Synthesis of Novel-*dl*-α-Tocopherol-Based and Sterically-Hindered-Phenol-Based Monomers and Their Utilization in Copolymerizations over Metallocene/MAO Catalyst Systems. A Strategy To Remove Concerns about Additive Compatibility and Migration

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ABSTRACT: In this paper we present an initial study on various synthetic routes to novel polymerizable *dl*-α-tocopherol derivatives and to a styrenic sterically hindered phenol which was stimulated by our desire to conduct copolymerization with these monomers with α-olefins over different metallocene/methylalumoxane (MAO) catalyst systems. The syntheses of 6-hydroxyl-2,5,7,8-tetramethyl-2-(but-3-enyl)-chroman (**1**) and 5,7,8-trimethyl-3-(hex-5-enyl)benzofuran-6-ol (**2**) were achieved by cyclocondensation of trimethylhydroquinone (TMHQ) with 3-methylhept-1,6-dien-3-ol and 2,7-octadienol, respectively. However, the latter tocopherol compound (**2**) could only be obtained in low yields, and all our attempts to isolate the product from its ring-opened isomers failed. This can be attributed to the fact that the reaction between TMHQ and 2,7-octadienol gave rise to a highly complex reaction mixture. Compound **3**, 6-hydroxyl-2,2,8,9-tetramethyl-6-allylchroman, was prepared from the corresponding allylchromanoxy ether via Claisen rearrangement. In addition facile synthetic pathways to 4-methylene(3,5-di-*tert*-butyl-4-phenoxy)styrene (**4**) and its trimethylsilylated derivative **5**, i.e., 4-methylene(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-styrene, were successfully developed. The chromanol **1** was copolymerized with ethylene over a *rac*-[dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system, and monomers **4** and **5** were copolymerized with styrene over an (η^5-indenyl)trichlorotitanium ($IndTiCl_3$)/MAO catalyst system. The copolymers contained from 2.3 to 6.8 wt % functional units and exhibit enhanced thermooxidative stabilities in comparison to the corresponding homopolymers as determined by TGA and DSC analysis.

Introduction

All organic materials, including polyolefins, are susceptible to oxidation in a process called "autoxidation".[1] This degradation process is irreversible and leads ultimately to polymer discoloration and loss of physical properties. Primary antioxidants, known as radical scavengers, are intended to interfere with the aforementioned degradation process, and they prevent the process from becoming autocatalytic.[2] α-Tocopherol, or vitamin E, is a fully substituted aromatic chromanol with a phenolic group situated *para* to the oxygen of the chroman ring. This antioxidant molecule, which has been perfected by nature, is well-known as an effective inhibitor of oxy radicals such as hydroxyl, alkoxyl, hydroperoxyl, phenoxyl, and other reactive species associated with oxidative damage in biological systems. Thus, tocopherols are implemented to prevent oxidative stress of lipid organelles, particularly the plasma membrane.[3] More recently, chemically synthesized versions of vitamin E derivatives such as 2,5,7,8-tetramethyl-2-(4′,8′,12′-trimethyltridecyl)-6-chromanol have shown potential as stabilizers for polyolefins, especially in food packaging and medical applications.[4] The current trend seems to be that vitamin E is displacing the conventional mononuclear phenols such as 2,6-di-*tert*-butylphenol (BHT) and 2-*tert*-butyl-4-methoxyphenol (BHA) as antioxidants for polyolefins in many applications.

Health authorities in many countries within the European Union (EU) and United States have stipulated strict directives and legislation to control the use of additives in plastics to minimize contamination risks associated with migration of additives into the human environment.[5] Recently, concerns have been raised especially about the role of hormone-like additives such as hydroxylbiphenyls, alkylphenols, phthalates, etc. which may exhibit adverse effects on male reproduction in wildlife and laboratory animals due to their xenoestrogenic activity.[6] As a rule, all low molecular weight antioxidants in plastic materials are prone to physical depletion and therefore constitute a potential threat to the environment after leaching and/or migration from the host polyolefin. For instance, the migration of α-tocopherol from LDPE into various food simulators was shown to be highest in olive oil and in the fatty food simulator heptane.[7]

As a consequence of this and to enhance the properties of polyolefins in regard to adhesion, dyeability, and compatibility, we have started to investigate polymer-bound stabilizers.[8] In this paper we report the synthesis of 6-hydroxyl-2,5,7,8-tetramethyl-2-(but-3-enyl)chroman (**1**), 5,7,8-trimethyl-3-(hex-5-enyl)benzofuran-6-ol (**2**), and 6-hydroxyl-2,2,8,9-tetramethyl-6-allylchroman (**3**), i.e., the synthetic route to three novel polymerizable analogues of tocopherols and the copolymerization of **1** with ethylene over a *rac*-[dimethylsilylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride/methylalumox-

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ane (MAO) catalyst system. In addition, the synthetic pathways to 4-methylene(3,5-di-*tert*-butyl-4-phenoxy)-styrene (**4**) and its siloxy-functionalized analogue 4-methylene(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)styrene **(5)** and their syndiospecific copolymerization with styrene over an (η^5-indenyl)trichlorotitanium ($IndTiCl_3$)/MAO catalyst system are also described.

Experimental Section

Materials. All materials used for the preparation of **1**−**5** were of reagent grade and purchased from Aldrich or Tokyo Chemical Industry (TCI). The *rac*-[dimethylsilanylenebis-(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride was prepared according to the literature.[9] The ^{1}H NMR spectra of the monomers and intermediates were recorded in $CDCl_3$ relative to that of TMS on a JEOL JNM-A-500 or JEOL JNM-L-400 spectrometer. The carbon nuclear magnetic resonance spectra were determined on a JEOL 500 operating at 125.78 MHz; chemical shifts in the proton-decoupled spectra are reported in parts per million downfield from the peak of TMS. GC−MS analyses were performed with an HP 5890 gas chromatograph and an HP 5970 mass-selective detector. The ionizing potential was 70 eV. Mass spectral peaks are given in units of mass per charge followed by the relative peak intensity in parentheses. High-purity ethylene and propylene were further purified over a series of columns containing molecular sieves, CuO, and Al_2O_3. High-purity toluene was refluxed over sodium and subsequently distilled under an argon atmosphere. MAO (10% w/w toluene) was purchased from Witco and used as received.

Polymerization Procedure. The sampling of catalyst, activator, and functional monomers was carried out under nitrogen in an MBRAUN 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. However, during the first 5 min an increase of temperature by 3−5 °C could be observed. The slurry ethylene polymerizations were carried out in a 0.5 L jacketed glass autoclave (Büchi, Switzerland) equipped with a blade turbine stirrer. The dry glass autoclave was evacuated and back-flushed with nitrogen. This procedure was repeated several times. Then 250 mL of freshly distilled toluene was pumped into the autoclave. Half of the methylalumoxane/toluene solution to be used was added to the reactor together with tocopherol monomer and stirred for 30 min. After 25 min the metallocene catalyst was dissolved in the remaining amount of the MAO/toluene solution and preactivated for 5 min by allowing the resulting mixture to stand at room temperature. Then the catalyst/activator mixture was charged into the reactor by using an ethylene overpressure. The pressure of ethylene was kept constant by controlling the gas feed automatically over the entire reaction period with a Büchi Pressflow gas controller, model bpc 1202. The copolymerization was quenched after 20 min by rapidly venting ethylene and adding 100 mL of ethanol. The catalyst residues of the produced copolymer were removed by treatment with 1 L of ethanol containing 40 mL of 10% HCl solution overnight. After filtration, the copolymer was washed again twice with ethanol, dried in a vacuum, and weighted to determine the polymerization yield. The copolymers were extracted with refluxing 2-propanol/cyclohexane[10] (volume ratio 1:1) for 24 h in a Soxhlet apparatus prior to the determination of the amount of bound chromanol and thermooxidative studies.

The syndiospecific styrene homo- and copolymerizations were carried out in a dried glass reactor (50 mL) equipped with a magnetic stirrer inside the glovebox. The dried amounts of toluene, styrene, and comonomer were added via separate syringes into the reactor. Then, the reactor was placed into a bath with the designated temperature and stirred for 10 min, after which half of the MAO amount (∼1.45 g) was added. The solution was stirred for another 10 min before the rest of the MAO and metallocene catalyst were loaded into the reactor. The polymerization was quenched after 20 min by adding a 10% solution of HCl in methanol. The reactor was removed from the glovebox, and the polymer was precipated from methanol and washed with an excess of methanol. The product was dried in an oven at 75−80 °C overnight. The polymer was then extracted with 2-butanone for 48 h in a Soxhlet extractor to remove any atactic polymer or residual comonomer.

Polymer Characterization. The melting temperatures and enthalpies of the polymers were determined using a Perkin-Elmer DSC 7 instrument. The samples were heated twice (heating rate 10 or 20 °C/min in the case of homo- and copolymers of syndiotactic polystyrene), and the second heating curve was analyzed. The crystallinities were determined from the DSC curves using the heat of fusion of folded-chain polyolefin crystals (293 J/g for PE[11] and 208 J/g for SPS[12]). Molecular weights and molecular weight distributions were determined by size exclusion chromatography on a Polymer Laboratories instrument equipped with a Waters Styragel or PLG gel MIXED-B column (exclusion limits for polystyrene 10^3, 10^4, 10^5, and 10^6 Å) in 1,2,4-trichlorobenzene at 135 °C (flow rate 1 mL/min). The basic calibration was made by using polystyrene standards with narrow molecular weight distributions and universal calibration using linear low-density polyethylene and polystyrene, respectively. ^{13}C and ^{1}H NMR spectra of polymers were recorded from solutions of 70−100 mg of polymer in 0.4 mL of $C_2D_2Cl_4$ or 1,2,4-trichlorobenzene at 120 °C. The spectrum was recorded using a 45° pulse by applying single-pulse excitation with gated decoupling to suppress NOE. The amount of bound chromanol was determined by UV analyses, and the numerical values were based upon polypropylene/vitamin E standard films, which had a thickness of ∼70 μm. UV−vis spectra were obtained with a Schimadzu UV-240 spectrometer. Spectra were recorded between 220 and 350 nm. The chromanol exhibits a strong absorbance in this region at 280 nm, and all measurements were carried out at this wavelength. The oxidation induction temperature was determined from data recorded during heating at a rate of 10 °C/min and keeping the sample under a constant oxygen flow (30 mL/min). The DSC was calibrated with an indium standard (T_{fus} = 156.6 °C). A polymer sample (∼6 mg) was placed in an aluminum pan and heated at 10 °C/min. The oxidation temperature was determined by extrapolating the exotherm associated with the beginning of oxidation to the baseline of the trace. A Mettler Toledo TA8000 system equipped with a TGA850 thermobalance was used for thermal analyses (TG and SDTA). A heating rate of 10 °C/min (starting from 25 °C and ending at 600 °C) was used under an atmosphere of flowing nitrogen or air.

Preparation of 6-Hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)chroman (1). To vinylmagnesium chloride (0.4 mol) in THF (160 mL) was added dropwise a solution of 5-hexen-2-one (24.8 g, 0.25 mol) in anhydrous THF (150 mL). After being stirred at room temperature for 20 h, the reaction mixture was cautiously poured into 450 mL of cold saturated aqueous NH_4Cl solution. The organic phase was concentrated and extracted with dichloromethane, dried over Na_2SO_4, and concentrated. The residue was distilled, giving 19.0 g (61.6%) of 3-methylhept-1,6-dien-3-ol, bp 45 °C, 10 mmHg. Then 3.73 g (29.6 mmol) of 3-methylhept-1,6-dien-3-ol together with trimethylhydroquinone (4.5 g, 29.6 mmol) was dissolved in 10 mL of formic acid (98%) in a 50 mL flask. The solution was heated to reflux and stirred at this temperature for 3 h. The reaction mixture was poured onto crushed ice and extracted with diethyl ether (3 × 50 mL). The organic phase was separated and filtered. After removal of solvent, the residue was dissolved in methanol, 1 mL of concentrated HCl was added, and the solution was refluxed for 30 min to hydrolyze the formate ester of **1**. The solvent was evaporated and the residue dissolved in diethyl ether. The organic phase was washed with water and aqueous saturated sodium carbonate solution and again with water. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford 4.33 g (54%) of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)chroman after distillation, bp 151 °C, 1 mmHg. MS: *m*/*e* (rel intens) M^+ 260 (69), 205 (9), 165 (100), 121 (10), 91 (7), 55 (7). ^{1}H NMR ($CDCl_3$, δ): 1.22 (s, 3H, CH_3C(2)); 1.65 (m, 2H, $ArCH_2CH_2$−); 1.8 (m, 4H,

−CH_2CH_2-−); 2.1, 2.12, 2.15 (3S, 9H, ArCH_3); 2.62 (t, 2H, CH_2-Ar); 4.23 (s, 1H,O*H*); 4.8−5.0 (m 2H, =CH_2); 5.7−5.9 (m,1H, =C*H*). ^{13}C NMR ($CDCl_3$, δ): 11.3, 11.8, 12.2, 20.7, 23.6, 28.0, 31.7, 38.7, 74.1, 76.7, 77.0, 77.3, 114.2, 117.1, 118.5, 139.1, 144.7, 145.4.

Preparation of 6-Allyl-7-hydroxy-2,2,8,9-tetramethylchroman (3). 6-Hydroxy-2,2,7,8-tetramethylchroman (3.0 g, 11.5 mmol; synthesized according to the procedure described in the literature[13]) was diluted in acetone, and then K_2CO_3 (1.60 g, 11.5 mmol) was added gradually. Then the reaction mixture was allowed to react for 30 min followed by dropwise addition of allyl bromide (1.40 g, 11.6 mmol). Finally, the solvent was removed, the residue was taken up in diethyl ether and washed with water, and the organic phase was dried over sodium sulfate. After removal of solvent, allylchromanoxy ether was obtained (2.55 g, 85 yield %). The produced allylchromanoxy ether was dissolved in DMF and heated to 155 °C, whereby via Claisen rearrangement, crude **3** was obtained. After distillation 2.3 g of **3** (bp 120 °C/0.1 mmHg) was obtained as a slightly yellow liquid. MS: *m/e* (rel intens) M^+ 246 (47), 190 (34), 175 (23), 149 (10), 127 (6), 113 (10), 97 (15), 85 (47), 71 (69), 57 (100). ^{1}H NMR ($CDCl_3$, δ): 1.25, 1.28 (2s, 6H, −CH_3); 1.77 (2s, 4H, CH_2); 2.11, 2.15 (2s, 6H, ArCH_3); 2.66 (m, 2H, −CH_2); 3.36−3.38 (m, 3H, CH_2C*H*=); 4.40 (s, 1H, O*H*); 5.01−5.08 (m, 2H, =CH_2), 5.9−6.0 (m, 1H, =C*H*,). ^{13}C NMR ($CDCl_3$, δ): 11.9, 12.1, 14.1, 20.5, 22.7, 26.7, 29.7, 30.5, 31.9, 33.1, 72.5, 115.4, 116.8, 120.0, 122.1, 123.8, 135.9, 145.1, 145.9.

Preparation of 4-Methylene-(3,5-di-*tert*-butyl-4-phenoxy)styrene (4). To a solution of 2,6-di-*tert*-butylphenol (103 g, 0.5 mol) in 300 mL of methanol was added dropwise a solution of KOH (32.74 g, 0.57 mol) in 200 mL of methanol. The mixture was stirred overnight, giving a potassium salt of the phenolic derivative. The methanol was evaporated, leaving a green powdery residue. The residue was dissolved in 500 mL of dimethylformamide (DMF), then vinylbenzyl chloride (91.5 g, 0.6mol) was added dropwise under agitation followed by addition of tetrabutylammonium bromide (1.6 g, 5.0 mmol), and the temperature was raised to 100 °C. After 12 h the solvent was evaporated, and the remaining residue was suspended in Et_2O and filtered through brine. Then, the solvent was evaporated, and the unreacted vinylbenzyl chloride and 2,6-di-*tert*-butylphenol were removed by distillation under reduced pressure. The residue was recrystallized four times from acetone to afford 9.82 g (6% yield) of **4** with a melting point of 129−131 °C. MS: *m/e* (rel intens) M^+ 322 (44), 307 (100), 265 (8), 139 (4), 117 (43), 91 (4), 57 (5). ^{1}H NMR ($CDCl_3$, δ): 1.40 (s, 18H, C(CH_3)$_3$), 3.88 (s, 2H, CH_2), 5.05 (s, 1H, O*H*), 5.19 (dd, 1H, J = 10.9, 1.0 Hz, =CH_2), 5.70 (dd, 1H, J = 17.6, 1.0 Hz, =CH_2), 6.69 (dd, 1H, J = 17.6, 10.9 Hz, C*H*=CH$_2$), 6.98 (s, 2H, Ar), 7.16 (d, 2H, J = 8.1 Hz, Ar), 7.33 (dt, 2H, J = 8.1, 1.7 Hz, Ar). ^{13}C NMR ($CDCl_3$, δ): 30.29, 34.27, 41.54, 112.94, 125.39, 126.21, 128.95, 131.40, 135.20, 135.82, 136.69, 141.56, 152.05.

Preparation of 4-Methylene-(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)styrene (5). To a solution of **4** (0.50 g, 1,55 mmol) in 3 mL of THF was added dropwise a solution of BuLi (2.5 M in hexanes, 0.62 mL) at −80 °C, and the reaction mixture was stirred for 10 min. Chlorotrimethylsilane (0.40 mL, 3.10 mmol) was then slowly added to the reaction mixture, and stirring was continued for 30 min at −80 °C and 1 h at 0 °C. The solution was neutralized with water (5 mL), hexane (50 mL) was added, and the organic phase was washed with water (50 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. Chromatography of the residue with hexane afforded **5** (570 mg, 93%) as a white solid, mp 48 °C. MS: *m/e* (rel intens): M^+ 394 (39), 379 (43), 323 (5), 305 (4), 117 (61), 73 (100), 57 (16). ^{1}H NMR ($CDCl_3$, δ): 0.38 (s, 9H, Si(CH_3)$_3$), 1.35 (s, 18H, C(CH_3)$_3$), 3.86 (s, 2H, CH_2), 5.18 (dd, 1H, J = 10.9, 1.0 Hz, =CH_2), 5.69 (dd, 1H, J = 17.6, 1.0 Hz, =CH_2), 6.68 (dd, 1H, J = 17.6, 10.9 Hz, C*H*=CH$_2$), 7.03 (s, 2H, Ar), 7.14 (d, 2H, J = 8.0 Hz, Ar), 7.32 (d, 2H, J = 8.0 Hz, Ar). ^{13}C NMR ($CDCl_3$, δ): 3.93, 31.24, 35.05, 41.34, 112.90, 126.18, 126.20, 129.01, 132.07, 135.17, 136.72, 140.50, 141.52, 151.38.

Results and Discussion

Synthetic Routes to Vitamin E Monomers. The structure of natural vitamin E is essentially based on a chroman skeleton having a phytyl chain attached to it containing three chiral carbons atoms on the 2, 4′, and 8′ positions. The high antioxidant activity of α-tocopherol has been attributed to stereoelectronic effects exerted by the chroman structure. Hence, its two-ring structure gives additional stability to the tocopheroxyl radical through interaction of the orbital overlap between the p-type lone pair orbital of the oxygen *para* to the −OH group and the semioccupied molecular orbital of the tocopheroxyl radical. Thus, the chroman structure is responsible for the intrinsic antioxidant activity of vitamin E, while the long side chain only acts to enhance the solubility of the polymer.[14] Therefore, in the present work, our primary synthetic strategy to produce polymerizable vitamin E derivatives was to preserve the chromanol moiety and replace the long phytyl side chain moiety with an α-alkenyl group at the 2 position. To the best of our knowledge, the number of α-tocopherol compounds having a polymerizable alkenyl group in the 2, 3, 4, 5, 7, or 8 position are unprecendented in the literature. However, in previous studies a large number of other model compounds of α-tocopherol have been synthesized such as 6-hydroxyl-2,2,5,7,8-pentamethylchroman, 6-hydroxyl-2,5-dimethyl-2-phytylbenzo[7,8]-chroman,[15] 2,3-dihydroxy-2,2,4,6,7-pentamethylbenzofuran,[16] and 6-hydroxylthiochroman[17] derivatives. The first model compounds of α-tocopherol were prepared by Smith, Kareer, and Bergel already during late 1930 by condensation of trimethylhydroquinone (TMHQ) with isophytol in the presence of various catalyst systems.[18]

During the following years, mainly modifications of this process in terms of solvents and catalyst systems, e.g., Lewis or Brønsted acids, were developed.[19] Using the same approach, we started to investigate synthetic procedures to polymerizable hydroxylchromans. First, we synthesized 3-methylhept-1,6-dien-3-ol due to the fact that it contains an α-olefinic moiety and is otherwise an analogous reagent to the first isoprenol unit of isophytol. The condensation of TMHQ with 3-methylhept-1,6-dien-3-ol in refluxing formic acid afforded **1** as a slightly yellow liquid with a boiling point of 151 °C, 1 mmHg, in a moderate yield (54% yield). Thus, this synthetic pathway depicted in Scheme 1a to polymerizable tocopherol derivatives could be of both industrial and academic interest. As anticipated, the normal condensation routes of TMQH with 3-methylhept-1,6-dien-3-ol using either $ZnCl_2$/HCl or $AlCl_3$/CH_3NO_2 were not convenient, due to the fact that the α-olefinic double bond was chlorinated.[20]

In recent years there has been a continuous search for vitamin E analogues with enhanced antioxidant activity. The most notable improvements in antioxidant activity have been measured for the class of five-membered heterocyclic ring analogues such as 2,3-dihydroxybenzofuran and for the α-naphthofuran class of derivatives such as 6-hydroxy-2,5-dimethyl-2-phytyl-7,8-benzochroman, which exhibit higher k_{inh} values 1.8−10 times that of α-tocopherol.[21] This encouraged us to try to develop a one-step synthetic route to **2** from cheap starting materials, i.e., TMHQ and a mixture of *cis*/*trans*-2,7-octadien-1-ol, as illustrated in Scheme 1b. However, despite numerous modifications of the reaction conditions, the result was always a complex reaction mixture.[22] This is in accordance with the results

Scheme 1. Synthetic Routes to (a) 1, 2, and 3

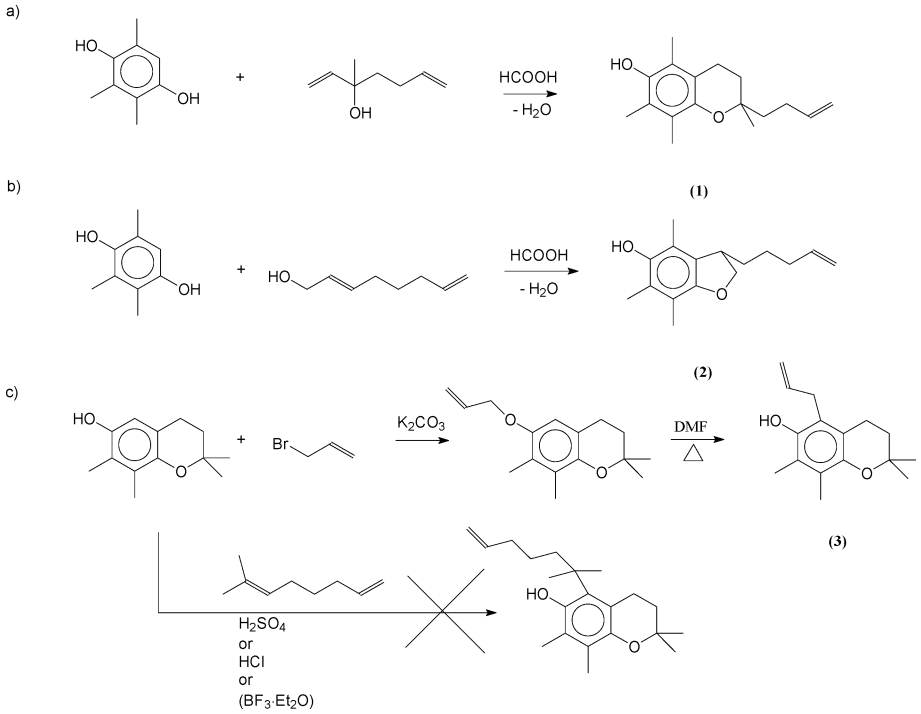


Table 1. Copoplymerization of Ethylene and 1 over a *rac*-[Dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium Dichloride/Methylalumoxane Catalyst System[a]

entry	concn of **1**, mmol /L	concn of α-tocopherol, mmol /L	cryst,[b] %	T_m,°C	M_n	M_w	M_n/M_w	activity, kg of polym/ (mol of Zr h)	concn of bound antioxidant, wt %[c]	OIT,[e] °C
1			73	128.4	10300	31300	3.0	5600		210
2		130[f]	tocopherol					3200		210
3		370[f]						2400		210
4	290		56	127.2	20500	41000	2.0	2500	2.3	244

[a] Copolymerization conditions: [Zr] = 44 μmol/L, Al/Zr = 3000, $P_{ethylene}$ = 2 bar, polymerization time 30 min, T = 80 °C, and $V_{toluene}$ = 250 mL. [b] Here, "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 293 J/g. [c] Determined by UV analysis. [e] The oxidation induction time (OIT) was determined after extraction of polymer samples. The OIT was determined from DSC curves by extrapolating the exotherm associated with the beginning of oxidation to the baseline of the trace. [f] Tocopherol was added instead of the functional monomer **1**.

reported by Robillard et al.[23] on their work with related hydroxythiochromans.

In our previous studies, we have noticed that certain sterically hindered phenolic derivatives such as 2,6-di-*tert*-butylphenol and 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol significantly enhance the polymerization rate of propylene and ethylene over different metallocene catalyst systems.[24] Other research groups have also verified this observation,[25] whereas other reports describing the copolymerization of α-olefins with various nonbulky polar monomers, such as 9-decen-1-ol and 5-hexen-1-ol, show that the molecular weight decreases with higher incorporation of polar monomer to the polymer backbone and also activity.[26] Furthermore, Ferreira and co-workers have studied the effect of copolymerizable and noncopolymerizable Lewis bases on propylene polymerization with an $Et(Ind_2)ZrCl_2$/MAO catalyst system, and they have also observed that deactivation occurs upon addition of Lewis bases.[27]

As a consequence of this and other considerations, we sought synthetic routes to more crowded hydroxylchromanol monomers than 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)chroman such as 6-hydroxyl-5-(1,1-dimethylhept-6-enyl)-2,2,7,8-tetramethylchroman and **3**. All of our attempts to prepare the former chromanol monomer from 7-methyl-1,6-octadiene and 6-hydroxyl-2,2,7,8-tetramethylchroman via Friedel−Crafts alkylation were more or less unsuccessful in terms of yields and problems with isolation of the desired product. On the other hand, we were able to synthesize the latter chromanol **3** by first treating 6-hydroxyl-2,2,7,8-tetramethylchroman with potassium carbonate and allyl bromide to give the corresponding allylchromanoxy ether. In the second step the produced allylchromanoxy ether was successfully converted by Claisen rearrangement to **3**, as shown in Scheme 1c.

In our opinion tocopherol **1** seemed to be the most promising candidate of the aforementioned tocopherol monomers **1**, **2**, and **3** in terms of synthetic yield, polymerizability, and tolerance by methylalumoxane-activated metallocene catalysts in terms of retained polymerization activity. In light of this, we copolymerized **1** with ethylene over a *rac*-[dimethylsilylenebis-(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride/MAO catalyst system, and the results are presented in Table 1. In addition, two standard ethylene polymerizations were conducted in the presence of various amounts of α-tocopherol to determine the degree of deactivation of active sites. The activity for ethylene and **1** copolymerizations was more or less half of that recorded for ethylene homopolymerization, whereas the molecular weights of the produced copolymers were similar to that

Table 2. Syndiospecific Copolymerization of Styrene with 4 and 5 over an $IndTiCl_3$/MAO Catalyst System[a]

entry	comonomer	amt of comonomer, mmol	syndiotactic,[b] %	T_m, °C	M_n	M_w	M_n/M_w	yield, g	concn of bound antioxidant, wt %[c]
3			92.5	269.5	52000	81000	1.6	0.92	
4	4	0.78	93.1	245.4	80000	120000	1.5	0.15	6.8
5	5	0.32	94.0	263.6	60000	100000	1.7	0.50	2.4

[a] Polymerization conditions: at 60 °C for 20 min, $V_{styrene}$ = 10 mL, $V_{toluene}$ = 20 mL, [Ti] = 130 μM, and Al/Ti = 2000. [b] Portion of the syndiotactic polymer insoluble in boiling 2-butanone. [c] Determined by ^{1}H NMR analysis.

Table 3. Results of Thermogravimetric Analysis of Polystyrene, Poly(styrene-*co*-4), and Poly(styrene-*co*-5)[a]

entry	atmosphere	temp interval of thermal decomp, °C	entry	atmosphere	temp interval of thermal decomp, °C
polystyrene	nitrogen	374−470	poly(styrene-*co*-**5**)	nitrogen	390−470
	air	268−430		air	285−430
poly(styrene-*co*-**4**)	nitrogen	405−470			
	air	300−430			

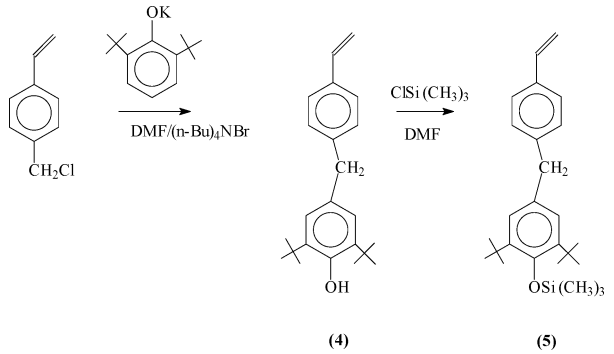
[a] A Mettler Toledo TA8000 system equipped with a TGA850 thermobalance was used for thermal analysis (TG and SDTA). A heating rate of 10 °C/min (starting from 25 °C and ending at 600 °C) under an atmosphere of flowing nitrogen or air.

of polyethylene prepared under similar reaction conditions. Thus, the novel tocopherol monomer **1** has a tendency of rendering the metallocene/MAO catalyst activity to a certain degree as also could be predicted from the results obtained from standard ethylene polymerizations in the presence of α-tocopherol.

The produced poly(ethylene-*co*-**1**) exhibited enhanced thermooxidative stability even after extraction with 2-propanol/cyclohexane for 24 h in a Soxhlet apparatus in comparison to polyethylene; i.e., the oxidation induction temperature in an oxygen atmosphere for the copolymer was around 244 °C, whereas the extracted polyethylene samples (entries 2 and 3) and the pure polyethylene sample (entry 1) showed an oxidation induction temperature of only ∼210 °C. Thus, on the basis of the thermooxidative stability tests, one can conclude that the comonomer **1** has indeed been copolymerized with ethylene.

Synthetic Routes to a Styrenic Phenol Derivative and Its Trimethylsilylated Analogue. In 1986, Ishihara and co-workers synthesized the first pure syndiotactic polystyrene over a titanium/MAO catalyst system.[28] After this announcement intensive work has been aimed at the synthesis of various homogeneous organometallic catalyst systems that would exhibit high productivity and stereospecificity in syndiotactic styrene polymerizations. More recently, approaches to functionalized syndiotactic polystyrenes with improved adhesion and compatibility with other polymers have been reported. Thus, Chung et al.[29] have successfully prepared a new family of syndiotactic styrenic polymers containing primary amino groups. Furthermore, 4-*tert*-butyldimethylsiloxystyrene has been successfully both homo- and copolymerized with styrene using a metallocene catalyst system.[30] However, to the best of our knowledge, there have been no reports where a styrenic type of antioxidant monomer would have been syndiospecifically copolymerized with styrene to give self-stabilized syndiotactic polystyrene grades. Prompted by this, we wanted to develop a synthetic route to styryl-substituted antioxidant monomers such as **4** and its trimethylsilylated analogue **5** (see Scheme 2) and copolymerize these novel monomers with styrene over a half-sandwich metallocene/MAO catalyst system to give syndiotactic polystyrenes with enhanced thermooxidative properties. The results of styrene copolymerizations with **4** and **5** over an $IndTiCl_3$/MAO catalyst system are

Scheme 2. Synthetic Pathway to 4 and 5



presented in Table 2. The results show clearly that the unprotected hydroxyl functionality of monomer **4** interacts with the active sites, since the recorded catalyst activity is significantly lower than in homopolymerization of styrene under similar conditions, whereas in the case of the trimethylsilyl masked monomer the catalyst activity was close to 60% of styrene homopolymerization. It is interesting to note that the copolymers had molecular weights and molecular weight distributions very similar to those of polystyrene, whereas in the aforementioned work[28] describing the copolymerization of styrene with 4-*tert*-butyldimethylsiloxystyrene using an $IndTiCl_3$/MAO catalyst system the obtained copolymer had a relatively low molecular weight (M_n = 9200 and Pd = 2.2). These experimental results clearly show the advantage of having bulky *tert*-butyl substitutions in the *ortho* positions of the phenol moiety in terms of retaining catalyst activity and producing copolymers of high molecular weight. In general, the effect is similar to that of generating steric hindrance in the catalyst substitution of Cp by bulky substitutions such as *n*-propyl and *n*-butyl.[31]

In addition, it can be seen from Table 2 that all polymer samples showed similar syndiotacticities and that the melting points were markedly lower for the copolymers. The ^{1}H spectra of the three prepared syndiotactic polymers, i.e., syndiotactic polystyrene, poly(styrene-*co*-**4**), and poly(styrene-*co*-**5**), are shown in Figure 1. There are four common strong signals in all three spectra. Thus, the first two peaks at 1.45 and 1.95 ppm (a triplet typical for syndiotacticity) corresponds to the CH_2 and C*H* protons in the polymer backbone, and the two later peaks at δ = 6.7 and 7.2 ppm are due

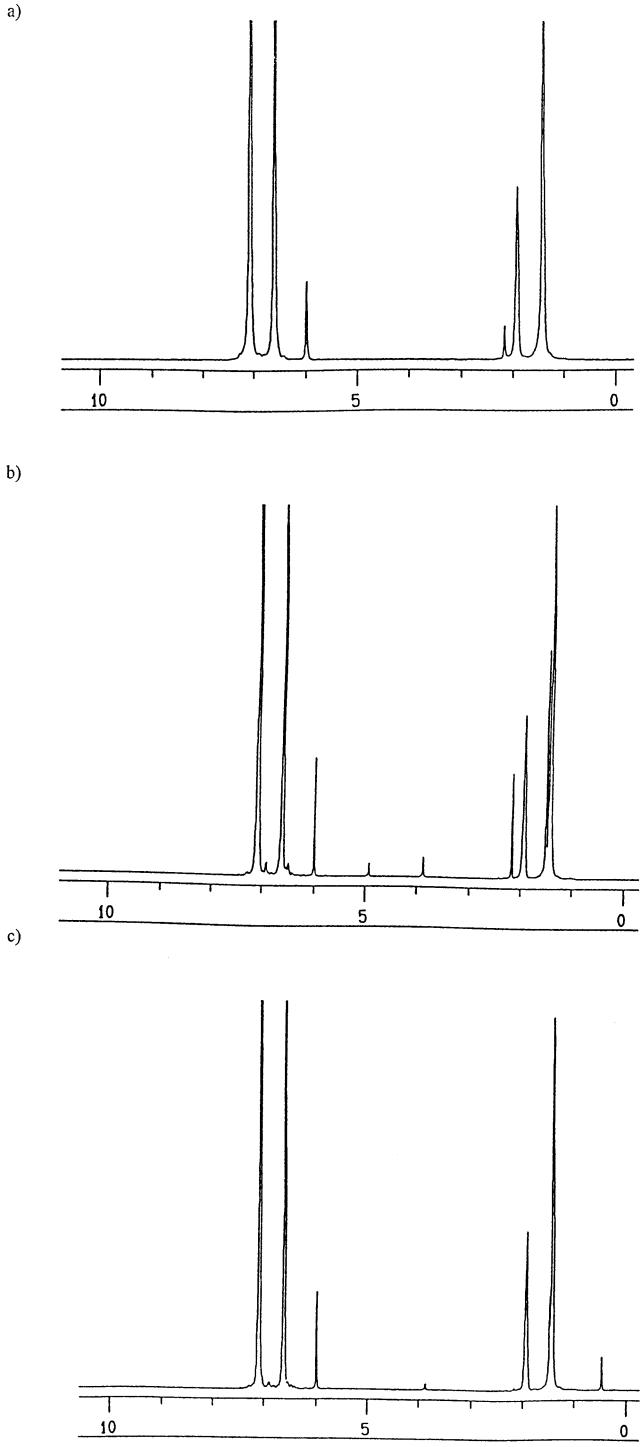


Figure 1. ^{1}H NMR spectrum of (a) syndiotactic polystyrene, (b) poly(styrene-*co*-**4**), and (c) poly(styrene-*co*-**5**).

to aromatic proton resonances. The spectrum of poly(styrene-*co*-**4**) shows the following additional peaks: the peak at $\delta = 1.48$ ppm can be assigned to the *tert*-butyl group protons, and the peaks at $\delta = 3.9$ and 4.9 ppm can be assigned to the methylene protons between the aromatic rings and the hydroxyl proton, respectively (18:2:1 ratio of integrated intensity). In addition, aromatic proton resonances from the functional monomer can be seen in the region of 6.5 and 6.9 ppm. The ^{1}H NMR spectrum of poly(styrene-*co*-**5**) is very similar to that of poly(styrene-*co*-**4**) except for the fact that the hydroxyl proton at $\delta = 4.9$ ppm is missing and a new peak at $\delta = 0.5$ ppm has appeared that can be assigned to the protons of the methyl groups adjacent to the silicon atom. The good agreement between expected and measured peak intensity ratios for the protons in each group indicates, within experimental error, that both copolymers are clean. On the basis of ^{1}H NMR spectral analysis the incorporation degree of functional styrene into the copolymer chain was determined to be 6.8 wt % in the case of poly(styrene-*co*-**4**) and 2.4 wt % for poly(styrene-*co*-**5**). The ^{13}C NMR spectrum of poly(styrene-*co*-**4**) reveals that the quaternary C1 carbon atom of the unsubstituted styrene gives a very sharp resonance at $\delta = 145.7$ ppm. This sharpness together with the characteristic shifts indicates a highly syndiotactic microstructure for the copolymer.

TGA of Syndiotactic Polystyrene, Poly(styrene-*co*-4), and Poly(styrene-*co*-5). The thermal degradation of syndiotactic polystyrene, poly(styrene-*co*-**4**), and poly(styrene-*co*-**5**) was investigated by TGA in both nitrogen and air atmospheres using a heating rate of 10 °C/min up to 600 °C. The TGA results are presented in Table 3. In nitrogen, the TGA curve showed that syndiotactic polystyrene degrades in a single step beginning at 374 °C and ending at 470 °C. In addition, the curve showed that the maximum rate of weight loss occurred at 416.5 °C. In the case of poly(styrene-*co*-**4**) and poly(styrene-*co*-**5**) the degradation takes place between 405 and 470 °C with maximum weight losses at 426.5 and 390−470 °C and at 420.5 °C, respectively. In the presence of air, the pure polystyrene sample degrades primarily in a single step starting at 268 °C and reaches zero mass at 430 °C. Thus, the degradation of syndiotactic polystyrene begins immediately after the melting point of the polymer has been reached. For poly(styrene-*co*-**4**) and poly(styrene-*co*-**5**) the weight loss due to thermooxidation starts to occur when the melting points of the copolymers have been exceeded by 20−50 °C, i.e., at 300 and 285 °C, respectively.

Conclusions

In this work we demonstrate that novel α-tocopherol comonomers such as **1** can be manufactured by acid-catalyzed condensation of TMHQ with 3-methylhept-1,6-dien-3-ol, whereas the tocopherol compound **2** could only be obtained in very low yields and isolation of the product turns out to be very difficult. Furthermore, a synthetic pathway to *ortho*-allylated tocopherol monomer was constructed and successfully completed. Thus, *ortho*-allylated chromanol denoted as **3** was obtained by Claisen-rearrangement of the corresponding allylchromanoxy ether. The tocopherol monomer denoted **1** was successfully copolymerized with ethylene over a metallocene/MAO catalyst system. The prepared self-stabilized copolymers exhibited improved thermooxidative stabilities in comparison to polyethylene. In addition, a novel styrene derivative, **4**, and its methylsilylated analogue **5** were successfully synthesized and copolymerized with styrene over an $IndTiCl_3$/MAO catalysts system. The copolymers produced exhibited relatively high syndiotacticities and molecular weights and high thermal stabilities.

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