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# Synthesis of Novel Hindered Amine Light Stabilizers (HALS) and Their Copolymerization with Ethylene or Propylene over Both Soluble and Supported Metallocene Catalyst Systems

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ABSTRACT: Novel polymerizable hindered amine light stabilizers (HALS) such 1-(but-3-enyl)-2,2,6,6-tetramethylpiperidine (**1**), 1-(undec-10-enyl)-2,2,6,6-tetramethylpiperidine (**2**), 4-(but-3-enyl)-1,2,2,6,6-pentamethyl-3,4-dehydropiperidine (**3**), 2-(but-3-enyl)-2,6,6-trimethylpiperidine (**4**), 4-(but-3-enyl)-1,2,2,6,6-pentamethyl-4-piperidyl ether (**5**), 4-(undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**6**), 4-((*N*-*n*-butyl)-undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**7**), and bis(*N*-*n*-butyl-*N*-2,2,6,6-tetramethylpiperidine)-*N*-*n*-butyl-*N*-allyltriazine (**8**) were synthesized. All the aforementioned HALS monomers except for **5** and **8** were successfully copolymerized in fair to high yields with ethylene or propylene over eight different group 4 metallocene catalysts using methylalumoxane (MAO) as cocatalyst. Copolymerizations were also performed over a supported metallocene/$SiO_2$/MAO/triisobutylaluminum(TIBA) catalyst system. The silica-supported metallocene catalyst system readily promoted copolymerization of the sterically hindered monomer **2** with ethylene, however, copolymerizations using either **6** or **7** as comonomer failed. Moreover, a catalyst derived from the reaction of *rac*-[dimethylsilylenebis(1-indenyl)]zirconium dichloride (**CA1)** with triethylaluminum and trityl tetra(perfluorophenyl)borate (TRI−FABA) afforded HALS copolymers in high yields. Surprisingly, it was found that TRI−FABA, a strong Lewis acid, could impede the Lewis base activity of HALS monomers such as **2**, **6** and **7** provided a sufficient relative amount of TRI−FABA was employed. Thus, once an equilibrium concentration between TRI−FABA and HALS monomer was established, the presence of HALS monomer no longer affected the rate of polymerization. Normally, metallocene catalysts are severely poisoned when traces of polar monomers (Lewis bases) are present, due to the Lewis acidic nature of the catalyst. Furthermore, a series of standard ethylene homopolymerizations over *rac*-[dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2)**/MAO catalyst system was performed in the presence of different sterically hindered amine model compounds such as 1-(1-methylene-2,6-di-*tert*-butylphenol)-2,2,6,6-tetramethylpiperidine (**A**), *N*,*N*-diisopropylaniline (**B**), 1-octyl-2,2,6,6-tetramethylpiperidine (**C**), 1-benzyl-2,2,6,6-tetramethylpiperidine (**D**), 2,2,6,6-tetramethylpiperidine (**E**), 1,2,2,6,6-pentamethylpiperidine (**F**), diisopropylethylamine (**G**), 1,2,2,6,6-pentamethyl-4-oxopiperidine (**H**), 2,2,6,6-tetramethylpiperidine-1-oxyl (**I**), 1-propargyl-2,2,6,6-tetramethylpiperidine (**J**), 4-*N*,*N*-bis(*n*-butylamino)-2,2,6,6-tetramethylpiperidine (**K**), tris(*N*-butyl-*N*-2,2,6,6-tetramethylpiperidineamino)triazine (**L**) and tris(dibutylamino)triazine (**M**). The results show that some of the amine model compounds are highly reactive and deactivating whereas others are less so. Much preferred are those HALS structures which have a sterically demanding substituent attached on nitrogen and no additional heteroatoms in 4-position of the piperidine ring in terms of metallocene/MAO catalyst activity. $^{13}C$ NMR analyses revealed that the produced materials are random copolymers containing isolated HALS branches and that the prepared propylene copolymers have highly stereoregular microstructures. According to size exclusion chromatography, the prepared copolymers have molecular weight distributions close to 2, which are characteristic for polymers produced over single-site catalysts. The prepared copolymers contained from 0.2 to 14.1 wt % of HALS units and exhibited high ultraviolet and thermooxidative stabilities even after exhaustive extraction with a mixture of refluxing (50:50) cyclohexane/2-propanol. For example, the poly(ethylene-*co*-**4**) copolymer with a HALS content of 0.2 wt % exhibited considerable improved thermooxidative stability in comparison to unstabilized polyethylene, i.e., for the copolymer the carbonyl peak had not appeared after one year of oven aging at 115 °C, whereas unstabilized polyethylene shows a strong increase in the carbonyl index within 2 days.

## Introduction

Hindered amine light stabilizers have gained prominence as effective light stabilizers for polyolefins; in particular, the derivatives of alkyl-substituted piperidines are widely used.[1] Beyond this, hindered amine compounds also significantly contribute to the long-term thermal stability of olefinic-based polymers in the solid state at temperatures closely related to actual polymer aging in practice.[2] The stabilizing mechanism has been studied intensively during the past decades and the original theory of Denisov has been improved and complemented.[3] Denisov's cycle suggests that the nitroxyl radicals formed during initial oxidation of the parent amine and those regenerated from alkoxylamine

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are the main stabilizing species. The low molecular weight hindered amine stabilizers such as 2,2,6,6-tetramethylpiperidine and its 4-substituted derivatives such as 4-hydroxyl or 4-acetyloxyl are excellent stabilizers from an intrinsic point of view. However, a drawback related to their structure is that they do not possess low volatility at high processing temperatures.[4] A further disadvantage is their low resistance to extraction by liquids. Thus, low molecular weight HALS derivatives are prone to physical depletion, which has significantly limited their use. In response to this, a recent trend for HALS development has been to improve the persistence of the stabilizer by preparing HALS derivatives of higher molecular weight, i.e., HALS molecules with an oligomeric or polymeric structure.[5] Such polymeric HALS compounds become entangled in the polymer, whereby their rate of diffusion is reduced. For example, polymeric HALS masterbatches have been synthesized by free radical polymerization of acryloyl- or methacryloyl-substituted hindered amine monomers or by copolymerization of these HALS monomers with styrene and/or various acrylates.[6] However, generally the effectiveness of these polymeric or oligomeric HALS derivatives is not very high. The reason for this is that these relatively polar HALS compounds exhibit poor compatibility and low solubility with the hydrophobic polyolefin substrate, which leads to dispersion problems. Recently, Malik and co-workers[7] studied the diffusion and solubility of HALS in polyethylene and polypropylene and correlated these parameters with the measured efficiency. The results obtained indicate that an effective HALS derivative should be highly soluble in the polymer, while its translation mobility is less important than has been previously proposed and should be low instead. Thus, increased solubility of the stabilizer improves its performance, whereas an increase in diffusion rate has the opposite effect. Consequently, polymer-bound stabilizers are likely to offer a favorable combination of these important properties, i.e., improved solubility (homogeneity) of functional groups in the polymer matrix and immobility which makes the HALS nonvolatile and nonextractable. In general, there are two routes of tethering HALS moieties onto the polyolefin backbone, including chemical modification of preformed polymers and direct copolymerization of HALS monomers with α-olefins. The former method of binding stabilizers have been thoroughly discussed by Al Malaika, in particular by different reactive processing technologies.[8] An intriguing method of attaching HALS molecules onto the polyolefin by using photoreactive HALS derivatives which become photografted on the polymer surface has also been reported.[9] The limitation of this approach is that it is restricted to out-door applications. Mani et al. have prepared a HALS end functionalized poly(ethylene-*alt*-propylene) copolymer via a rather long synthetic route, i.e., by terminating the living anionic polymerization of isoprene with 4-(2,3-epoxypropoxy)-1,2,2,6,6-pentamethylpiperidine followed by hydrogenation.[10] In general, most of the polymer post modification methods are accompanied by some undesirable side reactions, such as stabilizer homopolymerization, stabilizer consumption during grafting, uneven distribution of stabilizer in the matrix, cross-linking and/or degradation of the polyolefin. As a result of these and other considerations we have started to investigate the latter method, i.e., direct copolymerization of stabilizers with α-olefins. In previous papers we have reported the copolymerization of 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine with propylene over a heterogeneous Ziegler−Natta catalyst based on a $TiCl_4/MgCl_2/$TEA/DMS catalyst system[11] and the copolymerization of ethylene[12] and propylene[13] with 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol employing various metallocene/MAO catalyst systems. Especially, the discovery of metallocene methylalumoxane catalysts has opened new frontiers in polymer synthesis; they offer opportunities to make copolymers with precisely controlled molecular architecture and hence extremely uniform copolymers of narrow molecular weight distribution and narrow compositional distribution can be prepared. Thus, stabilizer/α-olefin copolymers made using metallocene catalysts may give very valuable information about the performance of chemically bound stabilizers in general—well beyond the capabilities of any previously known polyolefin based system containing chemically bound stabilizers prepared via other tethering methods. Prior to this work, to the best of our knowledge, there have been no reports in which HALS monomers have been copolymerized with α-olefins over homogeneous or heterogeneous catalysts based on group IV metallocene catalyst systems in order to produce self-stabilized polyolefins. However, Waymouth and co-workers have homopolymerized a variety of other polar monomers such as 5-*N*,*N*-diisopropylamino-1-pentene and 5-*tert*-butyldimethylsiloxyl-1-pentene using MAO-free cationic metallocene catalysts.[14] Moreover, Waymouth have more recently demonstrated an interesting approach to functional polyolefins by first copolymerizing an alkene-substituted alkoxylamine with propylene over metallocene/borate catalyst and then utilizing the incorporated alkoxylamine moieties for the initiation mediated radical polymerization of styrene to produce polyolefin graft copolymers.[15] Recently, Mülhaupt reported the copolymerization of *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene[16] with ethylene over *rac*-$Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO catalyst system as well as the homo- and copolymerization of monovinyl functional silsesquioxane[17] with ethylene or propylene over various metallocene catalyst systems. In another approach, Chung has demonstrated the versatility of alkenylborane monomers which can successfully be copolymerized with ethylene or propylene in high yields using metallocene catalysts. In a second step the pendant borane intermediates can be converted to a host of other organic functions under mild reaction conditions.[18] In an alternative process, *ω*-halogeno-α-olefins[19] and 4-vinylcyclohexene[20] have been copolymerized with ethylene in the presence of metallocene/MAO catalytic systems followed by chemical transformation of the halogen or unsaturated group into other desired functions.

This paper describes the synthesis of novel hindered amine light stabilizers (HALS) and their copolymerization with ethylene or propylene over various group 4 metallocene catalysts using MAO or TRI−FABA as cocatalysts. Furthermore, to find HALS structures which would be well-tolerated by the metallocene catalyst in terms of maintained polymerization activity, a series of standard ethylene polymerizations over a **CA2**/MAO catalyst system in the presence of different sterically hindered amine model compounds was also performed. The central purpose of this polymerization series was to find a correlation between amine structure and polymerization rate. We hypothesized that this type of amine screening would help us in selecting and designing such HALS monomer candidates that are unlikely to extinguish catalytic sites.

## Experimental Section

All chemicals used for the preparation of HALS monomers and model compounds were of reagent grade and purchased from Aldrich. The *N*,*N*-diisopropylaniline (**B**),[21] 1-allyl-2,2,6,6-tetramethylpiperidine (**1**),[22] 1-benzyl-2,2,6,6-tetramethylpiperidine (**D**)[23] and metallocene catalysts: *rac*-[dimethylsilylenebis(1-indenyl)]zirconium dichloride (**CA1**),[23] *rac*-[dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**),[24] *rac*-[ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA4**),[24] *rac*-[dimethylsilylenebis(2-methyl-4,5-benzoindenyl)]zirconium dichloride (**CA6**),[24] and isopropyl-(cyclopentadienyl-1-fluorenyl)zirconium dichloride (**CA7**)[25] and *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxyl-1-indenyl)]zirconium dichloride (**CA8**)[26] were synthesized according to reported procedures. *rac*-[Ethylenebis(1-indenyl)]zirconium dichloride (**CA3**) and bis(pentamethyl-$\eta^5$-cyclopenta-dienyl)zirconium dichloride (**CA5**) were purchased from Strem and Aldrich, respectively, and used as received. The silica-supported metallocene catalyst was prepared according to a reported procedure.[27] The rest of the used HALS monomers as well as the amine model compounds were donated by Ciba Specialty Chemicals. The $^1$H NMR spectra of the HALS monomers and intermediates were recorded in $CDCl_3$ relative to TMS on a JEOL GX 500 or JEOL GX 400 spectrometer. The splitting patterns for the $^1$H NMR are designated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet); addition of br indicates a broadened pattern. The carbon nuclear magnetic resonance spectra were determined on a JEOL 500 operating at 125 MHz; chemical shifts in the proton decoupled spectra are reported in ppm downfield from TMS. GC−MS analyses were performed with a HP 5890 gas chromatography and a HP 5970 mass selective detector. The ionizing potential was 70 eV. Mass spectral peaks are given in units of mass/charge followed by relative peak intensity in parentheses. 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 argon atmosphere. Methylalumoxane (MAO 10% w/w toluene) was purchased from Witco and trityl tetrakis(pentafluorophenyl)borate (TRI−FABA) as well as *N*,*N*-dimethylanilinium tetra(perfluorophenyl)borate (DAN−FABA) were purchased from Akzo Nobel and used as received.

**Polymerization Procedure.** The sampling of the catalyst, activator, and HALS monomer were carried out under nitrogen in a MBRAUN glovebox containing <2 ppm oxygen and <5 ppm water. The reaction temperature was controlled by a Lauda Ultra circulating water bath within ± 0.3 °C. The slurry polymerizations were carried out in a 0.5 L jacketed glass autoclave (Büchi) equipped with a blade turbine stirrer. The dry glass autoclave was evacuated and backflushed 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 HALS 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 standing at room temperature. Then the catalyst/activator mixture was charged into the reactor by using ethylene or propylene overpressure. The pressure of ethylene and propylene was kept constant by controlling the gas feed automatically over the entire reaction period with a Büchi Pressflow Gas Controller Model bpc 1202. After 20 or 60 min, the copolymerization was quenched by rapidly venting ethylene or propylene and adding 100 mL of ethanol. The catalyst residues of the produced copolymer was removed by treatment with ethanol/HCl(aq) solution overnight. After filtration, the polyolefin was washed twice with ethanol and stirred overnight in a NaOH(aq)/ethanol solution. Then the polyolefin was washed again twice with ethanol, dried in a vacuum and weighed to determine the polymerization yield. The copolymerizations with the MAO-free cationic catalyst system were carried out at −20 °C and 2.0 bar propylene pressure using triethylaluminum (TEA) as impurity scavenger and alkylating agent. The alkylated catalyst precursor were generated in situ. In a typical run, 0.3 g of TEA was stirred with 50 mL of toluene and the appropriate amount of HALS monomer for 30 min followed by the addition of 5 $\mu$mol of the metallocene catalyst. The copolymerization was initiated by flushing the cation-forming agent (TRI−FABA) with propylene overpressure. The copolymerization was interrupted after 60 min and subjected to the same washing procedure as described previously. The copolymerizations over the silica-supported metallocene catalyst system were performed at 80 °C and 5 bar ethylene pressure in 300 mL pentane. The catalyst suspension (100 mg of supported catalyst in 5 mL of pentane) was flushed with ethylene overpressure into the reactor to start the copolymerization. The copolymerization was interrupted after 180 min and subjected to the same washing procedure as described previously.

**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 °C/min), 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[28]and 208 J/g for PP[29]). Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C ALC GPC instrument equipped with Waters Styragel or PLG gel MIXED-B columns (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 polypropylene, respectively. $^{13}$C 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 spectra was recorded using a 45° pulse by applying single pulse excitation with gated decoupling to suppress NOE.

**Thermooxidative and Light Stability Measurements.** The amount of bound HALS was determined by elemental analyses after extracting the copolymers with refluxing 2-propanol/cyclohexane[30] for 24 h in a Soxhlet apparatus. The thermooxidative stability of the extracted copolymer films, thickness approximately 70 $\mu$m, was studied by oven aging at 115 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. For light stability tests the poly(propylene-*co*-**9**) copolymer was mixed with polypropylene powder (Profax6501) at 200 °C in a Brabender Plastograf□ using 0.1 wt % of Ca−stearate, 0.1 wt % tris(2,4-di-*tert*-butylphenyl) phosphite and 0.02 wt % octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxylphenyl)-propionate as costabilizers. The produced polymer material was then compressed to films with a thickness of 0.1 mm (3 min at 260 °C) prior to irradiation in a xenon Weatherometer (Weather-O-Meter 65 WR (Atlas Corp.), black panel temperature of 65 °C). The time (in hours) to reach 0.1 carbonyl index from the plot of absorbance of the carbonyl groups vs irradiation time was determined.[31]

## Results and Discussion

The degree to which polar compounds (i.e., Lewis bases) such as HALS derivatives react and generally deactivate conventional Ziegler−Natta as well as metallocene/MAO catalysts, due to their highly electrophilic nature, depends on the structure of the Lewis base and the constitution of the catalyst. Both electronic and steric effects are important in determining the mode of action of the HALS derivative. To be able to successfully design novel HALS monomer candidates, which would presumably be well-tolerated in terms of maintained

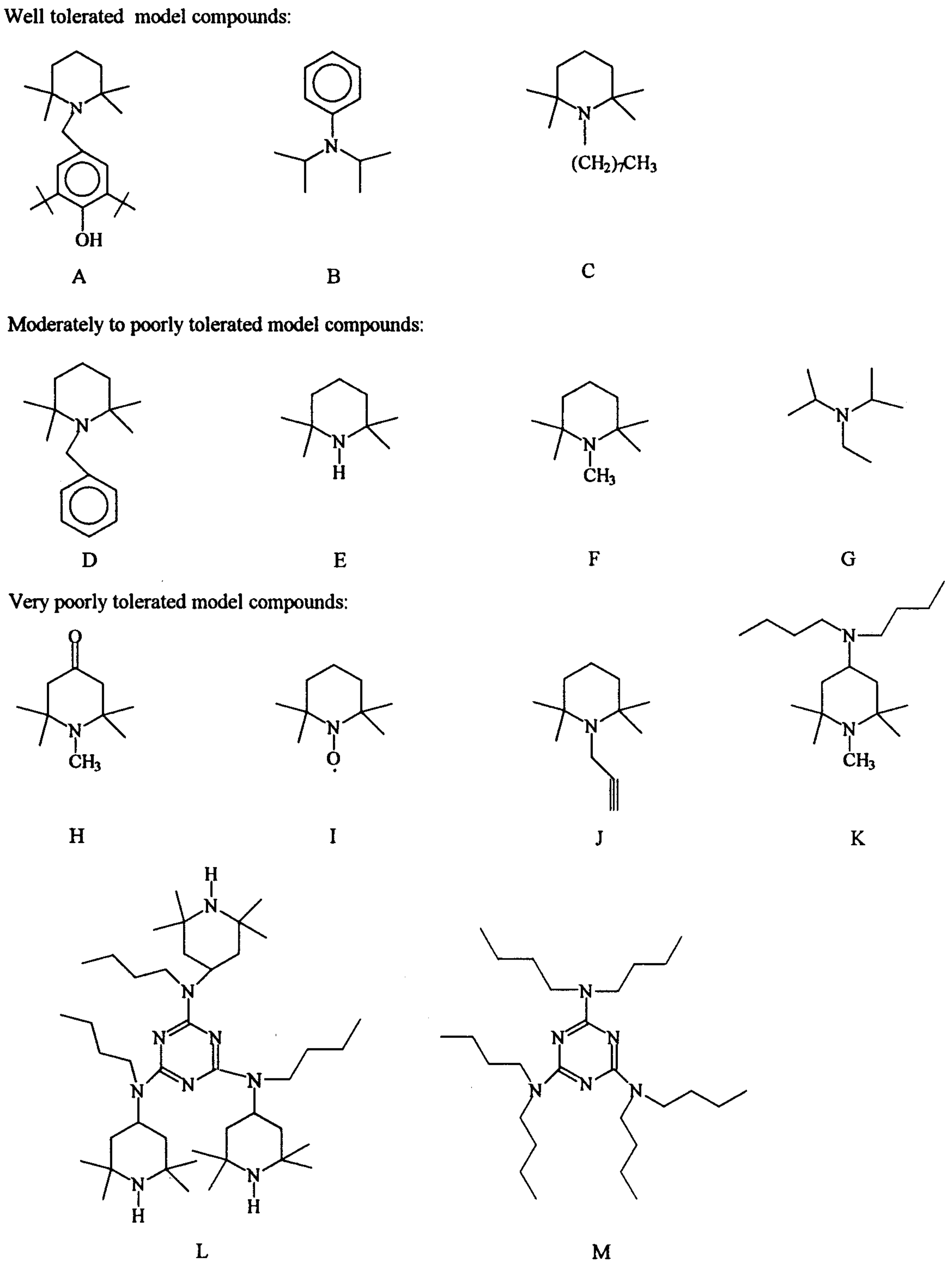


**Figure 1.** Amine model compounds: 1-(1-methylene-2,6-di-*tert*-butylphenol)-2,2,6,6-tetramethylpiperidine (**A**), *N*,*N*-diisopropylaniline (**B**), 1-octanyl-2,2,6,6-tetramethylpiperidine (**C**), 1-benzyl-2,2,6,6-tetramethylpiperidine (**D**), 2,2,6,6-tetramethylpiperidine (**E**), 1,2,2,6,6-pentamethylpiperidine (**F**), diisopropylethylamine (**G**), 1,2,2,6,6-pentamethyl-4-oxopiperidine (**H**), 2,2,6,6-tetramethylpiperidine-1-oxyl (**I**), 1-propargyl-2,2,6,6-tetramethylpiperidine (**J**), 4-*N*,*N*-bis(*n*-butylamino)-2,2,6,6-tetramethylpiperidine (**K**), tris(*N*-butyl-*N*-2,2,6,6-tetramethylpiperidineamino)triazine (**L**) and tris(dibutylamino)triazine (**M**).

catalyst activity, our initial efforts were directed toward conducting a series of standard ethylene polymerization over a *rac*-[dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/methylalumoxane catalyst system in the presence of various amine model compounds (see Figure 1) such as **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H**, **I**, **J**, and **K**, with the aim to find a correlation between HALS structure and polymerization activity. Generally, addition of Lewis bases such as amines reduce catalyst productivities with increasing Lewis base/Al or Lewis base/Zr molar ratios.[32] This behavior is expected on the basis of complex formation of the Lewis bases with Al and Zr complexes. The results presented in Table 1 clearly indicate that some of the amine model compounds are highly reactive and deactivating whereas others are less so. Much preferred are those HALS structures, which have a sterically demanding group in the 1-position of the piperidine ring and

**Table 1. Ethylene Polymerizations in the Presence of Various Amine Model Compounds over a CA2/MAO Catalyst System**[a]

| entry | stabilizer | Zr, μmol/L | Al, mmol/L | stab./Zr, mol/mol | stab./Al, mol/mol | activity [kg of polymer/mol of Zr·h·atm] |
|---|---|---|---|---|---|---|
| C70 | | 42 | 126 | | | 6000 |
| C92 | | 46 | 137 | | | 5300 |
| Well-Tolerated Amine Model Compounds **A**, **B**, and **C** | | | | | | |
| D81 | **A** | 23 | 70 | 295 | 0.100 | 6000 |
| D80 | **B** | 36 | 111 | 440 | 0.146 | 5200 |
| D79 | **B** | 34 | 103 | 934 | 0.311 | 5700 |
| C94 | **C** | 44 | 132 | 119 | 0.040 | 5300 |
| C95 | **C** | 44 | 132 | 457 | 0.153 | 4900 |
| C220 | **C** | 44 | 132 | 724 | 0.241 | 2500 |
| Moderately to Poorly Well-Tolerated Amine Model Compounds **D**, **E**, **F**, and **G** | | | | | | |
| C229 | **D** | 46 | 137 | 253 | 0.084 | 3800 |
| C228 | **D** | 46 | 137 | 500 | 0.167 | 2400 |
| C82 | **E** | 46 | 137 | 120 | 0.040 | 5400 |
| C83 | **E** | 46 | 137 | 230 | 0.076 | 4600 |
| C84 | **E** | 46 | 137 | 460 | 0.153 | 2700 |
| C227 | **E** | 46 | 137 | 684 | 0.228 | 1700 |
| C96 | **F** | 45 | 134 | 115 | 0.038 | 3900 |
| C88 | **F** | 45 | 134 | 230 | 0.077 | 2300 |
| C86 | **F** | 45 | 134 | 467 | 0.155 | 1200 |
| C230 | **F** | 24 | 67 | 704 | 0.235 | 1100 |
| C209 | **G** | 45 | 134 | 80 | 0.027 | 3000 |
| C210 | **G** | 42 | 126 | 250 | 0.085 | 2500 |
| C221 | **G** | 45 | 134 | 693 | 0.231 | 1200 |
| Very Poorly Tolerated Amine Model Compounds **H**, **I**, **J**, **K**, **L**, and **M** | | | | | | |
| C208 | **H** | 16 | 50 | 63 | 0.021 | 4200 |
| C207 | **H** | 42 | 126 | 129 | 0.043 | 2700 |
| C204 | **I** | 44 | 132 | 59 | 0.020 | 2700 |
| C203 | **I** | 45 | 134 | 113 | 0.037 | 1300 |
| C212 | **J** | 43 | 128 | 64 | 0.021 | 1000 |
| C211 | **J** | 46 | 137 | 120 | 0.040 | 500 |
| C91 | **K** | 46 | 137 | 112 | 0.037 | 500 |
| C108 | **L** | 46 | 137 | 150 | 0.050 | 500 |
| C110 | **M** | 44 | 132 | 64 | 0.021 | 2100 |
| C109 | **M** | 45 | 134 | 125 | 0.042 | 100 |

[a] Copolymerization conditions: *rac*-[1,1′-dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/MAO catalyst system, Al/Zr = 3000, $P_{\text{ethylene}} = 2$ bar, polymerization time = 20 min, $T = 80$ °C, and $V_{\text{toluene}} = 250$ mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution.

no additional heteroatoms in the 4-position in terms of maintained catalyst activity. The amine model compounds were divided into three groups: (1) well-tolerated, (2) moderately to poorly tolerated, and (3) very poorly tolerated model compounds based on how well they were tolerated by the **CA2**/MAO catalyst system. The following criteria was used for dividing the model compounds into these three different classes, those compounds which at Lewis base/Zr and Lewis/Al of up to 300 and 0.100, respectively only reduced the catalyst productivities marginally were considered to be well-tolerated; i.e., the recorded polymerization activities were in the range of 5000 [kg of polymer/mol of Zr·h·atm]. Representative amine model compounds of these well-tolerated compounds are **A**, **B**, and **C**. The compounds considered to be moderately to poorly tolerated were those for which polymerization activities in the range of 4600−2300 [kg of polymer/mol of Zr·h·atm] were recorded at Lewis base/Zr and Lewis base/Al molar ratios of 230 and 0.076, respectively, whereas compounds which reduced the polymerization activities to less than 2700 [kg of polymer/mol of Zr·h·atm] at already very low Lewis base/Zr molar ratios of 130 and Lewis base/Al molar ratios of 0.040 were considered to be very poorly tolerated. Representative examples of moderately to poorly tolerated amine model compounds are **D**, **E**, **F**, and **G**; and very poorly tolerated compounds are **H**, **I**, **J**, **K**, **L**, and **M**. The fact that model compound **A** is well-tolerated by the metallocene catalyst is consistent with our previous studies which show that sterically hindered phenols such as 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol and 2,6-di-*tert*-butylphenol enhances polymerization activity of ethylene and propylene by a factor of 2 and 6, respectively, under similar polymerization conditions.[12,13] In addition, the fact that sterically hindered phenol derivatives enhances the catalyst activity of various metallocene/MAO catalyst systems has also been verified by others.[33] Previous studies has shown that 5-amino-1-pentenes with diisopropyl or diphenyl substitution patterns on nitrogen are relatively well-tolerated, whereas dimethyl- or diethyl-substituted aminoalkenes are poorly tolerated by metallocene/borate catalysts systems.[14b] This observation can account for the fact that compound **B** which contain both a diisopropyl and a phenyl moiety on the nitrogen is well-tolerated, whereas compound **G** which have an ethyl group instead of phenyl group is far less well-tolerated than **B**. The 1-substituted-2,2,6,6-tetramethylpiperidine compounds with a hydrogen, methyl, benzyl, or octyl substituent at nitrogen exhibit quite different behavior in terms of recorded polymerization activities. The highest polymerization activity in this series was recorded for the octyl-substituted and the second highest for the benzyl- and hydrogen-substituted tetramethylpiperidine derivatives. The fact that the more sterically crowded benzyl-substituted model com-

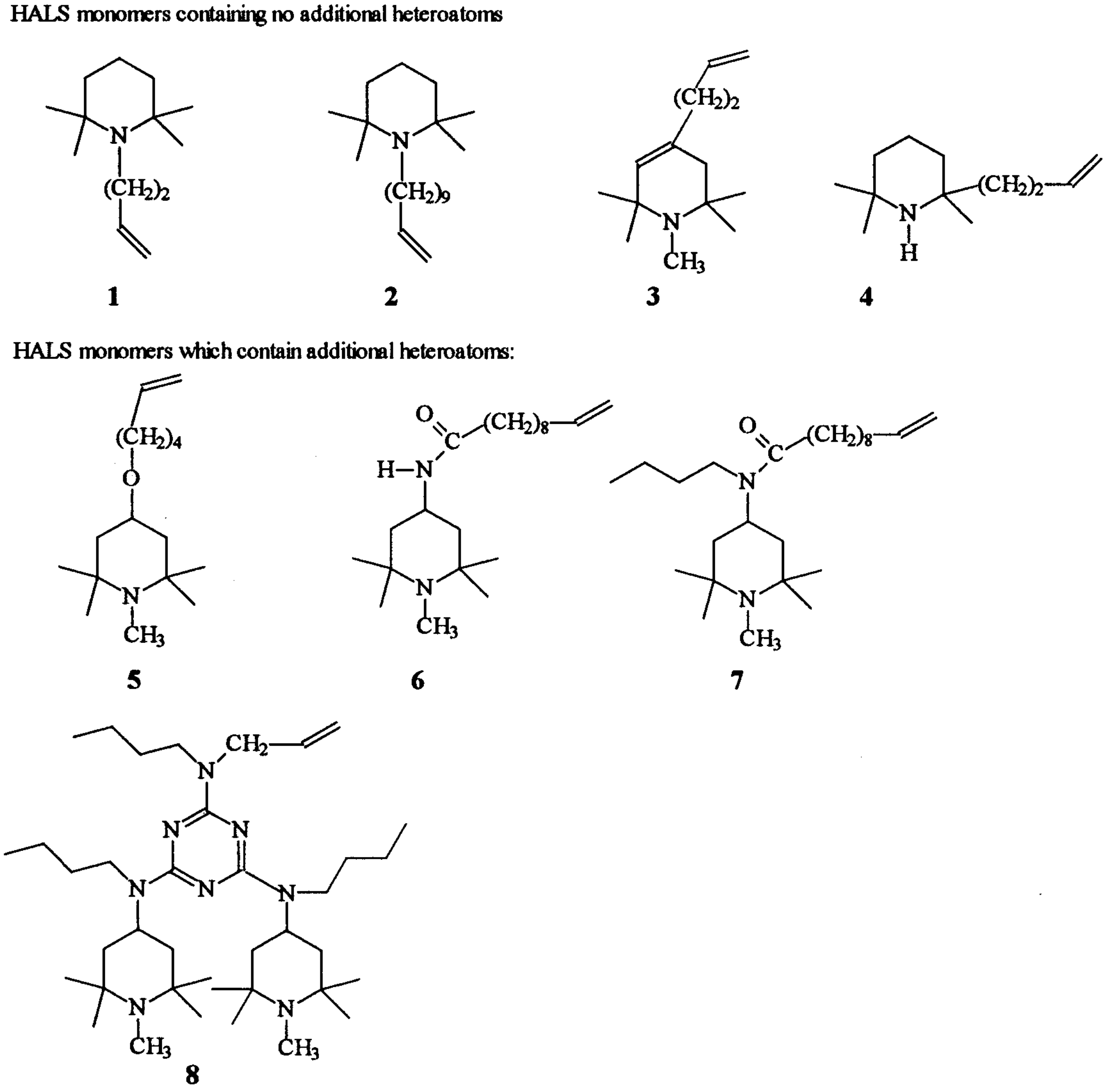
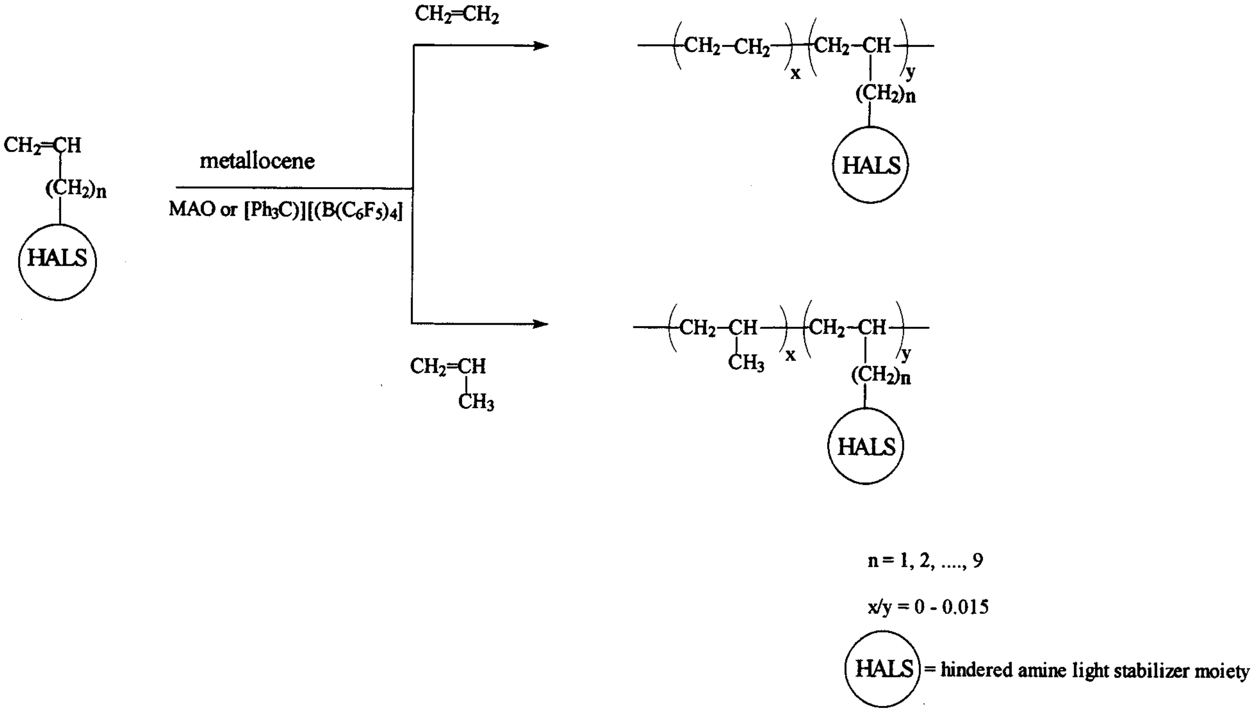


**Figure 2.** Developmental HALS monomers: 1-(but-3-enyl)-2,2,6,6-tetramethylpiperidine (**1**), 1-(undec-10-enyl)-2,2,6,6-tetramethylpiperidine (**2**), 4-(but-3-enyl)-1,2,2,6,6-pentamethyl-3,4-dehydropiperidine (**3**), 2-(but-3-enyl)-2,6,6-trimethylpiperidine (**4**), 4-(but-3-enyl)-1,2,2,6,6-pentamethyl-4-piperidyl ether (**5**), 4-(undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**6**), 4-((*N*-*n*-butyl)-undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**7**), and bis(*N*-*n*-butyl-*N*-2,2,6,6-tetramethylpiperidine)-*N*-*n*-butyl-*N*-allyltriazine (**8**)

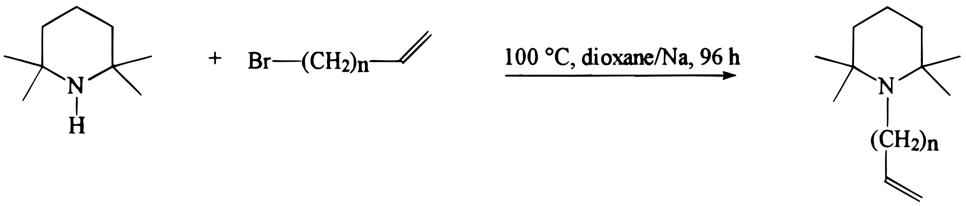
pound suppresses the polymerization activity to a greater extent than the octyl-substituted model compound **C** can rationally be explained by the fact that benzyl ligands have a tendency to coordinate to the cationic $d^0$ metal center and thus compete with the olefin for the coordination site, whereby the polymerization activity decreases.[34] The observation that **F** seem to depress catalyst activity to a larger extent than **E** may be attributed to the fact that the secondary HALS derivative forms a sterically crowded Al-amide compound with MAO (or with the "free" trimethylaluminum (TMA) which is an unavoidable part of MAO). This type of chemically altered 2,2,6,6-tetramethylpiperidine derivatives are according to our earlier trials generally well-tolerated, provided a sufficient relative amount of cocatalyst is employed.[11] On the other hand, in the case of 1,2,2,6,6-pentamethylpiperidine, the methyl substituent attached to the donor N atom provides only moderate steric hindrance. The net result is that the nonbonded electron pairs on N still tend to complex with the catalytic sites, thus inhibiting polymerization. In light of these results we decided to focus our synthetic efforts mainly on preparing novel HALS monomers based on polyalkylated piperidine templates containing no additional heteroatoms in the 4-position and preferable with a bulky substituent or an acidic hydrogen at the 1-position.

**Synthesis of HALS Monomers and Their Copolymerization.** We report herein our work on synthesis of our developmental HALS monomers and especially their copolymerization behavior with ethylene or propylene over various metallocene catalyst systems. These developmental HALS monomers are presented in Figure 2. Attempts to copolymerize the synthesized HALS monomers with ethylene or propylene over various metallocene catalysts as depicted in Scheme 1 were conducted. At present a large number of 2,2,6,6-tetramethylpiperidine derivatives has been prepared. The most numerous ones are those having an alcohol, ester, ether, amide or amine substituent in the four-position of the piperidine ring. These compounds are normally synthesized from the unique starting compound triacetonamine. Very few examples of polyalkylated piperidines with no additional heteroatoms and an alkenyl group in positions from 2 to 6 can be found. These type of HALS compounds would be potential candidates for

**Scheme 1. Copolymerization of HALS Monomers with Ethylene or Propylene over Soluble and Supported Metallocene Catalysts Employing MAO or TRI−FABA as Cocatalysts**



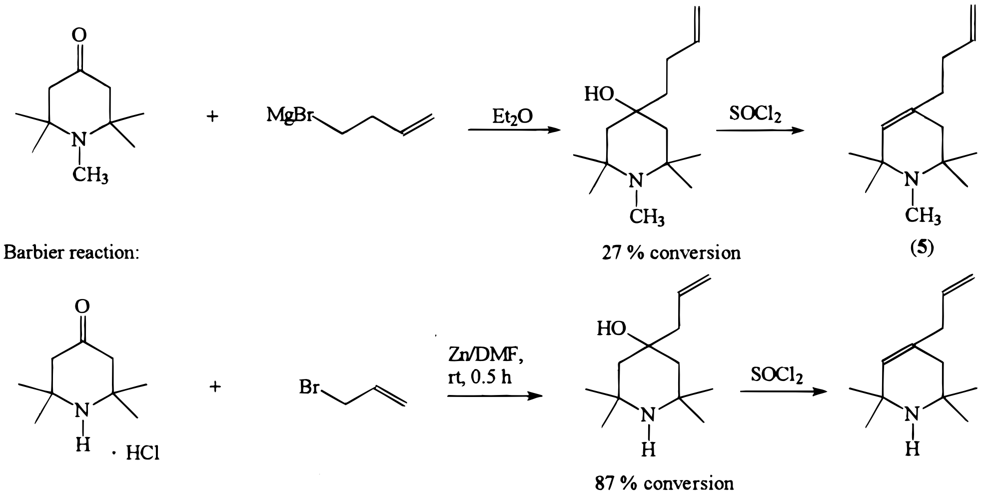
**Scheme 2. Synthetic Route for Obtaining 1-(ω-Alkenyl)-2,2,6,6-tetramethylpiperidines**



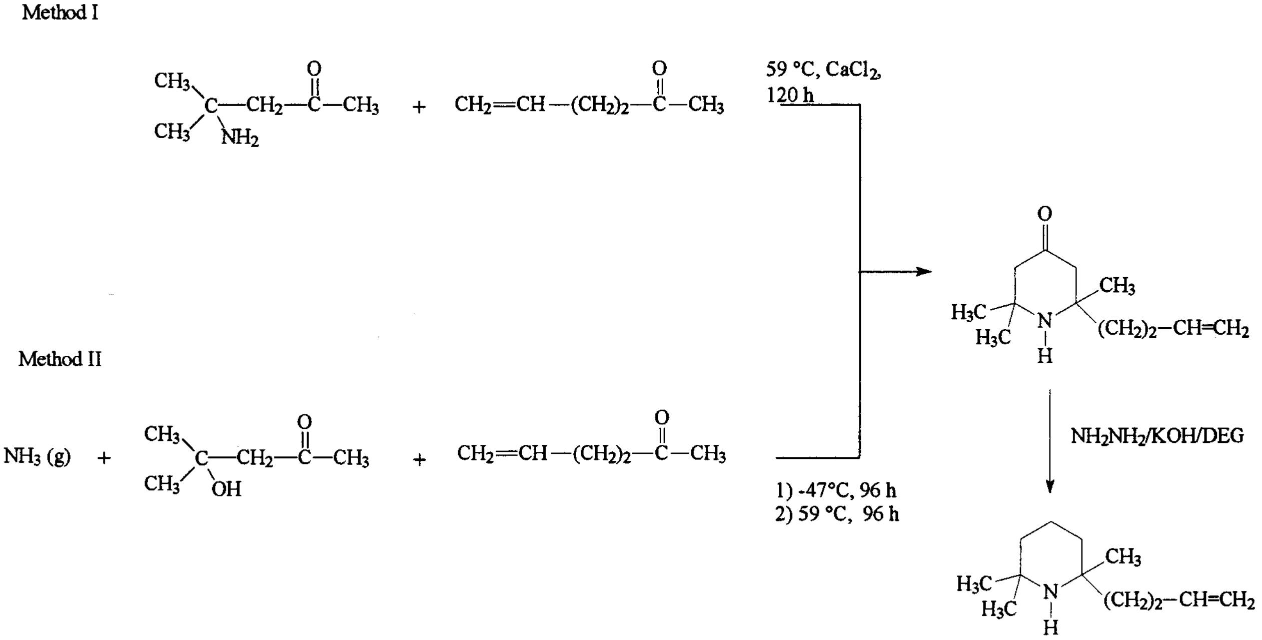
copolymerization with α-olefins over metallocene/MAO catalyst systems. As mentioned previously, we have reported the synthetic route to 4-alkenyl-2,2,6,6-tetramethylpiperidines. However, the presented long synthetic pathway to 4-(hex-5-enyl)-2,2,6,6-tetramethylpiperidine is impractical and expensive for the synthesis of 4-alkenyl-2,2,6,6-tetramethylpiperidines in large quantities. For this reason, other synthetic approaches to polymerizable piperidine derivatives were sought, i.e., pathways which would not be limited in terms of starting materials employed, multistep synthesis, generation of toxic byproducts, and/or low yield. The first potential HALS monomers we chose to synthesize were 1-(but-3-enyl)-2,2,6,6-tetramethylpiperidine (**1**) and 1-(undec-10-enyl)-2,2,6,6-tetramethylpiperidine (**2**) as shown in Scheme 2. These HALS monomers resembled closely nonfunctional α-olefins and therefore we expected that these monomer candidates would successfully be copolymerized with either ethylene or propylene in high yields. Moreover, we synthesized 4-(but-3-enyl)-1,2,2,6,6-pentamethyl-3,4-dehydropiperidine (**3**) (see Scheme 3a) for which we assumed that the rather sterically hindered double bond in the piperidine ring would not participate in the process of copolymerization. More recently, we have developed a new facile, high yield and fast reaction route to 4-allyl-2,2,6,6-tetramethyl-3,4-dehydropiperidine via a Barbier reaction[35] using Zinc powder as catalyst as shown in Scheme 3b. This route to the intermediate 4-allyl-4-hydroxyl-2,2,6,6-tetramethylpiperidine is more convenient than the ordinary Grignard reaction which proceeds in lower yields and requires inert atmosphere.

The general observation made during our previous investigations directed toward the development of a common pathway for the preparation of polymerizable HALS derivatives suggested that triacetonamine is perhaps not the only suitable starting material for the synthesis of polymerizable HALS derivatives. This new approach led us to develop an inexpensive general two-step reaction method to polymerizable HALS derivatives such as 2-(but-3-enyl)-2,6,6-trimethylpiperidine (**4**). The novel HALS monomer **4** was prepared by starting from diacetone amine (or diacetone alcohol), ω-alken-2-one, and calcium chloride as depicted in Scheme 4. It is a good practice to introduce the ultimate double bond, that is needed in the copolymerization, during the formation of the piperidine ring. The precursor 2-(but-3-enyl)-2,6,6-trimethyl-4-oxopiperidine was prepared from the reaction of diacetone amine and 5-hexen-2-one in the presence of calcium chloride. The isolated yield of 2-(but-3-enyl)-2,6,6-trimethyl-4-oxo-piperidine was only 9% due to problems with separation from the major byproduct triacetonamine. The low yield is partially balanced by the simplicity of the method and the availability of the starting materials. There are numerous reports describing the preparation of these starting materials, i.e., on the synthesis of diacetone amine,[36] diacetone alcohol,[37] and 5-hexen-2-one.[38] Alternatively 2-(but-3-enyl)-2,6,6-trimethyl-4-oxo-piperidine was prepared from the reaction of 5-hexen-2-one with diacetone alcohol in the

**Scheme 3. Preparation of HALS Monomers via (A) Grignard and (B) Barbier Routes**



**Scheme 4. Synthetic Pathways to 2-(but-3-enyl)-2,2,6-trimethylpiperidine (4)**



presence of ammonia and calcium chloride. The prepared 2-(but-3-enyl)-2,6,6-trimethyl-4-oxopiperidine was reduced by means of a modified Wolf-Kishner reaction which consisted in heating the 4-oxopiperidine with hydrazine hydrate under strongly alkaline conditions in the presence of the polar solvent diethylene glycol to give the desired **4** product in 43.3% isolated yield.

Next we explored routes for preparing 3-alkenyl-2,2,6,6-tetramethylpiperidines. Generally, it can be stated that 2,2,6,6-tetramethylpiperidine derivatives with substituents on the α-methylene group in the 3-position are unusual, due to considerable steric hindrance in this position. However, a plausible method for the preparation of 3-substituted alkenyl piperidines is mentioned in a patent application, i.e., the synthetic route to 3-allyl-2,2,6,6-tetramethylpiperidine.[39] This HALS compound could in theory be generated by treating triacetonemaine with a secondary amine to form the enamine which could be alkylated with allyl bromide to give 3-allyl-2,2,6,6-tetramethyl-4-oxopiperidine which in turn would be reduced by hydrazine to 3-allyl-2,2,6,6-tetramethylpiperidine. The enamine intermediate reacts only with reactive organic halides such as allyl bromide and benzyl bromide. This condition restricts the application of this method to introducing only an allylic group in the 3 position of the piperidine ring, since this reaction does not take place with bromo-*ω*-alkenyls longer than allyl bromide. Our attempts to prepare 3-allyl-2,2,6,6-tetramethylpiperidine according to this tentative route were unsuccessful. The enamine was obtained in high yield by the usual method:[40] a toluene solution of triacetonamine and pyrrolidine in the presence of a catalytic amount of benzoic acid was refluxed for 16 h with azeotropic distillation of the formed water. However, the alkylation of the enamine using allyl bromide lead to a complex mixture of products which were difficult to identify and isolate. It seems that the reaction is nonselective and it mainly proceeded at the ring nitrogen atom, whereby the piperidine ring is broken and various byproducts are formed. Therefore, it appears as if this reaction pathway for the synthesis of 3-allyl-2,2,6,6-tetramethylpiperidine is not recommendable.

In addition to the above-described 1-, 2-, and 4-alkenyl-substituted HALS monomers, we wish to report another family of HALS monomers, namely monomeric

**Scheme 5. Synthesis of HALS Monomers 6 and 7**

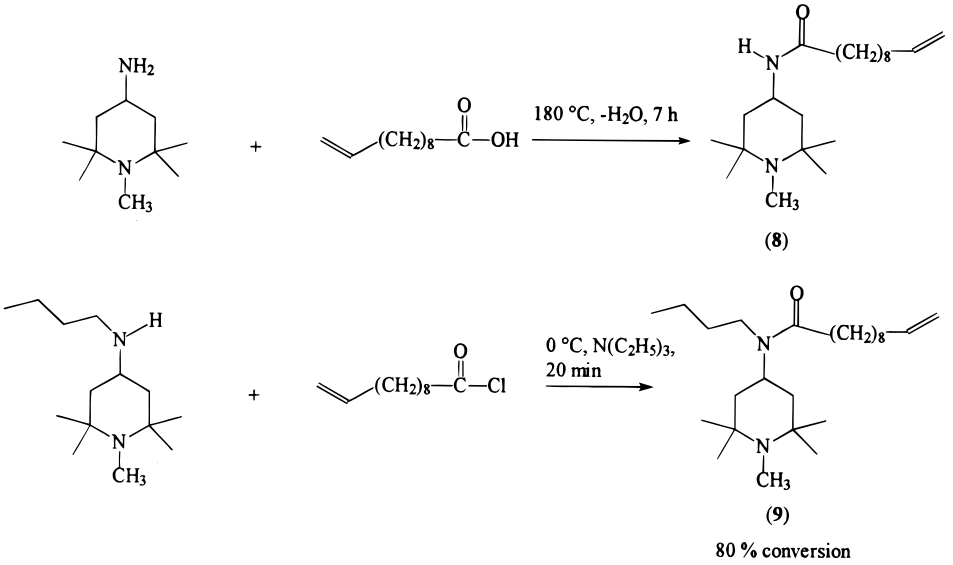


**Table 2. Copolymerization of Ethylene with 1, 2, 3, and 4 over a CA2/MAO Catalyst System**[a]

| entry | HALS | Zr, $\mu$mol/L | Al, mmol/L | HALS/Zr, mol/mol | HALS/Al, mol/mol | $T_M$, °C | cryst,[b] % | activity[c] | $M_n$ | $M_w$ | $P_d$ | bound nitrogen, wt %[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C70 | | 42 | 126 | | | 128.4 | 73 | 5600 | 10 300 | 31 300 | 3.0 | |
| C334 | **1** | 47 | 134 | 50 | 0.016 | 127.8 | 75 | 3900 | 12 200 | 26 900 | 2.2 | 0.4 (100%)[e] |
| C312 | **1** | 44 | 132 | 150 | 0.050 | 126.8 | 66 | 2800 | 10 600 | 23 900 | 2.3 | 0.8 (54%) |
| C313 | **1** | 43 | 129 | 600 | 0.2 | 122.4 | 46 | 2100 | 7100 | 18 500 | 2.6 | 5.4 (63%) |
| C333 | **2** | 44 | 132 | 50 | 0.016 | 126.8 | 77 | 4100 | 11 900 | 28 000 | 2.4 | 0.7 (100%) |
| C249 | **2** | 43 | 129 | 150 | 0.050 | 125.5 | 67 | 3300 | 12 200 | 27 700 | 2.3 | 2.0 (94%) |
| C241 | **2** | 44 | 132 | 600 | 0.2 | 121.8 | 46 | 3400 | 9200 | 17 300 | 1.9 | 6.4 (83%) |
| C242 | **2** | 45 | 134 | 1200 | 0.4 | 118.8 | 45 | 3300 | 5700 | 14 700 | 2.6 | 11.5 (74%) |
| C250 | **2** | 42 | 126 | 1875 | 0.625 | 114.8 | 31 | 3500 | n.d. | n.d. | n.d.[g] | 14.1 (61%) |
| C310 | **3** | 46 | 137 | 60 | 0.020 | 129.3 | 68 | 2300 | 14 100 | 29 300 | 2.1 | 0.8 (100%) |
| C309 | **3** | 45 | 134 | 120 | 0.040 | 127.8 | 60 | 1500 | 15 300 | 30 700 | 2.0 | 1.6 (65%) |
| C311 | **3** | 44 | 132 | 180 | 0.060 | 125.4 | 56 | 1700 | 14 900 | 31 400 | 2.1 | 1.9 (63%) |
| 558[f] | **4** | 31 | 92 | 110 | 0.036 | 130 | 70 | 5800 | 18 100 | 36 200 | 2.0 | 0.2 |

[a] Copolymerization conditions: *rac*-[1,1′-dimethylsilylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/MAO catalyst system, Al/Zr = 3000, $P_{ethylene}$ = 2 bar, polymerization time = 20 min, $T$ = 80 °C, and $V_{toluene}$ = 250 mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution. [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] Activity in [kg of polymer/mol of Zr·h·atm]. [d] Determined by elemental analysis. [e] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged HALS monomer into the reactor)·100%]. [f] $P_{ethylene}$ = 1 bar. [g] n.d. denotes not determined.

HALS derivatives which contain additional heteroatoms at the 4-position of the piperidine ring such as 4-(hex-5-enyl)-1,2,2,6,6-pentamethyl-4-piperidyl ether (**5**), 4-(undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**6**), 4-((*N*-*n*-butyl)undec-10-enylamide)-1,2,2,6,6-pentamethylpiperidine (**7**), and bis(*N*-*n*-butyl-*N*-2,2,6,6-tetramethylpiperidine)-*N*-*n*-butyl-*N*-allyltriazine (**8**). The synthetic routes to the 4-amide-substituted tetramethylpiperidines **6** and **7** are shown in Scheme 5. Being fully aware of the fact that these type of strong Lewis basic HALS monomers based on the screening experiments were likely to suppress polymerization productivities especially at higher Lewis base/Al and Lewis base/Zr molar ratios, we decided, nevertheless, to perform copolymerizations with both ethylene and propylene under uniform conditions over various metallocene/MAO based catalyst systems. We wanted to elucidate any correlation between metallocene structure and incorporation rate of HALS as well as between metallocene structure and tolerance to relatively strong Lewis bases.

**Ethylene Copolymerizations with 1, 2, 3, and 4 over a CA2/MAO Catalyst System.** The results of ethylene copolymerizations with **1**, **2**, **3**, **4**, and **5** over a **CA2**/MAO catalyst system are presented in Table 2. According to elemental analysis, copolymers with relatively high HALS content ranging from 0.2 to 14.1 wt % were obtained in high yields. In the case of ethylene copolymerization with **2** the catalyst activity initially decreases from 5600 to around 3500 [kg of polymer/mol of Zr·h·atm] upon the addition of 6.6 mmol of **2** which corresponds to HALS/Zr and HALS/Al molar ratios of 150 and 0.050, respectively. The catalyst activities remained unchanged within experimental error, when the HALS/Zr and HALS/Al molar ratios was further increased to 1875 and 0.6250, respectively. Overall, the amount of incorporated HALS units systematically increased with the concentration of HALS monomer in the feed. Kaminsky and co-workers have shown that in the course of copolymerization of ethylene with 4-vinylcyclohexene only the vinyl double bond of 4-vinylcyclohexene, and not the endocyclic double bond react during copolymerization over a $Ph_2C(CpFlu)ZrCl_2$/MAO catalyst system.[20] Therefore, it is not likely that the endocyclic double bond of **3** which is more sterically hindered than that in 4-vinylcyclohexene would participate in the copolymerization with ethylene. Therefore, we can as-

**Table 3. Terpolymerization of Ethylene/1-Hexene/2 over a CA2/MAO Catalyst System**[a]

| entry | HALS | [1-hexene], mol/L | Zr, µmol/L | Al, mmol/L | HALS/Zr, mol/mol | HALS/Al mol/mol | $T_M$, °C | cryst,[b] % | activity[c] | $M_n$ | $M_w$ | $P_d$ | bound nitrogen, wt %[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C70 | | | 42 | 126 | | | 128.4 | 73 | 5600 | 10 300 | 31 300 | 3.0 | |
| C318 | | 0.14 | 27 | 82 | | | 121.6 | 32 | 7200 | 7400 | 18 000 | 2.4 | |
| C314 | **2** | 0.14 | 27 | 82 | 243 | 0.08 | 116.8 | 17 | 4900 | 3500 | 9600 | 2.7 | 1.2 (57%)[e] |
| C315 | **2** | 0.14 | 27 | 82 | 972 | 0.32 | 114.5 | 23 | 5400 | 3900 | 8700 | 2.3 | 4.7 (60%) |
| C316 | **2** | 0.14 | 25 | 76 | 2040 | 0.68 | 109.3 | | 4400 | 3200 | 6000 | 1.9 | 11.4 (56%) |
| C317 | **2** | 0.14 | 25 | 76 | 3160 | 1.1 | 95.7 | | 4600 | 2500 | 4800 | 1.9 | 15.9 (53%) |

[a] Copolymerization conditions: *rac*-[1,1′-dimethylsilylenebis($\eta^5$-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/MAO catalyst system, Al/Zr = 3000, $P_{ethylene}$ = 2 bar, polymerization time = 20 min, $T$ = 80 °C, and $V_{toluene}$ = 250 mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution. [b] 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] Activity in [kg of polymer/mol of Zr·h·atm]. [d] Determined by elemental analysis. [e] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged HALS monomer into the reactor)·100%].

**Table 4. Copolymerization of Ethylene with 5, 6, 7, or 8 over a CA2/MAO Catalyst System**[a]

| entry | HALS | $T_p$, °C | Zr, µmol/L | Al, mmol/L | HALS/Zr, mol/mol | HALS/Al, mol/mol | activity[b] | $T_m$, °C | cryst,[c] % | $M_n$ | $M_n$ | $P_d$ | bound nitrogen, wt %[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C70 | | 80 | 42 | 126 | | | 5600 | 128.4 | 73.4 | 31 300 | 10 300 | 3.0 | |
| C85 | **5** | 80 | 45 | 134 | 110 | 0.035 | Tr[g] | | | | | | |
| D55 | **8** | 80 | 46 | 137 | 110 | 0.035 | Tr[g] | | | | | | |
| C71 | **6** | 80 | 48 | 145 | 50 | 0.016 | 4800 | 128.0 | 70.0 | 22 700 | 9600 | 2.4 | 0.5 (100%)[e] |
| C73 | **6** | 80 | 45 | 134 | 100 | 0.035 | 3000 | 128.0 | 57.6 | 20 500 | 8400 | 2.4 | 1.7 (93%) |
| C72 | **6** | 80 | 45 | 134 | 165 | 0.055 | 120 | n.d | n.d | n.d | n.d | n.d | n.d[f] |
| C78 | **6** | 60 | 45 | 134 | 110 | 0.035 | 3400 | 128.8 | 51.4 | 24 100 | 61 400 | 2.5 | 1.3 (85%) |
| C80 | **6** | 40 | 47 | 139 | 100 | 0.034 | 1000 | 125.8 | 33.3 | 62 300 | 121 000 | 1.9 | 3.6 (73%) |
| C74 | **7** | 80 | 46 | 137 | 50 | 0.016 | 5400 | 127.7 | 68.4 | 20 800 | 8400 | 2.5 | 0.5 (100%) |
| C75 | **7** | 80 | 46 | 139 | 100 | 0.032 | 2800 | 128.4 | 66.0 | 21 100 | 9300 | 2.3 | 2.0 (100%) |
| C76 | **7** | 80 | 45 | 134 | 150 | 0.050 | 380 | 122.8 | 44.1 | 3400 | 1500 | 2.3 | 8.0 (35.6%) |
| C77 | **7** | 60 | 44 | 132 | 100 | 0.034 | 3700 | 130 | 64.7 | 22 300 | 50 600 | 2.3 | 1.7 (100%) |
| C79 | **7** | 40 | 45 | 134 | 100 | 0.033 | 900 | 124.4 | 37.5 | 44 900 | 102 000 | 2.3 | 5 (70%) |

[a] Copolymerization conditions: *rac*-[1,1′-dimethylsilylenebis($\eta^5$-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/MAO catalyst system, Al/Zr = 3000, $P_{ethylene}$ = 2 bar, polymerization time = 20 min, $T$ = 80 °C, and $V_{toluene}$ = 250 mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution. [b] Activity in [kg of polymer/mol of Zr·h·atm]. [c] 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. [d] Determined by elemental analysis. [e] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged monomer into the reactor) × 100%]. [f] n.d denotes not determined. [g] Tr denotes trace of polymer.

sume that **3** has been copolymerized with ethylene via the alkenyl double bond. The catalyst productivities for homopolymerization of ethylene and copolymerization of ethylene with **4** were similar. Evidently, **4** is well-tolerated at this low level of HALS/Al molar ratio of 0.036. As previously mentioned, this can be attributed to the well-known reactivity of the N−H bond with organometallic cocatalyst compounds such as aluminumalkyls. Similarly to ethylene/1-hexene copolymers the melting points and crystallinities are reduced monotonically with an increase in short-chain branching.[41] Thus, increasing the HALS content from 0 to 14.1 wt % reduces the melting point from 128 to 115 °C and crystallinity from 73 to 30%. For the selected catalyst system and polymerization conditions polyethylene with a weight-average molar mass of $M_w$ = 31 300 g/mol was obtained. With growing content of HALS units, the weight-average molar mass decreases to 5700 g/mol for the HALS/ethylene copolymers. The molecular weight distribution was found to be narrow and it corresponded to the values expected for polymers produced by metallocene catalysts. Furthermore, terpolymerizations of ethylene/1-hexene/**2** were also carried out over the **CA2**/MAO catalyst system and the results are shown in Table 3. Again no correlation between HALS monomer concentration and catalyst activity could be observed. The catalyst activity remained basically unchanged after the initial decrease even at very high HALS/Al and HALS/Zr molar ratios of 1.1 and 3160, respectively. Both the melting point and crystallinity decreased markedly and eventually disappeared completely with an increase in HALS content.

**Ethylene Copolymerization with HALS Monomers Containing Additional Heteroatoms at the 4-Position such as 5, 6, 7, and 8 over a CA2/MAO Catalyst System.** Table 4 summarizes the copolymerizations of ethylene with **5**, **6**, **7**, and **8** over a **CA2**/MAO catalyst system. The results clearly indicate that the relatively sterically unprotected ether, amino and triazine moieties have a strong tendency to coordinate at the catalytic site, whereby polymerization is inhibited. In contrast to **5** and **8** under similar polymerization conditions at low HALS/Al and HALS/Zr molar ratios less than 0.035 and 100, respectively the copolymerization of **6** or **7** with ethylene proceeded smoothly up to complete HALS monomer conversion, whereas at HALS/Al ratios of greater than 100, copolymers were obtained in poor yields. This may be attributed to rapid catalyst poisoning. Copolymerizations were also conducted at different temperatures and the incorporation rate of **6** and **7** was found to be independent of the polymerization temperature and ranged from 1.3 to 5 wt % as shown in Table 4. Mülhaupt and co-workers reported similar copolymerization behavior in ethylene and 1-octene copolymerizations over a *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ (**CA6**)/MAO catalyst system. At constant ethylene

**Table 5. Copolymerization of Ethylene with 2, 6, and 7 over a Supported Metallocene Catalyst System[a]**

| entry | HALS | morphology[b] | HALS/Zr, mol/mol | $T_M$, °C | cryst,[c] % | $M_n$ | $M_w$ | $P_d$ | activity[d] | bound nitrogen, wt %[e] |
|---|---|---|---|---|---|---|---|---|---|---|
| C174 | | good | | 129 | 56 | 55 500 | 199 000 | 3.6 | 1320 | |
| C251 | **2** | good | 550 | 129 | 61 | 57 400 | 165 000 | 2.9 | 1946 | 0.1 (18%)[f] |
| C178 | **6** | good | 430 | 129 | 61 | 40 200 | 196 000 | 4.9 | 280 | ≈0 |
| C180 | **7** | good | 430 | 130 | 59 | 46 400 | 214 000 | 3.7 | 300 | ≈0 |

[a] Copolymerization conditions: heterogeneous metallocene/$SiO_2$/MAO catalyst system, MAO/Zr = 100, $P_{ethylene} = 5$ bar, polymerization time = 180 min, $T = 80$ °C, and $V_{pentane} = 300$ mL. In addition 0.3 g of TIBA was used as an impurity scavenger and external activator. [b] Spherical co- and homopolymer particles were formed, no reactor fouling or fine powder could be detected. [c] 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. [d] Activity in [kg of polymer/mol of Zr·h·atm]. [e] Determined by elemental analysis. [f] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged monomer into the reactor)·100%]

pressure of 2 bar and 1-octene concentration of 0.6 mol/L, poly(ethene-*co*-1-octene) copolymers with constant 1-octene incorporation of approximately 25 mol % were obtained independently of polymerization temperature which ranged from 0 to 60 °C.[42] The HALS copolymers produced at low polymerization temperatures exhibited large $M_w$ and $M_n$ values compared to those copolymers obtained at 80 °C. This is in accord with earlier observations that $\beta$-hybride elimination requires a significant activation energy whereby lowering the polymerization temperature should decrease the rate of $\beta$-hybride elimination and increase the molecular weight of the polymer.[43] In addition, as a consequence of lower solubility of ethylene at higher polymerization temperatures at constant ethylene pressure, polymers of lower molecular weights are obtained at higher polymerization temperatures. On the basis of $^{13}C$ NMR spectra all of the produced ethylene/HALS copolymers are random copolymers, which contain isolated HALS short-chain branches. The observed resonances at 27.4, 30.7, and 34.6 ppm for the methylene and 38.3 ppm for the methine backbone carbon atoms of the copolymers correspond to those reported for ethylene/1-octene copolymers with isolated hexyl branches.[44] No detectable traces of HALS homopolymers or block copolymer fragments could be found in any of the $^{13}C$ NMR spectrum of ethylene/HALS copolymers prepared in this study.

**Copolymerization of Ethylene and 2, 6, and 7 over a Supported Metallocene Catalyst System.** Next we have studied the copolymerization of ethylene with **2**, **6**, and **7** over a supported metallocene/MAO/$SiO_2$/triisobutylaluminum(TIBA) catalyst system. To the best of our knowledge there have been no reports of the successful copolymerization of unprotected functional monomers containing heteroatoms with ethylene over a silica-supported catalyst based on group IV metallocene/methylalumoxane catalysts. Generally it can be stated that supported metallocene catalysts are, as a rule, much more sensitive to Lewis bases than their unsupported counterparts. This seems reasonable given that the supported metallocene catalyst systems have normally very low MAO/Zr molar ratios ranging from 10 to 100, which are considerably less than those commonly employed under homogeneous conditions for maximum polymerization activities.[45] The implication of the relatively low MAO/Zr molar ratio is that the supported catalyst systems are easily poisoned by heteroatom-containing monomers due to the absence of excess MAO which would effectively prevent the destructive interaction between the heteroatoms and active sites. As a matter of fact, one important role of MAO (or TMA), besides alkylation, ionization and/or reduction of the transition metal and stabilization of cationic metallocene alkyl is to scavenge potential catalyst poisons. Against this background it is interesting to note that **2** can be successfully copolymerized with ethylene over the silica-supported metallocene catalyst system as shown in Table 5 entry C251. The prepared copolymer contained 0.1 wt % of HALS units and the catalyst productivity was even slightly higher than in the homopolymerization of ethylene under similar conditions. Evidently, the undecenyl group shields the nonbonded electron pair of nitrogen from complexation with the electronically deficient catalytic sites. Moreover, as may be seen from Table 5, the supported metallocene catalyst system failed to promote the copolymerization of ethylene with the more strongly basic HALS monomers **6** and **7**, due to a negative interference of the amide and *N*-methyl moieties with catalyst active sites. Hence, solely polyethylene was formed and the catalyst activities for runs C178 and C180 were approximately only one-fourth of the catalyst activity value for the homopolymerization of ethylene under similar reaction conditions. This result together with the results from the above-mentioned co- and terpolymerizations imply that **2** is a relatively weak Lewis base which is well-tolerated by the metallocene catalyst and easily copolymerized with ethylene or terpolymerized with ethylene and 1-hexene.

**Propylene Copolymerization with 6 and 7 over Eight Different Metallocene/MAO Catalyst Systems.** Propylene was copolymerized with **6** and **7** over eight different metallocene catalysts (**CA1**, **CA2**, ..., **CA8**) using a constant set of parameters. The copolymerizations were performed in toluene at 20 °C and constant propylene pressure of 2 bar and using HALS/Al and HALS/Zr molar ratios of 0.017 and 50, respectively. The obtained results are collected in Table 6. From this limited amount of copolymerization experimentation, conclusions from the comparative activity data must be drawn with some caution. However, some of these activity changes between homopolymerization and copolymerization are dramatic and instructive and some predominant structural pattern for metallocene structure vs high catalytic activity in copolymerization can be made. Overall the copolymerization results over the different metallocene/MAO catalyst systems show that the catalytic activity decreases in the series **CA2** ≈ **CA4** > **CA7** ≈ **CA8** > **CA6** ≈ **CA1** ≈ **CA3** ≈ **CA5** relative to propylene homopolymerization activities obtained for the respective metallocene/MAO catalyst systems under similar reaction conditions.

Several features are worth noting. Most remarkable is that the tetrahydroindenyl analogues of **CA1** and **CA3**, i.e., **CA2** and **C4**, are superior with respect to retained polymerization activity in the presence of

**Table 6. Copolymerization of Propylene with 6 and 7 over Seven Different Metallocene/MAO Catalyst Systems**[a]

| entry | catalyst | HALS | Zr, $\mu$mol/L | Al, mmol/L | HALS/Zr, mol/mol | HALS/Al, mol/mol | catalyst activity[b] | $T_m$, °C | cryst,[c] % | $M_n$ | $P_d$ | bound nitrogen, wt %[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C24 | CA1 | | 44 | 132 | | | 2200 | 142 | 37.8 | 30 100 | 1.8 | |
| C28 | CA1 | **6** | 46 | 136 | 49 | 0.016 | 250 | 140.7 | 30.9 | 16 900 | 2.1 | 2.4 (77%)[e] |
| C30 | CA1 | **7** | 44 | 132 | 51 | 0.017 | 400 | 141.6 | 38.0 | 22 800 | 1.9 | 1.4 (66.6%) |
| C58 | CA2 | | 44 | 132 | | | 500 | 145.5 | 39.2 | 32 000 | 1.8 | |
| C60 | CA2 | **6** | 48 | 134 | 50 | 0.017 | 300 | 141.7 | 40.5 | 3300 | 2.9 | 2.0 (63.6%) |
| C56 | CA2 | **7** | 44 | 132 | 52 | 0.017 | 450 | 143.2 | 38.5 | 10 100 | 2.3 | 1.5 (78.1%) |
| C160 | CA3 | | 46 | 137 | | | 2700 | 131.1 | 32.6 | 10 000 | 2.2 | |
| C159 | CA3 | **6** | 46 | 137 | 49 | 146 | 200 | 133.4 | 38.2 | 4800 | 2.4 | 2.7 (63%) |
| C158 | CA3 | **7** | 50 | 149 | 47 | 141 | 400 | 134.7 | 37.9 | 6900 | 2.7 | 1.4 (80%) |
| C50 | CA4 | | 46 | 137 | | | 400 | 137.5 | 31.9 | 16 500 | 2.0 | |
| C61 | CA4 | **6** | 50 | 150 | 45 | 0.015 | 350 | 135.1 | 34.5 | 2300 | 2.4 | 1.61 (52.3%) |
| C49 | CA4 | **7** | 48 | 144 | 47 | 0.016 | 450 | 135.6 | 34.6 | 3600 | 3.1 | 1.44 (80%) |
| C244 | CA5 | | 44 | 133 | | | 560 | atactic oligomeric polypropylene | | | | |
| C245 | CA5 | **6** | 45 | 135 | 48 | 0.016 | 150 | atactic oligomeric poly(propylene-*co*-**6**) copolymer | | | | |
| C162 | CA6 | | 29 | 140 | | | 3600 | 150 | 38.8 | 67 300 | 2.3 | |
| C156 | CA6 | **6** | 37 | 111 | 58 | 0.019 | 400 | 146.3 | 26.1 | 26 000 | 3.2 | 1.6 (55%) |
| C157 | CA6 | **7** | 34 | 102 | 66 | 0.021 | 650 | 147.5 | 29.7 | 55 300 | 2.3 | 0.9 (53%) |
| C54 | CA7 | | 47 | 142 | | | 800 | 140.8 | 16.0 | 54 700 | 1.8 | |
| C59 | CA7 | **6** | 47 | 142 | 47 | 0.016 | 200 | 138.5 | 16.7 | 18 700 | 2.2 | 1.9 (45%) |
| C53 | CA7 | **7** | 49 | 147 | 46 | 0.015 | 350 | 139.5 | 16.2 | 32 100 | 1.9 | 1.1 (52%) |
| C41 | CA8 | | 47 | 141 | | | 2300 | 143.7 | 46.7 | 8000 | 2.4 | |
| C45 | CA8 | **6** | 45 | 136 | 50 | 0.016 | 1100 | 147.0 | 40.1 | n.d.[e] | n.d | 0.42 (40%) |
| C51 | CA8 | **7** | 48 | 145 | 47 | 0.016 | 550 | 143.7 | 45.4 | 8300 | 2.2 | 1.2 (72%) |

[a] Copolymerization conditions: (**CA1**, **CA2**, ..., or **CA7**)/MAO catalyst system, Al/Zr = 3000, $P_{\mathrm{propylene}} = 2$ bar, polymerization time = 1 h, $T = 80$ °C, and $V_{\mathrm{toluene}} = 250$ mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution. [b] Activity in [kg of polymer/mol of Zr·h·atm]. [c] Here, 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 208 J/g. [d] Determined by elemental analysis. [e] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged monomer into the reactor)·100]. [f] n.d. denotes not determined.

HALS comonomers **6** and **7** when compared with the parent indenylmetallocenes **CA1** and **CA3**. The non-hydrogenated **CA1** and **CA3** catalytic activities were five to eight times lower in the co- than homopolymerizations whereas in the case of the tetrahydroindenyl analogues **CA2** and **CA4** the catalyst activities were only slightly lower during copolymerization. This observation, can at least partially be accounted for by the fact that non-hydrogenated congeners **CA1** and **CA3** have a tendency to undergo a slippage from $\eta^5 \rightarrow \eta^3$ causing bonding distortion and making the metallocene catalyst exceptionally Lewis acidic.[46] Hence, assuming one ligand slippage at a time, the catalytic species goes from being a cationic 14 electron species to a highly coordinatively and electronically unsaturated 12 electron species. Thus, the 12 electron species has a higher tendency to form complexes with already minute amounts of Lewis bases such as **6** and **7** than does the original cation which was a 14 electron species. Therefore, catalytic sites are easily extinguished after this type of a ligand slippage has occurred.

By comparing entries C24, C28 and C30 with C160, C158 and C159, it appears as if the replacement of the dimethylsilyl bridge in **CA1** by the ethylene bridge in **CA3**, does not influence the copolymerization behavior, presumably due to the fact that catalyst **CA1** and **CA3** have nearly identical spatial arrangements, whereas the introduction of a bulky substituent in the 2-position of the cyclopentadienyl ring (as in the case of metallocene structure **CA8)** seems to influence the catalytic activity. The decreased rate of deactivation relative to **CA1** and **CA3** in copolymerizations might result from the fact that the spacious *tert*-butyldimethylsiloxyl group in the 2-position near the central zirconium atom may sterically partially hinder the amide moieties of the HALS monomers **6** and **7** from approaching, coordinating, and deactivating the cationic zirconium center. Thus, relatively higher catalyst activities were recorded for 2-substitued indenyl structures in comparison to metallocenes with unsubstituted indenyl ligand frameworks. In addition, the syndiospecific metallocene catalyst **CA7** exhibited also substantially higher relative catalyst productivities in copolymerizations than did **CA1** and **CA3**. In addition, the experimental results indicate that HALS comonomer **6** is better tolerated by all of the metallocene/MAO catalyst systems used in this study compared to **7** in terms of retained polymerization activity and a significantly higher amount of **6** than **7** is incorporated into the synthesized copolymers under identical polymerization conditions. An other common feature is that by comparing poly(propylene-*co*-**6**) and poly(propylene-*co*-**7**) pairs the former copolymers exhibit much higher molar masses. These differences in activity, molar masses and incorporation rates of monomers **6** and **7** may be attributed to the fact that only monomer **6** due to its Brønstedt acidity is able to react selectively with MAO (or TMA) to give an aluminum-amide complex. The produced Al−amide complex increases the steric bulk around the amide moiety and in this manner suppresses the undesired interaction between vacant coordination sites and the nonbonded electron pairs on oxygen and/or nitrogen atoms of the amide group. The $^{13}$C NMR spectrum of poly(propylene-*co*-**6**) prepared over a **CA1**/MAO catalyst system is shown in Figure 3. The stereochemical triad composition of the copolymer, expressed as fractions of isotactic mm = 94.7, heterotactic mr = 3.9, and syndiotactic rr = 1.4, is similar to that of polypropylene, mm = 94.5, mr = 4.3, and rr = 1.2, synthesized over the same catalyst system. Since 2rr/mr is close to 1, the triad composition suggests that the propagation step is mainly enantiomorphic site controlled. On the basis of the $^{13}$C NMR spectrum the propylene homo- and copolymerizations proceeds dominantly via 1,2-additions with minor amounts of 2,1-

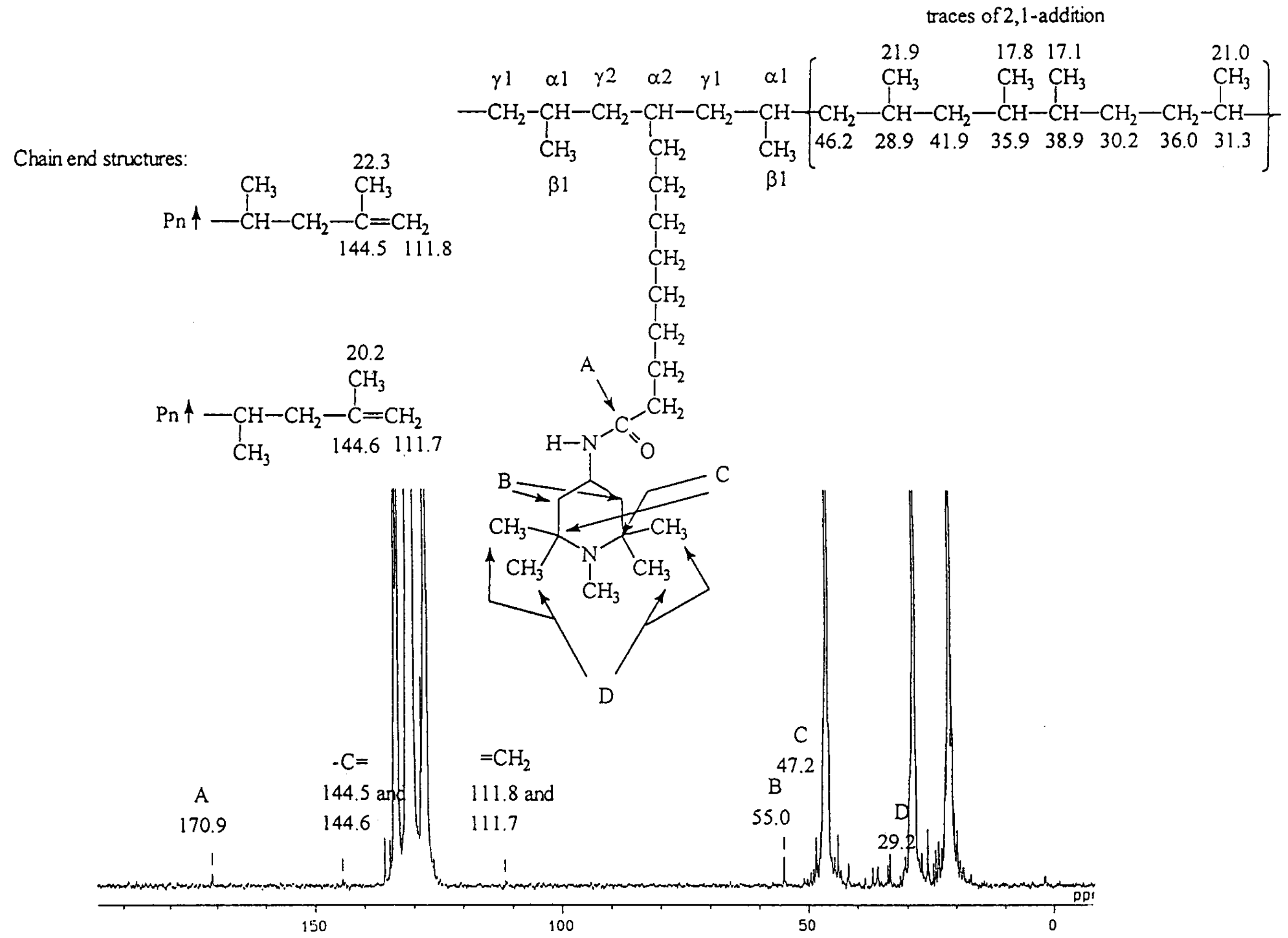


**Figure 3.** Typical $^{13}$C NMR spectrum of poly(propylene-*co*-**6**) copolymer.

additions. No traces of 1,3-additions can be detected in the $^{13}$C NMR spectrum. The chain-end groups are predominantly vinylidene and *n*-propyl, which suggest that the $\beta$-hydride elimination is the main chain-transfer process in both polymerizations. The $^{13}$C NMR spectra recorded for propylene/HALS copolymers unambiguously suggest that the HALS comonomers are copolymerized with propylene over metallocene/MAO catalyst systems. For instance, the observed resonances at 43.6 ppm for the methylene and 33.6 ppm for the methine carbon atoms in the mainchain of poly(propylene-*co*-**6**) copolymer (see Figure 3.) correspond to those recorded for poly(propylene-*co*-1-hexene)[47]copolymers. Generally, it can be said that the stereospecificity of the reaction over metallocene catalysts is insensitive to the presence of the HALS functionality according to $^{13}$C NMR and FTIR studies; i.e., in this study the **CA7**, **CA5** and the rest of the metallocene catalyst systems produced highly syndiotactic, atactic and isotactic copolymers, respectively.

**Copolymerization of Propylene with 2, 6, and 7 over a CA1/TEA/Triethylaluminum/(Trityltetra(perfluorophenyl)borate (TRI−FABA) or *N,N*-Dimethylanilinium Tetra(perfluorophenyl)borate (DAN−FABA)) Catalyst System.** Copolymerizations of propylene with **2**, **6**, and **7** were catalyzed by the ternary system **CA1**/TEA/(TRI−FABA or DAN−FABA), and the results are collected in Table 7. The activity for the propylene homopolymerizations using TRI−FABA as cocatalyst was 2300 [kg of polymer/mol of Zr·h·atm]. Our initial copolymerization effort employing **6** with propylene over the above-mentioned catalyst system failed, since virtually no polymerization activity was observed at a boron/**6** molar ratio of 0.5, entry C166, as shown in Table 7. On the other hand at boron/**6** molar ratios of greater than 0.8 catalyst activities similar to that of propylene homopolymerization were recorded (entries C163 and C165). This indicates that the catalyst system is totally deactivated up to a limiting boron/HALS molar ratio. We observed that TRI−FABA diluted in toluene changed color from yellow to white when the concentration of HALS monomer was increased. During polymerization of propylene the active catalyst complex was still slightly yellow. We were able to determine the limiting TRI−FABA/HALS molar ratio by titration as shown in Figure 4, i.e., as long as the molar ratio was such as that the solution was still yellow, copolymer was obtained in high yield. On the other hand, if the TRI−FABA/HALS solution turned white virtually no copolymer was obtained as shown in Table 7. The limiting boron/HALS molar ratio varied for the three different HALS monomers used in this study as follows: for monomers **2**, **6**, and **7** the limiting TRI−FABA/HALS molar ratio was approximately 0.3, 0.8, and 1.4, respectively. Thus, once an equilibrium concentration between TRI−FABA and HALS monomer was established, the presence of HALS monomer no longer affected the rate of polymerization. This observation deserves further investigation. In general, this finding may also be interesting in the sense that TRI−FABA may even potentially impede the basic activity of other functional monomers as well. However, the chemistry between the

**Table 7. Copolymerization of Propylene with 2, 6, and 7 over a CA2/TEA/(TRI−FABA or DAN−FABA) Catalyst System**[a]

| entry | HALS | borate cocatalyst | Zr, μmol/l | Al, mmol/L | HALS/Zr, mol/mol | HALS/Al, mol/mol | borate/HALS, mol/mol | $M_n$ | $P_d$ | activity[b] | $T_M$, °C | cryst,[c] % | bound nitrogen, wt %[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C140 | | | 90 | 33 | | | | 34 000 | 1.9 | 2300 | 148 | 38 | |
| C272 | **2** | TRI−FABA | 87 | 33 | 150 | 0.4 | 0.1 | n.d.[f] | n.d. | 900 | 144 | 36 | 1.7 (23%) |
| C273 | **2** | TRI−FABA | 89 | 33 | 96 | 0.26 | 0.2 | n.d. | n.d. | 1500 | 145 | 34 | 1.2 (42%) |
| C271 | **2** | TRI−FABA | 89 | 33 | 48 | 0.13 | 0.3 | n.d. | n.d. | 2800 | 149 | 39 | 1.1 (81%) |
| C163 | **6** | TRI−FABA | 89 | 33 | 36 | 0.1 | 1.05 | 19 200 | 2.6 | 2600 | 149 | 38 | 0.7 (90%) |
| C165 | **6** | TRI−FABA | 92 | 34 | 37 | 0.1 | 0.8 | 19 500 | 2.3 | 2200 | 149 | 40 | 0.8 (100%) |
| C166 | **6** | TRI−FABA | 81 | 34 | 34 | 0.1 | 0.5 | 9500 | 2.3 | 20 | t.d | t.d | 3.5 (3.7%) |
| C167 | | DAN−FABA | 92 | 34 | | | | n.d. | n.d. | 1300 | | | |
| C168 | **6** | DAN−FABA | 89 | 33 | 38 | 0.1 | 1.0 | n.d. | n.d. | 60 | n.d. | n.d. | n.d. |
| C169 | **6** | DAN−FABA | 89 | 33 | 38 | 0.1 | 1.5 | n.d. | n.d. | 40 | n.d. | n.d. | n.d. |
| C182 | **7** | TRI−FABA | 78 | 34 | 45 | 0.1 | 2.0 | 38 200 | 2.4 | 2500 | 151 | 37 | 0.6 (64%) |
| C172 | **7** | TRI−FABA | 97 | 34 | 34 | 0.1 | 1.4 | 44 200 | 2.9 | 1200 | 147 | 37 | 0.7 (40%) |
| C164 | **7** | TRI−FABA | 86 | 33 | 39 | 0.1 | 1.1 | 20 500 | 3.1 | 300 | 144 | 34 | 1.8 (22%) |

[a] Copolymerization conditions: *rac*-[1,1′-dimethylsilylenebis($\eta^5$-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**CA2**)/TEA/TRI−FABA or DAN−FABA catalyst system, polymerization time = 20 min, $P_{\text{propylene}}$ = 2 bar, $T_p$ = −20 °C, and $V_{\text{toluene}}$ = 250 mL. The appropriate stabilizer amount was precomplexed with half of the MAO amount for 30 min prior to addition of the metallocene/MAO solution. [b] Activity in [kg of polymer/mol of Zr·h·atm]. [c] Here, 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 293 J/g. [d] Determined by elemental analysis. [e] The number in parentheses denotes the conversion of the HALS monomer to copolymer; i.e., (%) = [(copolymerized HALS monomer/initially charged monomer into the reactor) × 100]. [f] n.d. denotes not determined.

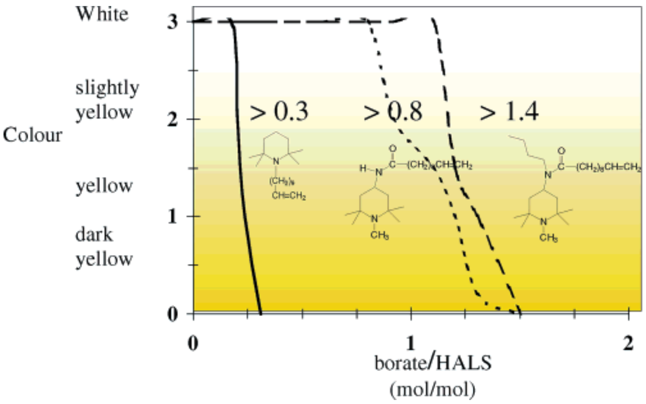


**Figure 4.** Titration of TRI−FABA with HALS monomers **2**, **6**, and **7**.

**Table 8. Results of Thermo-Oxidative and Light Stability Studies**

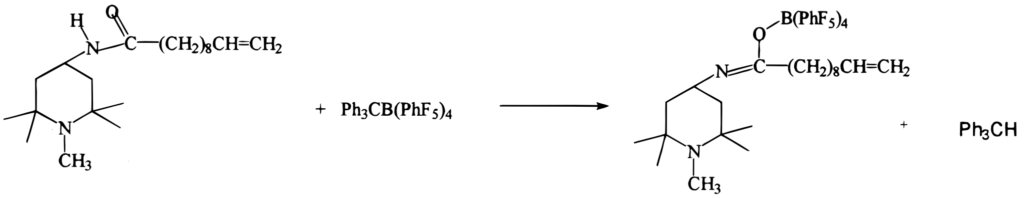
| polymer sample | bound nitrogen, wt % | time for the formation of the carbonyl peak, h |
|---|---|---|
| Thermo-Oxidative Stabilities after Oven Aging at 115 °C | | |
| polyethylene[a] | | 48 |
| poly(ethylene-*co*-**4**)[b] | 0.2 | >8544 |
| Light Stability | | |
| poly(propylene-*co*-**6**)[c] | 0.1 | 2500 |
| poly(propylene-*co*-**6**)[c] | 0.2 | 3900 |

[a] Entry C70 in Table 2; i.e., unstabilized polyethylene. [b] Entry 558 in Table 2; i.e., no additional stabilizers were added. [c] For light stability tests the poly(propylene-*co*-**8**) copolymer entry C163 was mixed with an appropriate amount of polypropylene powder (Profax6501) at 200 °C in a Brabender Plastograf using 0.1 wt % of Ca−stearate, 0.1 wt % tris(2,4-di-*tert*-butylphenyl) phosphite and 0.02 wt % octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxylphenyl-)propionate as costabilizers. The produced polymer material was then compressed to films with a thickness of 0.1 mm (3 min at 260 °C) prior to irradiation in a xenon Weatherometer (Weather-O-Meter 65 WR(Atlas Corp.), black panel temperature of 65 °C). The time (in hours) to reach 0.1 carbonyl index from the plot of absorbance of the carbonyl groups vs irradiation time was determined.

TRI−FABA and the HALS monomers needs to be investigated more thoroughly (by, e.g., $^{13}$C and $^1$H NMR studies) in order to determine what the equilibrium chemistry is and whether this approach is operational for copolymerizations of propylene with other functional groups. These results will be reported elsewhere. We believe that TRI−FABA reacts with **6** to give triphenylmethane and a [**6**:B($C_6F_4$)$_4$] complex (Scheme 6), whereas it is unclear at present how TRI−FABA reacts and/or coordinates with *N*-alkyl and carbonyl moieties of the HALS monomers. Besides TRI−FABA, attempts to use a weaker Lewis acid such as DAN−FABA as cocatalyst to initiate copolymerization was also investigated under similar reaction conditions; however DAN−FABA could not induce copolymerization under the conditions shown in Table 7. Obviously, in this case only a strong Lewis acid such as TRI−FABA can effectively impede the Lewis basicity of **6**.

**Stability Studies.** The thermooxidative stability of the poly(ethylene-*co*-**4**) copolymer was determined by oven aging at 115 °C in an air atmosphere in combination with FTIR analyses. The copolymer was extracted with both refluxing 2-propanol/cyclohexane and chloroform in a Soxhlet apparatus for 24 h prior to stability tests. The copolymer exhibited high thermooxidative stability in comparison to unstabilized polyethylene, i.e., for the copolymer the carbonyl peak had not appeared after 1 year of oven aging at 115 °C, whereas unstabilized polyethylene showed a strong carbonyl peak within 2 days, as shown in Table 8. The photostabilizing

**Scheme 6. Reaction of TRI−FABA with HALS Monomer 6**



efficiency of poly(propylene-*co*-**6**) copolymer was studied by blending the copolymer with unstabilized polypropylene as described in the experimental part. The time (in hours) to reach 0.1 carbonyl index from the plot of absorbance of the carbonyl groups vs irradiation time was determined and the results are shown in Table 8. In the case of stabilized polymer films containing 0.1 and 0.2 wt % of HALS monomer **6** units, the time to reach 0.1 carbonyl index was 2500 and 3900 h, respectively. Thus, as anticipated the produced poly(propylene-*co*-**6**) copolymer was highly photostable.

## Conclusion

This work demonstrates that a new class of HALS comonomers such as **1**, **2**, **3**, **4**, **6**, and **7** can be incorporated into copolymers with ethylene or propylene, via metallocene catalysis, using MAO as cocatalyst. We have also demonstrated that TRI−FABA, a strong Lewis acid, can impede the Lewis base activity of **2**, **6**, and **7** provided that a sufficient relative amount of TRI−FABA is employed, such that copolymers are obtained in high yields. This finding can also be interesting in the sense that TRI−FABA (or another related borate derivative) may potentially even impede the basic activity of other functional monomers as well. Furthermore, monomer **2** was successfully copolymerized with ethylene over a supported metallocene catalyst system in high yield. To the best of our knowledge, the copolymerization of amine functional monomers with ethylene over supported metallocene catalysts is unprecedented. As a rule, supported metallocene catalysts are very sensitive to Lewis bases; i.e., the supported catalyst is rapidly poisoned by even minute amounts of heteroatom-containing monomers. Against this background it is interesting to note that **2** can be successfully copolymerized with ethylene over a silica-supported metallocene catalyst with a very low MAO/Zr ratio of 100.

In addition, an inexpensive synthetic pathway to a 2-substituted HALS comonomer denoted as **4** has been constructed and successfully completed. The HALS monomer was prepared by condensation of 5-hexen-2-one with diacetone amine in the presence of calcium chloride and then reducing the formed 2-(but-3-enyl)-2,6,6-trimethyl-4-oxopiperidine with hydrazine under strong alkaline conditions by means of a modified Wolf−Kishner reaction to give the desired comonomer product **4**. In conclusion, we have prepared a new family of polymerizable hindered amine light stabilizers which can successfully be copolymerized with ethylene or propylene over both soluble and supported metallocene catalyst systems to give copolymers with good thermooxidative and light stabilities of both academic and industrial interest. Further work is in progress to elucidate the copolymerization behavior of 4-($\omega$-alkenyl)-1-(1-methylene-2,6-di-*tert*-butylphenol)-2,2,6,6-tetramethylpiperidine, dimeric-HALS derivatives and styrene analogues of HALS derivatives and their efficiencies as thermooxidative and light stabilizers.

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**Supporting Information Available:** Text giving syntheses of the HALS monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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