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The effect of phenolic compounds on salicylaldimine nickel-catalyzed ethylene oligomerization

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Abstract

A salen nickel complex has been prepared in good yield with ethylenediamine, salicylaldehyde and NiCl$_2$·6H$_2$O as raw materials. The structure of complex was characterized by FT-IR, ¹H NMR, UV, and ESI-MS. Upon activation with methylaluminoxane (MAO), the precatalyst showed high activity for ethylene oligomerization. In order to reduce the simultaneous production of insoluble polymers during the nickel-catalyzed ethylene oligomerization, a series of phenolic compounds were introduced as modifiers for the production of linear α-olefins. The researched result showed that the phenolic compounds have a significant impact on the selectivity of oligomers and the concentration of polymers. With the increase of phenolic compounds, the content of polymers decreased and the distribution of oligomers was gradually shifted toward lighter olefins. Especially, sterically hindered 4-tert-butyphenol was proved to be an efficient polymer-retarding modifier among the studied phenolic compounds in this work. Furthermore, the retarding effect of phenolic compounds toward insoluble polymers may be mainly related to their interaction with MAO, giving rise to larger MAO aggregates.

Keywords: Salen nickel complex, Catalyst, Ethylene oligomerization, Modifier

1. Introduction

Linear α-olefins are extensively used as comonomers in the production of linear low-density polymers (LLDPE) and manufacture of detergents, plasticizers, and synthetic lubricants.¹ Ethylene oligomerization, as one of the major processes for the production of linear higher α-olefins,² is of considerable academic and industrial interest. Nickel catalyst, one of transition-metal-based oligomerization catalysts has received high-profile since they provided selective ethylene
oligomerization. Since Shell Higher Olefins Process (SHOP) nickel (II)-based catalysts was discovered, metal nickel (II) complexes have been attracting much attention owing to the fact that they are less sensitive to protonic solvents and polar monomers.3-4

The first salen ligand, was discovered by Combes in the study of the reaction of diamines and dialdehydes.5 Subsequently, salen ligand derivative and their metal complexes were synthesized,6 with increasingly people noticing the value of salen metal complexes. Past decades have witnessed the wide study and application on salen metal complexes,7-10 with its importance being gradually recognized by people. Based on study above, we synthesized a salen nickel complex ([NOON]Ni) with salicylaldehyde-amine-based pro-ligand (scheme 1) to be catalyst for ethylene oligomerization to linear α-olefins. However, the distribution of the obtained ethylene oligomers was very broad, with the containing of insoluble polymers in the total products. Such simultaneous production of polymers during oligomerization serve as a potential limit for the commercialization.

Many efforts have been made to solve this problem, in which, one way is to change the ligand structure, while another is the addition of modifiers. Moreover we envisioned that some difference could be made through the addition of modifiers, on the basis that additives have already been used in a number of cases. For example, siloxanes were used as electron donor in propylene polymerization with MgCl2-supported Ziegler-Natta catalysts.11-12 Hydrogen was used as an efficient promoter for PNP/Cr(III)/MAO catalyzed ethylene tetramerization toward 1-octene.13 Ye. et al reduced the production of insoluble polymers by introducing siloxanes and phenols into the iron catalytic system.14-15 Encouraging us to introduce phenolic compounds into the nickel-catalyzed ([NOON]Ni) system, wishing the reduction of the formation of insoluble polymers and improvement of the content of C8-C12. We proposed an effective strategy to retard the simultaneous polymer
formation during ethylene oligomerization by treatment of MAO with phenolic compounds. The effect of phenolic compounds on nickel-catalyzed ethylene oligomerization was investigated at first, along with the discussion of the mechanism of phenolic functions.

2. Experimental Section

2.1 Materials

Solvents (cyclohexane, toluene) were analytical grade and dried by refluxing over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 10 wt % in toluene) was purchased from Sigma-Aldrich. Ethylenediamine, ether, cyclohexane, toluene and methanol were obtained by Tianjin Kermel Chemical Regent. Salicylaldehyde was provided by Tianjin Guanfu Fine Chemical Industry Research Institute. P-cresol, Phenol, 4-bromophenol (4-BrPhOH, 99%), 4-isopropylphenol (4-iPrPhOH), 4-tert-butylphenol (4-tBuPhOH), 1-Naphthol and 2-Naphthol were purchased from Aladdin. CDCl₃ was purchased from Sigma-Aldrich.

2.2 Synthesis of nickel catalyst

2.2.1 Synthesis of ligand

The procedure previously reported by Tao was followed, all synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in nitrogen glove-box, to a solution of ethylenediamine (2.67 mL, 0.04 mol) in methanol (20 mL), was added 2-hydroxy-benzaldehyde (12.8 mL, 0.12 mol) under nitrogen atmosphere, and the mixture was allowed to stir at 70 °C for 12 h. The mixture was filtered to remove Na₂SO₄, and the ligand solution was attained. The precipitate was obtained after the ligand solution crystallized at -15 °C for 24 h. The resulting precipitate was filtered off, and then washed three times with ether. The product was
dried under vacuum at 50 °C to a residue solid as light-yellow powders (6.83 g, 63%) (Scheme 1).

FT-IR (KBr, cm⁻¹): 3689 (m), 1635 (m), 1609 (m), 1283 (s). λmax (nm): 260, 317. ¹H NMR (400 HMz, CDCl₃, ppm): δ: 3.94 (t, 2H, CH₂), 6.93 (t, 1H, Ar-H), 7.08 (d, 1H, Ar-H), 7.21 (d, 1H, Ar-H), 8.31 (s, 1H, N=CH), 13.17 (s, 1H, OH). MS: m/z: 269.1 [M+H]⁺.

2.2.2 Synthesis of metal complex

The metal complex was synthesized by following the established literature procedure.¹⁶ The methanol solution (15 mL) of NiCl₂·6H₂O (1.93 g, 8.0 mmol) was added dropwise to the methanol solution (25 mL) of ligand (1.0 g, 3.7 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 24 h. The resulting suspension was filtered, and red-brown powders was obtained. The product was washed three times with ether. The residue was dried in vacuum to afford a light red-brown powder (0.901 g, 75%) (Scheme 1). FT-IR: (KBr, cm⁻¹): 3425 (m), 1627 (s), 1602 (s), 1294 (s). λmax (nm) 248, 331. MS: m/z 325.1 [M+H]⁺. Anal. Calcd. for C₁₆H₁₁N₂O₂Ni: C, 59.13, H, 4.31, N, 8.62, Found: C, 59.45, H, 4.39, N, 8.61.

2.3 General procedure for ethylene oligomerization reaction

Ethylene oligomerization reactions were carried out in a 1000 mL stainless steel reactor with magnetic stirring. The reactor was heated at 120 °C for about 30 min and purged with dry nitrogen. After cooling to the reaction temperature (50 °C), 200 mL of cyclohexane (solvent), then desired amounts of phenolic compound and MAO in solvent were injected into the reactor under N₂ protection and the resulting mixture was stirred at ≈500 rpm for 5 min. Finally, the solution of nickel complex in solvent (1.22 μmol/mL, 50 mL) was added to the reactor under ethylene atmosphere, the ethylene pressure was increased to desired value and maintained at this level by constant feeding of
ethylene. After 30 min, the reaction was stopped by releasing the excess ethylene. The product was then centrifuged to separate the oligomers in cyclohexane and the insoluble polyethylene wax. The wax was firstly put on a filter paper and washed sufficiently with cyclohexane to drip down the light fraction in the filtrate, which was then merged into the oligomers. Secondly, the wax was washed with ethanol (10% HCl) 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.

2.4 Characterization

Infrared spectra were recorded in a KBr disc matrix using a Bruker Vector 22 IR spectrophotometer. The UV-visible spectra were carried out on a UV-1700 ultraviolet-visible spectrophotometer by using methanol as a solvent. \(^1\)H NMR spectra were carried out on a Varian NOVA 400 MHz instrument in CDCl\(_3\). Electrospray ionization mass spectrometry (ESI-MS) datas were collected on the micrOTOF-Q I mass spectrometer. Elemental analysis was carried out on a Heraeus element analyzer (Germany). The total catalytic activity was quantified by the amount of products. For oligomers, individual olefins were identified by GC/MS. \(C_{12}\) olefin isomers were used to determine the linearity. Further quantitative analyses were performed by Fuli GC9720 equipped with a HP-PONA column (50m×0.2mm×0.5m) using n-heptane as the internal standard. The injector temperature was 300°C and the following temperature program was: 50 °C/5 min, 50-280 °C/10 °C·min\(^{-1}\). Under this temperature program, olefins ranging from \(C_4\) to \(C_{28}\) can be detected. The wt% of PE = (mass PE/total mass of products)-100, the yield of the soluble oligomers was based on GC yields determined by comparison to the internal standard, the yield of volatile \(C_4\) fraction was determined by extrapolation of \(\alpha\) value. The \(\alpha\) value is a characteristic coefficient of the ethylene oligomerization 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, \( C_{22} \) and \( C_{24} \) in this case (Equation).

\[
\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of termination}} = \frac{\text{mol}(C_{n+2})}{\text{mol}(C_n)}
\]

3. Result and discussion

3.1 Characterization of metal complex

The structure of salen ligand and nickel complex were characterized by FT-IR, \(^1\)H NMR, UV, elemental analysis and ESI-MS, with the characterization results being basically consistent with Tao’s previous work.\(^{16}\) Detailed results can be seen from the supplementary section.

3.2 Effects of phenolic compounds on ethylene oligomerization

3.2.1 Effect of phenol on ethylene oligomerization

Ethylene oligomerization reactions were undertaken with the \{NOON\}Ni pre-catalyst, with MAO as the cocatalyst ([Al]/[Ni] = 275) under ethylene pressure of 4 MPa at 50 °C. However, the distribution of the obtained ethylene oligomers ranging from \( C_4 \) to \( C_{28+} \), was very broad, and contained a large amount (43.90 wt%) of insoluble polymers (PE). The effect of phenolic compounds on ethylene oligomerization was investigated to reduce the formation of insoluble polymers and improve the content of \( C_8 \) to \( C_{12} \).

The effect of Phenol on the selectivity of oligomers and the concentration of polymers were showed in Table 1. Phenol, as is shown, exerted a significant impact on the selectivity of oligomers and the concentration of polymers. With the [Phenol]/[Al] molar ratio increasing from 0.1 to 0.4, the mass fraction of insoluble polymers in the total products decreased from 43.90 wt% to 30.20 wt%. However, a further increase of [Phenol]/[Al] to 0.5, instead of keeping reducing the polymer, greatly
deactivated the catalyst, deactivation process like which may be attributed to the interaction between the free phenol and the active centers. This result implied that the maximum phenol we could introduce into our system was around [Phenol]/[Al]=0.4. In addition, as can be seen from Figure. 1, at [Phenol]/[Al]≤0.4 with the increase of [Phenol]/[Al], the distribution of oligomers was gradually shifted toward lighter olefins, which may be attributed to the modification of MAO molecules by phenol. The decrease of the α indicated the enhanced relative rate of chain termination (mainly via β-H elimination).

Besides the influence on the product distribution, phenol also exerted remarkable effect on the activity. The total activity for ethylene oligomerization, as revealed in Table 1, increased firstly and then decreased with the increase of molar ratio of [Phenol]/[Al]. The total activity was largest when the molar ratio of [Phenol]/[Al] was 0.1, reaching up to 735 kg·(mol Ni)$^{-1}$·h$^{-1}$. However, the addition of phenol to the ethylene oligomerization system led to a decrease of the activities for insoluble polymers. The activity for insoluble oligomers, as shown in Figure. 2, dramatically decreased from 303 to 164 kg·(mol Ni)$^{-1}$·h$^{-1}$ when the molar ratio of [Phenol]/[Al] increased from 0 to 0.4. It seems that the phenol could reinforce the active intermediates responsible for the soluble oligomers while inhibit the active intermediates responsible for the insoluble polymers, confirming that both of the oligomerization activity and the product distribution can be efficiently tuned by the addition of phenol.

3.2.2 Effect of p-alkyl substituted phenolic compounds on ethylene oligomerization

To explore whether bulky substituents on the para-position could make the phenolic compounds more effective polymer-retarding modifiers, and improve the proportion of valuable α-olefins. 4-isopropylphenol (4-PrPhOH) and 4-tert-butylphenol (4-BuPhOH) were used as
modifiers to investigate the effects of p-alkyl substituted phenolic compounds on ethylene oligomerization, with the research results being shown in Table 2. The effect of 4-iPrPhOH and 4-tBuPhOH on ethylene oligomerization, as evident from Table 2, was very striking. The mass fraction of insoluble polymers in the total products, with concentration of phenolic compounds increasing, was found to be largely reduced compared with that of the pure {NOON}Ni/MAO catalytic system. The content of insoluble polymers reduced to 26.84 wt% and 19.21 wt%, respectively, when the molar ratio of [ArOH]/[Al]=0.4 was applied. The polymer-retarding ability of two phenolic compounds was proven to increase in the order of 4-iPrPhOH < 4-tBuPhOH. Two phenolic compounds not only exerted a greater influence on the proportion of polymers, but also on the distribution of oligomers. With the increase of molar ratio of [ArOH]/[Al], the distribution of oligomer, as shown in Figure 3, was gradually shifted toward lighter olefins, and the selectivity of C₈ to C₁₂ was best when the molar ratio of [ArOH]/[Al] was 0.2.

Furthermore, when 4-iPrPhOH and 4-tBuPhOH were used as modifiers, the catalytic activity increased firstly and decrease followingly with the increase of [ArOH]/[Al]. When the ratio of [ArOH]/[Al] were 0.1 (4-iPrPhOH) and 0.2 (4-tBuPhOH), the catalytic activities were highest, reaching up to 734 kg·(mol Ni)⁻¹·h⁻¹ and 808 kg·(mol Ni)⁻¹·h⁻¹, respectively. However, with the molar ratio of [ArOH]/[Al] increasing from 0 to 0.4, the activity of insoluble polymers decreased (Figure 4), which is consistent with the observations in phenol-mediated system.

On the other hand, the enlargement of para-substituent size ranging from isopropyl to tert-butyl would result in the reduction of the coefficient α, respectively (Table 2). The chain termination was supposed to be enhanced by the larger para-substituent modified MAO molecules, thus generating products with lower molecular weight. All of these combined results provide strong evidence that
both the oligomerization activity and the product composition can be significantly tuned by the p-alkyl substituted phenols.

### 3.2.3 Effect of para-halogen substituted phenolic compound on ethylene oligomerization

With a strong electron-withdrawing effect, the bromo group could reduce the electron-density of the -OH group and promote the reaction between the phenolic compounds and MAO, thereby helping explain that 4-BrPhOH was used as a modifier for further study. With the ethylene oligomerization results being shown in Table 3, the influence of the para-halogen substituted phenol was similar to para-alkyl substituted ones, with the obvious the polymer-retarding effect of 4-BrPhOH. With the increase of molar ratio of [ArOH]/[Al] from 0.1 to 0.4, the mass fraction of insoluble polymers in the total products reduced from 43.90 wt% to 24.32 wt%, with the distribution of the soluble oligomers shifting toward lighter olefins (Figure. 5) as well. When the molar ratio of [ArOH]/[Al] was 0.2, the content of C\textsubscript{8} to C\textsubscript{12} was largest.

At [ArOH]/[Al]≤0.4, the addition of [ArOH]/[Al] led to the decrease of activity of polymers (Figure. 6), but with only marginal changes being shown in the total activity, this was also consistent with the observations in phenol-mediated system. The increase of the ratio from 0 to 0.4 led to the reducing trend in α, indicating the enhanced relative rate of chain termination, implying that the large size of bromo group increased the reactivity of -OH group, and 4-BrPhOH could be highly effective in the interaction with MAO.\textsuperscript{17-18} 4-BrPhOH is thus proven to be an ideal modifier for the catalytic system in ethylene oligomerization.

### 3.2.4 Effect of Naphthol on ethylene oligomerization

In order to confirm the effect of naphthol, a kind of phenol reagent with large steric hindrance, on the activity and the product distribution of ethylene oligomerization, 1-naphthol and 2-naphthol
were used as modifiers for further study. The catalytic activity and product distribution, as can be seen from Table 4, were also largely influenced by 1-naphthol and 2-naphthol. With the increase of molar ratio of \([\text{ArOH}]/[\text{Al}]\) from 0 to 0.4, the mass fraction of insoluble polymers in the total products reduced to 28.53 wt\% and 23.46 wt\%, respectively, which was also accompanied by the gradual shift of the distribution of oligomers toward lighter olefins (Figure 7). The 2-naphthol exerted a greater effect on the selectivity compared with 1-naphthol, when the molar ratio of \([\text{ArOH}]/[\text{Al}]\) was 0.3, the content of C\(_8\) to C\(_{12}\) was largest.

When the naphthol was added to the system of ethylene oligomerization, the total activity of catalyst decreased to certain degree compared with the system without naphthol, which may be related to the bicyclic structure of naphthol. With the molar ratio of \([\text{ArOH}]/[\text{Al}]\) increasing from 0 to 0.4, the activity of polymers decreased (Figure 8).

These results support our hypothesis that naphthol could retard the formation of insoluble polymers. Its molecular volume, due to the bicyclic structure of naphthol, is significantly larger than that of benzene ring, and the larger group modified MAO molecules is supposed to enhance the chain termination, thus inducing the \(\beta\)-H elimination to \(\alpha\)-olefins, inhibiting the formation of polymers. The naphthol may be a more efficient polymer-retarding modifier compared with the system with phenol.

4. Reaction mechanism of the effect of phenolic compounds

According to Bryliakov's work,\(^{19-20}\) ion-pair active intermediates would be generated in (NOON)Ni systems with the activation of MAO, thereby making the active nickel centers be surrounded by huge anionic [Me-MAO]- clusters. By the cation-anion distance, additional steric hindrance from the MAO clusters could be imposed on the active centers, which may play a role in
regularly inhibiting the rotation of propagating chains and the β-H elimination to α-olefins.

The spectra of systems mixing 4-tBuPhOH and MAO, as shown in Figure 9, firstly, confirmed the trapping of AlMe₃ by phenolic compounds. The addition of 4-tBuPhOH to MAO led to the formation of AlMe₂(OAr) and CH₄, as demonstrated by appearance in the ¹H NMR spectrum of diagnostic resonance at δ = 1.09 ppm and the enhancement of a singlet at 0.11 ppm. On the other hand, 4-tBuPhOH could also react with part of the MAO-Al-Me bonds of MAO, leading to the formation of MAO-Al-OAr and further enhancing the CH₄ release. Secondly, a new broad resonance was significantly appeared around δ = 0.8-1.4 ppm by the addition of 4-tBuPhOH, with similar phenomenon being observed by Macchioni and co-workers, finding that a broad band at δ = 1.50 ppm was present with the reaction of DMAO and tBu₂PhOH, which was then tentatively assigned to large and polydisperse MAO/tBu₂PhOH adducts. Therefore, the new band around δ = 0.8-1.4 ppm in our study could be assigned to larger 4-tBuPhOH modified MAO aggregates. The interaction between the phenolic compounds and MAO should play a key role in accounting for the polymer-retarding effect. On the basis of the ¹H NMR studies, it occurred to us that the influence of 4-tBuPhOH on MAO, with the corresponding active species being simply illustrated as shown in Scheme 2.

5. Conclusions

In this contribution, a salen nickel complex was synthesized and characterized, the complex was evaluated as a catalyst in ethylene oligomerization. A series of phenolic compounds were used to research their effect on nickel complex. It was found that phenolic compounds were effective polymer-retarding modifiers, and with the increasing dosage of the phenols, the mass fraction of insoluble polymers in the total products would be largely reduced. Especially, sterically hindered
4-tert-butyphenol was proved to be an efficient polymer-retarding modifier among the studied phenolic compounds in this work, when the molar ratio of [ArOH]/[Al] was 0.2, it could improve the selectivity of C₈ to C₁₂ while maintaining a higher activity. From these work, we guess that the retarding effect of phenolic compounds toward insoluble polymers is mainly related to their interaction with MAO, giving rise to larger MAO aggregates. Which would betterly separate the nickel centers and the MAO cages in the ion-pair active species, and promote β-H elimination to lighter olefins. There is still a lot of work to be done, more detailed studies on the interaction of phenolic compounds with nickel complexes are going on our group.

Acknowledgement

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References


10.1021/ja0372412.


Figure and Scheme Captions

**Scheme 1.** Synthetic route of nickel complex.

**Figure 1.** Oligomer distributions with Phenol as modifier.

**Figure 2.** Activity for insoluble polymers with Phenol as modifier.

**Figure 3.** Oligomer distributions with 4-PrPhOH and 4-tBuPhOH as modifier (a: 4-PrPhOH; b: 4-tBuPhOH).

**Figure 4.** Activity for insoluble polymers with 4-PrPhOH and 4-tBuPhOH as modifier.

**Figure 5.** Oligomer distributions with 4-BrPhOH as modifier.

**Figure 6.** Activity for insoluble polymers with 4-BrPhOH as modifier.

**Figure 7.** Oligomer distributions with 1-Naphthol and 2-Naphthol as modifier (c: 1-Naphthol; f: 2-Naphthol).

**Figure 8.** Activity for insoluble polymers with 1-Naphthol and 2-Naphthol as modifier.

**Figure 9.** $^1$H NMR spectra of MAO/4-tBuPhOH solutions in CDCl$_3$ at different [ArOH]/[Al] molar ratios (a: 0; b: 0.1; C: 0.2; d: 0.3; e: 0.4).

**Scheme 2.** Reaction mechanism for the effect of phenolic compounds
Table 1 Effect of phenol on ethylene oligomerization

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<th>Entry</th>
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*Reaction conditions unless otherwise described: cyclohexane=200 mL, [Ni]=61 μmol, MAO, T=50 °C, P=4 Mpa, [Al/Ni]=275, reaction time=30 min.*
Table 2 Effect of p-alkyl substituted phenolic compounds on ethylene oligomerization

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Reaction conditions unless otherwise described: cyclohexane=200 mL, [Ni]=61 μmol, MAO, T=50 °C, P=4Mpa, [Al/Ni]=275, reaction time=30 min.
Table 3 Effect of para-halogen substituted phenolic compound on ethylene oligomerization

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*Reaction conditions unless otherwise description: cyclohexane=200 mL, [Ni]=61 μmol, MAO, T=50 °C, P=4Mpa, [Al/Ni]=275, reaction time=30 min.*
<table>
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<th>Entry</th>
<th>Modifier</th>
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<th>Total Activity (kg·(mol Ni)⁻¹·h⁻¹)</th>
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Reaction conditions unless otherwise description: cyclohexane=200 mL, [Ni]=61 μmol, MAO,

T=50 °C, P=4Mpa, [Al/Ni]=275, reaction time=30 min.
Scheme 1. Synthetic route of nickel complex.
Figure 1. Oligomer distributions with Phenol as modifier.
Figure 2. Activity for insoluble polymers with Phenol as modifier.
Figure 3. Oligomer distributions with 4-PrPhOH and 4-BuPhOH as modifier (a: 4-PrPhOH; b: 4-BuPhOH).
Figure 4. Activity for insoluble polymers with 4-iPrPhOH and 4-tBuPhOH as modifier.
Figure 5. Oligomer distributions with 4-BrPhOH as modifier.
Figure 6. Activity for insoluble polymers with 4-BrPhOH as modifier.
Figure 7. Oligomer distributions with 1-Naphthol and 2-Naphthol as modifier (c: 1-Naphthol; f: 2-Naphthol).
**Figure 8.** Activity for insoluble polymers with 1-Naphthol and 2-Naphthol as modifier.
Figure 9. $^1$H NMR spectra of MAO/4-tBuPhOH solutions in CDCl$_3$ at different [ArOH]/[Al] molar ratios (a: 0; b: 0.1; C: 0.2; d: 0.3; e: 0.4).
Scheme 2. Reaction mechanism for the effect of phenolic compounds.