Chapter 5. Alkylation of phenol with terminally vinylidene unsaturated poly(hexene-1)

5.1 Introduction

Functional poly(olefin)s have assumed importance because they contribute to new properties to otherwise inert poly(olefin)s [1-5]. Appropriately functionalized poly(olefin)s are useful as adhesion promoters, are capable of being coated, painted or dyed. Additionally, the functional groups either on the polyolefin backbone or at the chain end can be used for the synthesis of graft and block copolymers, which find application as compatibilizers and interfacial agents.

There are two broad approaches to the synthesis of functional poly(olefin)s, namely, "chain end" functionalization and "in chain" functionalization. Synthesis of functional poly(olefin)s by the first method involves either chemical reactions on preformed, terminally unsaturated poly(olefin)s or through use of appropriate chain transfer agents, whereas, the second approach involves the copolymerization of olefins with precursors which do not interfere in polymerization, followed by organic chemical transformations on the preformed polymers.

Synthesis of terminally functionalized poly(olefin)s by chain transfer method involves the use of appropriate chain transfer agent in metallocene catalyzed polymerization of olefins. The most commonly used chain transfer agents in heterogeneous Ziegler-Natta catalysts are molecular hydrogen [6-8] and ZnEt₂ [9]. Marks and coworkers studied silanes as efficient chain transfer agents in olefin polymerization using homogeneous catalysts[10, 11]. Xu and Chung [12, 13] demonstrated that organoboranes containing a B-H group are efficient chain transfer agents. Hessen and coworkers studied thiophene as a chain transfer agent in ethylene polymerization using neutral lanthanum catalyst system [14, 15]. More recently Chung and Dong reported the consecutive chain transfer to p-methylstyrene in presence of hydrogen during metallocene catalyzed copolymerization of propylene and p-methylstyrene [16]. There are several reports in the literature which define synthetic strategies for poly(olefin)s bearing various terminal functional groups such as OH, COOH, NH₂ etc by post polymerization functionalization of terminally unsaturated poly(olefin)s [17-25].

Metallocene and post metallocene catalysts offer significant advantages for the synthesis of functional poly(olefin)s. When α-olefins are polymerized using homogeneous
metallocene / MAO (methyl aluninoxane) catalysts, several chain transfer reactions (such as β-hydrogen transfer etc) are found to occur. Such chain transfer reactions result in terminally unsaturated poly(olefin)s. High degree of terminal unsaturation (> 95%) and narrow molecular weight distribution (MWD = 2) are some of the distinguishing features of poly(olefin)s obtained using metallocene catalysts.

In this chapter synthesis of phenol/2,6-dimethyl phenol terminated poly(hexene-l) by alkylation of phenol/2,6 dimethyl phenol with vinylidene terminated poly(hexene-l) will be discussed. Characterization of phenol terminated poly(hexene-l) by NMR, (especially $^{31}$P NMR), UV, IR etc. are presented.

5.2. Experimental

5.2.1 Materials
Vinylidene terminated poly(hexene-l) with Mn varying from 400-10 000 reported in chapter-3 was used for the alkylation of phenol / 2,6 dimethyl phenol. Phenol and n-hexane were obtained from s.d. fine chemicals, Boisar, India. Nonyl phenol was obtained from Herdillia Chemicals, Mumbai. 2,4,4-trimethyl 1-pentene, 2,6-dimethyl phenol, n-butylphenol, bisphenol-A, 2-chloro-1,3,2-dioxophospholane (DOP), and chromium tris (acetylacetonate) were obtained from Aldrich, USA. BF$_3$:OEt$_2$ was obtained from Fluka (Germany).

5.2.2 Purification
Vinylidene terminated poly(hexene-l)s obtained from chapter-3 were dissolved in n-hexane and dried over anhydrous sodium sulphate. Phenol and 2,6-dimethyl phenol were purified by distillation. n-Hexane was treated with H$_2$SO$_4$ to remove sulfur distilled and dried over sodium metal wire. 2,4,4-trimethyl 1-pentene was distilled under nitrogen atmosphere followed by distillation by freeze and thaw technique. BF$_3$:OEt$_2$ was distilled under reduced pressure and stored at 0°C. 2-Chloro-1,3,2-dioxophospholane (DOP), bisphenol-A and chromium tris (acetylacetonate) were used as received.

5.2.3 Functionalization
Alkylation of phenol/2,6-dimethyl phenol
The alkylation of phenol/2,6-dimethyl phenol with either 2,4,4-trimethyl 1-pentene or vinylidene terminated poly (hexene-1) was carried out as described below.
A four necked 250 mL round bottom flask equipped with a magnetic needle, reflux condenser, addition funnel, septum adapter and thermowell was flame dried and cooled under argon. 50 mL of dried n-hexane was transferred into the flask by syringe followed by 50 mmol of phenol/2,6-dimethylphenol. The terminally unsaturated oligomer (10 mmol of > C=C) (dried) was dissolved in 50 mL of n-hexane in a separate round bottom flask. The oligomer solution was transferred into the separating funnel of four-necked flask by cannula. The boron trifluoride etherate catalyst (7.6 mmol) was added into the phenol solution followed by dropwise addition of oligomer solution from a separating funnel at 40-45°C.

After the olefin addition (8-10 h), the temperature was raised to 50-55°C and stirring was continued for 30 h. The flask was cooled to room temperature and approximately 150 mL of water was slowly added and the content of the flask was transferred to a separating funnel. The aqueous layer was removed and the organic layer was washed 8-10 times with hot water (40-50°C) followed by washing repeatedly with alkali and 50% aqueous solution of methanol. The alkali and methanol were removed by washing with cold water. Washing was continued until the aqueous and organic layers were free of phenol.

The organic layer was washed with 0.1 N HCl. The acid was removed by further washings, and the organic layer was dried over anhydrous Na₂SO₄. Finally the solvent was removed by rotary evaporation and the product was dried at 60°C under vacuum.

Alkylation of bisphenol-A

Alkylation of bisphenol-A was carried in 1,2-dichloroethane at 70°C (since bisphenol-A is insoluble in n-hexane at 50°C) using procedures identical to that for phenol. The reaction was worked up by extracting the organic layer several times with water followed by washing the organic layer with acetone to remove all unreacted bisphenol-A. The acetone was removed by further washing with water.

5.2.4 Analysis

The number average degree of functionality (Fn) was calculated as

\[
Fn (\text{mol} \% ) = \left( \frac{Mn \text{ by VPO}}{Mn \text{ by NMR or UV}} \right) \times 100.
\]

Quantitative analysis of phenol end group using UV/Visible spectrophotometer

Concentration of phenol group in functionalized poly(hexene-1) was determined using UV/Visible spectrophotometer using n-butyl phenol as the standard. A standard experiment was carried out with n-butyl phenol.
First various solutions of n-butyl phenol in n-hexane was made in different concentration range. Absorbance for each solution was measured at $\lambda_{\text{max}} = 276.5$ nm. Taking absorbance in the X-axis and concentration in the Y-axis, a standard plot was made. A straight line was obtained passing through the origin, and slope was calculated. Then a known weight of phenol terminated poly (hexene-1) dissolved in 10 mL of n-hexane and absorbance for the corresponding solution was noted. Knowing the absorbance of phenol terminated poly (hexene-1) solution and the slope of the line for n-butyl phenol, the concentration of phenol group in the poly (hexene-1) was determined.

**Quantitative analysis of isomer composition (ortho / para) by $^{31}$P NMR**

A stock solution 0.4 mL of CDCl$_3$/pyridine (3:1, v/v) was prepared, in to which 200 mg (10%) of chromium tris (acetylacetonate) as a spin lattice relaxation reagent was added followed by 0.15 mL of 2-Chloro-1,3,2-dioxophospholane (DOP). The entire solution was transferred in to a 5 mm NMR tube containing approximately 100 mg of nonylphenol or phenol terminated poly (hexene-1). The solution was allowed to react for 10 min before analysis.

**FT-IR:** FT-IR spectra were obtained on a Perkin-Elmer 16 PC Spectrophotometer. A spectrum was recorded in chloroform solution. Spectra were corrected for CHCl$_3$ absorption.

**5.3 Results and discussion**

The alkylation of phenol with iso-olefins in presence of acid catalyst to produce alkyphenols is a well known reaction. Para alkyphenols impart improved performance properties to the class of metallic detergents used in lubricating oils, known as "phenates". Additionally alkyphenols are the starting material for the preparation of a wide range of non-ionic surfactants called "ethoxylates". Activating iso-olefins in presence of an acid catalyst results in the formation of a carbocation which undergoes electrophilic substitution to activated aromatic rings.

Patil reported the alkylation of hydroquinone with vinylidene terminated EP copolymer (Mn = 870) having terminal vinylidene group >95% using amberlyst-15 catalyst [24]. Alkylation of phenol with telechelic vinylidene poly (isobutylene) using BF$_3$:OEt$_2$ catalyst was reported by Kennedy *et al* [26]. In both cases, para isomer as high as 90% was obtained. Alkylation of phenol with either poly (α-olefin)s (known as PAO, oligomers of decene-1) using amberlyst-15 catalyst or oligo (isobutylene) using AlCl$_3$
catalyst was also reported [27, 28]. However, the alkylated product was found to be a mixture of ortho and para (40-60%) isomers.

We explored the alkylation reaction of phenols with vinylidene terminated poly(hexene-1) with Mn 400 - 10 000 using BF$_3$:OEt$_2$ catalyst (scheme-5.1).

**Scheme-5.1 Alkylation of phenol/2,6 DMPh with vinylidene terminated poly(hexene-1)**

5.3.1 Model alkylation of phenol with 2,4,4 trimethyl 1-pentene

To establish the experimental conditions, the alkylation of phenol with a model iso-olefin, namely, 2,4,4-trimethyl 1-pentene was carried out. Alkylation using BF$_3$:OEt$_2$ catalyst resulted in 4-(1,1,3,3-tetramethylbutyl) phenol in >95% yield and was characterized by melting point (84°C) and $^1$H NMR (fig-5.1). The results are in agreement with literature data.
5.3.2 Alkylation of phenol/2,6-dimethylphenol/bisphenol-A with terminally vinylidene unsaturated poly(hexene-1)

After establishing the alkylation reaction conditions with a model olefin, namely, 2,4,4-trimethyl 1-pentene, alkylation of phenol/2,6-dimethyl phenol/bisphenol-A was carried out with vinylidene terminated poly(hexene-1) using BF$_3$:OEt$_2$ catalyst under similar reaction conditions. The samples of poly(hexene-1) as well as stoichiometry used for alkylation of phenol, 2,6-dimethyl phenol and bisphenol-A is shown in table-5.1. In all cases satisfactory material balance was obtained.

Alkylation was carried out with poly(hexene-1) having Mn in the range of 400 – 10 000. Good yields were obtained in all the runs except in few runs, where the low yield may be due to the loss of oligomers during work up. The higher amount of catalyst was used for high molecular weight polymers as unreacted terminal vinylidene unsaturation was observed at lower catalyst concentration.
Table 5.1 Alkylation of phenol / 2,6-dimethylphenol/bisphenol-A with vinylidene terminated poly (hexene-1) using BF$_3$:OEt$_2$ catalyst*.

<table>
<thead>
<tr>
<th>Run no</th>
<th>Poly(hexene-1)</th>
<th>PhOH mol</th>
<th>BF$_3$:OEt$_2$ mmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>380</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>550</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
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<td>0.05</td>
</tr>
<tr>
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<td>0.0125</td>
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<tr>
<td>6</td>
<td>4260</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>7</td>
<td>6840</td>
<td>0.001</td>
<td>0.005</td>
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<tr>
<td>8</td>
<td>10020</td>
<td>0.001</td>
<td>0.005</td>
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</table>

Alkylation of 2,6-dimethyl phenol

<table>
<thead>
<tr>
<th></th>
<th>Poly(hexene-1)</th>
<th>PhOH mol</th>
<th>BF$_3$:OEt$_2$ mmol</th>
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<tbody>
<tr>
<td>9</td>
<td>380</td>
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</tr>
<tr>
<td>10</td>
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<td>0.05</td>
</tr>
<tr>
<td>11</td>
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<td>0.05</td>
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<tr>
<td>12</td>
<td>1760</td>
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Alkylation of bisphenol-A

<table>
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<th>Poly(hexene-1)</th>
<th>PhOH mol</th>
<th>BF$_3$:OEt$_2$ mmol</th>
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<tr>
<td>13*</td>
<td>380</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>14*</td>
<td>550</td>
<td>0.01</td>
<td>0.03</td>
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</table>

*Reaction conditions: [phenol] = 1 M in n-hexane, [olefin] = 0.2 M in n-hexane, Temp = 50°C, Time 36 h after addition of oligomer solution.

*Bisphenol-A was dissolved in 1,2-dichloroethane at 70°C.

5.3.3 Characterization of phenol/2,6-dimethylphenol/bisphenol-A terminated poly(hexene-1)

The phenol/2,6-dimethylphenol terminated poly(hexene-1) was characterized by elemental analysis, NMR, FT-IR, UV etc. The results obtained are discussed below.

5.3.3.1 Elemental analysis

The elemental analysis results are shown in table-5.2. Good agreement was observed between the values calculated and found with in the experimental errors.

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Table-5.2 Elemental analysis of phenol terminated poly(hexene-1)

<table>
<thead>
<tr>
<th>Run no</th>
<th>Before alkylation</th>
<th>After alkylation</th>
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<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>85.71</td>
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<td>5</td>
<td>85.71</td>
<td>14.29</td>
</tr>
</tbody>
</table>

5.3.3.2 NMR ($^1$H, $^{13}$C and $^{31}$P)

Structural analysis of phenol terminated poly(hexene-1) was carried out by $^1$H, $^{13}$C and $^{31}$P NMR. The $^1$H NMR obtained is shown in fig-5.2.

The $^1$H NMR spectra (tetrachloroethane-d$_2$ solvent was used to avoid peaks in aromatic region) shows exclusively para alkylated phenol. It was further confirmed by $^{13}$C NMR (fig-5.3).
Although, the $^{13}$C NMR spectrum differentiates the ortho and para isomers, however presence of small amount of ortho/para disubstituted phenol overlaps with para isomer. Hence, in order to confirm the isomer distribution in the phenol terminated poly(hexene-1), a derivatization method reported by Chan et al [29] was employed.

According to this method, derivatization of alkyl phenols with phosphitylating reagent followed by $^{31}$P NMR analysis results in quantification of para and ortho/para disubstituted phenols (scheme-5.2). However this method does not separate ortho and ortho/para disubstituted isomers. The best reagent for derivatization was found to be 2-chloro-1,3,2-dioxaphospholane (DOP).
Derivatization was first carried out with nonyl phenol as a reference. $^{31}$P NMR spectrum is shown in fig-5.4 and 5.5. The peaks at 127-129 ppm are due to the product. The peak at 167.5 ppm was also observed due to excess DOP. The protic impurities present in the system reacts with DOP resulting in a peak at 121 ppm.

Expanding the product region (127-129 ppm) revealed more information about different isomers. The major peak (>95%) between 126.8-127.8 was attributed para isomer. The minor peak between 128-129 was attributed to either ortho or ortho/para disubstituted phenol.
Derivatization was also carried out for phenol terminated poly(hexene-1) under conditions similar to that employed for nonyl phenol. $^{31}$P NMR spectrum is shown in fig-5.6 for the compound obtained from run number 2 (table-5.1).

The expanded region form 126 – 129 ppm shows presence of small amount of ortho or o/p disubstituted phenol. It was observed that use of higher molecular weight oligomers of poly(hexene-1) decreases the selectivity for para substitution as shown in fig-5.7.

![Fig-5.6 $^{31}$P NMR of derivatized phenol terminated poly(hexene-1) (from run no 2)](image)

![Fig-5.7 $^{31}$P NMR of high molecular weight phenol terminated poly(hexene-1)](image)
As shown in fig-5.7 the intensity of the peaks for corresponding ortho or ortho/para
disubstituted isomers increases from run no 6-8. The $^1$H NMR for run no 6-8 also
showed similar results as shown in fig-5.8.

![Fig-5.8 $^1$H NMR (aromatic region) of runs 6-8](image)

The $^{31}$P NMR results obtained are shown in table 5.3 including other characterization
data like UV and VPO.

### 5.3.3.3 Quantitative estimation of phenol by UV/titration

Concentration of phenol group in phenol terminated poly(1-hexene) was determined
using UV/Visible spectrophotometer by taking n-butylphenol as a standard. Known
concentrations phenol terminated poly(hexene-1) in n-hexane were made and their
corresponding absorbance were measured at $\lambda_{\text{max}} = 276.5$ nm. The concentration of
phenol in phenol terminated poly(hexene-1) was measured from the slope of n-butyl
phenol ($y = mx$). The number average molecular weight (Mn) was measured by
comparing the concentration of phenol and Mn obtained by VPO. The results obtained
are shown in table-5.3.

### 5.3.3.4 FT-IR

The FT-IR spectra for phenol terminated poly(hexene-1) showed a strong peak at 1512
cm$^{-1}$ due to aromatic C=C stretching and virtual absence of a shoulder at 3065 cm$^{-1}$ and
peaks at 1640 and 888 cm$^{-1}$ due to terminal vinylidene double bond (fig-5.9 and 5.10).

136
Fig-5.9 FT-IR spectra of poly(hexene-1) and phenol terminated poly(hexene-1)
(from run no 2)

Fig-5.10 Expanded region of FT-IR
Peaks: (a) 1640 cm\(^{-1}\) C=C stretching, (b) 888 cm\(^{-1}\) C-H alkene bending, (c) 1180 cm\(^{-1}\) C-O stretching, (d) 1512 cm\(^{-1}\) aromatic C=C stretching.
### Table-5.3 Characterization of the phenol terminated poly(hexene-1)s

<table>
<thead>
<tr>
<th>Run no</th>
<th>Mn before alkylation</th>
<th>Mn after alkylation</th>
<th>Isomer distribution by $^{31}$P NMR (%)</th>
<th>Fn mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VPO</td>
<td>NMR</td>
<td>End groups (mol%)</td>
<td>VPO</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>b</td>
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<td>d</td>
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<td>17</td>
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</table>

**a = vinylidene, b = internal**

The number average degree of functionality was found to decrease with increase in number average molecular weight. This is presumably a consequence of the decreased mol% of the vinylidene unsaturation in the oligomers.

The structure of 2,6 dimethyl phenol terminated poly(hexene-1) was also examined by $^1$H and $^{13}$C NMR (fig-5.11 and 5.12). The NMR analysis revealed that the alkylation of 2,6-dimethyl phenol with vinylidene terminated poly(hexene-1) occurs selectively at para position.
The alkylation of bisphenol-A (BPA) with vinylidene terminated poly(hexene-1) using BF$_3$OEt$_2$ catalyst in 1,2 dichloroethane at 70°C was attempted (run numbers 13 & 14 table-5.1). In this particular reaction, the unreacted bisphenol-A from the functionalized
oligomer was removed by further washings with acetone. The products obtained were characterized by VPO and NMR ($^1$H & $^{13}$C) as shown below (fig-5.13 to 5.15).

Although the $^1$H NMR showed two aromatic protons (peaks b and c), the presence another meta proton (peak d) (assuming mono akylation at ortho position) was not detected. However, the $^{13}$C NMR (fig-5.14) showed all the six expected carbons. The
assignment was further confirmed by the absence of three tetra substituted carbons (peaks a, b and d) in DEPT as shown below.

![DEPT spectra of BPA terminated poly(hexene-1) (run no 14)](image)

In both runs (13 and 14) the number average molecular weight of the alkylated products was found to be lower (560 and 750) than expected. Based on these results, it is not possible to conclusively establish the structure of the product. Further studies are necessary.

5.4 Conclusions

Poly(hexene-1) bearing terminal phenol/2,6-dimethylphenol functional group could be synthesized by alkylation of phenol/2,6-dimethylphenol with terminal vinylidene unsaturation of poly(hexene-1) using BF$_3$:OEt$_2$ catalyst. The number average degree of functionality (Fn) as high as 95 mol % was obtained for low molecular weight oligomers with >95 mol% para selectivity. The selectivity of para isomer was found to decrease with increase in number average molecular weight (Mn). Alkylation of bisphenol-A with poly(hexene-1) in 1,2-dichloroethane at 70°C gave preliminary indication of the formation of O,O'- alkylated bisphenol-A. However, further work is necessary to conclusively establish the structure of the product.

5.5 References


