.; Engehausen, R. ; Zoumis, K. *Makromol. Chem.* **1992**, *193*, 1643.

(17) The molecular weights of the homo- and copolymers prepared at 20 °C are very high and were not determined due to difficulties to solubility and anticipated problems with GPC columns. According to the literature (Heiland, K.; Kaminsky, W. *Makromol. Chem.* **1992**, *193*, 601) the viscosity-average molecular weight M_η is much higher than 350 000 for polyethylenes produced under these reaction conditions.

(18) Randall, J. C. *J. Polym. Sci. Phys. Ed.* **1973**, *11*, 275.

MA960830Q