

## **Chapter II**

**A Study of Shear Stability, Thickening and Viscosity Index**

**Properties of Homopolymer of Dodecyl Acrylate and its**

**Copolymer with Styrene and 1-Decene**

### 1.2.1 Introduction

Modern lubricants are composed of a base fluid and a package of chemical additives. When additives are added to the base fluid, they can improve the properties already present or add some new properties [1]. The most important additives which are commonly added to the base fluid are viscosity index improver (VII), pour point depressant (PPD), anti-wear, antioxidant, dispersant, extreme pressure additives, etc. The viscosity index is an indicator which indicates the change in viscosity with temperature change. A higher viscosity index indicates a small change in viscosity with change in temperature. Viscosity index improvers are long-chain, high molecular weight polymeric additives. They function by increasing the relative viscosity of base fluid more at high temperatures than at low temperatures [2]. Oil thickening property of the additives is a direct measure of a percentage increase in the viscosity of the base fluid for the addition of a unit amount of additive. This property indicates the extent of interaction of the additive with the base fluid. The greater is the thickening property, the greater is the extent of interaction. Shear stability is one of the important criteria that determine the suitability of a viscosity index improver in a lubricant composition which is an indicator to indicate the amount of viscosity of oil, may lose during operation [3].

The pour point is the lowest temperature at which the base fluid stops its flowing. The base fluid contains some dissolved paraffinic wax. At low temperatures, the wax crystallizes to form a rigid structure and trap the oil molecules. As a result, the oil will lose its capability to flow. To overcome this problem, some polymeric additives are used as a pour point depressant (PPD). The PPD functions by inhibiting the formation of a wax crystal structure that occurs at low temperatures [4]. In this article, we have prepared a homopolymer of dodecyl acrylate and two copolymers with styrene (10%,

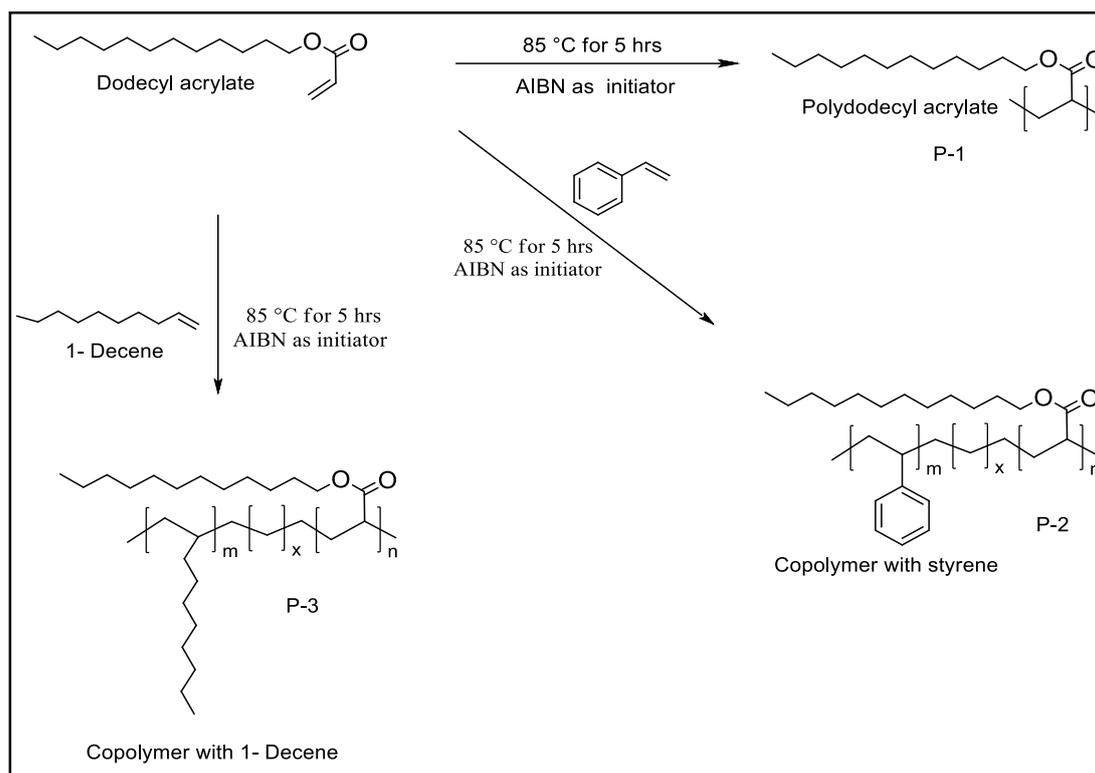
w/w) and 1-Decene (10%, w/w) by using AIBN as initiator and investigated the efficiency of the additives as viscosity index improver and pour point depressant in the base fluid. The shear stability and thickening property of each additive in base fluid have also been investigated and reported here.

## 1.2.2 Experimental Section

### 1.2.2.1 Synthesis of the polymers

The copolymers were prepared by taking the monomers of DDA (90%, w/w) and styrene or 1-Decene (10%, w/w) in presence of AIBN initiator without any solvent.

#### Scheme 1.2.1 Reaction for the synthesis of homopolymer of dodecyl acrylate and copolymer with and 1-Decene



The polymerization was completed in a three-necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. The mixture of monomers was heated to 85°C and then AIBN (0.5% w/w, with respect to the total monomer) was added and continuously heated for 5 hours keeping the temperature constant at 85°C. After the completion of reaction time, the product was

poured into methanol. A precipitate appeared which was filtered off and dried. The homopolymer of DDA was also prepared in the similar procedure. The prepared homopolymer and two copolymers with styrene and 1-Decene were designated as P-1, P-2, and P-3 respectively.

#### **1.2.2.2 Materials**

Benzoyl peroxide (LOBA Chemie, India) was used after recrystallization from chloroform-methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India) and the mineral base oil SN150 were collected from IOCL, Dhakuria, West Bengal, India.

### **1.2.3 Measurements**

#### **1.2.3.1 Spectroscopic measurements**

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm potassium bromide cells at room temperature within the wavenumber range of 400 to 4000  $\text{cm}^{-1}$ . Bruker Avance 300 MHz FTNMR Spectrometer was used for NMR spectra using  $\text{CDCl}_3$  as solvent.

#### **1.2.3.2 Molecular weight determination**

The average molecular weight was determined by the GPC method (Water 2414) in HPLC grade THF at 35<sup>0</sup>C at a flow rate of 1mL/min

#### **1.2.3.3 Thermogravimetric analysis (TGA)**

The thermogravimetric analysis was carried out on a Mettler TA – 3000 system, at a heating rate of 10<sup>0</sup>C / min.

#### **1.2.3.4 Determination of shear stability**

The shear stability of a lubricant is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The loss of viscosity of a lubricant under shearing conditions can be expressed in terms of permanent viscosity loss (PVL)

or permanent shear stability index (PSSI). The PVL/PSSI value was determined as per the ASTM D-3945 method by the following relation [3].

$$\text{PVL (\%)} = (V_i - V_s) / V_i \times 100$$

$$\text{PSSI (\%)} = (V_i - V_s) / (V_i - V_o) \times 100$$

Where,  $V_i$  = Kinematic viscosity of lubricant before shearing at 100°C

$V_s$  = Kinematic viscosity of lubricant after shearing at 100°C

$V_o$  = Kinematic viscosity of lube oil at 100°C

The higher the PVL/PSSI value, the lower is the shear stability of the polymer.

### **1.2.3.5 Evaluation of thickening property**

Kinematic viscosity of the lube oil and that of additive blended lube oil were evaluated at 40°C and 100°C. Thickening power of the lubricant was determined by calculating the percentage increase in viscosity of the lubricant composition by the addition of a unit amount of additive.

### **1.2.3.6 Determination of viscosity index (VI)**

VI of the lubricant composition was determined according to ASTM D 2270-10 method. The kinematic viscosity of the lubricant composition was determined at 40°C and 100°C. Different concentrations of additives [ranging from 1% - 5% (w/w)] were used to study the effect of additive concentration on VI.

### **1.2.3.7 Determination of pour point**

The pour point of the lubricant composition was determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different concentrations ranging from 1% - 5% (w/w).

## **1.2.4 Result and discussion**

### **1.2.4.1 Spectroscopic analysis**

The homopolymer of DDA (P-1) exhibited an IR absorption band at  $1735.5\text{ cm}^{-1}$  for the ester carbonyl group. The two peaks at  $2854.5\text{ cm}^{-1}$  and  $2924\text{ cm}^{-1}$  were due to the characteristic of  $\text{CH}_3\text{CH}_2$ - group. The peaks at  $1464.5$ ,  $1378$ ,  $1241$ , and  $1152.4\text{ cm}^{-1}$  due to CO stretching vibration and absorption bands at  $1068.5$ ,  $969.0$ , and  $868.2\text{ cm}^{-1}$  were due to bending of C-H bond (**Figure 1.2.1**). In the  $^1\text{H}$  NMR of homopolymer, methyl and methylene protons appeared in the range of  $0.890$  to  $1.934$  ppm. A broad peak at  $3.928$  ppm confirmed the protons of  $-\text{OCH}_2$  group. There is no peak in the range of  $5$ - $6$  ppm, indicated that polymerization was completed successfully (**Figure 1.2.2**). In the  $^{13}\text{C}$  NMR of homopolymer, the peaks at  $177.54$  ppm indicated the presence of ester carbon. There was no peak in the range of  $120$ - $150$  ppm and it confirmed the polymerization (**Figure 1.2.3**). In the IR spectrum of copolymer (P-3), the ester carbonyl group appeared at  $1728.2\text{ cm}^{-1}$ . Peaks at  $750.4\text{ cm}^{-1}$  and  $700.5\text{ cm}^{-1}$  indicated the C-H bond of the phenyl group of styrene (**Figure 1.2.4**). In the  $^1\text{H}$  NMR, multiplet peak in the range of  $3.933$  -  $4.156$  ppm indicated the protons of  $-\text{OCH}_2$ . A broad peak in the range of  $7.014$  -  $7.329$  ppm indicated the protons of the phenyl group. No peak in the range of  $5$ - $6$  ppm indicated the confirmation of polymerization (**Figure 1.2.5**). In the  $^{13}\text{C}$  NMR, the peaks in the range of  $176.8$  -  $177.7$  ppm confirmed the presence of ester carbons. The carbons in the phenyl group appeared in the range of  $125.04$  -  $128.56$  ppm (**Figure 1.2.6**). All the spectroscopic data of copolymer P-2 was found approximately the same with the homopolymer, P-1.

#### 1.2.4.2 Analysis of Molecular weight and TGA

The experimental value of number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and TGA values of the prepared additives (P-1 to P-3) are given in **Table 1.2.1**. From the data, it is observed that the copolymer P-3 has the highest molecular weight followed by homopolymer P-1. From the TGA values, it is

observed that the additive P-3 is thermally more stable than P-2 and P-1. It may be due to the presence of styrene moiety in P-3 which supports thermally stability.

#### **1.2.4.3 Analysis of shear stability**

PVL and PSSI values were calculated in additive doped lube oil at a different concentration ranging from 1% - 5 % ( w/w) at 100 ° C. The experimental values are listed in **Table 1.2.2**. From the values, it is found that copolymers are more stable under shear (lower PVL/PSSI value) than homopolymer. Among the three additives, the order of stability under shear is P-3 > P-2 > P-1. Moreover, it is also observed that with increasing the concentration of additive to the base oil, the shear stability decreases (higher PVL/PSSI value) [5].

#### **1.2.4.4 Analysis of thickening Property**

The thickening power of both homopolymer and copolymers is depicted in **Table 1.2.3** which indicated a gradual decrease with the increase in the concentration of the additive. This may be because of the fact that the additive molecules are assumed to be coiled like aggregation with the increase in concentration to the base oil [6]. From the results, it was observed that the thickening power of the additive P-1 was higher than that of additives P-2 and P-3. This indicated that from the point of view of fuel economy, the additive P-1 is better than additives P-2 and P-3.

#### **1.2.4.5 Analysis of viscosity index (VI) values**

VI values of the prepared additives in base oil are listed in **table 1.2.4**. The viscosity of base oil without any additive decreases with increasing temperature but when additives are added to the base oil, the decrement of viscosity does not occur. At high temperatures, additive molecules in the base oil medium swell up and as a result, the size of the micelle enhances. This enhanced micelle size resists the reduction of the viscosity of the lubricant composition and hence improves VI. It was also found that

at a higher concentration of the lubricant composition, the VI values are higher. This is because, at higher concentration, the micelle size increases and hence improves the VI property [7], [8]. The copolymer P-3 has better VI property than P-2 and P-1. It may be due to the higher molecular weight of P-3.

#### **1.2.4.6 Analysis of Pour point (PP) values**

The pour points of the base oil, as well as base oil containing different additives at different concentration levels [1%–5% (w/w)], are given in **Table 1.2.5**. From the experimental values, it is observed that base oil containing additives have lower PP than base oil and hence the prepared additives can be used as PPD. Moreover, it is observed that the efficiency as PPD increases with increasing concentration. The reason behind it may be, at higher concentrations, the interaction between the additive and paraffinic wax present in the base oil is more [9]-[11]. All the three prepared additives are approximately equally effective as PPD. The additive P-3 showed slightly higher performance as PPD than the others two additives.

### **1.2.5 Conclusions**

The study indicated that the copolymers are more stable under shear than homopolymer but the thickening property of a homopolymer is greater than copolymers. This study also indicated that the efficiency of the prepared additives as viscosity index improver and pour point depressant increases with increasing concentration of the additives in the base oil. The viscosity index property of the additives is directly proportional to the average molecular weight but there is no correlation between pour point and average molecular weight

### **1.2.6 References**

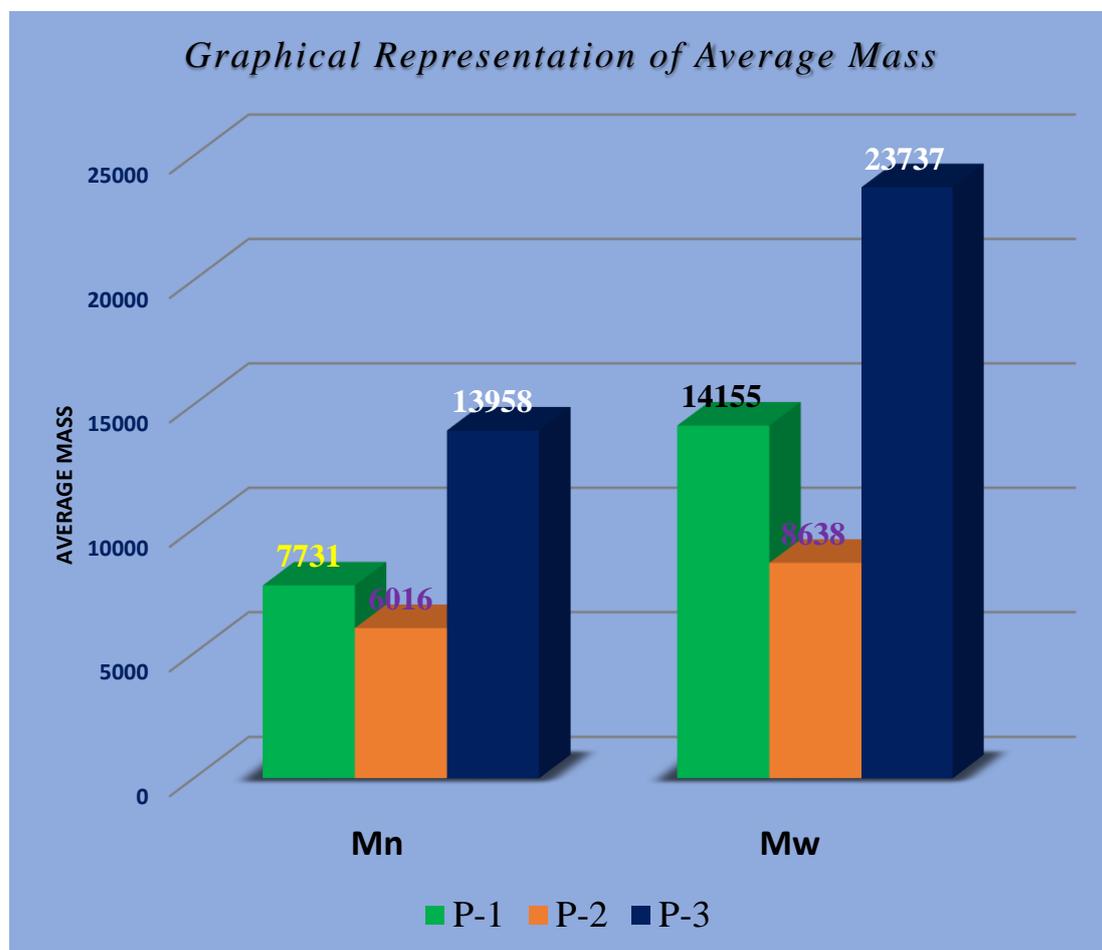
References are given in *BIBLIOGRAPHY* under “Chapter II of Part I” (Page No, 138-139).

## 2.2.7 Tables and figures

**Table 1.2.1: Average molecular weight and TGA values of the prepared polymers and its graphical representation**

Polymer code	Molecular weight			TGA value	
	$M_n$	$M_w$	PDI	Decom. Tem.	PWL
P-1	7731	14155	1.83	172/350	26/84
P-2	6016	8638	1.44	170/320	22/90
P-3	13958	23737	1.7	245/420	20/78

*$M_n$  = Number average molecular weight;  $M_w$  = Weight average molecular weight; PDI = Polydispersity index; Decom.Tem.=Decomposition temperature; PWL=Percent weight loss*



**Table 1.2.2: PVL and PSSI Values of the Additives Doped Base Oil**

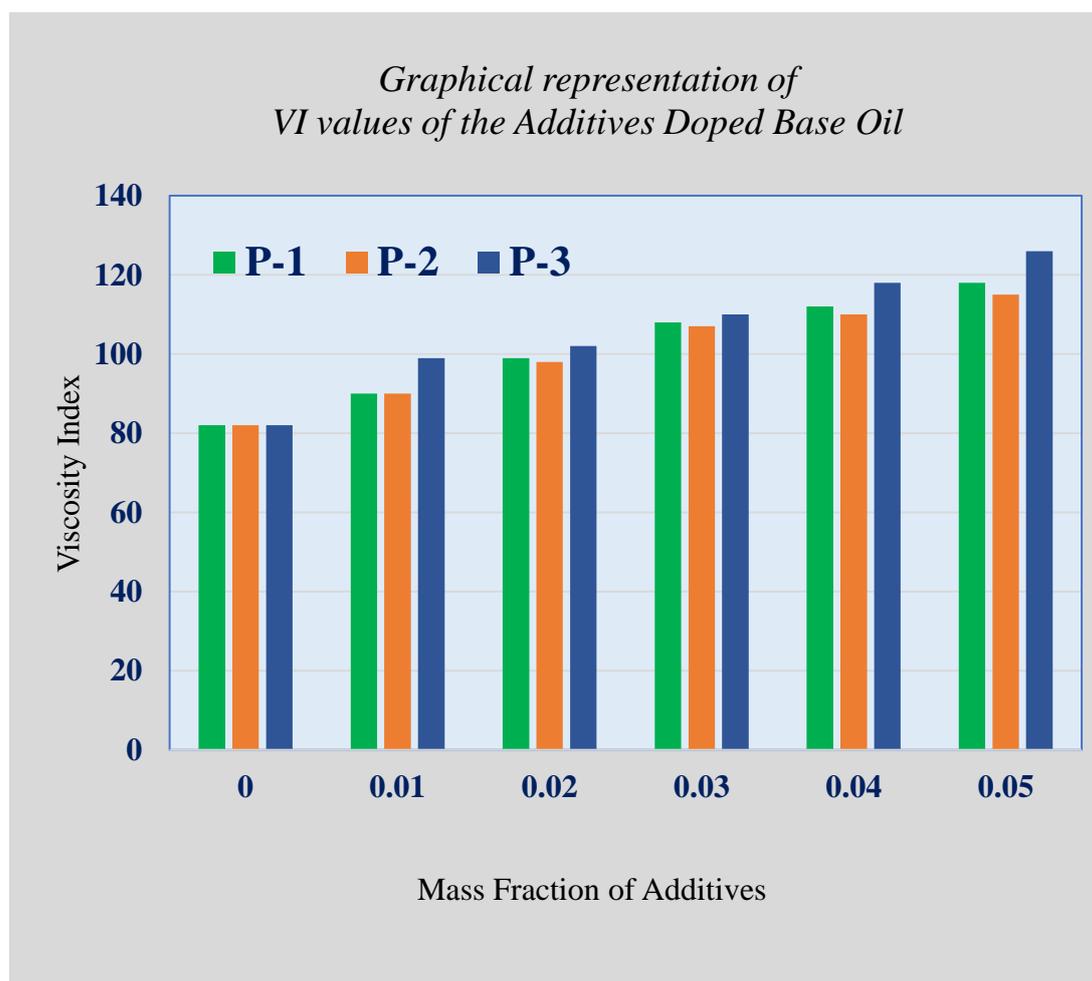
Mass fraction	KV (at 373K)						PVL			PSSI		
	before shear			after shear			P-1	P-2	P-3	P-1	P-2	P-3
	P-1	P-2	P-3	P-1	P-2	P-3						
0.00	3.68	3.68	3.68	3.68	3.68	3.68	0.00	0.00	0.00	0.00	0.00	0.00
0.01	3.84	3.82	3.80	3.83	3.81	3.80	0.23	0.18	0.13	5.76	5.10	4.03
0.02	3.95	3.93	3.92	3.93	3.91	3.90	0.53	0.43	0.38	7.77	6.80	6.35
0.03	4.16	4.14	4.12	4.11	4.10	4.09	1.03	0.84	0.77	9.01	7.67	7.25
0.04	4.29	4.26	4.25	4.22	4.20	4.19	1.67	1.35	1.27	11.84	10.00	9.54
0.05	4.49	4.47	4.46	4.39	4.38	4.37	2.24	2.07	1.97	12.40	11.78	11.34

**Table 1.2.3: Thickening power (THK) of the Additives Doped Base Oil.**

Mass fraction of the additive	THK(at 313K)			THK(at 373K)		
	P-1	P-2	P-3	P-1	P-2	P-3
0.01	3.07	2.97	2.92	4.23	3.71	3.36
0.02	2.21	2.14	2.12	3.66	3.39	3.2
0.03	1.9	1.87	1.86	3.31	3.12	2.98
0.04	1.74	1.72	1.71	3.12	2.93	2.83
0.05	1.66	1.64	1.63	2.41	2.28	2.21

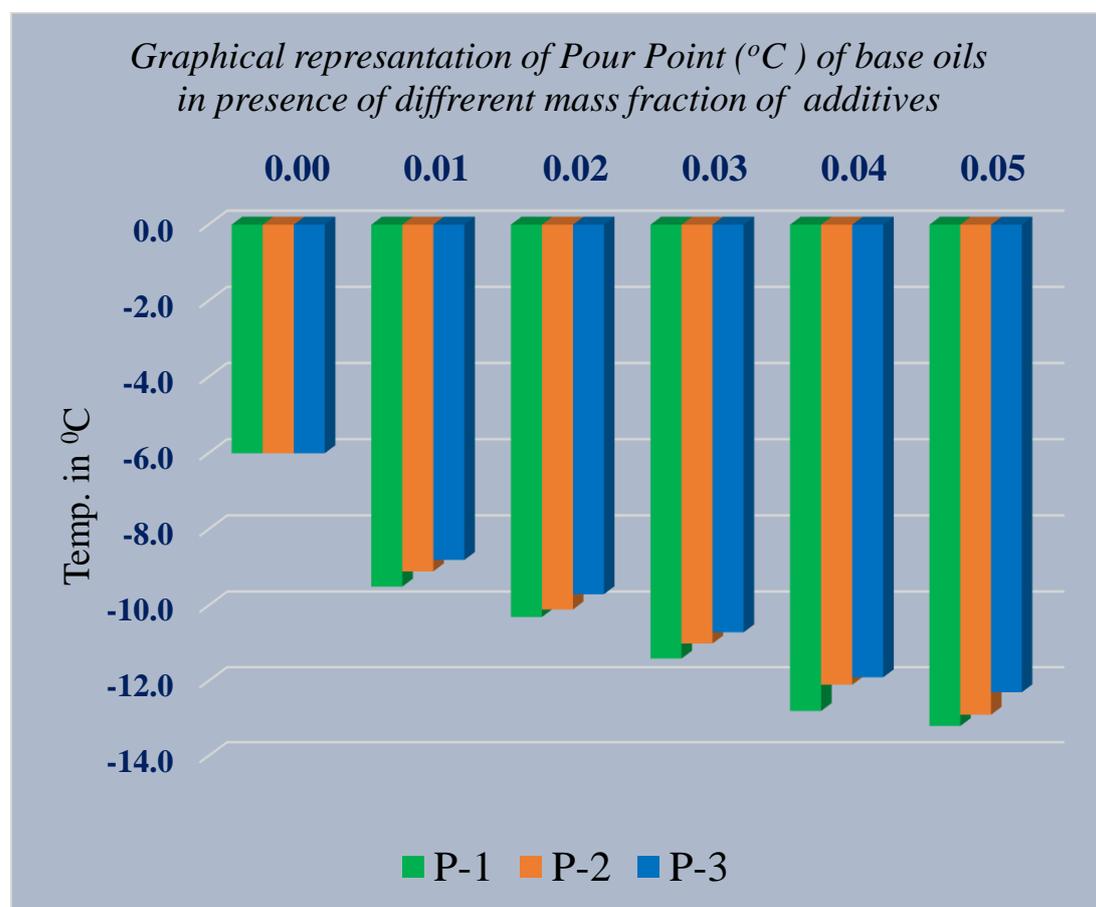
**Table 1.2.4: VI values of the Additives Doped Base Oil and its graphical representation**

Mass fraction of the additive	VI		
	P-1	P-2	P-3
0	82	82	82
0.01	90	90	99
0.02	99	98	102
0.03	108	107	110
0.04	112	110	118
0.05	118	115	126



**Table 1.2.5: Pour Point (PP) of the Additives Doped in Base Oil and its graphical representation**

Mass fraction of the additive	Pour Point ( $^{\circ}\text{C}$ ) of base oils in presence of		
	P-1	P-2	P-3
0.0	-6.0	-6.0	-6.0
0.0	-9.5	-9.1	-8.8
0.0	-10.3	-10.1	-9.7
0.0	-11.4	-11.0	-10.7
0.0	-12.8	-12.1	-11.9
0.1	-13.2	-12.9	-12.3



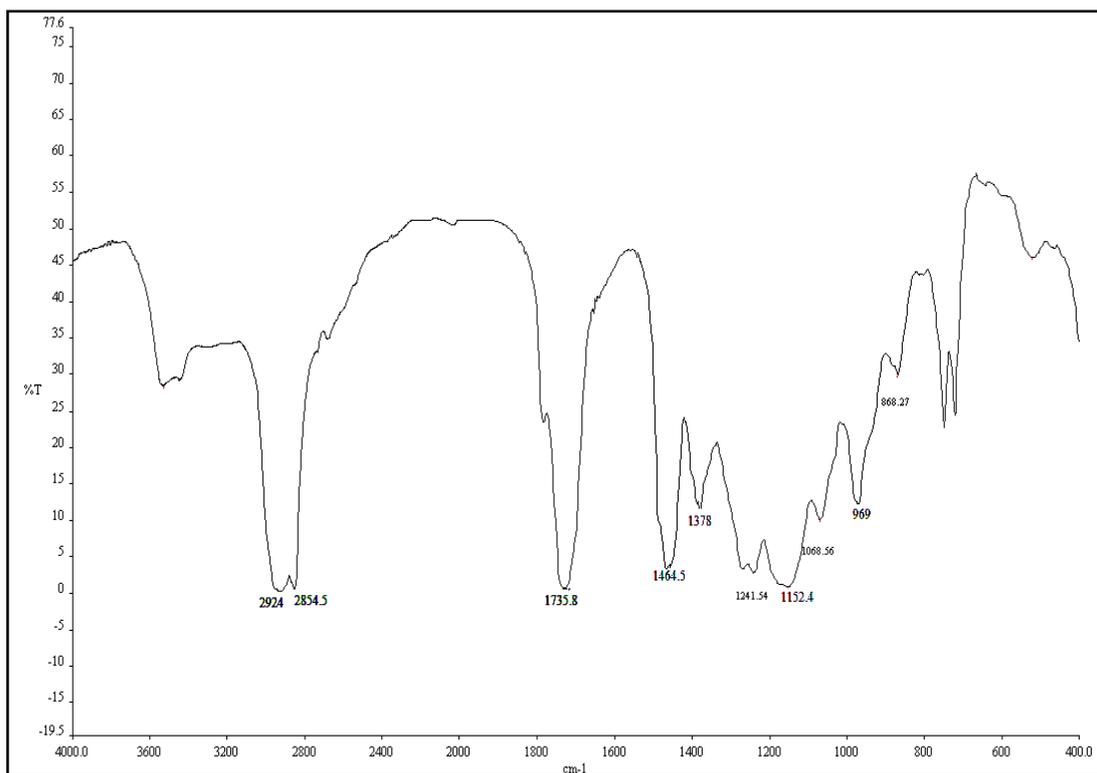


Figure 1.2.1: IR spectra of homopolymer (P-1)

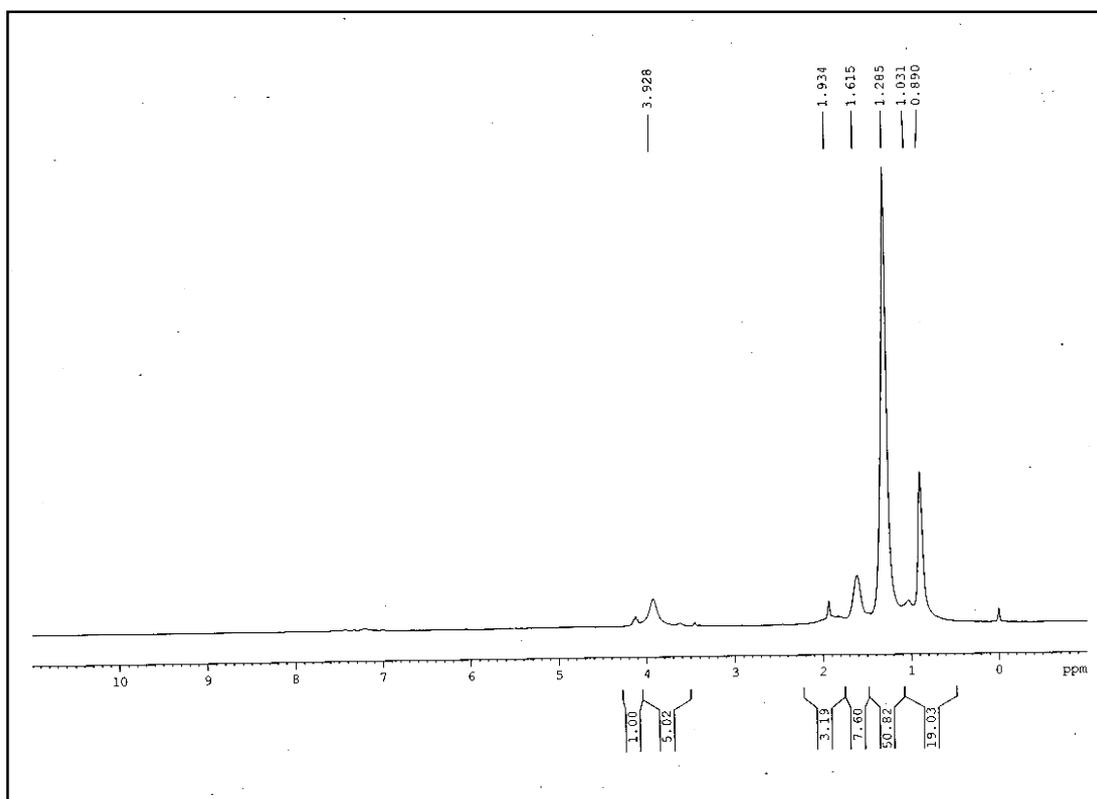


Figure 1.2.2: <sup>1</sup>H NMR spectra of homopolymer (P-1)

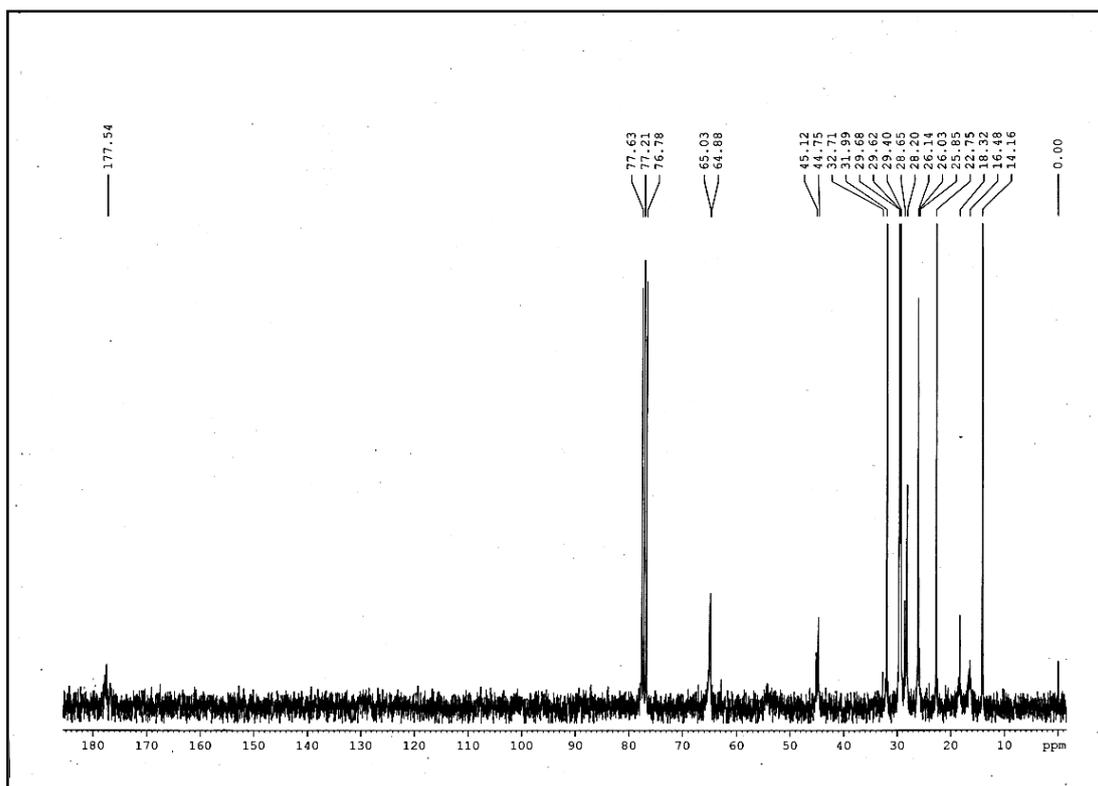


Figure 1.2.3:  $^{13}\text{C}$  NMR spectra of homopolymer (P-1)

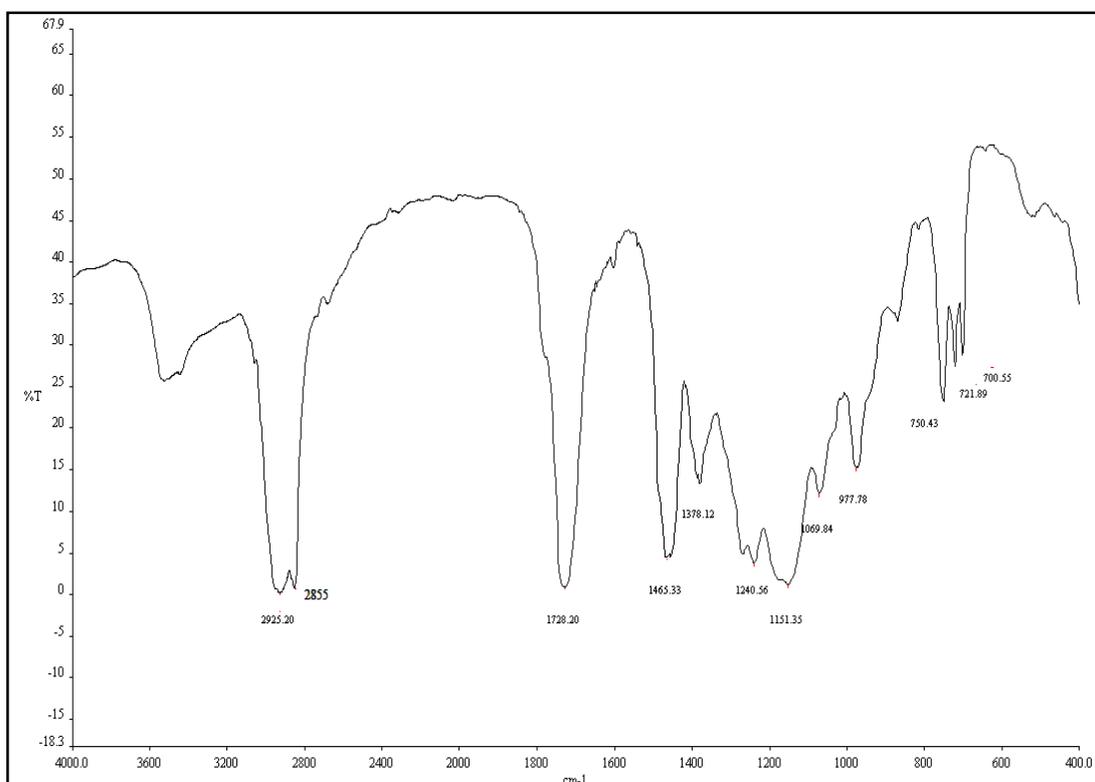


Figure 1.2.4: IR spectra of copolymer (P-3)

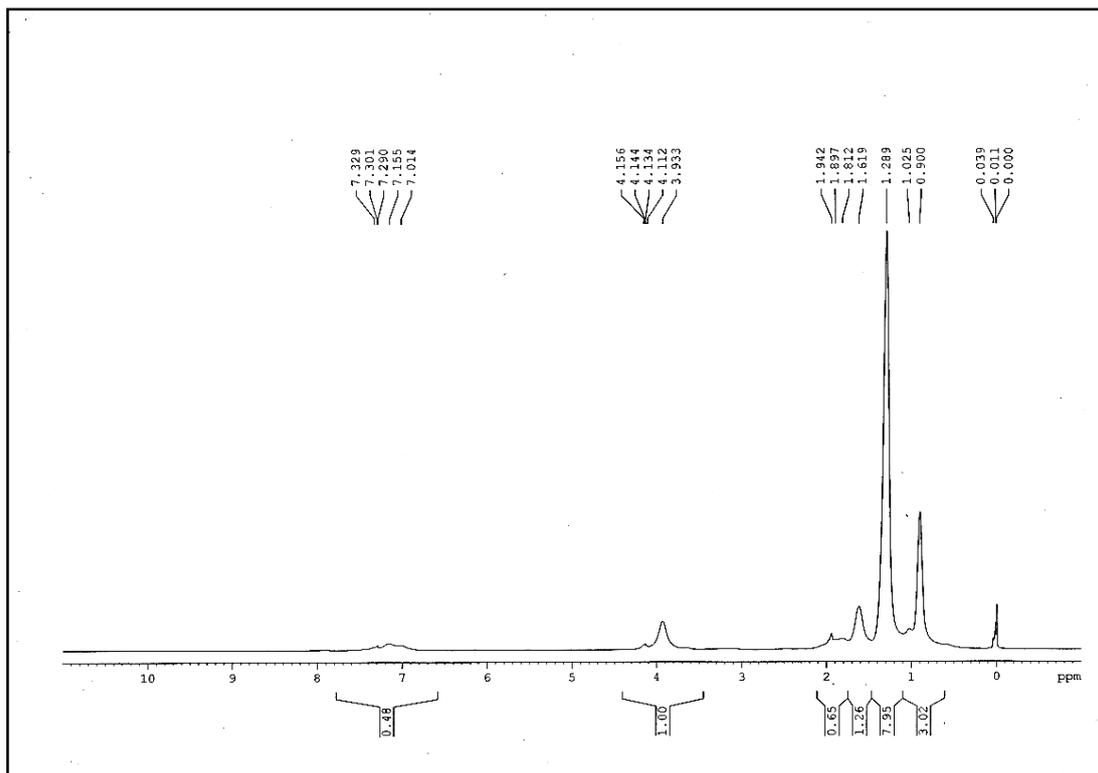


Figure 1.2.5:  $^1\text{H}$  NMR spectra of copolymer (P-3)

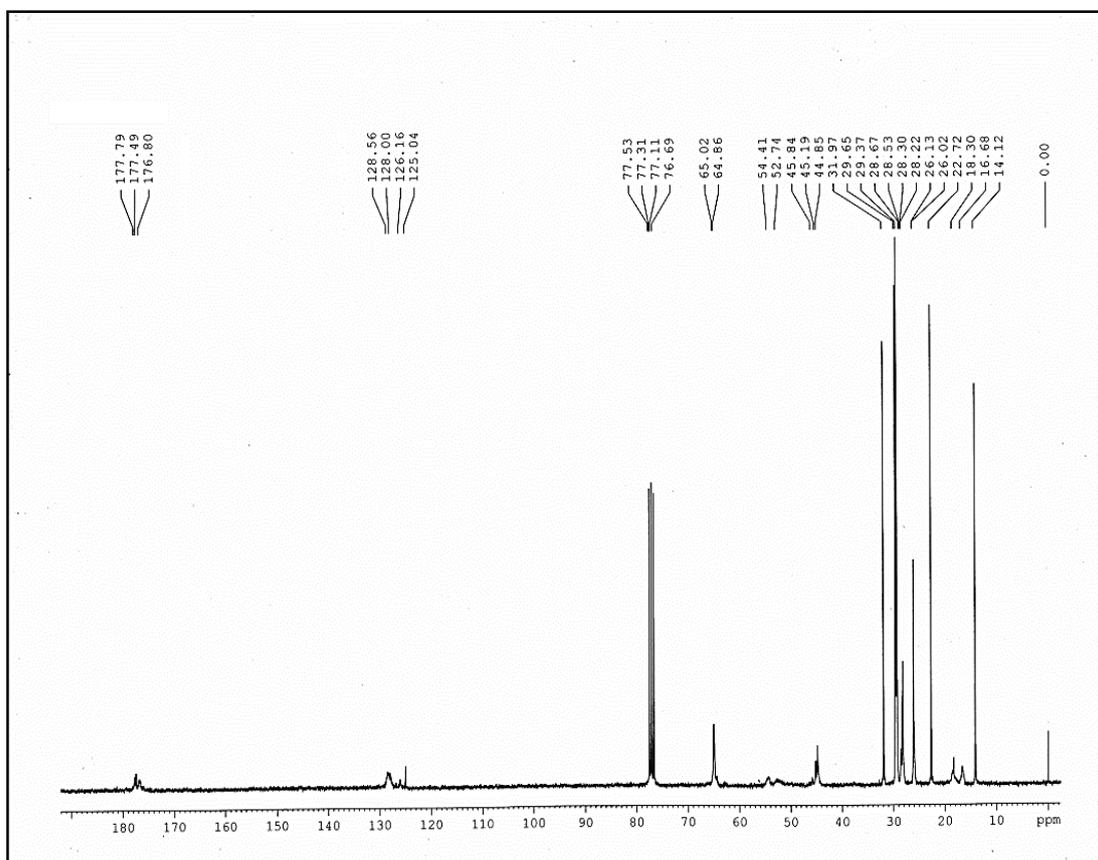


Figure 1.2.6:  $^{13}\text{C}$  NMR spectra of copolymer (P-3)