# Copolymerization of Ethene with Styrene Using Methylaluminoxane-Activated Bis(phenolate) Complexes

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ABSTRACT: Ethene was copolymerized with styrene using different titanium bis(phenolate) complexes $[R^1(4,6\text{-}R^2C_6H_2\text{-}O)_2]TiX_2$ ($R^1$ = $CH_2$, $C_2H_4$, S, SO; $R^2$ = $CH_3$, *t*-Bu; X = Cl, O(*i*-Pr)) activated with methylaluminoxane. The influence of ligand substitution pattern and polymerization conditions on catalyst activity, polymerization kinetics, styrene incorporation, molecular mass, and copolymer microstructure was investigated. Catalyst activity increased with decreasing styrene concentration and was affected by the type of the bridging group $R^1$ with an activity rating of $R^1$ = S > SO > $C_2H_4$. The opposite trend was observed for styrene incorporation where $R^1$ = $C_2H_4$ gave the highest styrene content. Polymerization kinetics primarily depended upon complex structure and was only marginally influenced by polymerization conditions. As a rule, styrene contents of more than 90 mol % in the monomer feed were needed to achieve more than 20 mol % styrene incorporation in the copolymer. Copolymerization parameters were calculated for ethene/styrene copolymerization using $[S(4\text{-Me-}6\text{-}t\text{-BuC}_6H_2O)_2]Ti(O\text{-}i\text{-Pr})_2$ to be $r_E = 111$ and $r_S = 0.055$, reflecting a pronounced tendency for ethene and much less for styrene to form long sequences. Solvent extraction of copolymers with subsequent NMR analysis revealed the presence of random poly(ethene-*co*-styrene) with inhomogeneity with respect to both styrene incorporation and molecular mass distribution, typical for multisite Ziegler−Natta catalysts. In contrast to earlier reports, only traces of syndiotactic polystyrene but no alternating ethene/styrene copolymer was detected.

## Introduction

Recently, early transition metal complexes with chelating phenolate ligands have attracted attention as possible catalyst precursors in α-olefin polymerization.[1,2] When activated with methylaluminoxane, some of these complexes afforded ethene/styrene copolymerization.[3] Most conventional Ziegler−Natta catalysts, however, are little effective in initiating copolymerization of ethene with styrene, and the copolymers are inhomogeneous with respect to styrene incorporation and molecular mass distribution. Typically, the styrene content of such copolymers is less than 1 mol %.[4,5] Contradictory results have been reported concerning the ability of methylaluminoxane-activated half-sandwich complexes such as $CpTiCl_3$ to copolymerize ethene with styrene.[6−8] Pellecchia et al.[9] reported formation of poly(ethene-*alt*-styrene) obtained in a mixture together with polyethene and syndiotactic polystyrene when polymerization was performed by means of $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$. The synthesis of monocyclopentadienyl−amide complexes, first reported by Bercaw and Okuda,[10,11] provided a new type of metallocene catalyst that is remarkably active in ethene/styrene copolymerization without producing detectable amouts of homopolymer impurities.[12,13] Kakugo et al. reported that titanium complexes with the substituted bis(phenolate) ligand 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) afforded ethene/styrene copolymerization with low catalyst activity, producing alternating ethene/styrene copolymer together with syndiotactic polystyrene.[3]

We were intrigued by Kakugo's conclusion that his catalytic system was supposed to consist of two different active centers, one producing poly(ethene-*alt*-styrene) and the other syndiotactic polystyrene in ethene/styrene copolymerization,[3] whereas only a single type active center was reported for ethene and propene homopolymerization.[14] Here we report ethene/styrene copolymerization using methylaluminoxane-activated bis(phenolate) complexes varying in the bridging unit between both phenolate moieties of the ligand as well in the chloride or isopropoxide ligand to understand the role of the ligand substitution pattern. In the case of diisopropoxo[2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)]titanium, catalyst concentration as well as monomer concentrations were varied in order to analyze the polymerization behavior with respect to catalytic activity, deactivation, comonomer incorporation, and copolymer thermal properties. To obtain information concerning the presence of different catalytically active centers solvent extraction of the resulting polymers was performed with subsequent analysis of polymer microstructure.

## Results and Discussion

**Influence of Ligand Substitution Pattern of Bis(phenoxo)titanum Complexes.** Figure 1 shows different bis(phenolate) complexes used for copolymerization of ethene with styrene. Complexes EBP, EBC,[15c] and SOBP [16c] were compared to complexes SBP, SBC, and MBC, previously described by Kakugo et al.[3] In Table 1 the results of copolymerizations as well as the polymerization conditions are listed.

In contrast to earlier conclusions,[3] as apparent from runs 5, 6, and 8 using complexes EBP, EBC, and SOBP, a ligand containing a sulfur bridge is not required for the formation of poly(ethene-*co*-styrene). With 35 mol % styrene incorporation, at 83 mol % styrene feed content, complexes EBP and EBC with an aliphatic ethylene bridge are surprisingly effective in styrene

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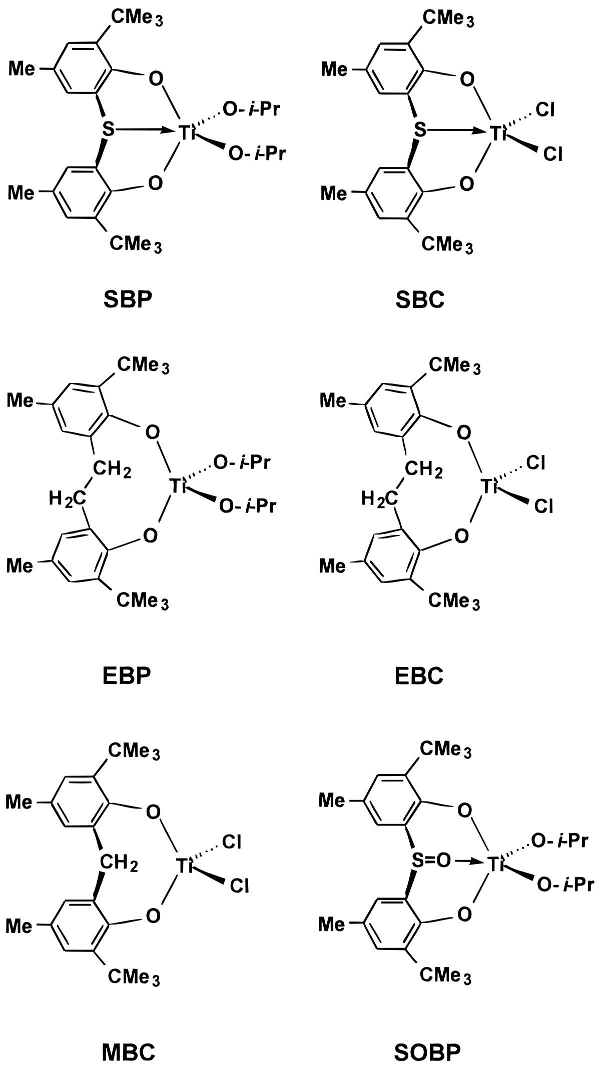

**Figure 1.** Bis(phenolate) complexes used for ethene/styrene copolymerization. SBP: diisopropoxo[2,2′-thiobis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-S(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]Ti(O-*i*-Pr)$_2$. SBC: Dichloro[2,2′-thiobis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-S(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]TiCl$_2$. EBP: Di-isopropoxo[2,2′-ethylenebis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-CH$_2$CH$_2$(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]Ti(O-*i*-Pr)$_2$. EBC: Dichloro[2,2′-ethylenebis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-CH$_2$CH$_2$(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]TiCl$_2$. MBC: Dichloro[2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-CH$_2$(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]TiCl$_2$. SOBP: Diisopropoxo[2,2′-sulfinylbis(6-*tert*-butyl-4-methylphenoxo)]titanium, [2,2′-SO(6-*t*-Bu-4-MeC$_6$H$_2$)$_2$]Ti(O-*i*-Pr)$_2$.

incorporation. Furthermore, complex SOBP, containing the sulfoxy bridge in the ligand, gave 10 mol % styrene incorporated under the same conditions. Figure 2 shows the $^{13}$C NMR spectrum of virgin poly(ethene-*co*-styrene) obtained with SBP. With resonances for $T_{\delta\delta}$ at $\delta = 46.0$ ppm, $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ at $\delta = 36.8$ ppm, $S_{\gamma\gamma}$, $S_{\gamma\delta}$, and $S_{\delta\delta}$ at $\delta = 29.7$ ppm, and $S_{\beta\gamma}$ and $S_{\beta\delta}$ at $\delta = 27.4$ ppm in the $^{13}$C NMR (C$_2$D$_2$Cl$_4$, 75.4 MHz, 100 °C), these copolymers contain predominantly isolated styrene units. Run 7, using methylene-bridged complex MBC, confirms earlier reports stating that this complex does not produce ethene/styrene copolymer but gives a mixture of both homopolymers.

The comparison of styrene content of the copolymers and catalytic activities of methylaluminoxane-activated bis(phenolate) complexes clearly indicates that complexes promoting high styrene incorporation are much less active. Ethylene-bridged complexes gave the highest styrene incorporation with 35 mol %, followed by sulfoxy-bridged complex SOBP with 10 mol % and sulfur-bridged complexes SBP and SBC with 6 mol % styrene incorporated under idendical conditions with a styrene/ethene molar feed ratio of 5. The catalyst activity of the complexes followed the opposite trend. The catalyst activity of SBP and SBC surpassed that of SOBP by 1 order of magnitude and those of EBP and EBC by 2 orders of magnitude. For interpretation of styrene incorporation and catalytic activity, both steric and electronic effects must be taken into account. Differences in styrene incorporation as well as in catalytic activity can be explained by comparing steric hindrance at the metal center, as a consequence of ligand geometry, and differences in electron-donating character of bis(phenolate) ligands. Figure 3 shows SCHAKAL plots based on the X-ray crystal structures of complexes SBP, SOBP, EBP, and MBC, clearly indicating the additional coordination of the metal center by the sulfur atom (complex SBP) or the oxygen atom (complex SOBP), respectively.

The methylene-bridged complex MBC gave very poor catalyst activity. In the case of complex MBC, the eight-membered ring, consisting of a metal atom, oxygen atoms, and carbon atoms of the phenyl ring and of the bridging methylene unit, adopts a boat conformation, which allows good $\pi$-donor interaction between oxygen atoms and the titanium atom (large C−O−Ti angle).[15a,b] This leads to high electron density at the metal center, thus accounting for low activity. Furthermore, it does not allow styrene incorporation, because the methylene group forces the complex into a conformation where both *tert*-butyl groups shield the metal center very effectively against styrene coordination.[15b]

In the ethylene-bridged complex EBP, the electronic situation at the titanium is similar to that in the methylene-bridged complex MBC, thus also accounting for low activity. But in contrast to complex MBC, steric hindrance at the titanium atom is much lower.[15c] Both phenyl rings are coplanar with the *tert*-butyl groups directed away from the metal center. As a consequence of this open coordination site, complex EBP affords high styrene incorporation in spite of low catalyst activity.

The sulfur-bridged complex SBP shows high activity with moderate styrene incorporation. In contrast to the methylene-bridged complex MBC, the sulfur bridge enforces octahedral coordination by forming a long titanium−sulfur bond.[16] This results in an apparent increase of Lewis acidity of the metal center, thus increasing the catalyst activity. However, this situation also gives rise to a geometry with relatively good shielding of the titanium atom by the ligand, resulting in low styrene incorporation.

The sulfoxy-bridged complex SOBP is rated between the ethylene-bridged and the sulfur-bridged complexes, with respect to both electronic influences and steric hindrance. Therefore, complex SOBP promotes higher styrene incorporation with respect to complex SBP but less than EBP, with activities less than complex SBP but higher than EBP.

Moreover, as demonstrated below, increasing styrene concentration adversely affected catalyst activity. A slower rate of polymerization in the presence of styrene monomer, possibly due to additional coordination of the metal center of the complex,[9] also makes plausible why complexes allowing higher styrene incorporation gave lower total activities.

**Table 1. Comparison of Different Methylaluminoxane-Activated Bis(phenolate) Complexes for the Copolymerizations of Styrene with Ethene**[a]

| run[a] | catalyst[b] | [cat], $\mu$mol/L | Al/Ti ratio, mol/mol | yield, g | activity,[c] g of polymer/ (mol of Ti·h·mol/L) | styrene content,[d] mol % |
|---|---|---|---|---|---|---|
| 1 | SBP | 20 | 20000 | 0.36 | 69 000 | 9.7 |
| 2 | SBC | 20 | 2000 | 0.27 | 52 000 | 1.2 |
| 3 | SBP | 100 | 1000 | 2.88 | 109 000 | 5.5 |
| 4 | SBC | 100 | 1000 | 2.17 | 82 000 | 6.0 |
| 5 | EBP | 100 | 1000 | 0.02 | 1 000 | 35.2 |
| 6 | EBC | 100 | 1000 | 0.03 | 1 000 | 36.4 |
| 7 | MBC | 100 | 1000 | 0.02 | 1 000 | e |
| 8 | SOBP | 100 | 1000 | 0.26 | 10 000 | 10.0 |

[a] Polymerization conditions: [styrene] = 1.1 mol/L, [ethene] = 0.22 mol/L ($P_E$ = 2.56 bar), styrene/ethene molar ratio 5/1, solvent toluene, total volume 200 mL, $t$ = 1 h, $T$ = 60 °C. [b] Catalysts are listed in Figure 1. [c] Monomer concentration is total olefin concentration (ethene + styrene). [d] Styrene content in copolymer, by $^1$H NMR spectroscopy. [e] No copolymer, mixture of homopolyethylene and homopolystyrene.

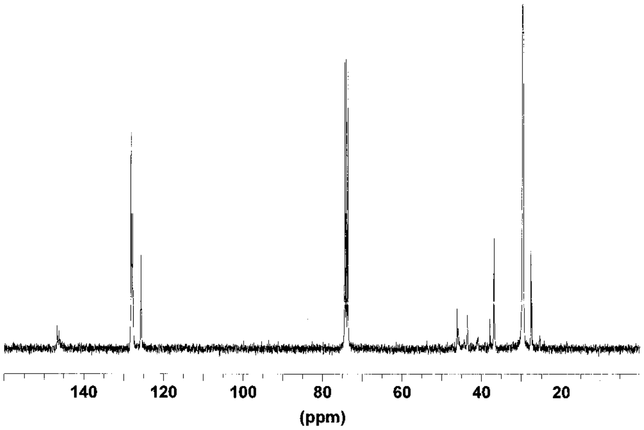

**Figure 2.** $^{13}$C NMR spectrum ($C_2D_2Cl_4$, 75.4 MHz, 100 °C) of a virgin poly(ethene-*co*-styrene) produced with MAO-activated SBC (sample 2).

**Influence of Polymerization Conditions.** Table 2 lists results of ethene/styrene copolymerizations using methylaluminoxane-activated diisopropoxo[2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)titanium (SBP) and varying catalyst concentration, monomer concentrations, and comonomer molar ratio. As apparent from runs 12−14 (Table 2), where the styrene concentration was kept constant and ethene concentration was varied, catalyst activity increased with increasing ethene concentration. As depicted in Figure 4 (runs 3, 9, 10, and 12, Table 2), catalyst activity also decreased rapidly with increasing styrene concentration. This is in agreement with observations typical for other catalytic systems, e.g. “constrained geometry complexes”, used in ethene/styrene copolymerization[13] and reflects the much slower insertion rate of styrene.

Catalyst activities of ethene/styrene copolymerizations usually exceed those of styrene homopolymerizations[3,16a] by 1 or 2 orders of magnitude. Under identical conditions, the catalyst activity in ethene homopolymerization exceeded that of styrene homopolymerization by 3 orders of magnitude. It has to be noted that comparison of catalytic activities should take the deactivation behavior of the catalytic center into account. Values for catalyst activity are usually normalized to polymerization time (1 h), thus leading to significant errors when very high initial activity is followed by very rapid decay. Therefore, we monitored catalytic activity as a function of time via mass flow measurement of ethene, maintaining constant ethene pressure.

From Figure 5 it is apparent that the catalyst diisopropoxo[2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)titanium (SBP)/MAO showed very high initial activity with subsequent rapid deactivation. This is not only important concerning kinetics of the polymerization reaction, but might also affect product composition. For instance, prolonged polymerization times at low catalyst activity are likely to produce larger relative amounts of byproducts such as styrene homopolymer.

With increasing styrene concentration copolymer molecular mass decreased. As can be seen in runs 9, 10, 3 and 12 (Table 2), when ethene concentration was kept constant and styrene concentration was raised from 0 to 2.2 mol/L, molecular masses decreased from $M_n$ = 28 000 g/mol for polyethene to $M_n$ = 14 000 g/mol for poly(ethene-*co*-styrene) containing 11.7 mol % styrene. With polydispersities of 2.4−4.9 molecular weight distributions are narrow when compared to conventional Ziegler−Natta catalysis but considerably broader when compared to those typical for “single site” metallocene-catalyzed ethene/styrene copolymerizations using mono-Cp−amido complexes.[13] Larger polydispersity is accompanied by inhomogeneity with respect to styrene incorporation when compared to poly(ethene-*co*-styrene) prepared with mono-Cp−amido complexes.[17] This was further investigated with solvent extraction experiments, which are reported below.

As apparent from Figure 6, styrene incorporation was proportional to the styrene/ethene molar ratio. With styrene concentrations varying between 0 and 2.2 mol/L, styrene incorporations varied between 0 and 36 mol % (67 wt %). However, Figure 6 also shows that a 30-fold molar excess was needed to achieve 30 mol % styrene incorporation. The corresponding copolymerization diagram is depicted in Figure 7, showing that more than 85 mol % styrene in the monomer mixture was required to give 10 mol % styrene incorporation. Copolymerization parameters were calculated by means of a Kelen−Tüdös plot, giving $r$ parameters of $r_E = 111$ for ethene and $r_S = 0.055$ for styrene ($r_E r_S = 6.1$). This clearly indicates that ethene monomer is likely to form blocks, whereas styrene sequences are very short or styrene units even remain isolated. This is suppoprted by the observation of a small relative abundance of signals for $S_{\alpha\alpha}$ and $T_{\beta\beta}$ in copolymer NMR spectra (Figure 3 and solvent extraction experiments). In contrast to reports by Kakugo, we were not able to detect the alternating ethene/styrene copolymer, even when using very similar conditions (run 16, Table 2).[18] In general alternating copolymerization results in $r$ parameters much smaller than 1 for both monomers. Even when copolymerization was performed at extremely high styrene molar excess (styrene/ethene molar ratio of 110/1, run 15, Table 2), followed by solvent extraction of the copolymer, there were no traces of

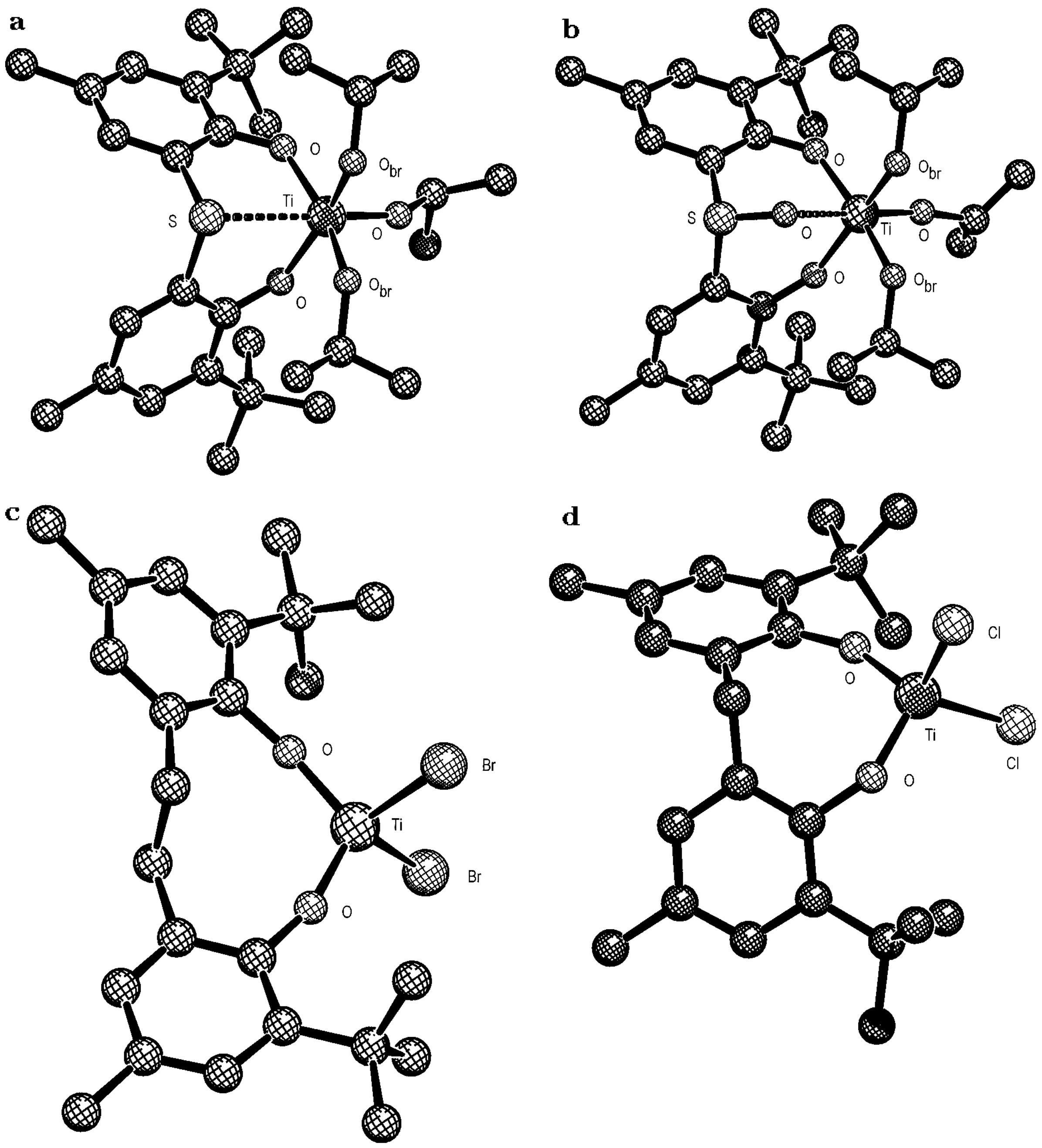

**Figure 3.** SCHAKAL plots of the bis(phenolate) complexes SBP (a), SOBP (b), EBP (c), and MBC (d) based on single crystal X-ray structure analyses of dimeric SBP,[16a] dimeric SOBP,[16c] [2,2′-$CH_2CH_2(6\text{-}t\text{-}Bu\text{-}4\text{-}MeC_6H_2)_2$]$TiBr_2$,[16c] and MBC,[15a] respectively.

alternating ethene/styrene copolymer. Extraction studies reveal formation of a mixture of poly(ethene-*co*-styrene) and traces of syndiotactic polystyrene, which is only found at very high styrene feed content.

According to characterization of thermal properties by means of DSC, all copolymers were semicrystalline. Melting temperatures varied beween 133 °C for polyethene and 109 °C for a copolymer containing 35 mol % styrene. Melting enthalpy, reduced from 179 J/g for polyethene to 4 J/g for a copolymer containing 35 mol % styrene, reflects reduced crystallinity due to styrene incorporation. Interestingly, in comparison to ethene/styrene copolymers obtained with mono-Cp—amido complexes,[13] the decay of crystallinity was much less pronounced. This is probably due to regioirregular arrangement of styrene units in copolymers obtained with mono-Cp—amido complexes because of exclusive tail-to-tail incorporation of styrene. In the case of copolymers produced with diisopropoxo[2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)]titanium (SBP) no such tail-to-tail coupling was detected, as verified by the absence of signals for $S_{\alpha\beta}$ in the $^{13}C$ NMR spectra (Figure 3).

**Microstructure of Ethene/Styrene Copolymers.** In order to obtain information on polymer microstructure and on the types of catalytically active centers, solvent extraction experiments were conducted with subsequent NMR analysis of the resulting fractions. According to Kakugo's hypothesis, this catalytic system is supposed to consist of two distinct active centers, one producing syndiotactic polystyrene and one producing alternating ethene/styrene copolymer.[3] The results of extraction experiments are given in Table 3.

Except for run 15, where a styrene/ethene molar ratio of 110 was used, causing formation of some syndiotactic polystyrene, all fractions were soluble in THF or toluene. Copolymer composition depended upon the type of solvent and extraction temperature. Copolymers with

**Table 2. Copolymerizations of Styrene with Ethene Using 2,2′-Thiobis(4-methyl-6-*tert*-butylphenoxo)titanium(O-*i*-Pr)$_2$/MAO[a]**

| run[a] | [cat], $\mu$mol/L | Al/Ti ratio, mol/mol | [styrene], mol/L | [ethene], mol/L | styrene to ethene ratio, mol/mol | yield, g | activity,[b] g of polymer/(mol of Ti·h·mol/L) | styrene content,[c] mol % | $T_g$,[d] °C | $T_m$,[d] °C | $\Delta H$, J/g | $10^{-3}M_n$,[e] g/mol | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 2000 | 1.1 | 0.22 | 5.0 | 0.360 | 69000 | 9.7 | | 118.4 | 48 | n.d.[f] | n.d. |
| 9 | 100 | 1000 | | 0.22 | | 4.42 | 1005000 | 0 | | 133.0 | 179 | 28 | 4.9 |
| 10 | 100 | 1000 | 0.55 | 0.22 | 2.5 | 4.32 | 281000 | 2.4 | | 119.9 | 120 | 25 | 3.6 |
| 11 | 100 | 1000 | 1.1 | 0.42 | 2.6 | 5.70 | 188000 | 3.9 | | 121.7 | 95 | 43 | 4.0 |
| 3 | 100 | 1000 | 1.1 | 0.22 | 5.0 | 2.88 | 109000 | 5.5 | | 119.0 | 75 | 21 | 3.4 |
| 12 | 100 | 1000 | 2.2 | 0.22 | 10.0 | 2.87 | 59000 | 11.7 | | 116.2 | 62 | 14 | 2.4 |
| 13 | 100 | 1000 | 2.2 | 0.13 | 16.9 | 1.35 | 29000 | 19.8 | | 110.2 | 33 | 6 | 3.2 |
| 14 | 100 | 1000 | 2.2 | 0.07 | 31.4 | 0.82 | 18000 | 35.6 | | 109.7 | 4 | 4 | 3.5 |
| 15 | 200 | 500 | 4.4 | 0.04 | 110 | 3.05 | 9000 | 72.8[g] | 71.7 | 121/259 | | n.d. | n.d. |
| 16 | 1812 | 450 | 0.22 | 0.02 | 11 | 0.59 | 7000 | 12.2 | | 120.5 | 15 | 1 | 4.0 |

[a] Polymerization conditions: solvent toluene, total volume 200 mL, $t = 1$ h, $T = 60$ °C. [b] Monomer concentration is total olefin concentration (ethene + styrene) in mol/L. [c] Styrene content in copolymer, by $^1$H NMR spectroscopy. [d] By differential scanning calorimetry (DSC), extrapolated on heating rate 0. [e] By gel permeation chromatography (GPC) vs polyethene standard. [f] n.d.: not determined. [g] Mixture of poly(ethene-*co*-styrene) and syndiotactic polystyrene.

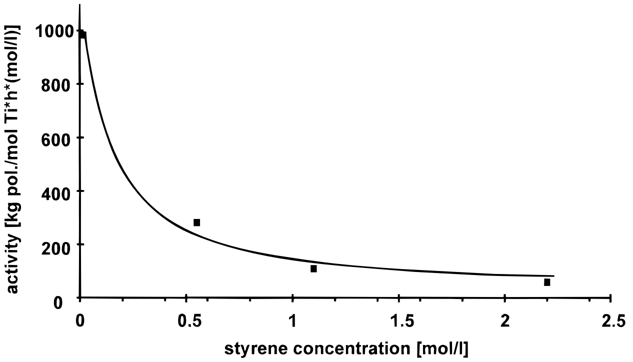

**Figure 4.** Catalyst activity of complex SBP as a function of styrene concentration (ethene concentration kept constant, [ethene] = 0.22 mol/L).

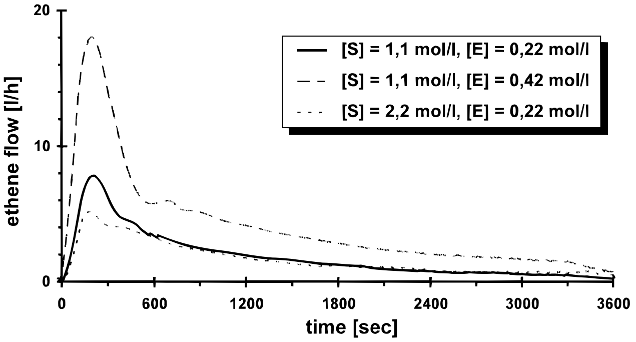

**Figure 5.** Kinetics of ethene/styrene copolymerization with SBP: catalytic activity, measured via ethene consumption, as a function of polymerization time.

higher styrene content are much more soluble than those with low styrene content. Typically, such copolymers are insoluble in THF but soluble in toluene. Samples 3, 12, and 13, obtained at styrene/ethene molar ratios of 5, 10, and 17, respectively, show a broad inhomogeneity with respect to styrene incorporation. For example, the copolymer sample of run 3 shows average styrene contents of the different fractions of 23.6, 14.7, and 4.4 mol %, respectively. According to investigations on catalyst active centers of alkoxytitanium complexes employed in syndiospecific styrene polymerization,[19] this is a clear indication for a multicenter active catalyst. These results also differ from poly(ethene-*co*-styrene) prepared with mono-Cp−amido complexes, where temperature rising elution fractionation (TREF) experiments confirmed a single-site mechanism.[17] Figures 8 and 9 depict the $^{13}$C NMR spectra of THF soluble and toluene soluble fractions of samples 3 and 12, obtained at a styrene/ethene molar ratio of 5 and 10, respectively. Spectra of the different fractions of sample 13 were very similar to that of sample 12. Sample 15 was a poly(ethene-*co*-styrene) with 49 mol % styrene incorporation of the hexane soluble fraction, whereas the hexane insoluble fraction consisted of syndiotactic polystyrene. Table 4 reports the relative intensities of the signals in $^{13}$C NMR spectra of samples 12 and 13.

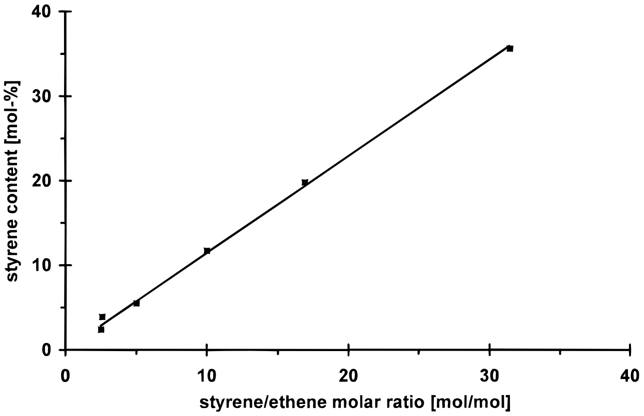

**Figure 6.** Styrene incorporation as a function of styrene/ethene molar ratio of the monomer feed.

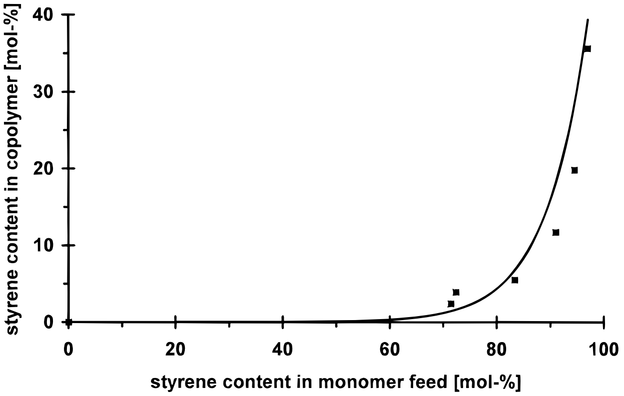

**Figure 7.** Copolymerization diagram of ethene/styrene copolymerization with MAO-activated SBP: styrene content in the copolymers as a function of styrene content of the monomer feed.

$^{13}$C NMR spectra of sample 3, obtained at a styrene/ethene molar ratio of 5, show reduced styrene incorporation with decreasing solubility. All signals indicating high styrene incorporation decreased in relative abun-

**Table 3. Solvent Extraction and Analysis of Copolymer Composition**

| run[a] | fraction[b] | solvent[b] | yield, g | fraction, % | styrene content, mol % |
|---|---|---|---|---|---|
| 3 THF | 1 | THF, ambient | 0.072 | 8 | 23.6 |
| 3 REF | 2 | THF, reflux | 0.061 | 6 | 14.7 |
| 3 INS[c] | 3 | THF insoluble[c] | 0.788 | 79 | 4.4 |
| 12 THF | 1 | THF, ambient | 0.085 | 11 | 27.2 |
| 12 TOL | 2 | toluene, reflux | 0.680 | 89 | 7.8 |
| 12 INS | 3 | toluene insoluble | 0 | 0 | 0 |
| 13 THF | 1 | THF, ambient | 0.020 | 5 | 36.1 |
| 13 TOL | 2 | toluene, reflux | 0.350 | 95 | 13.0 |
| 13 INS | 3 | toluene insoluble | 0 | 0 | 0 |
| 15 HEX | 1 | hexane, reflux | 0.328 | 33 | 49.3 |
| 15 INS | 2 | hexane insoluble | 0.568 | 57 | >99 |

[a] Run 3: S:E = 5:1. Run 12: S:E = 10:1. Run 13: S:E = 17:1. Run 15: S:E = 110:1. For further polymerization conditions see Table 2. [b] Extraction time: 24 h. Amount of solvent: 100 mL. Extraction under reflux with a 100 mL Soxhlet extractor (total volume 200 mL). [c] This fraction was completely soluble in boiling toluene.

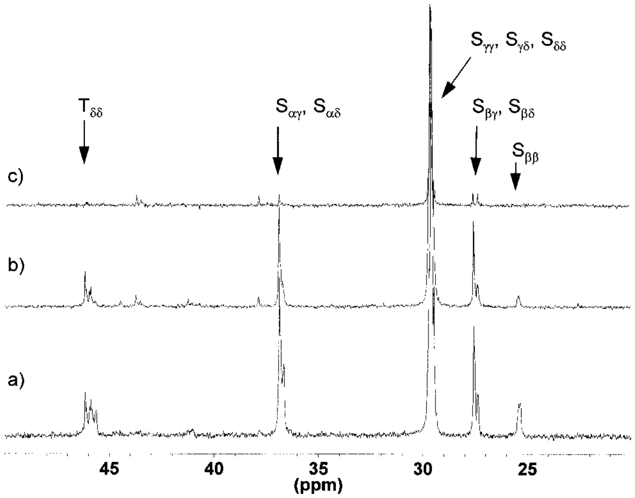

**Figure 8.** Methylene and methine region of the $^{13}$C NMR spectra ($C_2D_2Cl_4$, 75.4 MHz, 100 °C) of solvent-extracted fractions of sample 3: soluble in THF at ambient temperature (a); soluble in THF at reflux (b); insoluble in THF (c). S = secondary carbon, T = tertiary carbon, greek letters indicate the nearest tertiary carbon in either direction.

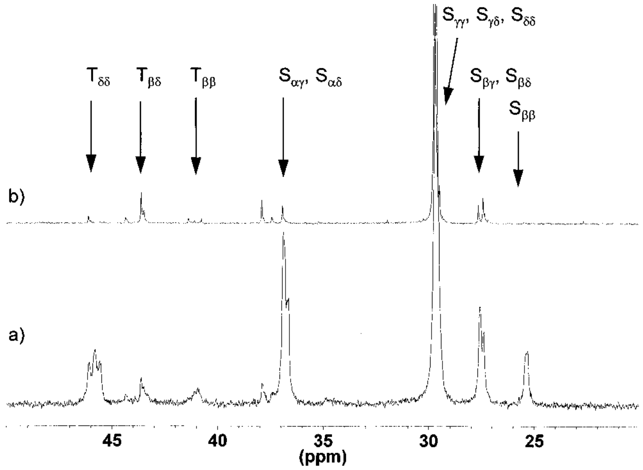

**Figure 9.** Methylene and methine region of the $^{13}$C NMR spectra ($C_2D_2Cl_4$, 75.4 MHz, 100 °C) of solvent-extracted fractions of sample 12: soluble in THF at ambient temperature (a); insoluble in THF at ambient temperature but soluble in toluene under reflux (b). (Copolymer was completely soluble in refluxing toluene.) S = secondary carbon, T = tertiary carbon, greek letters indicate the nearest tertiary carbon in either direction.

dance. Signals for $S_{\alpha\alpha}$ and $T_{\beta\beta}$ were not detectable in the THF insoluble fraction, indicating only isolated styrene units. The same trend was observed for the THF soluble and toluene soluble fractions of sample 12 (Figure 9). From Table 4, reporting the relative intensities of signals in the $^{13}$C NMR spectra of samples 12 and 13, it is apparent that the relative abundance of all signals is approximately the same for THF soluble and toluene soluble fractions of samples 12 and 13 with 11.7 mol % and 19.8 mol % styrene incorporated, respectively, except that for $S_{\gamma\gamma+\gamma\delta+\delta\delta}$. Only the signal for $S_{\gamma\gamma+\gamma\delta+\delta\delta}$ is reduced in relative abundance going to higher styrene incorporation, confirming the tendency of ethene monomer to form longer sequences. The relative abundance of all signals, especially the high intensities for $S_{\gamma\gamma+\gamma\delta+\delta\delta}$ and $S_{\beta\gamma+\beta\delta}$, also confirms that no alternating ethene/styrene copolymer is present in all copolymer samples. At this point it has to be noted that under extreme reaction conditions with styrene/ethene molar ratios of 31 (run 14) to 110 (run 15) or at complex concentrations unusually high for metallocene catalysis (run 16, [cat] = 1812 $\mu$mol/L) some syndiotactic polystyrene was detected in the copolymer in contrast to samples 1−13, obtained at styrene/ethene molar ratios of 0−17 and catalyst concentrations of 100 $\mu$mol/L (Table 2).

It can be concluded that in contrast to results by Kakugo,[3] under the reaction conditions reported above with styrene/ethene molar ratios of 0−110, no alternating ethene/styrene copolymer was detected. Instead, random poly(ethene-*co*-styrene) with inhomogeneity concerning both styrene incorporation and molecular mass distribution was produced. The question arises why Kakugo was able to observe poly(ethene-*alt*-styrene) in contrast to the present results. This might be explained looking at the extreme reaction conditions employed.[18,20] With very high styrene concentrations and very low ethene concentration, as employed by Kakugo, the last inserted ethene monomer unit will be followed by subsequent styrene insertion. Therefore, under these conditions there might be a certain probability for the formation of alternating ethene/styrene copolymer, though rather small taking *r* parameters into account as reported above. However, this cannot lead to the conclusion that two distinct active centers exist. Obviously, the catalytic system SBP/MAO does not consist of two different active centers, one of which produces poly(ethene-*alt*-styrene). In contrast, it consists of various active centers producing random poly(ethene-*co*-styrene) with broad distributions of molecular mass and comonomer incorporation.

Syndiotactic polystyrene was found together with random poly(ethene-*co*-styrene) at very high styrene or catalyst concentrations.[20] However, syndiotactic polystyrene was also found as byproduct in ethene/styrene copolymerizations with certain mono-Cp−amido complexes, which are unable to produce styrene sequences

**Table 4. Relative Intensities of Signals in $^{13}$C NMR Spectra of Samples Obtained by Solvent Extraction**

| fraction[a] | in NMR as | fraction wt % | relative intensities, normalized, % | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $T_{\delta\delta}$ | $T_{\beta\delta}$ | $T_{\beta\beta}$ | $S_{\alpha\gamma+\alpha\delta}$ | $S_{\gamma\gamma+\gamma\delta+\delta\delta}$ | $S_{\beta\gamma+\beta\delta}$ | $S_{\beta\beta}$ |
| 12 THF | *a* | 11 | 11 | 2 | 2 | 20 | 47 | 11 | 6 |
| 12 TOL | *b* | 89 | 1 | 3 | 1 | 2 | 89 | 4 | 0 |
| 12 INS | *c* | 0 | | | | | | | |
| 13 THF | *a* | 5 | 11 | 5 | 5 | 20 | 40 | 11 | 7 |
| 13 TOL | *b* | 95 | 1 | 6 | 2 | 2 | 83 | 6 | 0 |
| 13 INS | *c* | 0 | | | | | | | |

[a] THF: soluble in THF at ambient temperature. TOL: soluble in refluxing toluene. INS: insoluble in refluxing toluene.

longer than two monomeric units, even at high styrene concentrations.[21] The production of syndiotactic polystyrene might be explained in analogy to results by Chien who investigated the active centers in syndiospecific styrene polymerization with methylaluminoxane-activated alkoxytitanium and benzyltitanium complexes.[19] A very small number of syndiospecific centers was responsible for the formation of syndiotactic polystyrene, as these centers promote polymerization much faster than aspecific centers. Therefore, syndiotactic polystyrene as byproduct in ethene/styrene copolymerization might be due to prolonged reaction times. This interpretation is in agreement with the kinetics of the polymerization (Figure 5). With rapid decay of the activity of centers promoting ethene/styrene copolymerization, small amounts of syndiotactic polystyrene byproduct become detectable at long polymerization times.

## Conclusion

Bis(phenolate) complexes of titanium, when activated with methylaluminoxane, produce random poly(ethene-*co*-styrene). Comparison of different ligand substitution patterns showed that the bridging unit between bis(phenolate) moieties plays a decisive role with respect to styrene incorporation and catalyst activity. Additional coordination of the bridging unit to the metal center that leads to increased Lewis-acidity was found responsible for increased activity. Steric hindrance at the active center, when the ligand was forced into a conformation that effectively shields against styrene coordination, was responsible for decresased styrene incorporation.

Increasing styrene concentration was found to adversely affect the catalytic activity as well as molecular mass of the copolymers. After high initial activity, catalysts are rapidly deactivated. Styrene incorporation was found to be proportional to styrene concentration. Very high styrene/ethene molar ratios are required to achieve high styrene incorporation. Copolymerization parameters were calculated for SBP to be $r_E = 111$ and $r_S = 0.055$, reflecting formation of ethene blocks and isolated styrene units.

Solvent extraction of different copolymer samples revealed heterogeneity of the copolymers with respect to molecular mass and styrene incorporation. Kakugo's mechanistic two-center catalyst scheme[3] involves centers which produce either alternating ethene/styrene copolymer or syndiotactic polystyrene. Our experiments do not support this hypothesis. Formation of poly(ethene-alt-styrene) might result from Kakugo's unusual experimental conditions involving high styrene concentration and very high catalyst concentration. When the styrene/ethene molar ratio is varied over a wide range, no alternating ethene/styrene copolymer was detected. Both molecular mass distribution and inhomogeneity with respect to styrene incorporation strongly support the conclusion that this bis(phenolate)-based catalyst system is a typical multicenter catalyst. It is therefore similar to conventional Ziegler catalysts, containing centers with different reactivity in ethene and ethene/styrene polymerization.

## Experimental Section

**Materials.** All manipulations involving air and moisture sensitive compounds were carried out under a dry argon atmosphere, using Schlenk tube and glovebox techniques. Methylaluminoxane (MAO) was provided by Witco GmbH as a 10 wt % solution in toluene. Toluene (Roth, p.a., >99.7%) was purified by passing it through a column with acidic $Al_2O_3$, distilled over $LiAlH_4$ and refluxed over Na/K alloy, from which it was freshly distilled prior to use. Ethene was supplied by GHC Gerling, Holz & Co., Handels, GmbH. Styrene (Fluka, >99%) was purified by distillation over $LiAlH_4$ and stored under argon at 0 °C.

**Copolymerization.** Copolymerizations were carried out in a 500 mL glass autoclave (Büchi AG, Uster/CH). The reactor was filled with toluene, styrene, and part of the methylaluminoxane (MAO) needed. After thermostating, argon was removed under vacuum and the reaction mixture saturated with ethene. The metallocene solution (in 10 wt % MAO solution) was then injected into the reactor/flask, so that an in-situ start of the copolymerization was achieved. The preactivation time of the catalyst was 10 min. The ethene pressure was kept constant during the polymerization by a Dräger-Tescom (Dräger-Tescom, Hamburg, Germany) pressure reducer. The ethene flow was messured by a Brooks mass flow controller 5850E (Brooks Instrument B.V.). Copolymerizations were stopped by injecting $C_3H_7OH$ and venting off excess ethene. The copolymers were precipitated by pouring into 1 L of acidic (containig 10 mL of half-concentrated HCl) $CH_3OH$, filtered, and dried under vacuum to a constant weight.

**Catalyst Synthesis.** Titanium bis(phenolate) complexes SBP,[16a] SBC,[1,16a] EBP,[15c] EBC,[15c] MBC,[15a,b] and SOBP[16c] were synthezised according to the literature and completely characterized by elemental analysis, $^1$H and $^{13}$C NMR spectra, and mass spectra.

**Characterization.** NMR spectra of polymers were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz for $^1$H and at 75.4 MHz for $^{13}$C. Spectra were taken at 100 °C using $C_2D_2Cl_4$ as solvent. The chemical shifts are reported in ppm versus tetramethylsilane (TMS), setting the signal for $C_2DHCl_4$ at 74.06 ppm. Signals were assigned according to the literature.[3,6,22] Molecular weights and molecular weight distributions of polymers reported were determined by gel permeation chromatography (GPC) versus a polyethene standard. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-4 thermal analyzer using different heating rates for each sample and extrapolating on heating rate 0. Copolymer extraction was performed with a 100 mL Soxhlet extractor, using a total amout of solvent of 200 mL.

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