

Chapter II

**Homo and copolymers of decyl methacrylate – synthesis,
characterization and performance evaluation for lube oil**

1.2.1 Introduction

Base oil is the major component of lubricating oil. Some additives are to be added to the base oil to meet the requirement of modern lubricating oil. Additives are the chemical substances which when added to the base oil they can enhance the properties already present or add some new properties. Some of the important additives added in lube oil are viscosity index improver (VII),¹ pour point depressant (PPD),² antiwear,³ antioxidant, dispersant⁴ etc.

Viscosity index improvers are long chain, high molecular weight polymers and are used to resist the change of viscosity and function by increasing the relative viscosity of oil more at high temperatures than at low temperatures.⁵ It is believed that polymer molecules in cold oil adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the polymer molecules tend to straighten out and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. As the temperature increases, the solubility improves and the polymer coils expand to some maximum size and in so doing donate more and more viscosity. The process of coil expansion is entirely reversibly as coil contraction occurs with decreasing temperature.^{6, 7} The viscosity index is an indicator which indicates the change in viscosity when the temperature is changed. A higher viscosity index indicates the less change in viscosity of oil for a given temperature changes.⁸

Shear stability is an indicator which indicates the amount of viscosity of oil may lose during operation. Lube oil experiences very high stresses in certain areas of engine such as in the oil pump, piston rings and any other areas where two mating surface areas compress the oil film out momentarily. Most of the lubricating oils contain viscosity modifier which are composed of very large viscosity- controlling molecules.⁹

The pour point of oil is the lowest temperature at which the oil stops its flowing. Most of base oil contains some dissolved paraffinic wax. The complete removal of wax from oil is difficult and expensive. Pour point depressants provide an economical alternative way of facilitating the proper flow of the oil in an engine at low temperature.^{10, 11} At low temperature, the wax crystallizes to form a rigid structure that traps the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil will no longer capable to flow. To overcome this problem some high molecular weight polymers are used as pour point depressant (PPD). The high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperature.^{12, 13}

In this present work, author has prepared homopolymers of decylmethacrylate and its copolymers with styrene at different percentage composition by using two types of initiators (BZP and AIBN) and investigated the efficiency of the polymers as viscosity index improver and pour point depressant in two types of base oil. Shear stability, which is an indicator to indicate the amount of viscosity of oil, may lose during operation, of each of the polymer have also been investigated. Finally a comparison of the efficiency of the polymers in terms of their performances in lube oil is investigated and reported in this chapter.

1.2.2 Experimental section

1.2.2.1 Chemicals used

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), styrene (99%, Sigma-Aldrich), decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), hexane (99.5%, S. d Fine Cheme Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.), benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) and azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Base oil was collected from IOCL and BPCL, India. Physical properties of the base oils are given in **table 1.2.1**.

1.2.2.2 Preparation of ester (monomer)

Decylmethacrylate (DMA) was prepared by reacting methacrylic acid with n-decyl alcohol in the molar ratio of 1.1:1 in the presence of conc. H₂SO₄ as a catalyst, 0.25% (w/w) hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as solvent by using Dean Stark apparatus. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants were mixed with toluene and heated gradually from room temperature to 130° C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester.

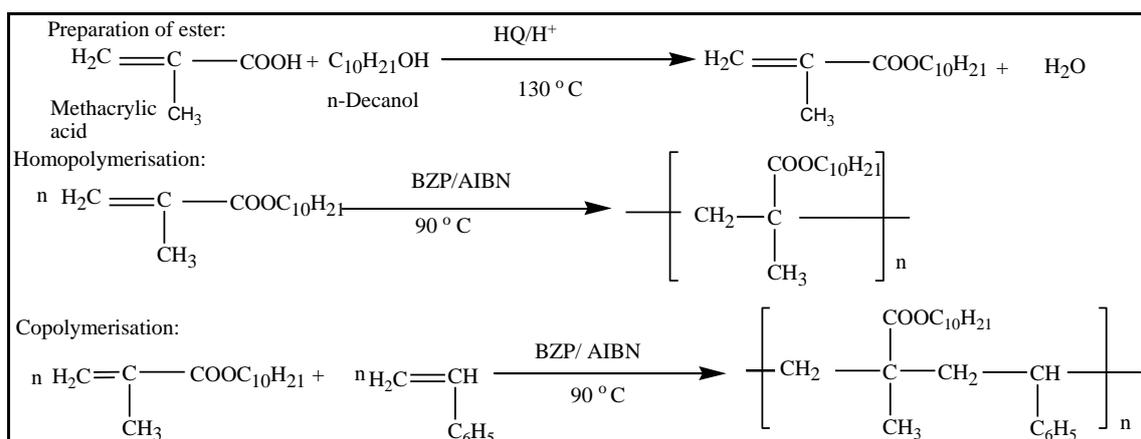
1.2.2.3 Purification of prepared ester

A suitable amount of charcoal was added to the prepared ester. It was allowed to reflux for 2 ½ h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide solution in a separating funnel and then shaken well. This process was repeated several times to ensure the complete removal of unreacted acid and hydroquinone. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide. The ester was then dried by Na₂SO₄ and distillation under reduced pressure and was used in the polymerization process.

1.2.2.4 Preparation of copolymers and homopolymers

The polymers were prepared by free radical polymerization of different percentage ratios of styrene with DMA in presence of different initiators (BZP and AIBN). The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. In the flask, the desired amounts of DMA and styrene in toluene solvent were heated to 90 °C for half an hour. AIBN/BZP (0.5% w/w, with respect to the total monomer) was then added and heated for 6 hours keeping the temperature constant at 90°C. At the end of the reaction time, the mixture was poured into cold methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K temperature. The homopolymer of DMA was also prepared and purified in the same procedure.

By the above process, the author had prepared five polymers by using initiator BZP (one homopolymer and four copolymers) and another five polymers by AIBN (one homopolymer and four copolymers) at different percentage composition, shown in **table 1.2.2**.



Scheme 1 Preparation of ester, homopolymer and copolymer

1.2.3 Measurements

1.2.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

1.2.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45- μ m Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 μ L. The polydispersity index¹⁴ which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

1.2.3.3 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 of rate of 10 °C/min.

1.2.3.4 Determination of shear stability

Shear stability of the polymer blended lube oil is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The shear stability of the doped VM's has a strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant when it is used. The loss of viscosity of a lubricant under shearing condition can be of two types, temporary viscosity loss (TVL) and permanent viscosity loss (PVL). The PVL values are generally expressed in terms of permanent shear stability index (PSSI). The PVL/PSSI value was determined as per ASTM D-3945 method by the following relation.¹⁵

$$\text{PVL (\%)} = (V_i - V_s) / V_i \times 100 \quad (1)$$

$$\text{PSSI (\%)} = (V_i - V_s) / (V_i - V_o) \times 100 \quad (2)$$

Where V_i = Kinematic viscosity of lube oil with polymer before shearing at 100 °C

V_s = Kinematic viscosity of lube oil with polymer after shearing at 100 °C

V_o = Kinematic viscosity of lube oil at 100 °C

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

1.2.3.5 Performance evaluation as viscosity index improver

Viscosity index was calculated by dissolving prepared polymer in two different base oils (BO1 and BO2) using an Ostwald Viscometer (size 200, No 3205), thoroughly cleaned, dried and calibrated at the experimental temperatures (313K and 373K) with distilled water and purified methanol.¹⁶ It was then filled with experimental solution and placed vertically in a

glass sided thermostat. After reaching thermal equilibrium, the time flow of solutions was recorded with a digital stopwatch. In all the determinations an average of three measurements was taken into account and precautions were taken to minimize the losses due to evaporation. The kinematic viscosity (ν) of the sample solution, which was used to calculate Viscosity index (VI), was determined at 313K and 373K temperatures from the following equation¹⁷

$$\nu = (Kt - L/t) d \quad (3)$$

Where K and L are the viscometric constants and their values are $0.06853\text{cm}^2\text{s}^{-2}$ and 5.2706cm^3 respectively, are determined by taking toluene as a solvent, t and d are the time of flow and density of the experimental solution respectively. The densities were measured with a density meter (Anton Paar, DMA 4500M). Before measurements, the density meter was calibrated with distilled water and acetone at the experimental temperature and atmospheric pressure. VI was calculated from the following empirical equation¹⁷

$$VI = 3.63 (60 - 10^n) \quad (4)$$

Where n is given by

$$n = (\ln \nu_1 - \ln \nu_2) / \ln v_2 \quad (5)$$

Where ν_1 and ν_2 are the kinematic viscosities at lower and higher temperatures respectively, K is a constant which is equal to 2.714 for the temperature range performed and n is the characteristic constant for each oil.¹⁷

Different concentrations ranging 1% - 5% (w/w) were used to study the effect of additive concentration on VI.

1.2.3.6 Performance evaluation as pour point depressant

Pour point was determined in polymer doped different base oils (BO1 and BO2) through the pour point test 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 doping concentrations ranging 1% - 5% (w/w).

1.2.4 Results and discussion

1.2.4.1 Spectroscopic analysis

The IR and NMR spectra of the two homopolymers (P-1 and P-6) of decylmethacrylate are similar. IR absorption band at 1736cm^{-1} represents the ester carbonyl group. The peaks at 2854.5cm^{-1} and 2924cm^{-1} represent the CH_3CH_2 - group. The peaks at 1466cm^{-1} , 1404cm^{-1} , 1229cm^{-1} , 1211cm^{-1} and 1149.5cm^{-1} due to CO stretching vibration and absorption bands at 1064.6cm^{-1} , 710cm^{-1} and 690cm^{-1} were due to bending of C-H bond (**figure 1.2.1**). In the ^1H NMR of homopolymer, the methyl protons appear in the range of 0.890 to

1.29 ppm, the methylene protons appear in the range of 1.62 to 1.93 ppm for all alkyl groups. A broad peak at 3.93 ppm indicates the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm confirms the polymerisation (**figure 1.2.2**). In the ^{13}C NMR of homopolymer, the peak at 177.54 ppm indicates the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirm the presence of $-\text{OCH}_2$ carbon. Peaks in the range of 14.16 - 45.12 ppm represent all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbons and confirms the polymerization (**figure 1.2.3**).

The IR and NMR spectra of all copolymers are similar. The ester carbonyl group at 1736 cm^{-1} of homopolymer shifted to 1728 cm^{-1} in the copolymer. Peaks at 750.4 cm^{-1} , 722 cm^{-1} and 702 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene (**figure 1.2.4**). In the ^1H NMR of copolymer, a broad peak in the range of 3.933 - 4.15 ppm indicates the $-\text{OCH}_2$ protons. A broad peak at 7.01 - 7.33 ppm appears due to the protons of phenyl group. All the sp^3 protons appear in the range of 0.9 - 1.94 ppm. Absence of peaks in the range of 5-6 ppm indicates that the polymerisation was carried out successfully (**figure 1.2.5**). In the ^{13}C NMR of copolymer, the peaks in the range of 176.8 - 177.79 ppm confirm the presence of ester carbons. The phenyl carbons appear in the range of 125.04 - 128.56 ppm. The $-\text{OCH}_2$ carbon peaks appear at 64.86 ppm and 65.02 ppm. Peaks in the range 14.12 - 54.41 ppm represent all the sp^3 carbons (**figure 1.2.6**).

1.2.4.2 Analysis of molecular weight

The experimental values of M_n and M_w for the polymer P-1 to P-10 (determined by GPC) are given in **table 1.2.3**. The data indicated that molecular weight of homopolymer prepared by BZP (P-1) initiator is higher than homopolymer prepared by AIBN initiator (P-6). But the copolymers prepared by BZP have lower molecular weight than the copolymers prepared by AIBN. Moreover, it is also seen that with increasing the percentage of styrene in copolymers the molecular weight as well as PDI values increase.

1.2.4.3 Analysis of TGA data

The TGA values of all the polymers are given in **table 1.2.4**. From the experimental data, it is found that the homopolymer prepared by BZP initiator (P-1) is thermally less stable than homopolymer prepared by AIBN initiator. It may be due to higher molecular weight and higher PDI value of P-1. From the values, it is also observed that thermal stability of copolymers (P-2, P-3, P-4 and P-5) is more than homopolymer, P-1. Similarly, the copolymers P-7, P-8 and P-9 are thermally more stable than homopolymer, P-6 except P-10, which is thermally less stable than P-6. It may be because of the higher PDI value P-10, that

may lead to more degradation. The higher thermal stability of copolymers may be due to the presence of phenyl group. On the other hand, the homopolymer containing only the ester group may easily undergo degradation by producing gaseous products.^{18, 19} Moreover, it is also observed that with increasing the styrene content in the feed of copolymers, the thermal stability decreases which is also reflected in their higher PDI value.

1.2.4.4 Analysis of permanent shear stability index (PSSI) data

PSSI values were calculated in polymer doped base oil (BO2) at 2% (w/w) and 5 % (w/w) concentrations at 100 ° C. The experimental values are given in **figure 1.2.7**. From the figure, it is found that homopolymer P-1 is less shear stable (higher PSSI value) than homopolymer P-6. It may be due to higher molecular weight of P-1. The copolymer P-2, P-3, P-4 and P-5 are more shear stable than P-1 at low concentration but at higher concentration P-4 and P-5 is less shear stable. In case of copolymers prepared by AIBN initiator, P-7 and P-8 are more shear stable than homopolymer P-6 but P-9 and P-10 are less shear stable than P-6. It may be due to higher PDI value of P-9 and P-10. Moreover, it is also found that at a higher concentration polymer - base oil blend is less shear stable than at lower concentration. From the figure 1.2.7, it also is observed that with increasing the styrene content in copolymers the shear stability decreases (higher PSSI value) which may be due to their increased PDI values.²⁰

1.2.4.5 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at the concentrations of 1% - 5 % (w/w) to the two types of base oil (BO1 and BO2). The experimental values of VI are given in **table 1.2.5**. From the experimental data, it is found that for all the polymers VI values increase with increasing the concentration of polymer in base oils. With increasing temperature, the lube oil viscosity decreases but the expansion of polymer molecules take place at high temperature due to increase in solvation power and increased size of micelle. This increased in micelle size minimize the reduction of the viscosity of the polymer doped lube oil. Therefore, with increasing the concentration of polymer in lube oil leads to an increase in the total volume of polymer micelle in lube oil, thus exerting higher thickening effect and improves the VI property.^{21, 22} Between the two homopolymers (P-1 and P-6), P-1 (prepared by BZP initiator) has greater effect on VI for both the base oils than P-6 (prepared by AIBN initiator). It may be due to higher molecular weight of P-1. From the experimental values, it is also found that the performance of the prepared copolymers as VI increases by increasing the styrene content. It may be due to increase of the molecular weight with

increasing styrene content. In case of P-5 and P-10 (% of styrene 10), the molecular weight has increased but VI remain approximately same with P-4 and P-9 respectively. It may be due to higher PDI value and hence reduces the solubility.^{23, 24} The VI value is somewhat better in case of copolymers prepared by AIBN initiator than copolymers prepared by BZP initiator. The lower decomposition temperature of AIBN compared to BZP may be responsible for giving higher molecular weight and hence the VI.²⁵ All the polymers are more effective in BO1 (lower viscous) than BO2 as VM.

1.2.4.6 Analysis of pour point data

The polymer doped base oils (BO1 and BO2) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table1.2.6**. From the values, it is observed that all the polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oils. It may be due to decrease in solvation power. The efficiency as PPD of homopolymer, P-1(prepared by BZP initiator) is better than homopolymer, P-2 (prepared by AIBN initiator). It may be due to higher PDI value of P-1.²⁶ The copolymers P-2, P-3, P-4 and P-5 are less efficient as PPD than the homopolymer, P-1. It may be due to presence of phenyl group in the copolymers that reduces the adsorption of the polymer molecule on the wax crystals.²⁷ From the experimental values, it is clear that there is no significant change of pour point with increasing the styrene content among the copolymers of P-2, P-3, P-4 and P-5 (prepared by BZP initiator). The copolymers P-7 and P-8 (prepared by AIBN initiator) are more efficient as PPD than homopolymer P-6 (prepared by AIBN initiator) but P-9 and P-10 are less efficient compare to homopolymer. With increasing the styrene content among the copolymers P-7, P-8, P-9 and P-10, it is found that PPD property gradually decreases and may be due to increase of percentage of phenyl group. By comparing the PPD property of copolymers, prepared by BZP initiator and AIBN initiator, it is seen that copolymers prepared by AIBN initiator are more effective as PPD. The lower decomposition temperature of AIBN compare to BZP may be responsible for this observation.

1.2.5 Conclusions

From the above study, it is found that all the prepared decyl methacrylate based polymers are effective as VII and PPD. The homopolymer prepared by BZP initiator is more effective as VII and PPD than the homo polymer prepared by AIBN initiator. The efficiency of the copolymers as VII increases with increasing the styrene content up to 7.5% of styrene but at 10% of styrene, it does not increase. The performance as VII of the copolymers prepared by

AIBN initiator is better than the copolymers prepared by BZP initiator. The efficiency of the copolymers as PPD prepared by AIBN initiator decreases with increasing styrene content. Therefore, a critical observation can be made from the above study that initiator and percentage of styrene has a significant role in relation to the performance of the additive as VII and PPD.

1.2.6 References

References are given in bibliography section under Chapter II of Part I (Page No. 180 - 182).

1.2.7 Tables and figures

Table 1.2.1 Physical properties of the base oils

Base oil properties	Base oil	
	BO1	BO2
Density (g cm ⁻³) at 40 ° C	0.83	0.84
Viscosity at 40 °C in c St	7.102	23.502
Viscosity at 100 °C in c St	1.850	3.98
Viscosity index	84.56	85.15
Pour point (° C)	-3	-6
Cloud point (° C)	-1	-4

Table 1.2.2 Different percentage composition of the prepared polymers

Polymer code	% of DMA	% of styrene	Initiator	Polymer code	% of DAMA	% of styrene	Initiator
P-1	100	-	BZP	P-6	100	-	AIBN
P-2	97.5	2.5	BZP	P-7	97.5	2.5	AIBN
P-3	95	5	BZP	P-8	95	5	AIBN
P-4	92.5	7.5	BZP	P-9	92.5	7.5	AIBN
P-5	90	10	BZP	P-10	90	10	AIBN

DMA = Decyl methacrylate; BZP = Benzoyl peroxide; AIBN = Azobisisobutyronitrile

Table 1.2.3 M_n , M_w and PDI values of the polymers, P-1 to P-10

Polymer	M_n	M_w	PDI	Polymer	M_n	M_w	PDI
P-1	21,112	58,917	2.7906	P-6	20,482	49,682	2.43
P-2	19,121	40,571	2.1217	P-7	21,592	58,982	2.73
P-3	19,842	39,918	2.0117	P-8	27,457	77,688	2.83
P-4	22,982	56,121	2.4419	P-9	28,946	81,556	2.82
P-5	23,245	68,712	2.9559	P-10	30,345	93,842	3.09

M_n = Number average molecular weight; M_w = Weight average molecular weight;

PDI = Polydispersity index;

Table 1.2.4 TGA values of the polymers (P-1 to P-10)

Polymer	Decom. temp. /° C	PWL	Polymer	Decom. temp. /° C	PWL
P-1	170/350	28/82	P-6	248/315	20/76
P-2	250/412	16/81	P-7	280/382	20/78
P-3	250/410	15/81	P-8	275/350	18/82
P-4	210/360	14/85	P-9	275/336	19/88
P-5	190/362	31/90	P-10	172/300	20/92

Decom. temp = Decomposition temperature; PWL = Percent weight loss

Table 1.2.5 Viscosity Index (VI) of polymer doped base oils

Polymer code	VI in BO1					VI in BO2				
	Conc. of the polymer (% in w/w)					Conc. of the polymer (% in w/w)				
	1	2	3	4	5	1	2	3	4	5
P-1	96	114	123	144	153	96	104	109	118	128
P-2	91	96	98	107	122	92	98	110	112	107
P-3	96	108	115	126	128	108	116	118	120	126
P-4	112	120	128	138	162	104	105	119	128	136
P-5	112	122	134	156	162	108	114	116	124	138
P-6	103	105	123	130	136	98	102	112	114	118
P-7	99	102	106	116	125	106	110	108	119	126
P-8	101	104	115	122	132	106	108	114	122	132
P-9	99	118	128	148	163	105	122	138	142	143
P-10	102	124	124	142	160	102	115	132	142	142

Table 1.2.6 Pour point of polymer doped base oils

Polymer code	Pour point ($^{\circ}\text{C}$) in BO1					Pour point ($^{\circ}\text{C}$) in BO2				
	Conc. of the polymer (% in w/w)					Conc. of the polymer (% in w/w)				
	1	2	3	4	5	1	2	3	4	5
P-1	-10	-10	-8	-7	-7	-12	-12	-10	-9	-9
P-2	-7.4	-7.4	-6	-5.5	-5.5	-8.8	-8.8	-7.5	-7.5	-7.5
P-3	-7.8	-7.8	-6.8	-6.8	-6	-9.6	-9.6	-9	-9	-9
P-4	-9.4	-9.4	-7.5	-7	-7	-10	-10	-9	-9.5	-9
P-5	-9	-9	-8	-8	-8	-8	-8	-7.5	-7.5	-7.5
P-6	-9	-9	-8	-7	-7	-10	-11	-10	-10	-10
P-7	-15	-15	-13	-10	-10	-12	-12	-10	-10	-9.5
P-8	-12	-12	-10	-10	-10	-12	-12	-10	-10	-10
P-9	-9.4	-9.4	-8.5	-7.5	-7.5	-10	-9.5	-9.5	-9.5	-8.5
P-10	-9	-10	-8	-7	-7	-9.4	-9	-8.5	-8	-8

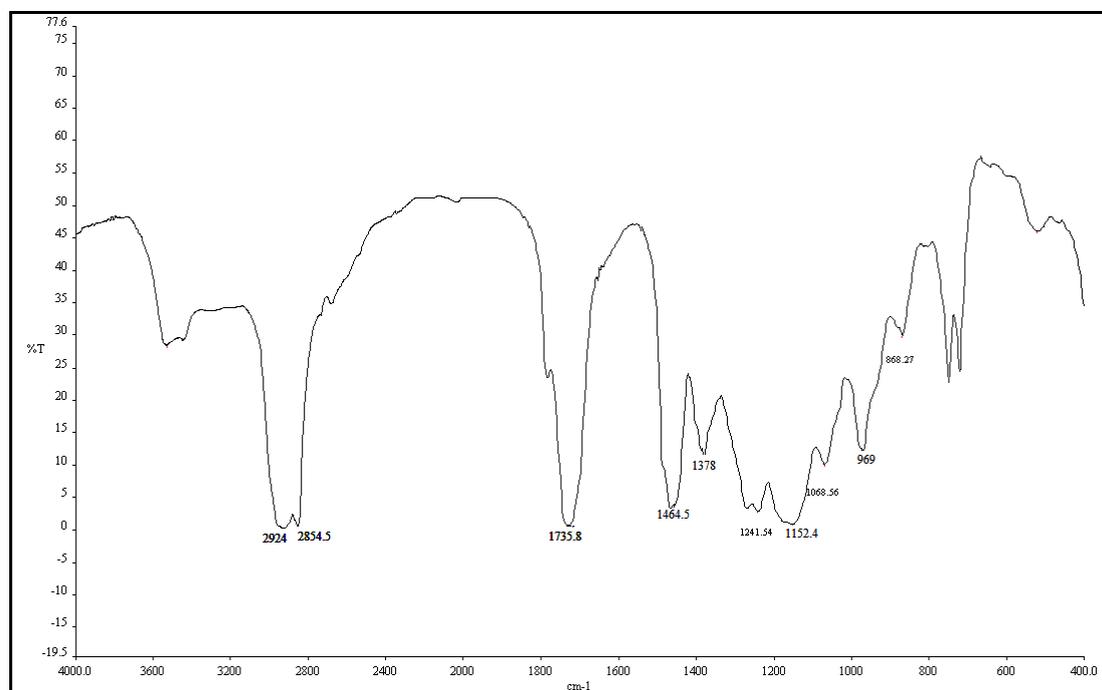


Figure 1.2.1 IR spectra of homopolymer (P-1)

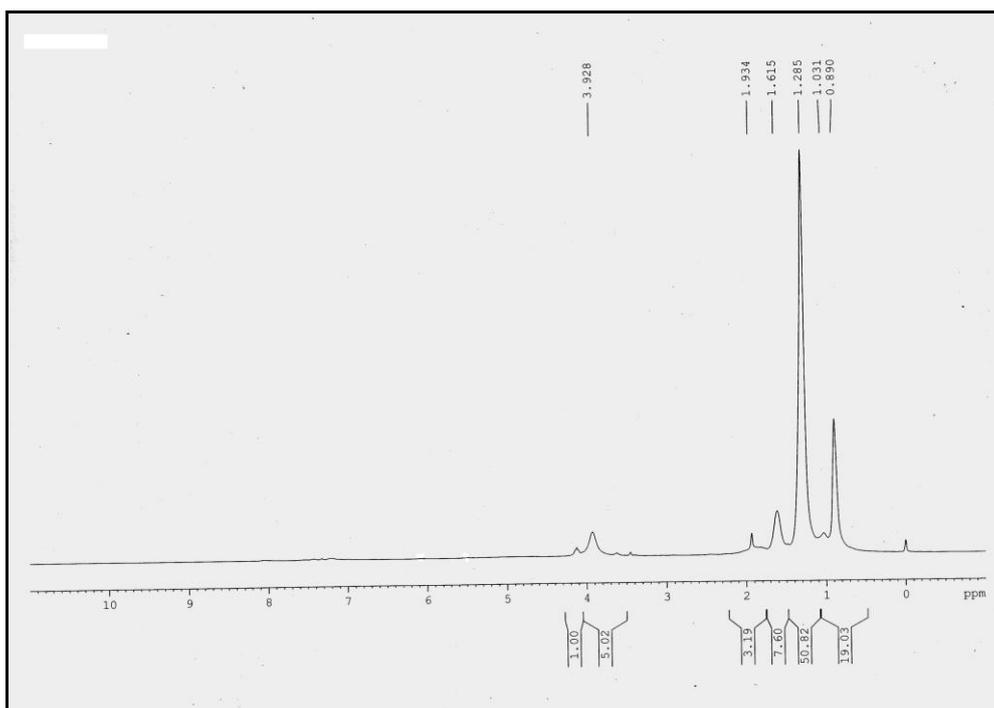


Figure 1.2.2 ^1H NMR spectra of homopolymer (P-1)

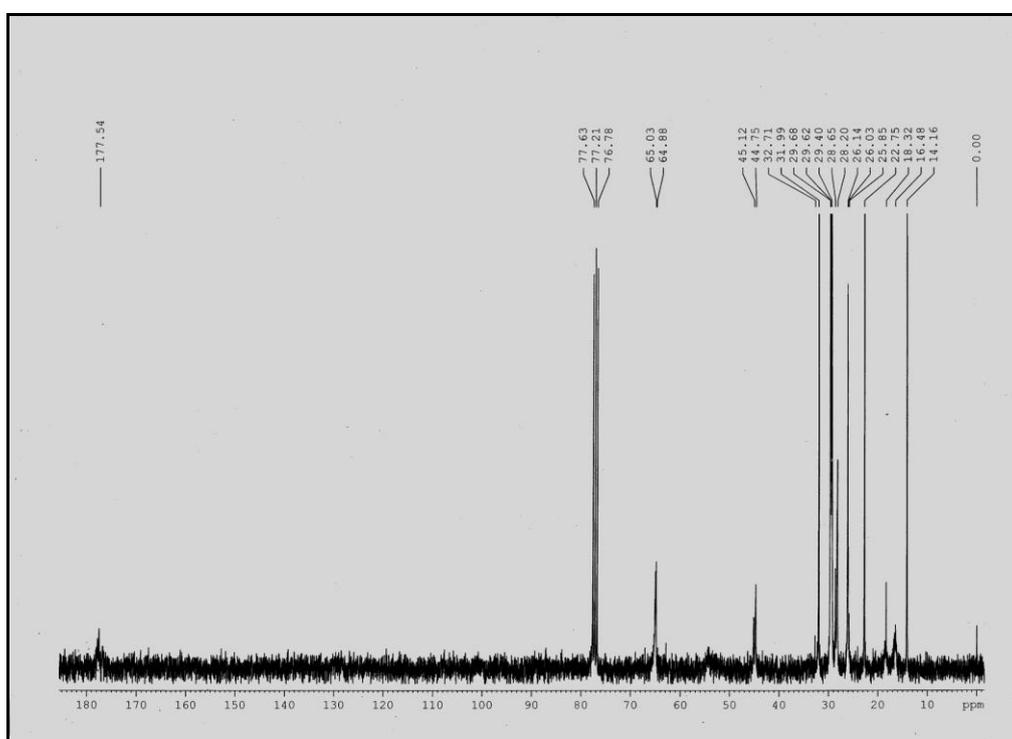


Figure 1.2.3 ^{13}C NMR spectra of homopolymer (P-1)

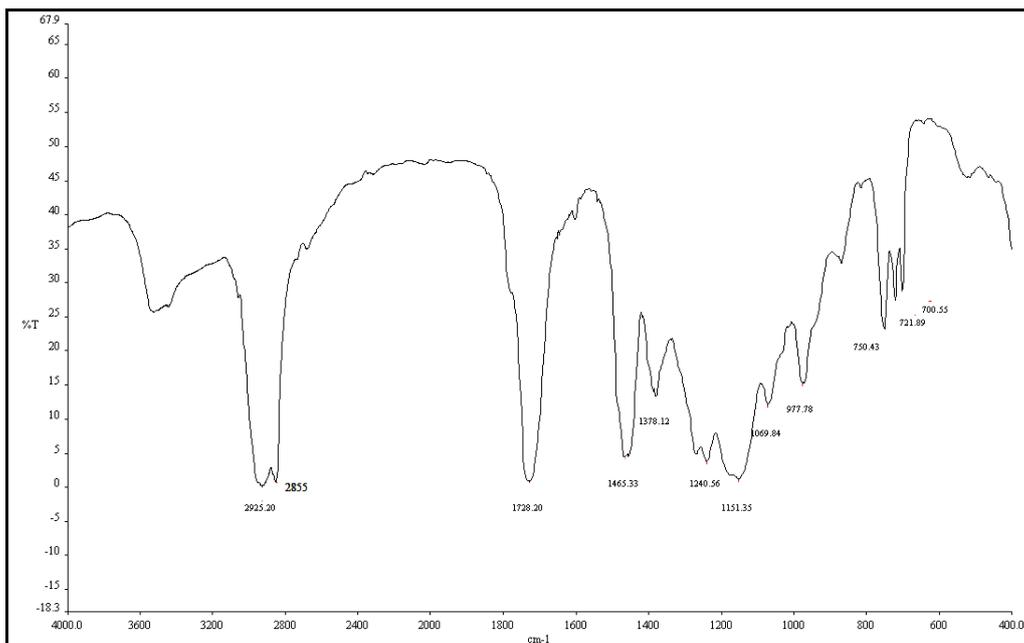


Figure 1.2.4 IR spectra of copolymer (P-2)

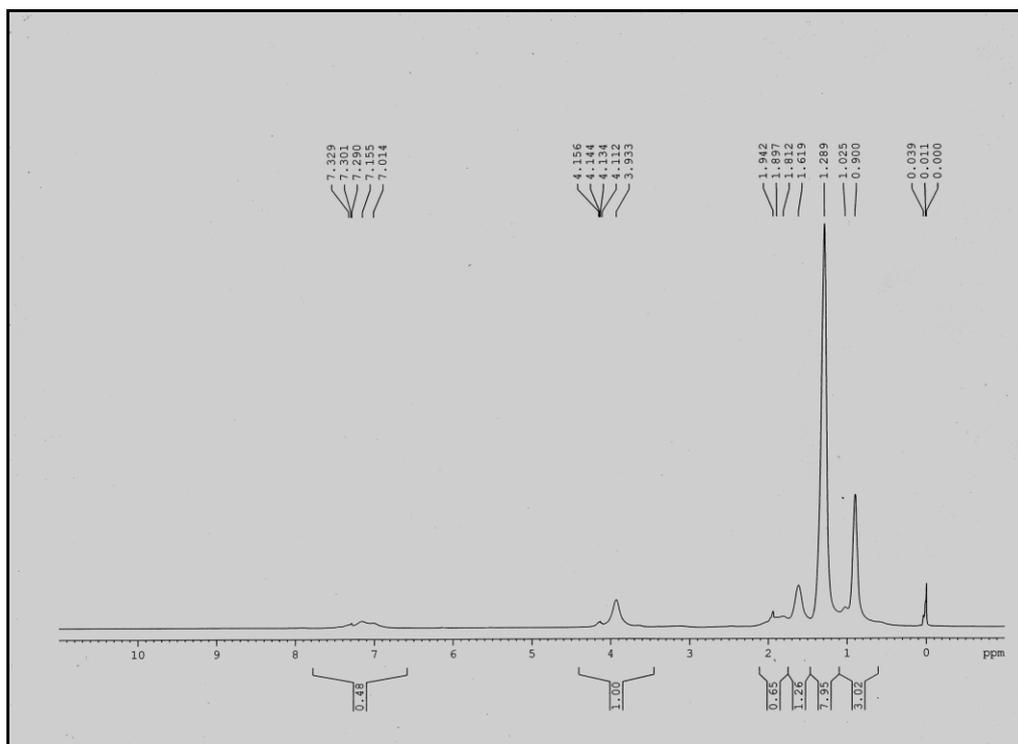


Figure 1.2.5 ¹H NMR spectra of copolymer (P-2)

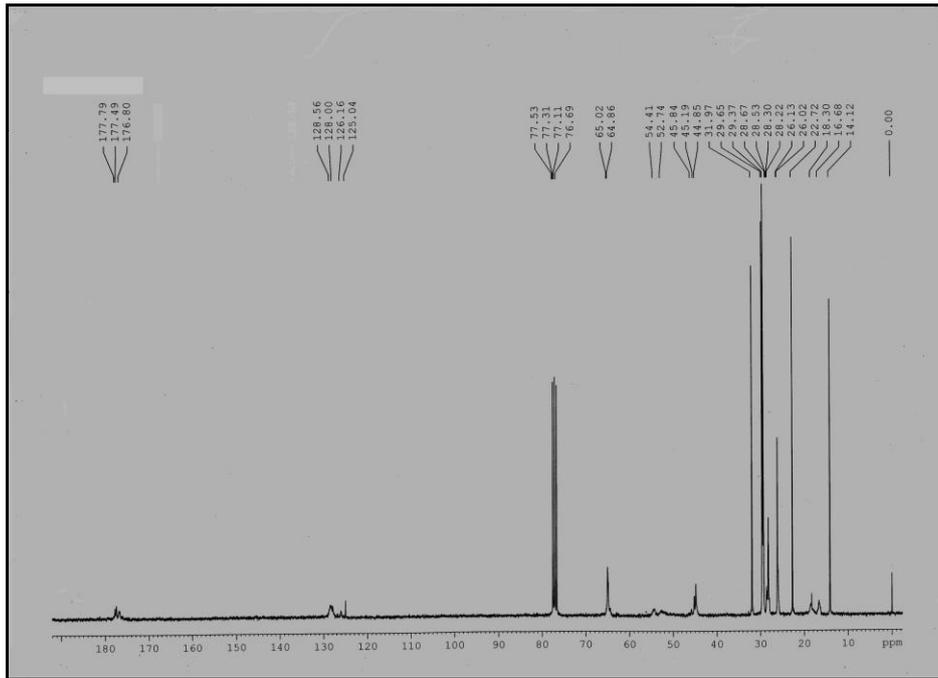


Figure 1.2.6 ^{13}C NMR spectra of copolymer (P-2)

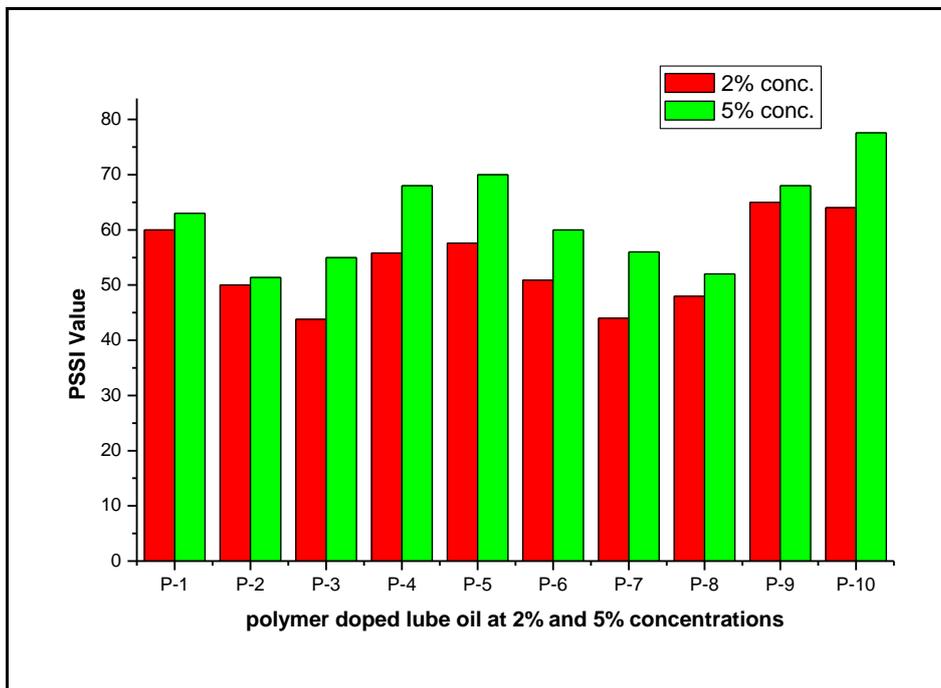


Figure 1.2.7 Variation of PSSI values of polymer doped base oil (BO2) at 2% and 5% concentrations