

## **Chapter III**

### **Synthesis and performance evaluation of vinyl acetate maleic anhydride based polymeric additives for lubricating oil**

### 2.3.1 Introduction

Lubricant comprises a base fluid and a package of additives.<sup>1, 2</sup> The basic function of lubricant is to lubricate modern engines to prolong its lifetime. Base fluids also known as base oils, the basic building block of a lubricant, are a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with low volatility and high viscosity index.<sup>3, 4</sup> The percentage of different hydrocarbon components determines the characteristics of the base oils.<sup>5</sup> Additives are the specific chemical compounds when added to base oil, impart new and useful properties to the oil. Some additives enhance the properties already present and some act to reduce the rate at which undesirable changes take place in the product during its service life.<sup>6</sup> The most important additive is viscosity index improver (VII). The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). A higher VI value signifies a lesser effect of temperature on viscosity. Viscosity index improvers (VII) or viscosity modifiers (VM) are additives that resist the change of viscosity of oil with change in temperature.<sup>7-10</sup> The performance of VII mainly depends on the behaviour of polymer molecule in the base stock, polymer solubility, molecular weight, resistance to shear degradation.<sup>11</sup>

Pour point is the lowest temperature at which the lube oil loses its flow ability. The freezing of lube oil is caused by the formation of crystal network of paraffinic wax present in the lube oil. The pour point of lube oil can be lowered with additives, called pour point depressants (PPDs), also known as cold flow improvers. The PPD additive works by destroying the wax crystal network and thereby lowering the pour point. The flow property at low temperature is thus maintained.<sup>12,13</sup> The additives which are used as pour point depressants should have some pendant alkyl groups and there should be an appropriate distance between the pendant alkyl group and there should be a suitable ratio of monomers when a copolymer is used.<sup>14, 15</sup>

In this present work, author prepared maleic anhydride - vinyl acetate copolymer. Due to insolubility of the copolymer in lube oil, it was esterified with three types of long chain alcohol (1-octanol, 1-decanol and 1-dodecanol) to get the corresponding esterified polymeric products. The author have investigated the efficiency of each of them as viscosity index improver or viscosity modifier and pour point depressant in three types of base oils.

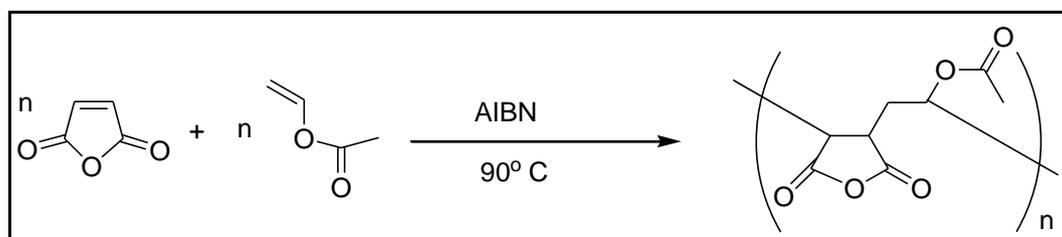
## 2.3.2 Experimental section

### 2.3.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and vinyl acetate (99%, Sd. fine chemicals, India) were used without further purification. Azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd. India) was used without purification. Toluene (98%, Sd. fine chemicals, India) was purified by distillation and used as solvent for polymerisation as well as esterification of polymer. P-toluene sulphonic acid (98%, LOBA chemie) was used as catalyst after complete drying. 1-Octanol (99%, LOBA chemie, India), 1-decanol (99%, Sd. fine chemicals, India) and 1-dodecanol (98%, Sd. fine chemicals, India) were used in esterification without further purification. Base oils were collected from IOCL and BPCL, India. Physical properties of the base oils are given in **table 2.3.1**.

### 2.3.2.2 Preparation of maleic anhydride-vinyl acetate copolymer

The copolymerization of maleic anhydride and vinyl acetate was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. Vinyl acetate and maleic anhydride was mixed in the molar ratio of 1:1 in the presence of azobisisobutyronitrile (AIBN, 0.5% w/w, with respect to the monomer) as an initiator and toluene was used as a solvent. The reactants were mixed and temperature was kept constant at 90° C for half an hour and then AIBN was added and heated for 6 hours. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.

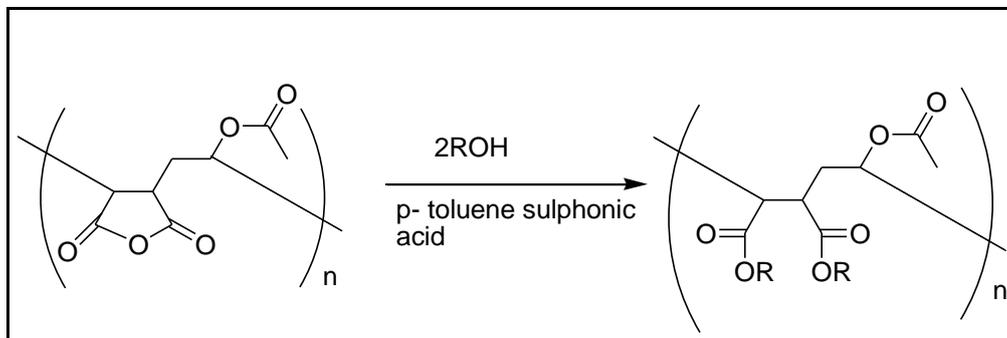


**Scheme 1** Preparation of copolymer of maleic anhydride and vinyl acetate

### 2.3.2.2 Esterification of the copolymer with different alcohols

The prepared copolymer was reacted separately with 1-octanol, 1-decanol and 1-dodecanol in presence of catalytic amount of p-toluene sulphonic acid to prepare three esterified product A, B and C respectively of the copolymer. In a four necked round bottom flask fitted with a mechanical stirrer, an efficient condenser with Dean Stark apparatus, a thermometer and a nitrogen gas inlet. The dried copolymer was esterified with different alcohols in the presence of p-toluene sulphonic acid as a catalyst and toluene as a solvent. The copolymer and alcohol

were taken in 1:1(w/w) ratio. Reaction mixture was slowly heated up to 130°C until all water of esterification is removed. The ester was purified by washing with distilled water and drying over Na<sub>2</sub>SO<sub>4</sub>. Finally methanol was added to precipitate the product and was filtrated and dried.



**Scheme 2** Esterification of copolymer by three types of alcohols.

ROH = C<sub>8</sub>H<sub>17</sub>OH (octyl alcohol) gives polymeric additive **A**, ROH = C<sub>10</sub>H<sub>21</sub>OH (decyl alcohol) gives polymeric additive **B**, ROH = C<sub>12</sub>H<sub>25</sub>OH (dodecyl alcohol) gives polymeric additive **C**

## 2.3.3 Measurements

### 2.3.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the range of 400 to 4000 cm<sup>-1</sup>. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) as reference material.

### 2.3.3.2 Determination of intrinsic viscosity and viscometric average molecular weight of the prepared polymeric additives

Viscometric properties were determined at 40°C in toluene solution using an Ubbelohde OB viscometer. The time flow was counted at eight different concentrations (g/c.c) of the polymer solution. Intrinsic viscosity and viscometric molecular weight were determined by Huggins (equation-1) and Mark- Houwink- Sukurda equation (equation-2) respectively.<sup>16</sup>

$$\text{Huggins equation (H), } \eta_{sp}/C = [\eta]_h + K_h [\eta]_h^2 C \quad (1)$$

Where, C is the mass concentration,  $\eta_{sp} = \eta_r - 1$ ,  $\eta_{sp}$  is the specific viscosity,  $\eta_r = t/t_0$ ,  $\eta_r$  is the relative viscosity or viscosity ratio, where t is the flow of time of the polymer solution and t<sub>0</sub> is the flow of time of the pure solvent.  $[\eta]_h$  = intrinsic viscosity, respective to Huggins equation, K<sub>h</sub> is the Huggins coefficient. According to Mark- Houwink–Sukurda (equation-2),

the value of intrinsic viscosity changes with the molecular weight of the additive in a solvent as:  $[\eta] = KM^a$  (2)

Where  $[\eta]$ , the intrinsic viscosity can be calculated by using Huggins equation, parameter 'K' and 'a' depends on the type of polymer, solvent and temperature. For the determination of viscosity average molecular weight, the constants,  $K = 0.00387$  dl/g and  $a = 0.725$  were used in Mark Houwink- Sukurda equation.<sup>17</sup>

### 2.3.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating rate of 10°C/min.

### 2.3.3.4 Performance evaluation of the polymers as viscosity index improver

Viscosity index (VI) was calculated by dissolving prepared polymer in three different base oils (BO1, BO2 and BO3) through the viscosity index test according to ASTM D 7042 method.<sup>18</sup> The kinematic viscosity of the polymer doped base oil was determined at 40°C and 100°C. Different concentrations ranging 1% - 5% (w/w) were used to study the effect of additive concentration on VI.

### 2.3.3.5 Performance evaluation of the polymers as pour point depressant

Pour point of the additive doped base oils (BO1, BO2 and BO3) were recorded through the pour point test according to the ASTM D 97-09 method<sup>19</sup> using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 5% (w/w).

## 2.3.4 Results and discussion

### 2.3.4.1 Spectroscopic data analysis

In the IR spectra of copolymer of maleic anhydride and vinyl acetate (**figure 2.3.1**), the peaks at 1782 cm<sup>-1</sup> and 1851.5 cm<sup>-1</sup> indicate the presence of anhydride group. The peak at 1728 cm<sup>-1</sup> indicates the presence of ester carbonyl group in the copolymer due to vinyl acetate moiety. The peaks at 2862 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> are the characteristic of CH<sub>3</sub>- group. The peaks at 1458 cm<sup>-1</sup>, 1365.5 cm<sup>-1</sup>, 1219 cm<sup>-1</sup> and 1033.8 cm<sup>-1</sup> due to CO stretching vibration and absorption bands at 933.5 cm<sup>-1</sup> and 725 cm<sup>-1</sup> were due to bending of C-H bond.

The spectroscopic data (IR and NMR) of the three polymers A, B and C are similar. In the IR spectra of polymer A (**figure 2.3.2**), peak at 1735.8 cm<sup>-1</sup> indicates the presence of ester carbonyl group. The peaks at 2854.5 cm<sup>-1</sup> and 2925 cm<sup>-1</sup> are the characteristic of CH<sub>3</sub>CH<sub>2</sub>- group. The peaks at 1466 cm<sup>-1</sup>, 1404 cm<sup>-1</sup>, 1373 cm<sup>-1</sup>, 1211 cm<sup>-1</sup> and 1156 cm<sup>-1</sup> due to CO stretching vibration and absorption bands at 818 and 725 cm<sup>-1</sup> were due to bending of C-H

bond. The disappearance of two anhydride peaks at  $1782\text{ cm}^{-1}$  and  $1851.5\text{ cm}^{-1}$  indicate that esterification of copolymer was carried out successfully.

In the  $^1\text{H}$  NMR (**figure 2.3.3**), a broad peak in the range of 3.37 ppm to 3.98 ppm indicates the protons of  $-\text{COCH}_3$  group. Another broad peak ranging from 4.002 ppm to 4.185 ppm indicates the protons of  $-\text{OCH}_2$  groups. The hydrogens attached to  $\text{sp}^3$  carbons appear in the range of 0.90 ppm to 2.43 ppm. Absence of any peak in the range of 5-6 ppm indicates the disappearance of  $\text{C}=\text{C}$  bond and confirms the polymerisation.

In  $^{13}\text{C}$  NMR (**figure 2.3.4**), the peak at 165.53 ppm indicates the presence of ester carbonyl group. The peak at 62.56 ppm indicates the presence of  $-\text{COCH}_3$  methyl carbon. The peaks at 64.83 ppm and 65.56 ppm confirm the presence of all  $-\text{OCH}_2$  carbons. The peaks ranging from 14.18 – 32.65 ppm represents all other  $\text{sp}^3$  carbons. No peak in the range of 120 -150 ppm indicates the absence of  $\text{sp}^2$  carbons and confirms the polymerization.

#### **2.3.4.2 Molecular weight and TGA data analysis**

The experimental values of intrinsic viscosity and viscometric molecular weight of polymer A, B and C are given in **table 2.3.2**. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the molecular weight increases. From TGA values of all the three polymers (**table 2.3.2**), it is seen that polymer A is thermally less stable than polymer B and C. Polymer B and C are thermally almost equal stable.

#### **2.3.4.3 Analysis of viscosity index (VI) data**

VI was calculated by dissolving the prepared polymers at a concentration range of 1% - 5% (w/w) in different base oils. The values are given in **table 2.3.3**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oils. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI.<sup>20, 21</sup> The VI value of polymer C is higher than polymer B and B is higher than A in all the three base oils. The lube oil viscosity decreases with increasing temperature but expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature.<sup>22, 23</sup> This effect is greater in case of polymer C which may be due to its higher molecular weight.

#### **2.3.4.4 Analysis of pour point data**

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table 2.3.4**.

From the values, it is observed that all the three polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power.<sup>24, 25</sup> Among the three polymers (A, B and C), the polymer A is more efficient as PPD in all the three base oils. It may be due to presence of short alkyl chain in polymer A. The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is inhibited.<sup>26, 27</sup> From the experimental pour point values, it is also observed that all the three polymers are more effective in base oil, BO1 i.e. in the lower viscous base oil.

### **2.3.5 Conclusions**

From the above study, it is found that all the prepared three polymers are effective as VII and PPD. Among the three polymers, polymer C is more efficient than B and B is more efficient than A as VII. This indicates that with increasing the alkyl chain length of alcohols used in esterification, the VI property increases. The PPD property of polymer A is higher than polymer B and C, it indicates that with decreasing the alkyl chain length of alcohols used in esterification, the PPD property improves. Therefore, alkyl chain length has a significant role in polymerization to enhance the property of VII and PPD for lube oil polymeric additives.

### **2.3.6 References**

References are given in the bibliography section of Chapter III of Part II (Page No. 188 - 190).

### **2.3.7 Tables and figures**

**Table 2.3.1** Physical properties of the base oils

Base oil properties	<u>Base oil</u>		
	BO1	BO2	BO3
Density ( g cm <sup>-3</sup> ) at 40 ° C	0.83	0.84	0.87
Viscosity at 40 °C in c St	7.102	23.502	107.120
Viscosity at 100 °C in c St	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point (° C)	-3	-6	-0.5
Cloud point (° C)	-1	-4	+2

**Table 2.3.2** Intrinsic viscosity, Viscometric molecular weight and thermo gravimetric analysis (TGA) values of polymer A, B and C

Polymer	$[\eta]_h$	$[M]_h$	Deco.tem/°C	PWL
A	4.12	14,973	180/306	32/91
B	4.38	16,220	198/ 355	26/88
C	4.52	16,916	203/365	25/87

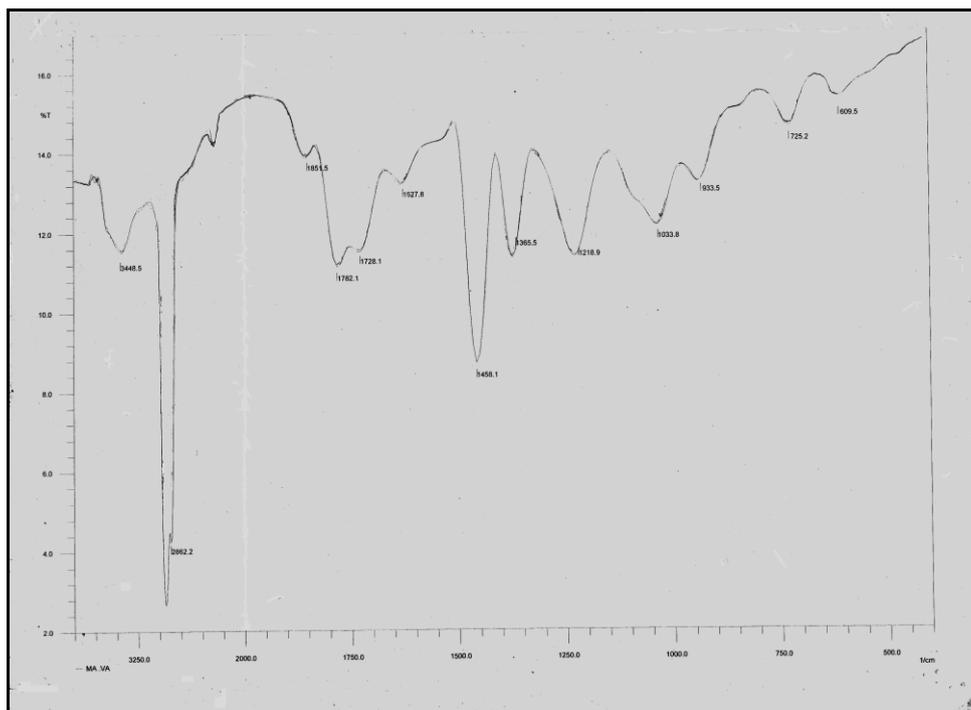
A = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-octanol; B = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-decanol; C = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-dodecanol;  $[\eta]_h$ = intrinsic viscosity respective to Huggins;  $[M]_h$  = Viscometric molecular weight according to Mark Houwink–Sukurda equation; Deco.tem = decomposition temperature; PWL = percentage weight loss.

**Table 2.3.3** Viscosity index (VI) of polymer of A, B and C at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3)

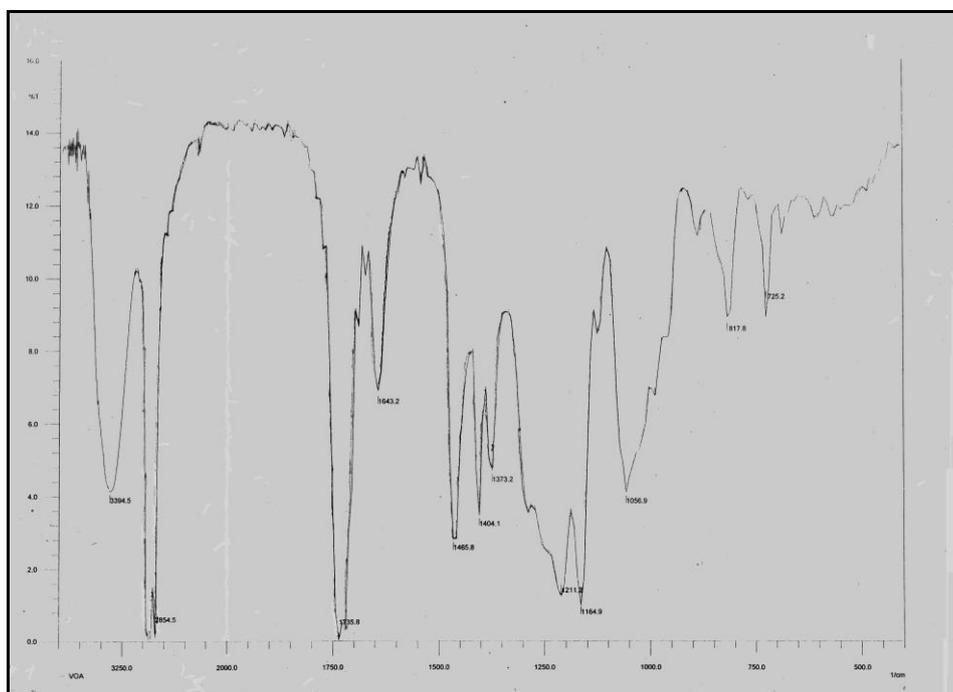
Polymer	Base oil	<u>VI of Polymer doped base oil</u>					
		0%	1%	2%	3%	4%	5%
A	BO1	84.6	90	96	96	100	104
	BO2	85.2	92	95	95	100	103
	BO3	81.5	87	92	92	98	105
B	BO1	84.6	93	97	97	104	106
	BO2	85.2	95	98	100	106	108
	BO3	81.5	88	90	96	96	105
C	BO1	84.6	96	96	99	108	112
	BO2	85.2	98	98	102	110	112
	BO3	81.5	89	94	94	102	107

**Table 2.3.4** Pour point of polymer A, B and C at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3)

Polymer	Base oil	<u>Pour point of Polymer doped base oil</u>					
		0%	1%	2%	3%	4%	5%
A	BO1	-3	-10	-12	-9	-9	-9
	BO2	-6	-12	-12	-10	-10	-10
	BO3	-0.5	-6	-7	-6	-5	-5
B	BO1	-3	-10	-10	-9	-8	-8
	BO2	-6	-10	-10	-10	-9	-9
	BO3	-0.5	-6	-6	-5	-5	-5
C	BO1	-3	-9	-9	-7	-7	-7
	BO2	-6	-9	-10	-8	-8	-8
	BO3	-0.5	-6	-4	-4	-4	-3



**Figure 2.3.1** IR spectra of copolymer of maleic anhydride and vinyl acetate



**Figure 2.3.2** IR spectra of polymer A

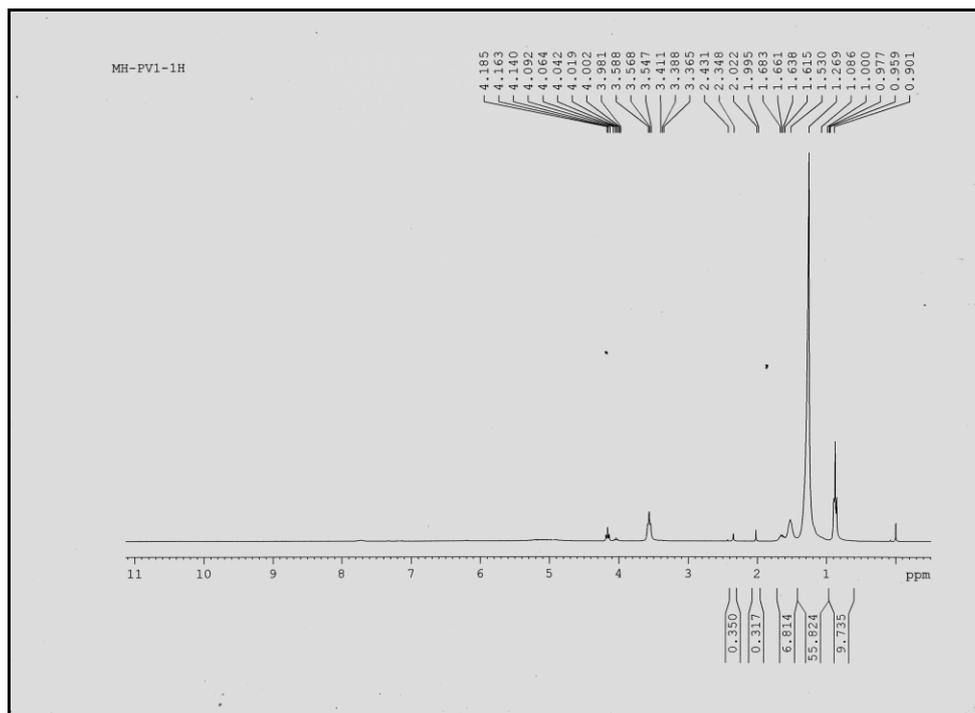


Figure 2.3.3  $^1\text{H}$  NMR spectra of polymer A

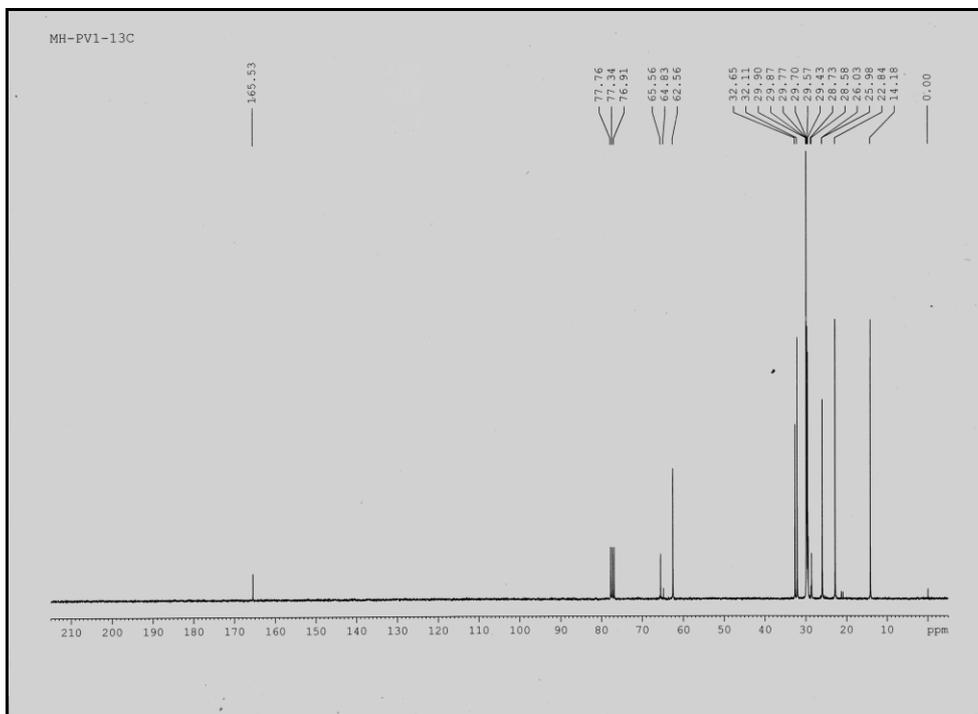


Figure 2.3.4  $^{13}\text{C}$  NMR spectra of polymer A