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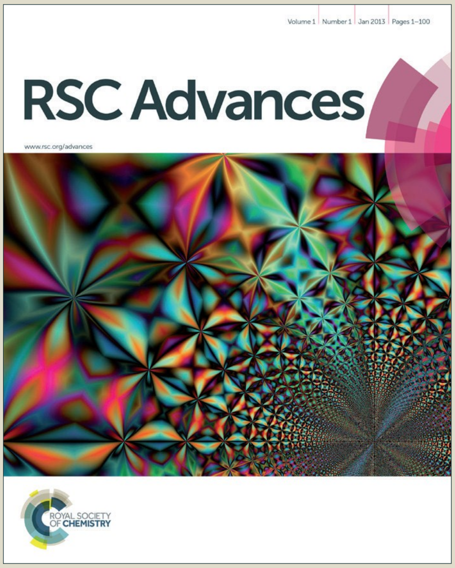

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# Exploring the effects of phenolic compounds on bis(imino)pyridine iron-catalyzed ethylene oligomerization

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In order to reduce the simultaneous production of insoluble polymers during the iron-catalyzed ethylene oligomerization, a series of phenolic compounds were introduced as modifiers. It was found that the polymer share in the total products would be largely reduced with the increasing dosage of the phenols and the enlargement of *para*-substituent size from methyl to *tert*-butyl. Further $^1$H NMR studies showed that the phenols could provide methylaluminoxane (MAO) profound structural modifications, giving rise to larger MAO aggregates and decoration of phenoxy groups on its surface. This would thus facilitate the active ion pair separation, leading the phenols to be effective polymer-retarding modifiers. Starting from the reaction between 4-*tert*-butylphenol, $AlMe_3$ and water, a novel phenoxy-aluminoxane could be prepared. Its combination with $AlMe_3$ enabled the catalyst activation, and gave us a further verification about the important role of phenoxy groups on the MAO surface. Furthermore, introduction of electron-withdrawing groups would improve the reactivity of the -OH group, promoting the interaction between the phenols and MAO. A series of *para*-halogen substituted phenols were thus developed. With the relatively large size of bromo group and the highest reactivity of -OH group, 4-bromophenol was proved to be the most efficient polymer-retarding modifier among the studied phenols in this work. An almost polymer-free ethylene oligomerization could be achieved by this strategy without altering the mono *ortho*-methyl substituted BIP ligand.

## Introduction

As one of the major processes for production of linear higher α-olefins, ethylene oligomerization is of considerable academic and industrial interest. Iron complexes with 2,6-bis(imino)pyridine (BIP) ligands, which were discovered more than 15 years ago,[1-3] have exhibited excellent catalytic performance in such ethylene upgrade reactions. These iron complexes represent a remarkable new generation of ethylene oligomerization catalysts that have extended our understanding of the impact of electronic and steric properties of the ligands. It is now apparent that those complexes bearing a single *ortho*-alkyl substituent (especially methyl) on the aryl rings, on activation by methylaluminoxane (MAO), exhibited the highest activity among all iron pre-catalysts in affording α-olefins with Schulz-Flory distribution to the best of our knowledge.[3] However, the distribution of the obtained ethylene oligomers can be very broad, ranging from $C_4$ to $C_{40+}$.[3,4] And the proportion of heavy byproducts, insoluble polymers, can be higher than 40 wt% in the total products even the iron complexes with mono *ortho*-methyl substituted BIP ligands were employed.[5,6] Such limitation of simultaneous production of undesired waxes or polyethylene (PE) imminently needs to be addressed for the further commercialization of a catalytic system.

The nature of the active species can be a decisive factor for the reaction behaviours and the product properties. It thus becomes important to solve the above-mentioned problem by mediating the nature or the micro-chemical environment of the active species. Tuning the ligand structure is then believed a direct method for such purpose, and modifications on the central pyridine moiety, the imino arms or the aryl rings have been extended.[7] Particularly, to introduce electron-withdrawing substituents could be a potential way in tuning the oligomer distribution. Several *ortho*-halogen substituted bis(imino)pyridine iron catalysts have been proved to trigger no ethylene to polymer.[8] However, these *ortho*-halogen substituted complexes suffer from poorer resistibility against deactivation than their *ortho*-methyl substituted analogues, especially at elevated temperatures. This is due to the strong electron-withdrawing effect of the halogens, making the complex of ligand and iron more prone to decomposition. Besides, the iron complexes bearing a novel generation of ligands, 2-imino-1,10-phenanthrolines, reported by Sun[9] would in some cases produce fewer polymers than the BIP systems.

On the other hand, the nature of the active species could also be modulated by co-catalyst modification. As we all know, the bis(imino)pyridine iron catalysts must be activated with

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cationizing co-catalysts for the active species to form. And it seems MAO still acts as the most active and used co-catalysts at present. Although the structure and detailed functioning principles of MAO still remain enshrouded by mystery, many modification methods can be applied to modify its structure, and further modulate the active ion pairs and their catalytic performances.[10] Especially, addition of bulkier $Al^{i}Bu_3$ into the MAO would cause the $^{i}$Bu/Me exchange and lead to an [$^{i}$Bu-MAO]$^-$ anion that has a weaker coordinating ability than the [Me-MAO]$^-$ ion, thus enhancing the activity.[11]

Recently, we proposed an effective strategy for retarding the simultaneous polymer formation during ethylene oligomerization by treatment of MAO with alkoxysilanes.[12] Owing to the electron-donating nature, alkoxysilanes could well modify the structure of MAO and further make a pronounced reduction of the polymer share in the total products. Noteworthy, this strategy is quite simple without the modification or alteration of the mono *ortho*-methyl substituted catalyst precursor. In that work, we tried to remove the free trimethylaluminum from MAO by reaction of sterically hindered phenol, *i.e.* 2,6-di-*tert*-butylphenol ($^{t}Bu_2PhOH$), with the commercial MAO solution according to the literature.[13] An interesting phenomenon we found was that the addition of $^{t}Bu_2PhOH$ could also retard the formation of insoluble polymers to some extent. This inspired us to explore another class of potential modifiers based on the phenolic compounds. Since the hydroxyl of $^{t}Bu_2PhOH$ was bulkily shielded, its interaction with the catalytic components may be less efficient.[14] We thus removed the *tert*-butyls on the *ortho*-positions of the phenolic compounds, and tried to investigate the effects of a series of substituents on the *para*-position in this work.

## Experimental

### Materials

All manipulations involving air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen glove-box. Solvents and reagents (toluene, *n*-hexane, *n*-heptane, *n*-butanol) were dried over 4 Å molecular sieves for at least 10 days. Toluene and *n*-hexane were then purified by solvent purification system of Innovative Technology (PS-400-5-SD, USA). Iron(III) acetylacetonate ($Fe(acac)_3$, 99%), 2,6-diacetylpyridine (97%), 4-methoxy-2-methylaniline (98%) were purchased from J&K Chemical Corp. (Shanghai, China) and were used as received. Phenol (98%) was provided by Sinopharm Chemical Reagent Co., Ltd., 4-methylphenol (4-MePhOH, 99%), 4-isopropylphenol (4-$^{i}$PrPhOH, 98%), 4-*tert*-butylphenol (4-$^{t}$BuPhOH, 98%) and 2-bromo-4-*tert*-butylphenol (2-Br-4-$^{t}$BuPhOH, 97%) were purchased from TCI China (Shanghai, China), while 4-fluorophenol (4-FPhOH, 99%), 4-chlorophenol (4-ClPhOH, 99%) and 4-bromophenol (4-BrPhOH, 99%) were purchased from J&K Chemical Corp. (Shanghai, China). All of these phenolic compounds were used as received. Benzene-$d_6$ ($C_6D_6$, 99.5 atom % D) was purchased from J&K Chemical Corp. (Shanghai, China). $C_6D_6$ was then transferred into a sealed Schlenk bottle with 4 Å molecular sieves in the nitrogen glove-box. Trimethylaluminum ($AlMe_3$, 1.0 M in hexane) was purchased from J&K Chemical Corp. (Shanghai, China) and used without further purification. MAO (10 wt% solution in toluene) was purchased from Albermarle Chemical Corp. (Baton Rouge, LA, USA) and stored at -18 ℃. It was 1 year old at the time of this work. High-purity nitrogen and polymerization-grade ethylene were obtained from SINOPEC Shanghai Corp. (Shanghai, China) and were passed through the oxygen- and moisture-scrubbing columns prior to use.

### Synthesis of the ligand

Synthesis of the ligand used in this study follows the established procedure[1,3] and its $^1$H NMR, MS and Elemental analyses can be referred to our previous work.[12] Scheme 1 shows that the ligand is an *ortho*-methyl and *para*-methoxy substituted bis(imino)pyridine (**L**), which is believed that an electron-donating group at *para*- or *meta*-position could be beneficial for better stabilizing the corresponding iron complexes, thus enhancing the activity with little effect on the product distribution.[3]

**Scheme 1** Structure of 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine (**L**).

### Preparation of the catalyst precursor

Throughout this study, we have employed an *in situ* formed catalyst system composed of $Fe(acac)_3$ and the BIP ligand **L**. They should be premixed, and an optimal molar ratio is 1:1 according to our previous work.[15] The homogeneous orange-red mixture in toluene was therefore prepared, abbreviated as **L-Fe(acac)$_3$**. The concentration of the catalyst precursor in toluene, in terms of iron atoms [Fe], was 2 $\mu$mol/ml.

### Ethylene oligomerization

Oligomerizations were carried out in a 250-ml glass reactor equipped with an ethylene inlet, vacuum line and magnetic stirrer. The reactor was heated by a heat gun with the operating temperature to be 650 ℃ for at least 15 min and purged with dry nitrogen. After cooling to the reaction temperature (50 ℃), 50 ml of toluene (solvent) and the desired amount of phenolic compound and MAO (or $AlMe_3$) were successively charged into the reactor, which were allowed to react for 20 min. The reaction was monitored by the bubbling (mainly methane) via an oil-filled bubbler. An agitation speed around 700 rpm was adopted. Nitrogen was then removed after 20 min and a continuous flow of ethylene was introduced to make the system saturated with ethylene. To maintain a constant 1.0 bar pressure of ethylene over the reaction, the ethylene was allowed to exit via the oil-filled bubbler. The oligomerization was then initiated by injection of a solution of the catalyst precursor in toluene. At the end of a run, the reaction was terminated by addition of 3 ml of acidified ethanol and the reactor was cooled down to room temperature. The product mixture was then centrifuged to separate the oligomers in toluene and the insoluble polyethylene wax. The wax was firstly put on a filter paper and washed sufficiently with toluene to drip down the light fraction in the filtrate, which was then merged into the oligomers. Secondly, the wax was washed with ethanol to remove the residual MAO, then filtered, dried, and weighed. An internal standard (*n*-heptane, 1.0 ml) was injected into the resultant liquid phase, prior to a GC-FID analysis.

### Preparation and oligomerization tests of the phenoxy-aluminoxane activator

The experiments were carried out in the same 250-ml glass reactor as above-mentioned. First step: to a solution of $AlMe_3$ (4.0 mmol) in dry toluene (50 ml) was added 4-$^{t}$BuPhOH (4.0 mmol) by dropwise for a period of 40 min. The mixture was then allowed to react for 30 min at 50 ℃ under $N_2$ protection. Second step: 3.6 mmol of water was added by dropwise to the product of the first step, which was then reacted for another 30 min. Third step: ethylene and **L-Fe(acac)$_3$** were introduced to initiate the oligomerization runs after the addition of an appropriate amount of extra $AlMe_3$ or not.

### Characterization

The catalytic activity was quantified by the amount of products. For oligomers, individual olefins were identified by GC/MS (Nicolet HP GC6890/MS5973). $C_{12}$ olefin isomers were used to determine the linearity. Further quantitative analyses were performed by Agilent GC 6890 equipped with a HP-5 column (5 % phenylmethylsiloxane, 30 m × 0.32 mm × 0.25 $\mu$m) using *n*-heptane as the internal standard. The injector temperature was 320 ℃ and the following temperature program was: 50 ℃ /2 min, 50-300 ℃/20 ℃•min$^{-1}$, 300 ℃/10 min. Under this temperature programme, olefins ranging from $C_4$ to $C_{32}$ can be detected. The yield of volatile $C_4$ fraction was determined by extrapolation of α value. The α value is a characteristic coefficient of Schulz-Flory distribution, which can be calculated from the relative rate of chain propagation and chain termination or the quotient of the molar amounts of two subsequent oligomer fractions, $C_{14}$ and $C_{12}$ in this case (eq. (1)).

$$\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of termination}} = \frac{\text{mol}(C_{n+2})}{\text{mol}(C_n)} \qquad (1)$$

The weight- (Mw) and number-average (Mn) molecular weights and polydispersity indices (PDI=Mw/Mn) of the insoluble polymers were estimated by a PL-GPC-220 gel permeation chromatography (GPC) system (Polymer Laboratories, UK) with 1,2,4-trichlorobenzene as solvent at 150 ℃. $^{1}$H NMR spectra of the mixtures of MAO and various amounts of 4-*tert*-butylphenol in a 5 mm sealed NMR tube were recorded on an Agilent 600MHz DD2 (DirectDrive2) spectrometer. Benzene-*d*$_6$ was used as the solvent and each sample was allowed to stabilize for 20 min at 25 ℃ before analysis.

## Results and discussion

### Influence of phenol on ethylene oligomerization

The oligomerizations using pre-catalyst **L-Fe(acac)$_3$** were initiated by MAO activation applying a molar ratio Al/Fe=1000 and routinely performed at a temperature of 50 ℃ over 30 min. Compared to the popular iron source $FeCl_2$, Fe(acac)$_3$ can be more soluble in toluene. It can be simply mixed with the BIP ligands, while the active species would *in situ* formed with the activation of MAO. As shown in Table 1, the system **L-Fe(acac)$_3$**/MAO triggered ethylene to linear α-olefins with exceptionally high activity and selectivity, much differing from those LFeCl$_3$ precursors, which produced a great deal of internal and branched olefins.[16] Noteworthy, this system produced a large amount of insoluble waxy polymers beyond the α-olefins, possessing higher than 30 wt% in the total products.

As mentioned in the Introduction, we found the addition of $^{t}$Bu$_2$PhOH into the system **L-Fe(acac)$_3$**/MAO could help reduce the formation of insoluble polymers, although such effect was not remarkable enough. It was deduced that the bulky *tert*-butyl groups would prevent the hydroxyl from sufficient interaction with the catalytic components, especially MAO. Therefore, as the start of the exploration of effective polymer-retarding compounds, phenol was firstly caught up in our minds. Without any substituents on *ortho*-positions, phenol was supposed to be a more reactive modifier than $^{t}$Bu$_2$PhOH. The results of phenol-mediated oligomerizations under otherwise identical conditions in pure **L-Fe(acac)$_3$**/MAO system are presented in Runs 2-5, Table 1.

As we can see, phenol indeed acted as an active polymer-retarding modifier. With the [-OH]/[Al] molar ratio increased from 0 to 0.7, the mass fraction of insoluble polymers in the total products decreased from 31.9 wt% to 5.5 wt%. The activity for α-olefins, at the meantime, remained very high with a remarkable increase compared to that of the system without phenol. Similar to the sterically hindered phenols, phenol can also react with $AlMe_3$, and scavenge it. These reactions can be referred to the eq. (2) and eq. (3) below.[17]

$$AlMe_3 + PhOH \rightarrow AlMe_2OPh + CH_4 \qquad (2)$$

$$AlMe_3 + 2PhOH \rightarrow AlMe(OPh)_2 + 2CH_4 \qquad (3)$$

As we have known, those $AlMe_3$ contained in MAO would reduce the activity of bis(imino)pyridine iron catalysts[12] and promote the catalyst deactivation via the reduction of cationic species, the formation of Fe-Al heterodinuclear dormant species[6] or the transmetallation involving transfer of the ligand from the iron to aluminum[18]. Trapping $AlMe_3$ would result in the formation of aluminum phenoxides, e.g. $AlMe_2OPh$ and $AlMe(OPh)_2$, though less effective in activating pre-catalysts,[19] could help inhibit the catalyst deactivation and thus enhance the activity.

By comparison, the polymer-retarding effects of $^tBu_2PhOH$ and phenol are summarized in Fig. 1. It is apparent that phenol was much more effective than $^tBu_2PhOH$. The mass fraction of polymers in the case of [Phenol]/[Al]=0.7 was only 1/3 of that in the case of [$^tBu_2PhOH$]/[Al]=0.9. Objectively speaking, a polymer share of 5.5 wt% was still unsatisfactory, it would still make the product a slurry. However, a further increase of [Phenol]/[Al] to 0.9 didn't keep reducing the polymer share, but greatly deactivated the catalyst. Such deactivation process may be due to the interaction between the free phenol and the active centers. This result implied that the maximum phenol we could introduce in our system was around [-OH]/[Al]=0.7.

**Fig. 1** Mass fraction of insoluble polymers in $^tBu_2PhOH$- and phenol-mediated systems as a function of [-OH]/[Al] molar ratio. The data of $^tBu_2PhOH$ can be referred to ref 12.

Therefore, the problem became how to achieve further reduction of the insoluble polymers under the limited phenol dosage. Still kept the *ortho*-positions of phenol unsubstituted, we envisioned that the introduction of a bulky *para*-substituent would lead to a better separation of the active ion pairs when the phenoxy groups decorated on MAO and thus make some difference. The steric effects of the *para*-substituents were therefore studied in the following sections.

### Steric effects of *p*-alkyl substituted phenolic compounds

To explore whether bulky substituents on the *para*-position could make the phenolic compounds to be more effective polymer-retarding modifiers or not, 4-methylphenol (4-MePhOH), 4-isopropylphenol (4-$^i$PrPhOH) and 4-*tert*-butylphenol (4-$^t$BuPhOH) with different size alkyl groups were studied. The oligomerization results are shown in Table 2.

**Table 2** Steric effects of the *para*-alkyl substituents on oligomerization promoted by **L-Fe(acac)$_3$**/MAO[a].

Let's focus on the formation of insoluble polymers preferentially. Very striking was the significantly strong polymer-retarding effect of 4-MePhOH, 4-$^i$PrPhOH and 4-$^t$BuPhOH. With the increasing concentration of such phenolic compounds, the mass fraction of insoluble polymers in the total products was found to be largely reduced compared to that of the pure **L-Fe(acac)$_3$**/MAO catalytic system (except the case of [4-MePhOH]/[Al]=0.3). As evident from Table 2, when a molar ratio of [-OH]/[Al]=0.7 was applied, the polymer fraction could be reduced to only 1.6 wt%, 0.4 wt% and 0.2 wt% in the 4-MePhOH-, 4-$^i$PrPhOH- and 4-$^t$BuPhOH-mediated oligomerizations, respectively. That is to say an almost polymer-free iron-catalyzed ethylene oligomerization could be achieved by the mediation of *para*-substituted phenols without altering the mono *ortho*-methyl substituted BIP ligand.

Taking the performances of these three phenolic compounds into comparison, the steric effect of the *para*-substituents was found to play a crucial role in tuning the oligomerization activity and product distribution. Firstly, let's take a look on the relationship between the insoluble polymer activity and the phenolic compound, which is more clearly illustrated in Fig. 2. As the steric size of the *para*-substituent enlarged from methyl to *tert*-butyl, a decrease in the activity for insoluble polymers resulted under each adopted [-OH]/[Al] molar ratio. The polymer-retarding ability of these three phenolic compounds was proved to increase in the order of 4-MePhOH < 4-$^i$PrPhOH < 4-$^t$BuPhOH.

**Fig. 2** Activity for insoluble polymers in the 4-MePhOH-, 4-$^i$PrPhOH- and 4-$^t$BuPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

Besides this influence on insoluble polymers, phenolic compounds also exerted remarkable effect on the α-olefins. As the molar ratio of [-OH]/[Al] was increased from 0 to 0.5, the activity for α-olefins was increased. While a further increase of [-OH]/[Al] to 0.7 would somewhat result in the activity drop. When the amount of the phenolic compound was kept increasing, *e.g.* [4-$^t$BuPhOH]/[Al]=0.9, the oligomerization system was greatly deactivated. This paralleled the observations in phenol-mediated system.

On the other hand, the increase of [-OH]/[Al] from 0.3 to 0.7 and the enlargement of *para*-substituent size from methyl to *tert*-butyl would result in the reduction of the Schulz-Flory coefficient α, respectively (Fig. 3). A larger *para*-substituent was supposed to enhance the chain termination, thus producing lower molecular weight products.

**Fig. 3** Schulz-Flory coefficients α of the 4-MePhOH-, 4-$^i$PrPhOH- and 4-$^t$BuPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

However, when the α value of the non-modifier system (Run 1) was taken into comparison, the result was out of our expectation. It was found that the α values in Runs 6, 7 and 9 ([4-MePhOH]/[Al]=0.3, 0.5 and [4-$^i$PrPhOH]/[Al]=0.3) were higher than that of the non-modifier system. A higher α value directly corresponds to an increased propagation probability resulting in higher molecular weight products. This is more visually depicted in Fig. 4 (a/b/c), which shows the distributions of the obtained oligomers. Taking the oligomerization run under the mediation of 4-MePhOH with [-OH]/[Al]=0.3 as an example, the α value raised to 0.83, thus making the distribution of oligomers significantly shifted toward $C_{20}$-$C_{32}$ at the expense of $C_4$-$C_{10}$ fractions. In the 4-$^t$BuPhOH-mediated system, however, the α value was reduced even when the applied [-OH]/[Al] molar ratio was 0.3. Therefore, the distributions were gradually shifted toward lighter olefins.

**Fig. 4** Oligomer distributions and polymer GPC curves obtained after the mediation of various *para*-alkyl phenolic compounds (a/d: 4-MePhOH; b/e: 4-$^i$PrPhOH; c/f: 4-$^t$BuPhOH).

Similar phenomenon was observed in molecular weight of the insoluble polymers. As evident from Fig. 4 (d/e/f) and Table 3, the molecular weight was found to increase at first and then decrease with the increasing concentration of the phenolic modifiers. All of these combined results provide strong evidence that both the oligomerization activity and the product composition can be significantly tuned by the *para*-alkyl substituted phenols. 4-$^t$BuPhOH was found to be the most effective polymer-retarding modifier among the current studied phenolic compounds.

**Table 3** Influence of *para*-alkyl substituents on MW and MWD of the insoluble polymers.

### Mechanistic considerations

Based on the facts that the phenolic compounds should be pre-contacted with MAO, while an excess amount (> [-OH]/[Al]=0.7) or pre-mixing them with the catalyst precursor would cause a severe deactivation, we believe that the interaction between the phenolic compounds and MAO should be paid especially sufficient attention. Therefore, we investigated by $^1$H NMR the reaction of 4-$^t$BuPhOH and MAO in benzene-$d_6$ at 25 ℃.

It is generally accepted that MAO is a mixture of oligomeric clusters with three-dimensional cage structures,[20] and often contains some unreacted $AlMe_3$. As evident from Fig. 5a, the free $AlMe_3$ containing in the MAO gave a singlet at $\delta$ = -0.42 ppm, overlapped with the very broad resonance of the methyl protons of MAO centered at around $\delta$ = -0.22 ppm.

**Fig. 5** $^1$H NMR spectra of MAO/4-$^t$BuPhOH solutions in benzene-$d_6$ at different [-OH]/[Al] molor ratios (a: [-OH]/[Al]=0; b: 0.15; c: 0.3; d: 0.5; e: 0.7; f: 0.9).

The spectra of systems mixing 4-$^t$BuPhOH and MAO, firstly, confirmed the trapping of $AlMe_3$ by phenolic compounds. The addition of 4-$^t$BuPhOH to MAO with [-OH]/[Al]=0.15 led to the formation of $AlMe_2(OAr)$ (Ar = 4-*tert*-butylphenyl) and $CH_4$, as demonstrated by the appearance in the $^1$H NMR spectrum of two diagnostic resonances at $\delta$ = 1.11 and $\delta$ = -0.26 ppm of the former and the enhancement of a singlet at 0.11 ppm typical of the latter.[11a,13,14,21] There may exist monomeric and dinuclear forms of $AlMe_2(OAr)$, where the dinuclear compound is exclusively phenoxide bridged,[6,14b] the resonance at $\delta$ = -0.26 ppm was thus ascribed to the terminal Al-Me protons. Further addition of 4-$^t$BuPhOH up to [-OH]/[Al]=0.3 resulted in the appearance of resonance at $\delta$ = 0.24 ppm. Ittel and co-workers have studied by $^1$H NMR the reaction of trimethylaluminum and 2,6-di-*tert*-butyl-4-methylphenol (BHT), and species like $Al_2Me_6$, $Al_2Me_5BHT$, $AlMe_2BHT$ and $AlMeBHT_2$ were observed in dynamic equilibrium at intermediate stages of reaction.[22] By analogy with this study, we tentatively conclude that similar equilibrium could exist in our system and different species could be in fast exchange of -OAr and -Me groups due to the lack of bulky *ortho*-substituents on the -OAr group. The resonance at $\delta$ = 0.24 ppm could therefore be assigned to the bridged Al-Me-Al protons.

At the same time, the MAO resonance at $\delta$ = -0.22 ppm was faded out and a new broad resonance was significantly appeared around $\delta$ = 0.9-1.5 ppm by the addition of 4-$^t$BuPhOH. Similar phenomenon was observed by Macchioni and co-workers.[23] They found that a broad band at $\delta$ = 1.50 ppm was present with the reaction of DMAO and $^t$Bu$_2$PhOH, which was then tentatively assigned to large and polydisperse MAO/$^t$Bu$_2$PhOH adducts. Generally, a shift of resonance to a higher frequency corresponds to a lower electron density on the protons. For MAO, this could be ascribed to the enlargement of MAO size, thus promoting the electron delocalization. Therefore, the new band around $\delta$ = 0.9-1.5 ppm in our study could be assigned to larger 4-$^t$BuPhOH-modified MAO aggregates. This also indicates that the modifications of MAO induced by 4-$^t$BuPhOH are parallel and not consecutive to $AlMe_3$ depletion. One reason leading to larger average size of MAO is the removal of $AlMe_3$,[24] although the findings of Sinn[25] and Ystenes[26] suggested that no clear relationship between the amount of $AlMe_3$ and the Mw of MAO. According to Macchioni's hypothesis, a further structural modification or backbone rearrangement of MAO-cages may be enabled by the absence of $AlMe_3$.[23]

As the [-OH]/[Al] molar ratio kept increasing, the resonances at $\delta$ = 0.24 and $\delta$ = -0.26 ppm were gradually diminished, while a further increment of the resonance typical of $CH_4$ was observed even when the [-OH]/[Al] molar ratio reached 0.9. In Ittel's studies, formation of $AlBHT_3$ was unlikely, but a smaller *t*-BuOH could react with the third Al-Me bond.[22] Since 4-$^t$BuPhOH is free of *ortho*-substituents, we tend to believe that the formation of $Al(OAr)_3$ is possible in our study (eq. (4)), which would account for the Al-Me resonances decay and the $CH_4$ resonance increment.

$$AlMe(OAr)_2 + ArOH \rightarrow Al(OAr)_3 + CH_4 \qquad (4)$$

On the other hand, 4-$^t$BuPhOH could also react with part of the Al-Me bonds of MAO (eq. (5)), leading to the formation of -OAl(OAr) "decorated" MAO[23] and again enhancing the $CH_4$ release.

$$\text{MAO-Al-Me} + ArOH \rightarrow \text{MAO-Al-OAr} + CH_4 \qquad (5)$$

Such decoration of -OAr groups could also be achieved through alkyl/phenoxy exchange between MAO and the aluminum phenoxides.[10d,27] Reactions of MAO and 4-$^t$BuPhOH in *n*-hexane showed that this -OAl(OAr) "decorated" MAO had a higher solubility in aliphatic solvents than the original MAO. Those -OAr groups may improve the stability of MAO and make it lesser tendency to further aggregate.

In summary, three main conclusions can be made from this NMR monitoring of the reaction of MAO and 4-$^t$BuPhOH: 1) 4-$^t$BuPhOH can trap the $AlMe_3$ containing in the MAO solution and lead to the formation of aluminum phenoxides, even the tri-substituted Al(OAr)$_3$, thus improving the oligomerization activity; 2) 4-$^t$BuPhOH provide MAO further structural modifications and give rise to larger MAO aggregates; 3) 4-$^t$BuPhOH can react with MAO and decorate -OAr groups on its surface, thus improving the solubility and stability of MAO. Beyond these, the variation trend of the resonance at $\delta$ = 1.11 ppm was somewhat out of our expectation. This resonance typical of methyl protons of $^t$Bu groups was found to be gradually faded out with the increasing molar ratio of [-OH]/[Al]. To be frank, we have no idea about it at the moment. But fast exchange of -Me and -OAr groups may be present between species like MAO (or MAO-Al-OAr) and aluminum phenoxides, giving rise to the broadening of the signal around $\delta$ = 0.9-1.5 ppm.

According to Bryliakov's work, ion-pair active intermediates would be generated in BIP-iron systems with the activation of MAO.[28] The active iron centers are thus surrounded by huge anionic [Me-MAO]$^-$ clusters. By the anion disassociation and re-association involving a change in the cation-anion distance, additional steric hindrance from the MAO clusters could be imposed on the active centers. This may regularly inhibit the rotation of propagating chains and the β-H elimination to α-olefins, thus favoring the simultaneous formation of higher-Mw polymers during the ethylene oligomerization. Holding these in minds, the interaction between the phenolic compounds and MAO should be the key factor accounting for the polymer-retarding effect. On the basis of the NMR studies, it occurred to us that the influence of 4-$^t$BuPhOH on MAO and the corresponding active species can be simply illustrated as shown in Scheme 2.

**Scheme 2** Proposed active ion-pair species of **L-Fe(acac)$_3$**/MAO system with or without the mediation of 4-$^t$BuPhOH. (MAO is referred to as a linear chain structure for the sake of simplicity, and m > n)

Firstly, the phenolic compounds would promote MAO aggregation, which would then result in a larger MAO anion. As above-mentioned, it could be deduced that larger anionic clusters would impose more remarkable steric hindrance on the iron centers, thus giving rise to an increment of product molecular weight.

Secondly, the decorated -OAr groups would make the novel [Me-MAO-OAr]$^-$ ion have a weaker coordinating ability than the [Me-MAO]$^-$ ion and lesser tendency to aggregate with the cationic species, leading to a better separation of the iron centers and the MAO anions. On the one hand, this would promote the formation of active outer-sphere ion pair (OSIP) instead of the dormant inner-sphere ion pair (ISIP),[29] which has a positive influence on the catalyst activity. On the other hand, the additional steric hindrance around the active centers that imposed by MAO clusters would be reduced, thus promoting β-H elimination to lighter product. The gradually reduced α values obtained with the increasing concentration of each phenolic compound strongly indicated such effect.

Combining these two effects together, our observations on the catalytic performance of *para*-alkyl substituted phenolic compounds could be well interpreted. For 4-$^t$BuPhOH, the large *p*-$^t$Bu group would make it highly efficient in separating active ion pairs and counteracting the effect of MAO enlargement even when its amount was small. However, situation for the 4-MePhOH-mediated system was more complex. 4-MePhOH would mainly react with AlMe$_3$ when its amount was small, and few (4-MePhO) units would be grafted onto the MAO. Since the *p*-Me is a relative small group, the strengthening steric hindrance resulted from MAO aggregation would therefore be dominant in this situation, thus shifting the oligomers to higher Mw ones. It was found that the mass fraction of insoluble polymers in the total products raised to 36.0 wt%, even higher than the original system, when [-OH]/[Al]=0.3. Further addition of 4-MePhOH would cause more (4-MePhO) units decorating on the MAO, thus leading to a better separation of the iron centers and the anionic MAO clusters. A molecular weight reduction was then observed.

Furthermore, the aluminum phenoxides, especially Al(OAr)$_3$, may also be beneficial to the oligomerization process. On the one hand, Al(OAr)$_3$ may reversibly coordinate with the cationic Fe center through a bridging oxygen donor. This would in a manner prevent the α-olefins from re-incorporation into the propagating chains. The linearity of the obtained α-olefins was thus slightly increased with the increase of [-OH]/[Al] molar ratio. Similar interaction between cationic Cr center and Al(OC$_6$F$_5$)$_3$ was also proposed by McGuinness and co-workers.[30] On the other hand, the existence of Al(OAr)$_3$ may alter the environment of the active sites and facilitate the cation-anion separation. A bulky phosphine P$^t$Bu$_3$ was previously reported by Stephan and co-workers to have such potential, thus increasing the ethylene polymerization activity of the non-metallocene [CpTiMe$_2$(NP$^t$Bu$_3$)]/B(C$_6$F$_5$)$_3$ system.[31]

### Development of a novel phenoxy-aluminoxane activator

On the basis of these studies, it is apparent that MAO could be structural modified by a phenolic compound ArOH with the incorporation of -OAr units into its backbone. By analogy with this, to give MAO a more thorough modification starting from its preparation via the reaction between 4-$^t$BuPhOH, AlMe$_3$ and water could also be envisioned. According to the established procedure of Kissin,[19] a novel phenoxy-aluminoxane was thus prepared through two consecutive reactions: first, a reaction between AlMe$_3$ and equimolar 4-$^t$BuPhOH and, second, a reaction between the product of the first step and water ([H$_2$O]/[Al]=0.9). The detailed procedures can be found in Experimental section. The oligomerization results using this phenoxy-aluminoxane as activator are present in Table 4.

**Table 4** Oligomerizations activated by the reaction products of 4-$^t$BuPhOH, AlMe$_3$ and water[a].

Before the ethylene oligomerizations activated by the phenoxy-aluminoxane, performance of equimolar AlMe$_3$ (Al/Fe=2000) was provided to be a baseline measure. As evident from Table 4, the activity of **L-Fe(acac)$_3$**/AlMe$_3$ was only 56 kg•(mol-Fe)$^{-1}$•h$^{-1}$, much lower than that of the **L-Fe(acac)$_3$**/MAO system, and the product consisted of only $C_4$ (92 wt%) and $C_6$ (8 wt%) fractions. Oligomerization activated by the phenoxy-aluminoxane alone was proved to be even less active, a very low activity of 27 kg•(mol-Fe)$^{-1}$•h$^{-1}$ was observed (Run 17, Table 4). We tentatively attributed this to the lack of methyl groups on the phenoxy-aluminoxane, making it less effective in catalyst methylation. Therefore, 0.5 mmol of extra $AlMe_3$ was added in Run 18. To our surprise, this combined system exhibited a relatively high activity (590 kg•(mol-Fe)$^{-1}$•h$^{-1}$). More importantly, the olefin product was well distributed with the Schulz-Flory coefficient $\alpha$ to be 0.66, while no insoluble polymers were formed. It was deduced that there existed an exchange between the -OAr groups and the -Me groups from the extra $AlMe_3$, which would replace part of the -OAr groups on the phenoxy-aluminoxane with -Me groups. Such exchange would make the activator to be more effective in catalyst activation, and the remained -OAr groups would facilitate the active ion pair separation and retard the formation of polymers.

To confirm this phenomenon, more $AlMe_3$ was added in Run 19. The oligomerization result showed that the activity and the olefin distribution remained almost the same as Run 18. However, some polymers were also obtained in this situation. One can deduce that more -OAr groups would be replaced by -Me groups when the addition of extra $AlMe_3$ was increased. The aluminoxane activator would thus be more similar in structure with MAO and its polymer-retarding effect would be alleviated. This section gives us a further verification about the mechanistic discussions on the effects of the phenolic compounds.

### Influence of halogen-substituted phenolic compounds

Now we have preliminarily understood the functional mechanism of the phenolic compounds. Their influence on the catalytic performance was realized via the interaction with MAO. To achieve a satisfactory polymer-retarding effect, the amount of a *para*-alkyl substituted phenolic compound should be as higher as [-OH]/[Al]=0.7 in this work. However, such amount was close to the critical point, further addition would deactivate the catalyst. Therefore, the dosage of the phenolic compounds should be strictly controlled, which will largely limit their applicability.

As we all know, introduction of an electron-withdrawing substituent onto the benzene ring would reduce the electron density of the -OH group, thus increasing the reactivity of the O-H bond. This may further promote the reaction between the phenolic compounds and MAO. Aiming at largely retarding the polymer formation with fewer amount of the phenolic modifier, a bromo group was introduced while the bulky *tert*-butyl group was remained on the *para*-position. 2-Br-4-$^t$BuPhOH was thus tested. The results are present in Table 5. It is apparent that introduction of a halogen substituent indeed enhance the polymer-retarding effect of the phenolic compounds. 2-Br-4-$^t$BuPhOH was proved to be a more effective polymer-retarding modifier than 4-$^t$BuPhOH as evident from Table 5. The polymer share was significantly reduced to 9.3 wt% with [-OH]/[Al] molar ratio to be only 0.1. When this ratio was up to 0.2, the obtained product was nearly free of polymers.

However, the activity was also remarkably decreased with the mediation of 2-Br-4-$^t$BuPhOH. This deactivation process could be tentatively ascribed to the co-coordination of both oxygen and bromo donor from (2-Br-4-$^t$BuPhO)$_x$-AlMe$_{3-x}$ (x = 1-3) with the cationic Fe center. As a consequence, the vacant coordination site for ethylene would be occupied. The monomer insertion and the chain propagation would then be largely depressed.

**Table 5** Influence of 2-Br-4-$^t$BuPhOH on oligomerization promoted by **L-Fe(acac)$_3$**/MAO$^a$.

Following this exploration, one can deduce that the *para*-$^t$Bu substituted phenol with a halogen on the *meta*-position would be more ideal in balancing the polymer-retarding effect and the oligomerization activity. However, such a phenolic compound is somewhat less obtainable, which may be due to the strong *ortho*-/*para*-directing nature of the -OH group in the electrophilic aromatic substitution according to the orientation rules.[32] Therefore, we attempted to investigate the effects of *para*-halogen substituents preferentially at this stage. Three phenols, 4-fluorophenol (4-FPhOH), 4-chlorophenol (4-ClPhOH) and 4-bromophenol (4-BrPhOH), which contained only one substituent and paralleled the previous series of *para*-alkyl substituted phenols in structure, were thus studied in the following part of this work. The oligomerization results are summarized in Table 6.

**Table 6** Influence of the *para*-halogen substituted phenols on oligomerization promoted by **L-Fe(acac)$_3$**/MAO$^a$.

Overall, the influence of the *para*-halogen substituted phenols was similar with the *para*-alkyl substituted ones. It can be seen from Fig. 6, this series of phenols also exhibited strong polymer-retarding ability. With the increasing concentration of each phenolic compound, the activity for insoluble polymers was largely reduced, giving rise to a remarkable decrease of the polymer share in the total products. What out of our expectation was the performance of 4-ClPhOH. When the [-OH]/[Al] molar ratio was 0.7, a product free of polymers could be obtained in both 4-FPhOH- and 4-BrPhOH-mediated systems, while the mass fraction of polymers in 4-ClPhOH-mediated system was still up to 6.9 wt%.

**Fig. 6** Activity for insoluble polymers in the 4-FPhOH-, 4-ClPhOH- and 4-BrPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

Generally, the electronic effect of the halogens on a benzene ring would be more complicated than that of the alkyls.[32] Although the electronegativity of the halogens follows the order of F > Cl > Br, the general effect on the halogenated phenols would be different when both the electron-withdrawing inductive effect and the electron-donating conjugative effect are taken into consideration. Since the atomic radius of the halogens follows the order of Br > Cl > F, such conjugative effect of the bromo group is supposed to be the weakest. As a comprehensive consequence, the net electron-withdrawing effect of the bromo group would be the strongest, and the electron density on the -OH group would be reduced with the *para*-halogen altering from F to Br. For this reason, the reactivity of the -OH group would thus follow the order of 4-BrPhOH > 4-ClPhOH > 4-FPhOH.

With the largest size of bromo group and the highest reactivity of -OH group, 4-BrPhOH could be highly effective in the interaction with MAO and well facilitate the cation-anion separation. This made it to be the most efficient polymer-retarding modifier among the *para*-halogenated phenols in this work without question. As evident from Table 6 and Fig. 6, the applicability of 4-BrPhOH was therefore improved. It could largely retard the polymer formation with low dosage and would not deactivate the catalyst.

Meanwhile, the product molecular weight and its distribution were also largely influenced by the *para*-halogens, which was somewhat in line with the *para*-alkyl substituted systems. As can be seen in Fig. 7 and Table 7, due to the relatively small size of fluoro group, the variation trend of oligomer distribution and polymer molecular weight in 4-FPhOH-mediated system replicated the phenomenon when 4-MePhOH was adopted. And 4-BrPhOH, again, exhibited the strongest ability in tuning the product molecular weight.

**Fig. 7** Oligomer distributions and polymer GPC curves obtained after the mediation of various *para*-halogen phenolic compounds (a/d: 4-FPhOH; b/e: 4-ClPhOH; c/f: 4-BrPhOH).

**Table 7** Influence of *para*-halogen substituents on MW and MWD of the insoluble polymers.

## Conclusions

In this work, the effects of phenolic compounds on bis(imino)pyridine iron-catalyzed ethylene oligomerization were investigated. It was found that the *para*-alkyl substituted phenols with the *ortho*-positions unsubstituted acted as effective polymer-retarding modifiers. With the increasing dosage of the phenols and the enlargement of *para*-substituent size from methyl to *tert*-butyl, the polymer share in the total products would be largely reduced. It could be deduced from the $^1$H NMR studies that the interaction between the phenolic compounds and MAO was the key factor accounting for their effects. They would provide MAO further structural modifications, giving rise to larger MAO aggregates and decoration of phenoxy groups on the MAO surface. This would thus facilitate the active ion pair separation and promote the β-H elimination to α-olefins. A more thorough modification of MAO could be started from its preparation via the reaction between 4-$^t$BuPhOH, $AlMe_3$ and water. The combination of the resultant phenoxy-aluminoxane and an appropriate amount of $AlMe_3$ could be a potential alternative of MAO for the activation of iron-based oligomerization catalysts. We have now been trying to improve the catalytic performance of the phenoxy-aluminoxane activator via the optimization of the preparation conditions. In order to promote the interaction between the phenolic compounds and MAO, halogens were introduced into the benzene ring of the phenols. The electron-withdrawing nature of the halogens would improve the reactivity of the -OH group. With the relatively large size of bromo group and the highest reactivity of -OH group, 4-BrPhOH was proved to be the most efficient polymer-retarding modifier among the studied phenols in this work. An almost polymer-free ethylene oligomerization could be achieved by this strategy without altering the mono *ortho*-methyl substituted BIP ligand. Nevertheless, not all of the observed phenomena have been well interpreted at this stage. More detailed investigations are now in progress.

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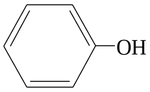
# Tables

**Table 1** Influence of phenol on oligomerization promoted by **L-Fe(acac)$_3$**/MAO[a].

| Run | Modifier | [-OH]/[Al] | Oligomer | | | Polymer | | *Act.*[f] |
|---|---|---|---|---|---|---|---|---|
| | | [mol/mol] | $Y_o$[b] [g] | α | % LAO[c] | $Y_p$[d] [g] | wt% PE[e] | |
| **1** | None | 0 | 2.35 | 0.76 | 98 | 1.10 | 31.9 | 3450 |
| **2** |  Phenol | 0.3 | 3.03 | 0.79 | 97 | 1.26 | 29.4 | 4290 |
| **3** | | 0.5 | 3.71 | 0.75 | 97 | 0.52 | 12.3 | 4230 |
| **4** | | 0.7 | 2.90 | 0.73 | 98 | 0.17 | 5.5 | 3070 |
| **5** | | 0.9 | 0.12 | 0.73 | 99 | trace | — | 120 |

[a] General conditions: pre-cat.: [Fe]=2 μmol; Al/Fe=1000; solvent: toluene, 50 ml; *T*=50 ℃; *P*=1 bar; t=30 min.

[b] Yield of the soluble oligomers, determined by GC.

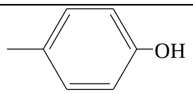
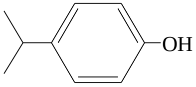
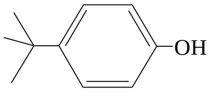
[c] % linear α-olefin content in oligomers determined by GC.

[d] Yield of the insoluble polymers.

[e] The mass fraction of insoluble polymers in the total products (soluble oligomers + insoluble polymers);

[f] Total Activity: kg•(mol-Fe)$^{-1}$•h$^{-1}$.

**Table 2** Steric effects of the *para*-alkyl substituents on oligomerization promoted by **L-Fe(acac)$_3$**/MAO[a].

| Run | Modifier | [-OH]/[Al] | Oligomer | | | Polymer | | *Act.*[b] |
|---|---|---|---|---|---|---|---|---|
| | | [mol/mol] | $Y_o$ [g] | α | % LAO | $Y_p$ [g] | wt% PE | |
| **1** | None | 0 | 2.35 | 0.76 | 98 | 1.10 | 31.9 | 3450 |
| **6** |  | 0.3 | 2.65 | 0.83 | 96 | 1.49 | 36.0 | 4140 |
| **7** | | 0.5 | 3.37 | 0.80 | 97 | 0.82 | 19.6 | 4190 |
| **8** | 4-MePh-OH | 0.7 | 2.20 | 0.74 | 99 | 0.036 | 1.6 | 2236 |
| **9** |  | 0.3 | 2.82 | 0.80 | 98 | 0.92 | 24.6 | 3740 |
| **10** | | 0.5 | 3.69 | 0.75 | 98 | 0.44 | 10.7 | 4130 |
| **11** | 4-$^i$PrPh-OH | 0.7 | 3.16 | 0.72 | 99 | 0.013 | 0.4 | 3173 |
| **12** |  | 0.3 | 2.83 | 0.75 | 97 | 0.66 | 18.9 | 3490 |
| **13** | | 0.5 | 2.86 | 0.72 | 98 | 0.20 | 6.5 | 3060 |
| **14** | 4-$^t$BuPh-OH | 0.7 | 2.02 | 0.70 | 99 | 0.004 | 0.2 | 2024 |
| **15** | | 0.9 | 0.20 | 0.67 | 99 | 0 | 0 | 200 |

[a] General conditions: pre-cat.: [Fe]=2 μmol; Al/Fe=1000; solvent: toluene, 50 ml; *T*=50 ℃; *P*=1 bar; t=30 min; [b] Total Activity: kg•(mol-Fe)$^{-1}$•h$^{-1}$.

**Table 3** Influence of *para*-alkyl substituents on MW and MWD of the insoluble polymers.

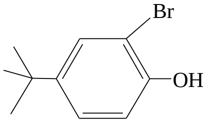
| Modifier | [-OH]/[Al] [mol/mol] | $M_w$ [g/mol] | $M_n$ [g/mol] | $M_w/M_n$ |
|---|---|---|---|---|
| None | 0 | 1815 | 639 | 2.84 |
| 4-MePhOH | 0.3 | 3307 | 1019 | 3.25 |
| | 0.5 | 3354 | 914 | 3.67 |
| | 0.7 | 950 | 632 | 1.50 |
| 4-$^i$PrPhOH | 0.3 | 2355 | 860 | 2.74 |
| | 0.5 | 1950 | 733 | 2.66 |
| | 0.7 | 711 | 564 | 1.26 |
| 4-$^t$BuPhOH | 0.3 | 2205 | 856 | 2.58 |
| | 0.5 | 1693 | 758 | 2.23 |
| | 0.7 | — | — | — |

**Table 4** Oligomerizations activated by the reaction products of 4-$^t$BuPhOH, $AlMe_3$ and water[a].

| Run | [-OH]/[Al] [mol/mol] | $[H_2O]/[Al]$ [mol/mol] | $AlMe_3$ [mmol] | Oligomer $Y_o$ [g] | Oligomer α | Oligomer % LAO | Polymer $Y_p$ [g] | Polymer wt% PE | *Act.*[b] |
|---|---|---|---|---|---|---|---|---|---|
| **16** | — | — | 4.0 | 0.056 | — | 99 | 0 | 0 | 56 |
| **17** | 1:1 | 0.9:1 | — | 0.027 | — | 99 | 0 | 0 | 27 |
| **18** | 1:1 | 0.9:1 | 0.5 | 0.59 | 0.66 | 99 | 0 | 0 | 590 |
| **19** | 1:1 | 0.9:1 | 1.0 | 0.50 | 0.66 | 99 | 0.022 | 4.2 | 522 |

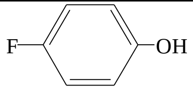
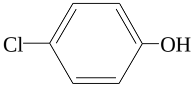
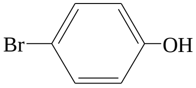
[a] General conditions: pre-cat.: **L-Fe(acac)$_3$**, [Fe]=2 *μ*mol; solvent: toluene, 50 ml; *T*=50 ℃; *P*=1 bar; t=30 min; [b] Total Activity: kg•(mol-Fe)$^{-1}$•h$^{-1}$.

**Table 5** Influence of 2-Br-4-$^t$BuPhOH on oligomerization promoted by **L-Fe(acac)$_3$**/MAO[a].

| Run | Modifier | [-OH]/[Al] | Oligomer | | | Polymer | | *Act.*[b] |
|---|---|---|---|---|---|---|---|---|
| | | [mol/mol] | $Y_o$ [g] | α | % LAO | $Y_p$ [g] | wt% PE | |
| **1** | None | 0 | 2.35 | 0.76 | 98 | 1.10 | 31.9 | 3450 |
| **20** | <br>2-Br-4-$^t$BuPh-OH | 0.1 | 1.85 | 0.70 | 98 | 0.19 | 9.3 | 2040 |
| **21** | | 0.2 | 0.82 | 0.69 | 99 | trace | — | 820 |
| **22** | | 0.3 | 0.27 | 0.69 | 99 | 0 | 0 | 270 |

[a] General conditions: pre-cat.: [Fe]=2 $\mu$mol; Al/Fe=1000; solvent: toluene, 50 ml; $T$=50 ℃; $P$=1 bar; t=30 min; [b] Total Activity: kg•(mol-Fe)$^{-1}$•h$^{-1}$.

**Table 6** Influence of the *para*-halogen substituted phenols on oligomerization promoted by **L-Fe(acac)$_3$**/MAO[a].

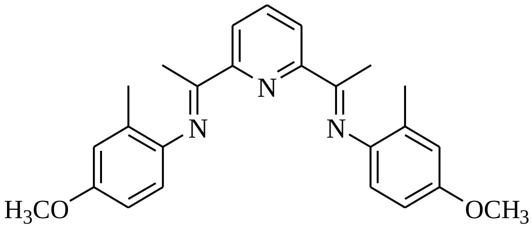
| Run | Modifier | [-OH]/[Al] | Oligomer | | | Polymer | | *Act.*[b] |
|---|---|---|---|---|---|---|---|---|
| | | [mol/mol] | $Y_o$ [g] | α | % LAO | $Y_p$ [g] | wt% PE | |
| **1** | None | 0 | 2.35 | 0.76 | 98 | 1.10 | 31.9 | 3450 |
| **23** |  | 0.3 | 4.08 | 0.82 | 96 | 1.31 | 24.3 | 5390 |
| **24** | | 0.5 | 2.29 | 0.73 | 98 | 0.10 | 4.2 | 2390 |
| **25** | 4-FPh-OH | 0.7 | 2.71 | 0.72 | 97 | 0.003 | 0.1 | 2713 |
| **26** |  | 0.3 | 3.62 | 0.75 | 96 | 0.85 | 19.0 | 4470 |
| **27** | | 0.5 | 2.94 | 0.73 | 97 | 0.33 | 10.1 | 3270 |
| **28** | 4-ClPh-OH | 0.7 | 2.69 | 0.73 | 97 | 0.20 | 6.9 | 2890 |
| **29** |  | 0.3 | 3.52 | 0.70 | 97 | 0.032 | 0.9 | 3552 |
| **30** | | 0.5 | 2.89 | 0.69 | 97 | 0.026 | 0.9 | 2916 |
| **31** | 4-BrPh-OH | 0.7 | 1.98 | 0.69 | 98 | 0.002 | 0.1 | 1982 |

[a] General conditions: pre-cat.: [Fe]=2 *μ*mol; Al/Fe=1000; solvent: toluene, 50 ml; *T*=50 ℃; *P*=1 bar; t=30 min; [b] Total Activity: kg•(mol-Fe)$^{-1}$•h$^{-1}$.

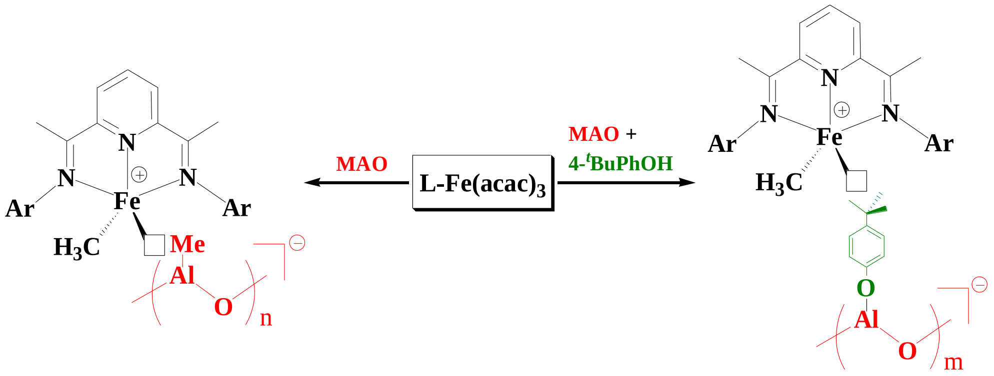
**Table 7** Influence of *para*-halogen substituents on MW and MWD of the insoluble polymers.

| Modifier | [-OH]/[Al] [mol/mol] | $M_w$ [g/mol] | $M_n$ [g/mol] | $M_w/M_n$ |
|---|---|---|---|---|
| None | 0 | 1815 | 639 | 2.84 |
| 4-FPhOH | 0.3 | 2220 | 792 | 2.80 |
| | 0.5 | 1626 | 743 | 2.19 |
| | 0.7 | — | — | — |
| 4-ClPhOH | 0.3 | 1398 | 631 | 2.22 |
| | 0.5 | 1180 | 635 | 1.86 |
| | 0.7 | 1202 | 698 | 1.72 |
| 4-BrPhOH | 0.3 | 551 | 429 | 1.28 |
| | 0.5 | 506 | 399 | 1.27 |
| | 0.7 | — | — | — |

# Schemes



**Scheme 1** Structure of 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine (**L**).



**Scheme 2** Proposed active ion-pair species of **L-Fe(acac)$_3$**/MAO system with or without the mediation of 4-$^t$BuPhOH. (MAO is referred to as a linear chain structure for the sake of simplicity, and m > n)

# Figures

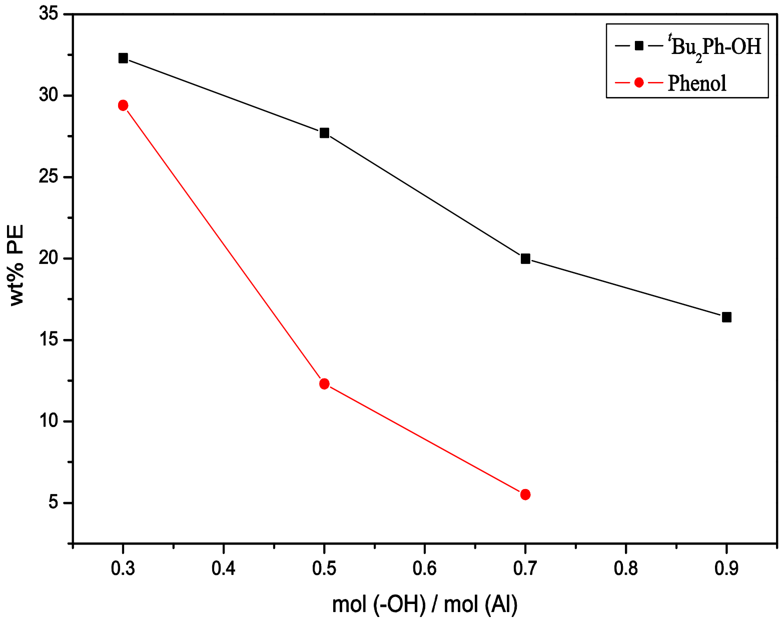


**Fig. 1** Mass fraction of insoluble polymers in $^t$Bu$_2$PhOH- and phenol-mediated systems as a function of [-OH]/[Al] molar ratio. The data of $^t$Bu$_2$PhOH can be referred to ref 12.

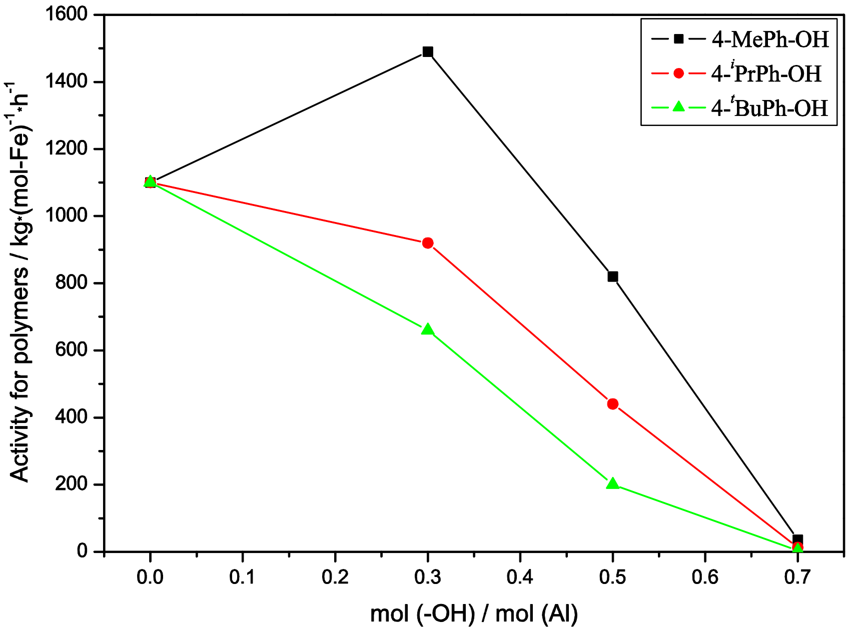


**Fig. 2** Activity for insoluble polymers in the 4-MePhOH-, 4-$^{i}$PrPhOH- and 4-$^{t}$BuPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

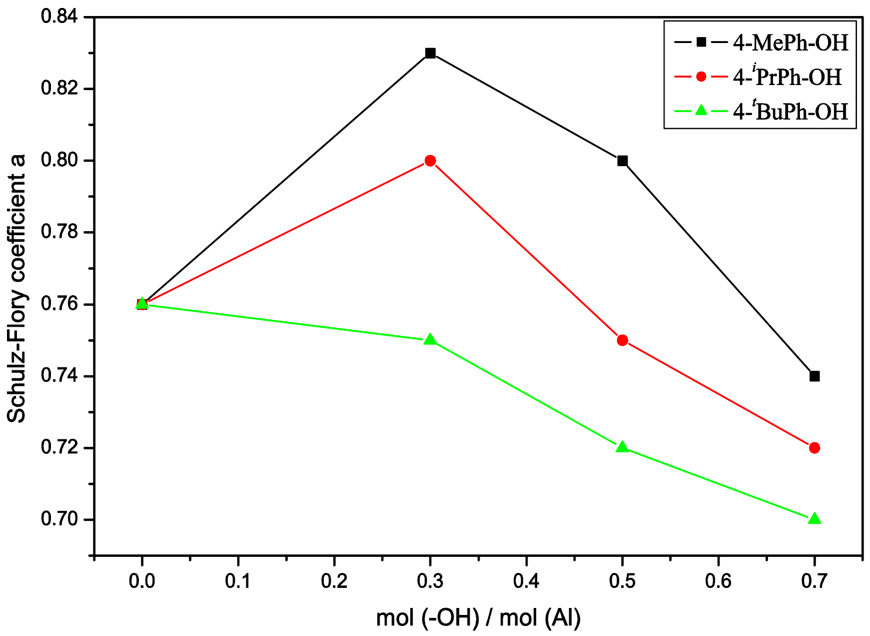


**Fig. 3** Schulz-Flory coefficients α of the 4-MePhOH-, 4-$^i$PrPhOH- and 4-$^t$BuPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

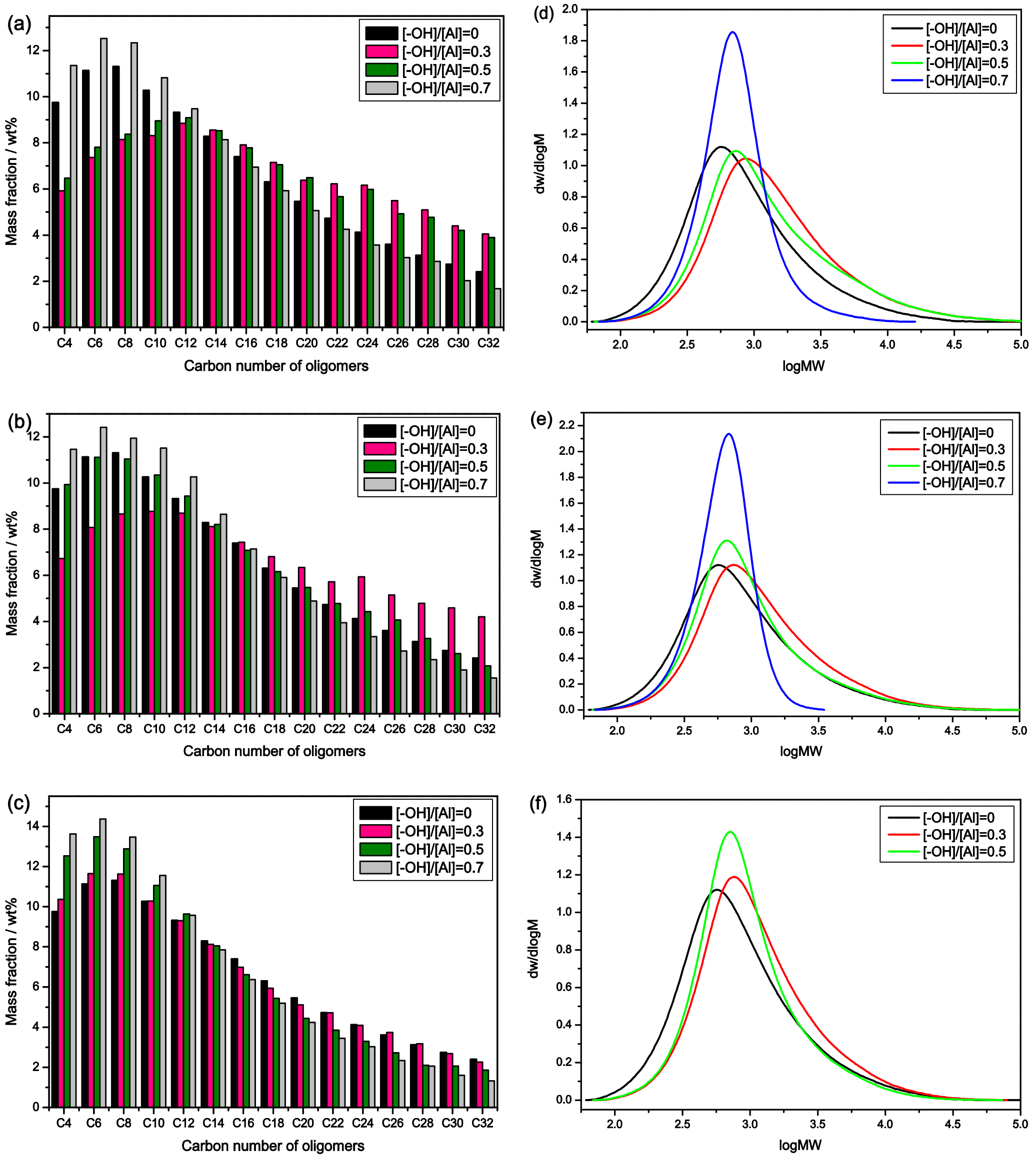


**Fig. 4** Oligomer distributions and polymer GPC curves obtained after the mediation of various *para*-alkyl phenolic compounds (a/d: 4-MePhOH; b/e: 4-$^i$PrPhOH; c/f: 4-$^t$BuPhOH).

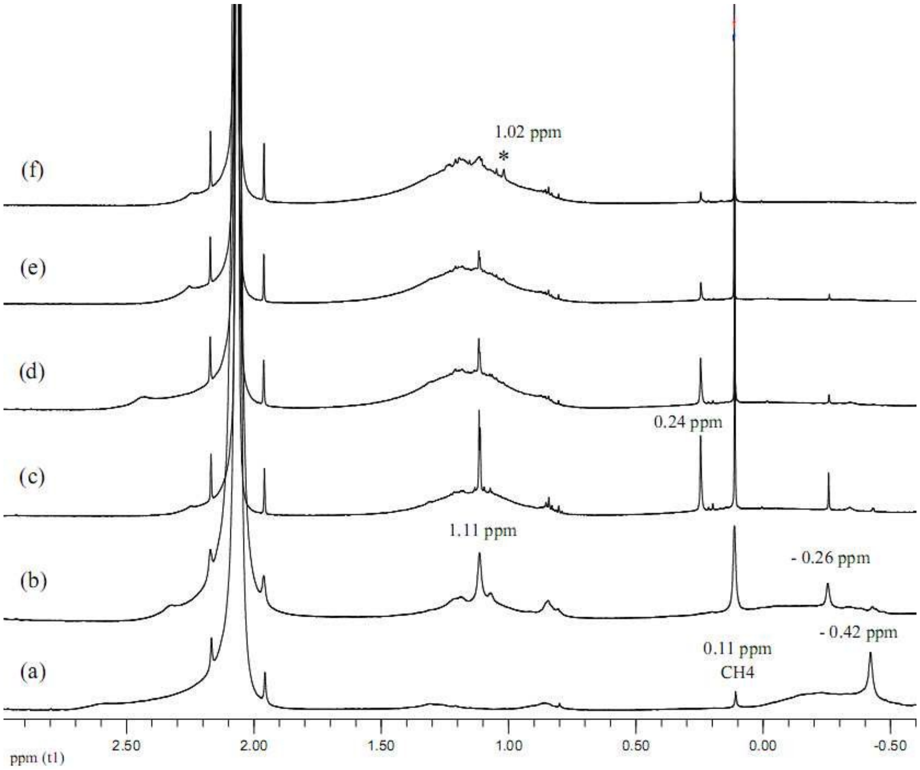


**Fig. 5** $^1$H NMR spectra of MAO/4-$^t$BuPhOH solutions in benzene-$d_6$ at different [-OH]/[Al] molor ratios (a: [-OH]/[Al]=0; b: 0.15; c: 0.3; d: 0.5; e: 0.7; f: 0.9).

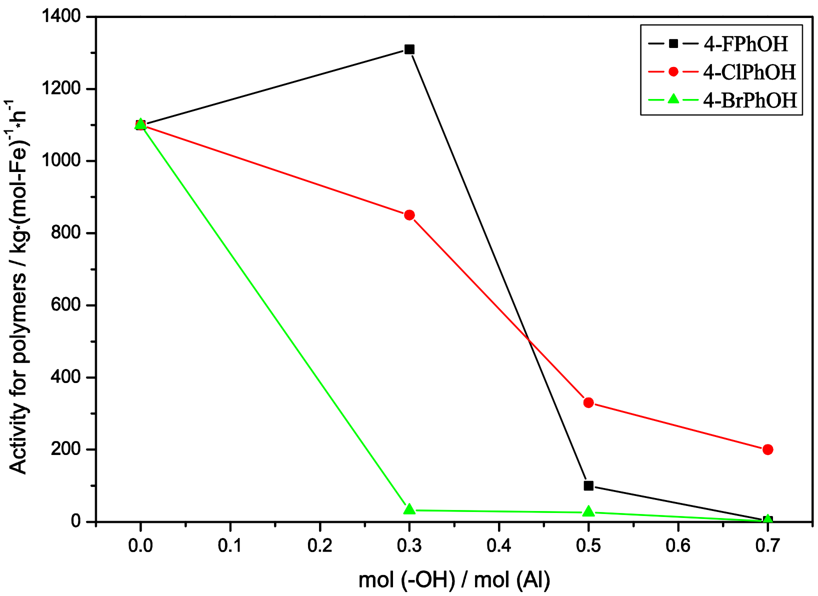


**Fig. 6** Activity for insoluble polymers in the 4-FPhOH-, 4-ClPhOH- and 4-BrPhOH-mediated systems as a function of [-OH]/[Al] molar ratio.

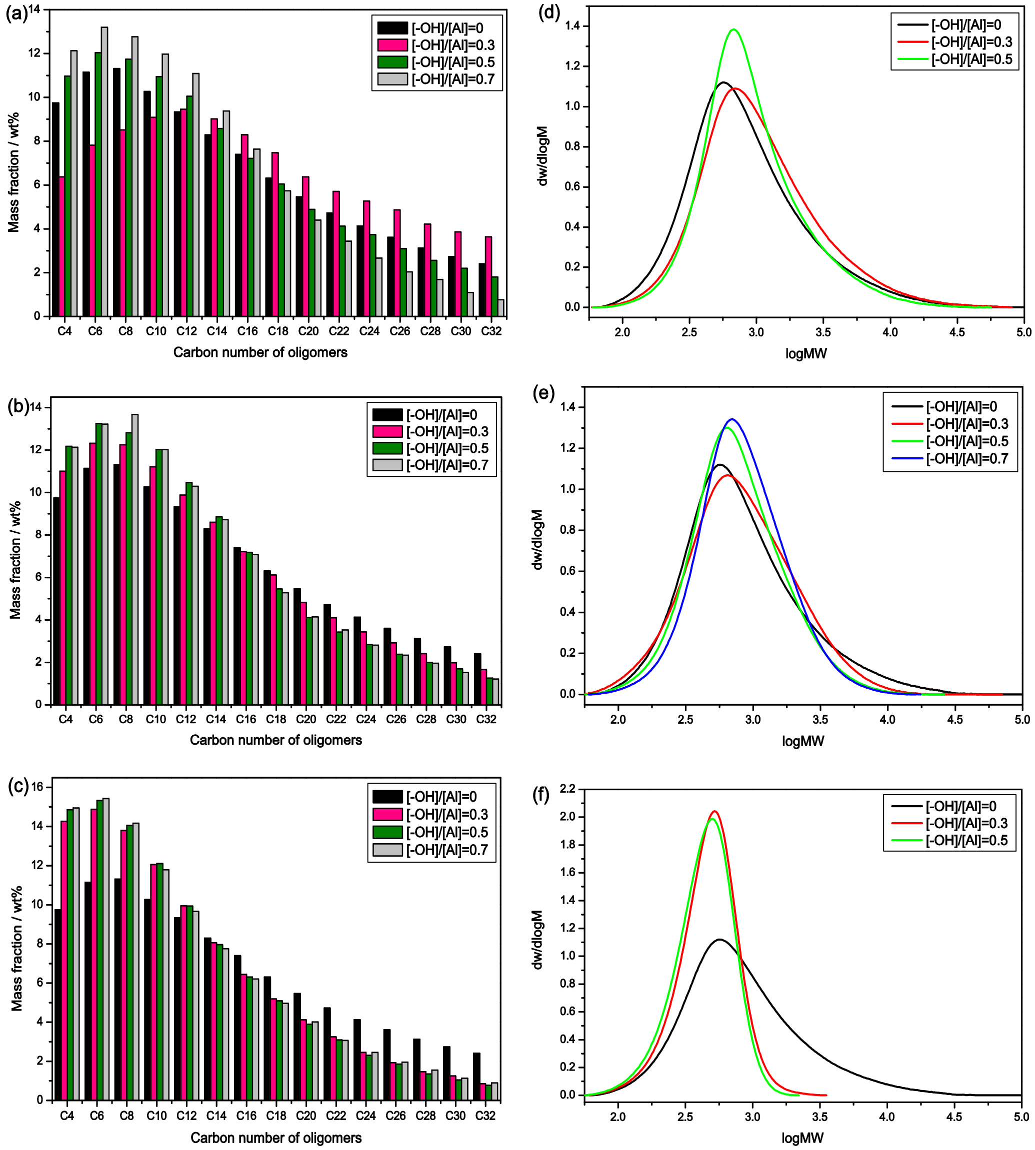


**Fig. 7** Oligomer distributions and polymer GPC curves obtained after the mediation of various *para*-halogen phenolic compounds (a/d: 4-FPhOH; b/e: 4-ClPhOH; c/f: 4-BrPhOH).