Chapter 7. Synthesis of carboxylic acid functionalized poly(olefin) from hexene-1 / 2,5-norbornadiene copolymer

7.1 Introduction

One approach to the synthesis of functional poly(olefin)s is via copolymerization of olefins with a precursor monomer, which can be later converted into functional groups. This approach leads to poly(olefin)s having pendant functional groups. Three types of precursor monomers are generally reported in the literature. These are α,ω-dienes, ω-borane-α-olefins and para-methyl styrene. Copolymerization of olefins with such co-monomers result in copolymers having pendant either double bonds, borane moiety or p-methylstyryl groups respectively. These pendant functionalities can be subsequently transformed.

Copolymerization of olefins with α,ω-dienes catalyzed by metallocenes has attracted considerable attention. Copolymerization of olefins with symmetrical dienes usually results in side reactions such as “cyclopolymerization” or “crosslinking”. However, such side reactions can be avoided by selecting an appropriate metallocene catalyst. Copolymerization of olefins with unsymmetrical dienes, where one of the double bonds is more reactive than the other, gives poly(olefin)s having pendant double bonds.

Several reports are available in the literature regarding post polymerization conversion of pendant double bonds to various functional groups by simple organic chemical transformations. Recently Uozomi et al [1] reported the hydrosilylation of pendant double bond present in poly(ethylene-alt-1,9-decadieene). Marathe and Sivaram [2] reported the conversion of pendant double bonds of ethylene/VNB copolymer to epoxy and hydroxyl groups. Kaminsky [3] et al. reported the conversion of the cyclohexenyl pendant groups on ethylene/4-vinylcyclohexene copolymer to hydroxyl groups.

Hackman et al [4] reported the epoxidation and bromination of isocitronellene / propene copolymer. The pendant double bonds in poly(ethylene-co-1,4 hexadiene) were hydroborated followed by chemical reaction on boron to give various functional groups by Chung et al [5]. Suzuki et al [6] studied the copolymerization of ethylene with endo-dicyclopentadiene using Cp₂ZrCl₂, Et(Ind)₂ZrCl₂ and Ph₂C(Cp)(Flu)ZrCl₂/MAO catalysts. The enchainment was found to occur through norbornene double bond. The pendant double bond in the copolymer was then epoxidized by reacting with m-
chlorobenzoic acid. The quantitative conversion of double bond to epoxy group was found from NMR. Recently Song et al reported the ozonolysis of pendant double bonds present in poly(propene-co-methyloctadiene) to give aldehyde and carboxylic acid containing poly(olefins) [7].

Synthesis of carboxylic acid functionalized poly(olefin)s by direct copolymerization is difficult compared to the synthesis of hydroxyl functional poly(olefin)s due to the presence of two kinds of groups, namely, a carbonyl and a hydroxyl group which are known to interfere in the copolymerization reaction. It has been reported that the copolymerization activity as well as incorporation is only one half of that for the hydroxyl functional analogue when carboxylic acid or ester containing functional monomers are used for copolymerization [8].

Copolymerization of ethylene with a symmetrical diene namely, 2,5-norbomadiene (NBD) using various metallocene/MAO catalysts have been previously explored [9]. It was found that the copolymerization occurs exclusively through one of the equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts (scheme-41 in chapter-1). However, crosslinking occurs during copolymerization with dimethylsilylene bridged catalyst, probably due to the higher coordination angle along the Zr-Cl vector of the metallocene [10].

Oxidation of pendant double bonds present in poly(hexene-1-co-2,5 norbornadiene) was attempted with an objective of synthesizing a carboxyl functional poly(olefin). The synthesis of a copolymer having pendant endocyclic double bonds was described in chapter-4.

7.2 Experimental

7.2.1 Materials

Poly(hexene-1-co-2,5 norbornadiene) with different mol% NBD incorporation and Mn are reported in chapter-4, was selected for functionalization. Poly(ethylene-co-2,5 norbornadiene) was synthesized according to the literature [9]. Norbornene (Aldrich Chemical Company, USA), potassium permanganate (KMnO4), sodium sulfite (Na2SO3), hydrochloric acid (HCl), dimethylsulfoxide (DMSO), toluene (all from s.d. fine chemicals, Boisar, India) and tetrabutylammonium bromide (Fluka A. G., Switzerland) were used as such.
7.2.2 Purification

Purification of the solvents was carried out as described in chapter-3.

7.2.3 Oxidation of norbornene to cyclopentane-1,3-dicarboxylic acid (model studies)

In a 100 mL round bottom flask, 1 g norbornene (10.6 mmol) was taken and 50 mL of toluene was added. Into this 0.34 g (1.06 mmol) of tetrabutylammonium bromide was added and was stirred well for 30 min. To this 5.17 g (31.8 mmol) of KMnO₄ dissolved in 50 mL of distilled water was added. After 3 h of continuous stirring, 4.56 g (38.0 mmol) of Na₂S₀₃ was added into the reaction mixture to oxidize the excess KMnO₄ and then 14 mL of conc. HCl in 14 mL of water was added. The solution color changed from brown to white. It was then stirred for 24 h to remove all the MnO₂ formed. Two layers, water and benzene, were clearly visible. The lower water layer was separated by a separating funnel. The water layer was extracted with ether in a continuous extractor for 48 h. The product was obtained by evaporating ether and was purified by recrystallization from benzene-ether mixture to give 95 % yield. ¹H NMR (DMSO-d₆, ppm) 1.67-1.94 (5H), 2.11 (IH), 2.64-2.80 (2H) and 12.1 (2H).

Oxidation of poly(hexene-1-co-2,5-norbornadiene)

In a 100 mL round bottom flask, 3 g (10 mol% NBD incorporation) of the copolymer (Mn 1100, 3.5 mmol of cyclic unsaturation and 2.7 mmol of terminal unsaturation) was taken and 50 mL toluene and 0.2 g (0.62 mmol) of tetrabutylammonium bromide were added. To this 2.9 g (18.6 mmol) of KMnO₄ dissolved in 50 mL of distilled water was added. The stirring was continued for 24 h at ambient temperature. To the reaction mixture 2 g (17 mmol) of Na₂S₀₃ was added to oxidize the excess KMnO₄ and then 5 mL of conc. HCl in 5 mL of water was added. The color of the solution changed from brown to white. It was then stirred for 24 h to remove all the MnO₂ formed. The functionalized oligomer was found to be in the interphase of the two layers. The lower water layer was removed using a separating funnel and from the remaining organic layer the insoluble fraction (1.1g) was filtered and dried. The solvent was removed from the soluble fraction under vacuum to collect the unfunctionalized oligomer (1.7g).

7.2.3 Analysis

The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ¹H NMR spectra of the copolymers before and after oxidation were recorded on a 200 MHz
Bruker NMR spectrometer at room temperature in CDCl$_3$ and CDCl$_3$/DMSO-d$_6$ (85/15, v/v) respectively. Quantitative $^{13}$C NMR spectra of the copolymer before and after oxidation were recorded on a Bruker MSL 500 model spectrometer with a pulse delay 10 sec. Approximately 5000 scans were made.

7.3 Results and discussion

A number of procedures are reported in the literature for the oxidative cleavage of the double bond in norbornene to dicarboxylic acid. Clark [11] used a catalyst combination of hydrated ruthenium trichloride and sodium periodate in chloroform for the oxidation. Henry and Weinreb [12] used Jone's reagent/osmium tetra oxide catalyst system in a mixture of acetone and water for the oxidation of norbornene. Hronowski and Szarek [13] employed KMnO$_4$ in a mixture of 2,2,4-trimethyl pentane and water in 1:5 ratio (v/v) with continuous bubbling of carbon dioxide and later sulfur dioxide for the oxidation of norbornene. In our earlier study, the limited solubility of poly(ethylene-co-2,5 norbornadiene) precluded the utilization of these methods for the oxidative cleavage of norbornene moiety in the copolymer. There was a report by Herriott and Picker [14] that stilbene could be oxidized under phase transfer conditions using tetrabutylammonium bromide/KMnO$_4$ in benzene/water biphasic medium.

We studied the oxidation of the endocyclic double bonds in poly(ethylene-co-2,5 norbornadiene) according the procedure by Herriott and Picker. Since poly(ethylene-co-2,5 norbornadiene) was only partially soluble in benzene at ambient temperatures it was decided to carry out the reaction in toluene where the copolymer is completely soluble.

Though the parent copolymer was soluble in toluene at room temperature, the carboxylic acid functionalized copolymer was found to be insoluble in toluene even at high temperatures, presumably, because of the presence of highly polar carboxylic acid groups. The product was also not soluble in any of the common solvents of polyolefins like xylene, o-dichlorobenzene etc. However, it was found to be soluble in a mixture of xylene or ODCB and DMSO (85:15 (v/v) ratio) at temperatures above 80° C.

The same oxidation procedure was extended for the synthesis of carboxylic acid functionalized polyolefin from poly(hexene-1-co-2,5 norbornadiene) (Scheme-7.1). It was felt that a higher $\alpha$-olefin like hexene-1 in copolymer would improve its solubility after functionalization and thus enable better characterization of the copolymer.
Scheme 7.1 Synthesis of carboxylic acid functionalized hexene-1-2,5 norbornadiene copolymer

Table 7.1 Oxidation of hexene-1-NBD copolymer under phase transfer conditions

<table>
<thead>
<tr>
<th>Run No</th>
<th>Copolymer (g)</th>
<th>NBD in copolymer(\text{mol}%)</th>
<th>Mn</th>
<th>End groups (mol%)</th>
<th>Yield (g)</th>
<th>Solubility in toluene (%)</th>
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<th>Insoluble</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Vinylene</td>
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<td>1070</td>
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<td>43</td>
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<td>&gt;99.0</td>
<td>&lt;1.0</td>
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<td>45</td>
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</tr>
<tr>
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<td>14.0</td>
<td>1300</td>
<td>48</td>
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<td>79</td>
<td>3.6</td>
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*Reaction conditions*: KMnO\(_4\)/olefin/TBAB = 30/10/1 (mol/mol), Reaction time = 12h, Based on \(^1\)H NMR. Oxidation in DCM.

As shown in table 7.1, oxidation of the copolymer resulted in toluene soluble and insoluble (found at interphase of two layers) fractions (except run numbers 1 and 2). The analysis revealed that the toluene soluble fraction is the unfunctionalized oligomer. The insoluble fraction was found to be a carboxylated poly(olefin). A copolymer
containing <10 mol% NBD (run no-1 and 2) resulted in a single toluene soluble fraction and was found to be a carboxylated poly(olefin).

The increase in NBD incorporation in copolymer gave more toluene insoluble fraction (run numbers 3-5). No significant change was observed on Mn of copolymer with solubility. The oxidation reactions carried out in dichloromethane (runs 9 & 10 compared to 3 & 4) gave higher carboxylated poly(olefin) than in toluene.

7.4 Characterization of the oxidized copolymer

7.4.1 NMR

Near complete conversion of the pendant endocyclic double bonds to dicarboxylic acids was evident by the absence of any residual pendant unsaturation in the copolymer as evidenced by $^1$H NMR (fig-7.1). The peaks due to the cyclopentane rings in the copolymer could not be properly identified in the NMR spectra due to overlapping with DMSO peaks. The $^{13}$C NMR (fig-7.2) spectrum showed a peak at 179 ppm due to carboxylic acid carbon and absence of peak at 139 ppm indicative of the absence of unsaturation.

![Fig-7.1 $^1$H NMR of carboxylic acid functionalized copolymer (toluene insoluble from run no 3, solvent CDCL3/DMSO-D6, 85/15 V/V)](image-url)
In both $^1$H and $^{13}$C spectrum, the absence of terminal unsaturation was also observed. The toluene soluble carboxylic acid functionalized copolymer showed traces of terminal vinylidene unsaturation (fig-7.3).

Fig-7.2 $^{13}$C NMR of carboxylic acid functionalized copolymer (toluene insoluble fraction from run no 2, solvent CDCL3/DMSO-D6, 85/15 V/V)

Fig-7.3 $^{13}$C NMR of carboxylic acid functionalized copolymer (toluene soluble fraction from run no 1, solvent CDCL3)
7.4.2 FTIR

IR spectrum of the copolymer showed a very strong peak at 1725 cm\(^{-1}\) due to C=O stretching vibration of the diacid and virtual absence of a shoulder at 3065 cm\(^{-1}\) and peaks at 1583 and 908.7 cm\(^{-1}\) due to C=C double bonds.

![FTIR spectrum](image)

Fig-7.4 IR spectrum of copolymer before and after functionalization (run no 5)

Peaks: (a) = 1725 cm\(^{-1}\) C=O stretching, (b) 1240 cm\(^{-1}\) C-O stretching, (c) 3065 cm\(^{-1}\) C-H alkene stretching, (d) 1483 cm\(^{-1}\) C=C stretching.

7.4.3 Quantitative analysis of carboxylic acid of carboxylated poly(olefin)

Quantitative carboxylic acid analysis of toluene soluble carboxylated polyolefin obtained from run numbers 1 and 2 was determined by dissolving samples in toluene/ethanol mixture and titrating the solution against alcoholic KOH. The carboxylic acid content obtained from titration (3.6 and 4.2 \(\times 10^{-3}\) mol/g respectively) was higher than the theoretical values calculated from mol% NBD in copolymer. It could be due to the oxidation of terminal unsaturation as well.

7.5 Copolymer properties

Though all the parent copolymer was soluble in toluene at room temperature, the carboxylated oligomers were found to be only partially soluble in toluene. It was found that the soluble fraction had no acid functionality where as the insoluble fraction showed the presence of carboxylic acid functional group. However, when the mol % NBD was <6% all the product formed was soluble, and was found to be the carboxylated oligomer. The presence of intermolecular hydrogen bonding between the -COOH groups in the
functionalized co-polymer may result in poor solubility. The toluene insoluble fraction was found to be soluble in a mixture of CDCl$_3$/DMSO (85:15 (v/v) ratio) at room temperature.

7.6 Conclusions

Copolymerization of hexene-1 with a symmetrical diene, namely, 2,5-norbornadiene, was found to occur through only one of the highly strained endocyclic double bonds leaving the other one as a pendant group. The pendant double bonds could be converted into carboxylic acid groups under mild conditions. The functionalized copolymer was found to be insoluble in toluene with NBD incorporation more than 6 mol%. The fact that the double bond was part of a strained endocyclic [2.2.1] skeleton enabled it to be oxidized under a very mild condition. Such oxidized poly(olefin)s are likely to possess interesting applications as adhesion promoters, tie layers in multilayer barrier packaging and emulsifiable polyolefin waxes for coating applications.

7.7 References