

PART-1/CHAPTER-2

DODECYL METHACRYLATE –VINYL ACETATE HOMO AND COPOLYMERS- A MULTIFUNCTIONAL PERFORMANCE ADDITIVE FOR LUBRICATING OIL

1.2.1 INTRODUCTION

The primary component of lubricating oil used in the modern machine to reduce rolling friction and heat generated is base oil and is derived from a petroleum source, but base oil alone cannot satisfy all engineering requirements. Hence, they are blended with some chemical entities to modify lube behavior or to add extra attributes needed to call additives[1]. Among the various important additives, PPDs, VIIs, and AWs are of prime importance for the effective formulation of the lubricant for their field application. Poly alkyl acrylates, poly alkyl methacrylates, styrene-butadiene copolymers are some of the widely used additives applied in specific composition and architecture for improving the tribological and rheological properties of base lubricating fluids[2]. However, most of the reported additives developed in this area so far, function either simply as VM or as PPD. Moreover, despite their promising properties, only a few of them have been evaluated as multifunctional additives. Therefore, in continuation of our quest to further explore this area of chemistry and to synthesize the effective multifunctional performance additives for lube oil at a reduced cost, this investigation is an attempt to ascertain whether a combination of acrylate and VA group can effectively control the rheological properties of the base fluid. This present work thus reveals the synthesis, characterization, and performance evaluation of additives based on the copolymers of long-chain dodecyl methacrylate and vinyl acetate[15]. A comparative assessment of

the outcome of copolymers as an additive in contrast to the homopolymer of dodecyl methacrylate was also studied. Homopolymer of the prepared dodecyl methacrylate (DDMA) monomer was synthesized and a series of copolymers of it were prepared by varying the ratio between DDMA and vinyl acetate (VA) by free radical polymerization using BZP as initiator. The synthesized polymers were characterized by spectral studies (FT-IR, ¹H NMR, ¹³C NMR) and by Gel Permeation Chromatography (GPC)[13]. Thermogravimetric analysis (TGA) was also carried out to investigate the thermal behavior of the polymers at high temperatures. Performances of the polymers as additives and their responses as PPD and viscosity modifiers in the base oil were evaluated by standard ASTM methods in terms of pour point and viscosity index[15]. Wax crystallization behavior of the additives was analyzed by Photo Micrographic image. The copolymers showed better thermal stability, better flow improving efficiency, and induced better viscosity modification than the homopolymer. It is also observed that the viscosity modification and the pour point performance of the additives depend on the concentration of the additives in the base fluid.

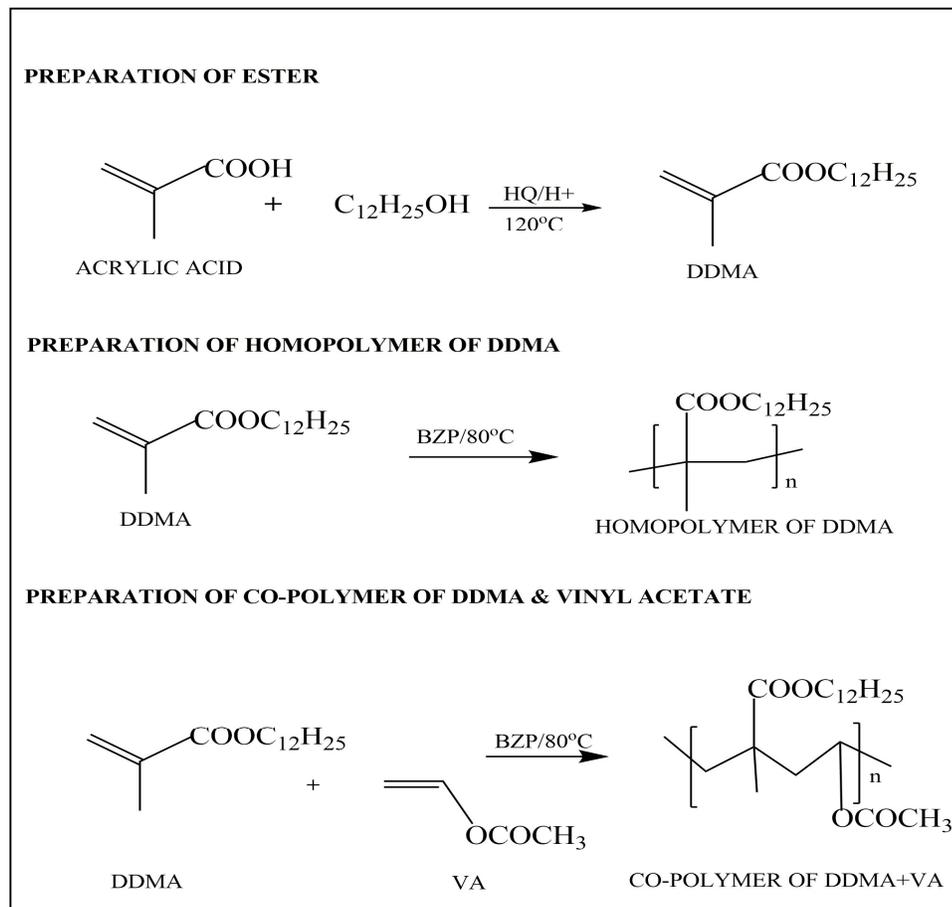
1.2.2 EXPERIMENTAL

1.2.2.1 MATERIALS USED

Dodecyl alcohol (DDA) methacrylic acid was obtained from SRL Pvt., Ltd., (India). and hexane was from SD Fine-Chemical Ltd., (India). Vinyl acetate (VA) was purchased from Acros Organics and methanol was from Thomas Baker Chemicals Pvt., Ltd., (India). Toluene and H₂SO₄ were obtained from Merck Specialties Pvt., Ltd., (India). Benzoyl peroxide (BZP) obtained from Spectrochem Pvt., Ltd. (India) was recrystallized from CHCl₃-CH₃OH before use. Other chemicals were used as received. Indian Oil Corporation Ltd. (IOCL), Dhakuria,

WB, India, provided base oil, and its properties are summarised in the footnote of Table:- 1.2.7.2.

Scheme 1.2.1 Preparation of ester followed by homo and copolymerization



1.2.2.2 PREPARATION OF ESTER (MONOMER) AND ITS PURIFICATION

The ester (dodecyl methacrylate, DDMA) was prepared by reacting 1.1 moles of methacrylic acid with 1 mol of dodecyl alcohol using concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone concerning the total reactants as a polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication[3].

1.2.2.3 PREPARATION OF POLYMERS

The polymers (homo and copolymers) were prepared by free radical polymerization (Scheme:-1.2.1) at different percentage compositions of monomers in presence of BZP as the initiator (0.4% w/w, concerning the total monomer). The process of polymerization and purification was carried out by the procedure as reported in our earlier publication[6].

1.2.3 MEASUREMENTS

1.2.3.1 INSTRUMENTATIONS

- **FT-IR AND NMR SPECTROSCOPY**

Shimadzu FT-IR 8300 (Japan) spectrometer was used within the wavenumber range of 400 to 4000 cm^{-1} at room temperature for recording the IR spectra, using 0.1 mm KBr cells. The NMR spectra were recorded in Bruker Avance 300 MHz (Germany) FT-NMR instrument using CDCl_3 as a solvent and TMS as a reference and 5 mm BBO probe[13].

- **GEL PERMEATION CHROMATOGRAPHY (GPC)**

The average molecular weight (number-average and weight-average) of the additives were measured in Waters (USA) GPC equipment using HPLC grade THF as eluent at room temperature. The system was fitted with a 2414 refractive index detector (polystyrene calibration) and Waters 515 HPLC pump. The PDI (M_w/M_n) was also calculated by GPC[14].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

The thermo-oxidative stabilities (TGA) or the decomposition pattern of the prepared additives were determined by a Shimadzu TGA-50 (Japan) thermogravimetric analyzer, at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The percent weight loss (PWL) of mass (of the additives) with a temperature rise was used to measure the

thermal stability of the additives. The PWL was measured according to the following equation,

$$\text{PWL} = [(M_0 - M_1)/M_0] \times 100$$

where M_0 = original mass taken and M_1 = Remaining mass after the test. The initial decomposition temperature and the temperature of the complete decomposition of the additives were obtained from the TGA curve[13].

- **PHOTOMICROGRAPH AND WAX MODIFICATION**

The effectiveness of an additive in controlling the crystallization of wax can be studied by a photomicrographic image of the base fluid. The wax modification pattern of the base fluid was analyzed using a Banbros polarizing microscope (BPL-400B, India), with magnification 200X. To control the temperature at 0°C The microscope was connected with a cooling thermostat [13].

1.2.3.2 PERFORMANCE EVALUATION

- **PERFORMANCE EVALUATION AS POUR POINT DEPRESSANTS IN THE BASE OIL**

The effect of additive concentration on the pour point of the lube oil was tested by using different doping concentrations ranging (1% to 5% (w/w) for each of the prepared polymer according to the ASTM D 97-09 method. The Pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India).

- **EVALUATION OF VISCOSITY INDEX**

The VI of the additive doped base fluid was determined using an Ubbelohde viscometer. The viscometer was dried and calibrated with distilled, degassed water, and purified methanol at the experimental temperatures (40°C and 100°C) to determine the value of the viscometric constants[3]. The variation of kinematic

viscosity (ν) of doped lube oil with the change of temperature, was evaluated putting data obtained in the equation,

$$\nu = (Kt - L/t) \rho$$

where ρ = density of the experimental solution, t = time of flow of the solution, and K and L are the viscometric constants[4]. The time of flow was recorded using a digital stopwatch. The densities of the solutions were determined with a density meter (Austria, Anton Paar, DMA 4500 M.). The VI, which reflects the variation of kinematic viscosity of oil with temperature, was calculated according to the ASTM D2270 method at five different doping concentrations (ranging between 1 to 5%) of the additives according to the equation,

$$VI = 3.63(60 - 10^n)$$

and n was determined by the equation,

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2$$

where ν_1 and ν_2 are the kinematic viscosities of the additive doped oil at lower and higher temperatures respectively. For the given temperature range, the value of k was determined to be 2.71[5].

1.2.4 RESULT AND DISCUSSION

1.2.4.1 MOLECULAR WEIGHT ANALYSIS

From the experimental values of M_n , M_w , and PDI (polydispersity index) of the prepared homo and copolymers (Table:- 1.2.7.1), the number average molecular weight and weight average molecular weight gradually increases with the increasing percentage of vinyl acetate in the copolymer. DDMA homopolymer. are found more dispersed than The DDMA-VA copolymer.

1.2.4.2 SPECTROSCOPIC ANALYSIS

The homopolymer of dodecyl methacrylate shows an IR absorption band at 1722 cm^{-1} (Figure:-1.2.7.2) corresponds to the ester carbonyl group. For the copolymers of dodecyl methacrylate and vinyl acetate (P-2 to P-5), the IR spectrum(Figure:-1.2.7.5) showed the absorptions ranged between 1716.5 cm^{-1} and 1732.9 cm^{-1} indicate the presence of ester carbonyl groups. In its ^1H NMR spectra, the homopolymer(Figure:-1.2.7.3) showed the presence of the methyl and methylene protons in the range of 0.881 to 1.812 ppm for all alkyl groups and a broad peak at 3.93 ppm for the protons of $-\text{OCH}_2$ group. The absence of any peak in the range of 5-6 ppm confirms the absence of any sp^2 hydrogens in the system and hence indicated the conversion of the monomer into the polymer. In the ^1H NMR of the DDMA-VA copolymers,(Figure:1.2.7.6) a broad peak at 3.93 - 4.16 ppm indicated the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. Methyl & methylene carbons appeared in the range of 0.87 ppm to 2.63 ppm. The absence of any peak in the range of 5-6 ppm confirmed the conversion of the homopolymer into polymerization successfully.

In ^{13}C NMR of the homopolymer,(Figure:-1.2.7.4) the peaks at 167.60 ppm indicated the presence of ester carbon. The peaks at 64.71 ppm and 64.88 ppm confirmed the presence of $-\text{OCH}_2$ carbon and peaks in the range of 14.13–31.38 ppm accounted for all sp^3 carbon atoms of alkyl groups. The absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In ^{13}C NMR of the copolymers,(Figure:-1.2.7.7) of vinyl acetate, the peaks at δ 176.73 -177.86 ppm were due to the presence of ester carbonyl group. The peaks at 63.06 - 65.40 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2$ carbons, peaks ranging from 14.13–45.22 ppm for all other sp^3 carbons. The absence of a peak

in the range of 120-150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization[15].

1.2.4.3 ANALYSIS OF POUR POINT VALUES

The experimental values of the pour point are given in Table:- 1.2.7.2. The values indicate that all the prepared polymers (P-1 to P-5) perform effectively as better pour point depressants (PPD) and flow improvers (FI) when doped in base lube. The copolymers (P-2 to P-5) are found to better flow improver than the homopolymer (P-1). But with varying concentration, the pour point values do not maintain a linear correlation. The vinyl acetate copolymers (P-2 to P-5) exhibit better results than the homopolymers of DDMA. These polymers are better as FI and may be due to the presence of acetate group in the polymer backbone which reduces the adsorption of the polymer molecule on the wax crystals[7](Abdel-Azim et al., 2005) that happened in the case of flat DDMA homopolymer architecture. The P-5 copolymer having 6% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers[15].

1.2.4.4 ANALYSIS OF THE INFLUENCE OF ADDITIVES ON THE VISCOSITY INDEX VALUE

The data presented in Table:- 1.2.7.3, compared the dependence of the VI values with nature and on the concentrations of the additive, and the results indicated that all the prepared additives modified the viscosity properties of the base fluid. The additive DDMA homopolymer showed the least viscosity modification and with the increase of VA content in the additive feed, the VI values are found to rise gradually in the case of the copolymer. For any viscosity modifier, the potential to improve the VI relies on the conduct of the additive molecules in the base fluid, where its molecular weight, solubility, and chain topology are crucial parameters[11]. Also,

the viscosity of the base fluid depends on the temperature, wherewith an increase in temperature, the viscosity normally decreases[9]. Various researchers suggested that at low temperatures, the additive molecules are poorly soluble in the base fluid and remain in a round coiled up conformation with a minimal effect on the base fluid viscosity[10]. But with the increased solubility and interaction between the additive chains and the solvent molecules at the higher temperature, the additives change their shape from tightly coiled to inflated spread out ones. This successfully thickens the oil and counters the normal reduction in viscosity of the base fluid with increasing temperature[11]. Here the DDMA-VA copolymer additive with 10% VA content in doped lube, P-5 showed the highest VI increment, and this is possibly due to increased degree of solvation and enhanced interaction of the additive having oleophilic ends with the paraffinic base fluid. On the other hand, the additive DDMA, which only consists of dodecyl methacrylate monomers, has a more polar character compared with the others. Due to this polar nature, the additive has less interaction with the base fluid and, therefore, has a lesser solvated volume, consequently leaving it with the lowest VI among others[6]. Moreover, following our earlier publication[13,14], the VI values become more pronounced on increasing the overall additive doping percentage in the base fluid. This is because the increase in the concentration of the additive leads to an increase in the total volume of the polymer coils. These inflated coils, together with their increased interaction with the base fluid leads to a greater thickening effect and subsequently increases the viscosity index of the base stock[12].

1.2.4.5 ANALYSIS OF THE PHOTOMICROGRAPHIC IMAGE

A comparison of the photomicrographs,(Figure:1.2.7.1) of the SN-150 base fluid and the base fluid blended with different polymeric additives indicated that the

original base fluid (pour point = -6°C) showed long rod liked wax crystals in its photomicrographic image whereas additive doped base oils (4%, w/w of DDMA homopolymer solution PP -11.5°C) showed a significant reduction in the shape and size of the wax crystals in their images. Thus, the reduction in the size of wax crystals seems to be responsible for improving the pour point values. Hence, the pour point values obtained earlier are incomplete in correlation with the wax modification results[15].

1.2.5 CONCLUSION

In conclusion, the copolymers of dodecyl methacrylate with vinyl acetate are found effective as a multifunctional additive (flow improver and viscosity improver) for the lube oil. Copolymers with lower molecular weight are more effective as low-temperature flow improvers than copolymers with higher molecular weight. Therefore, the molecular weight of polymer has a significant role concerning the performance of the polymers as flow improvers for lube oil. In addition, the VA copolymer induced excellent VM properties as well when added to the base oil[15].

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

1.2.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-2 of Part -1**”.

1.2.7 TABLES AND FIGURES

TABLE 1.2.7.1

PERCENTAGE COMPOSITION, M_n , M_w , AND PDI VALUES OF POLYMERS (P-1 TO P-5) & GRAPHICAL REPRESENTATION

Polymer code	% of DDMA	% of VA	M_n	M_w	PDI
P-1	100	-	20482	49682	2.4256
P-2	97.5	2.5	22475	33018	1.53
P-3	95	5	24613	35842	1.492
P-4	92.5	7.5	54766	66210	1.164
P-5	90	10	60790	81219	1.31

DDMA = Dodecyl methacrylate, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

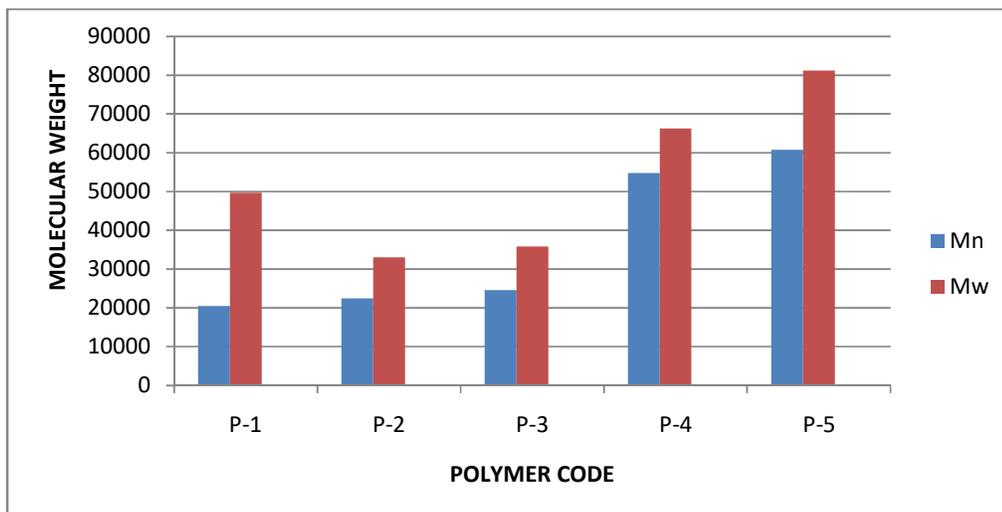


TABLE 1.2.7.2

POUR POINT DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN THE BASE OIL

Polymer	Pour point (°C) of additives doped base oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	-6	-13.5	-12.9	-12	-11.5	-10	-10.3
P-2	-6	-8	-7.8	-7.5	-8.1	-9.2	-10
P-3	-6	-7.5	-6.5	-6	-5.5	-4	-4.5
P-4	-6	-8.5	-8	-7.5	-8	-8.5	-9
P-5	-6	-10	-10.5	-12	-12.5	-13	-13.8

* Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

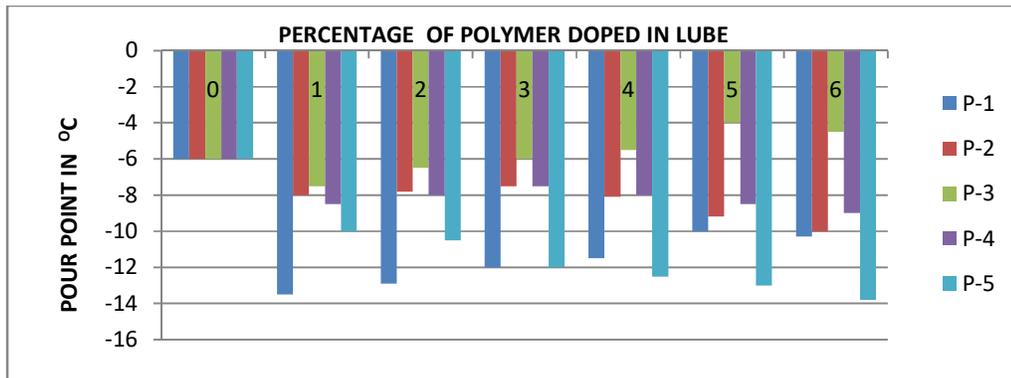


TABLE 1.2.7.3

VISCOSITY INDEX DATA CONCERNING THE DIFFERENT CONCENTRATIONS OF THE ADDITIVES IN THE BASE OIL & GRAPHICAL REPRESENTATION.

Polymer	The viscosity index of additives doped base oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	86	89	92	102	111	116	120
P-2	86	94	101	107	119	121	126
P-3	86	98	118	123	127	131	135
P-4	86	112	126	128	131	135	139
P-5	86	118	129	130	132	137	138

* Properties of the base oil - Density (g.cm⁻³) at 40 °C: 0.855; Viscosity at 100 °C in cSt 3.979; Viscosity index: 86; Pour point, °C: -6:

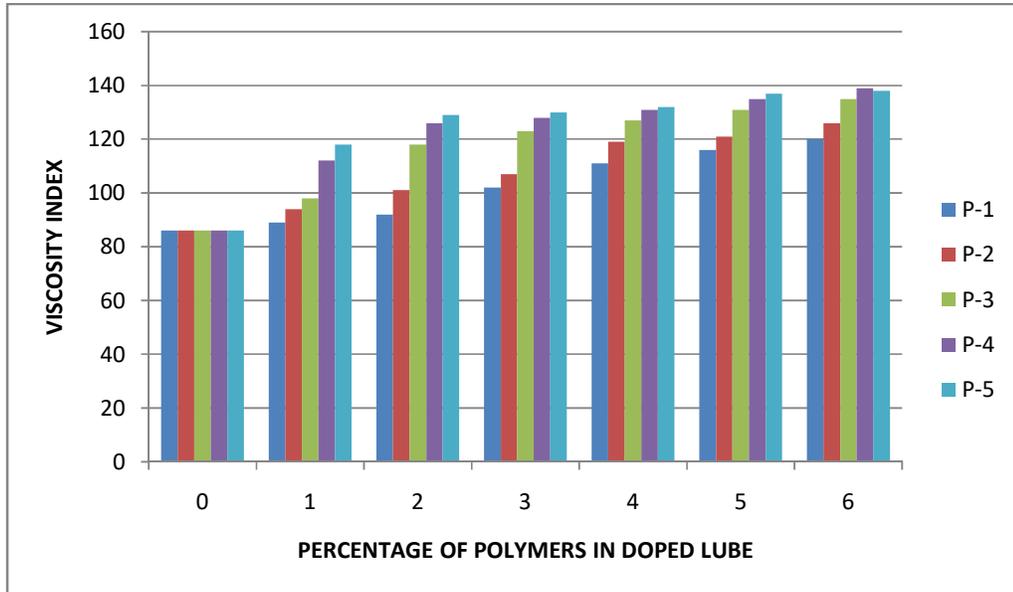
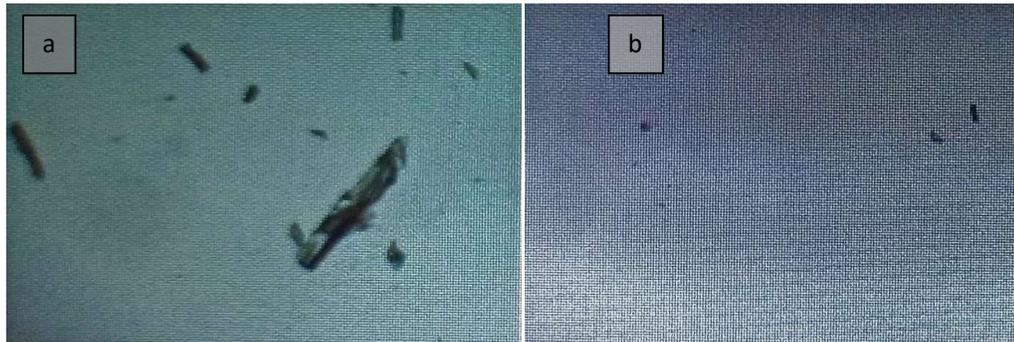


FIGURE 1.2.7.1

PHOTO MICROGRAPHIC IMAGE OF WAX CRYSTAL FORMATION.



Photomicrograph images of (a) pure lube oil ,PP-6°C, (b) lube oil + 4% (w/w) of DDMA homo polymer PP -11.5°C

FIGURE 1.2.7.2

FT IR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

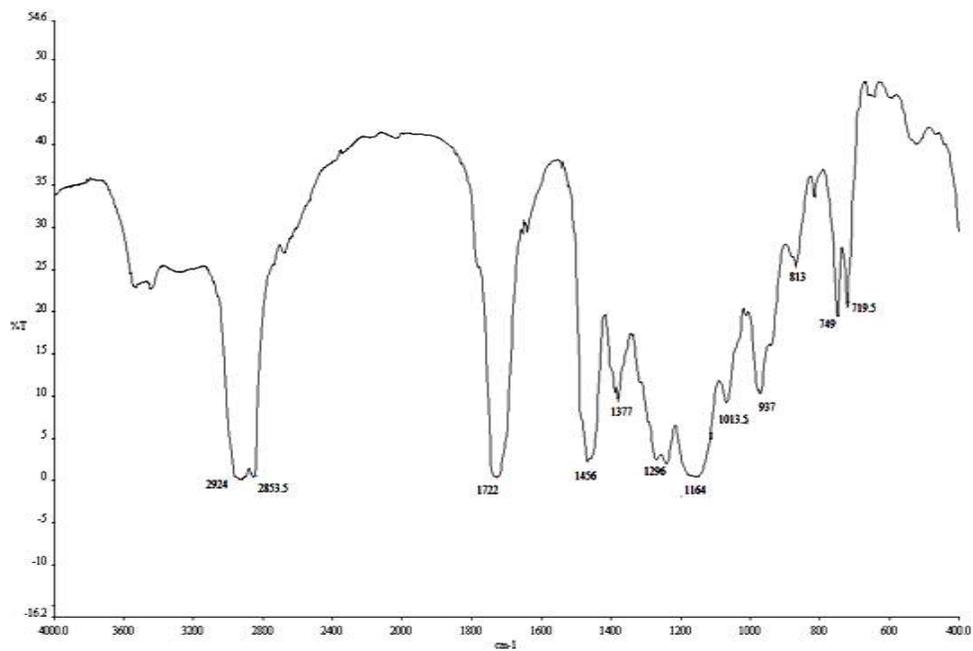


FIGURE 1.2.7.3

¹H NMR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

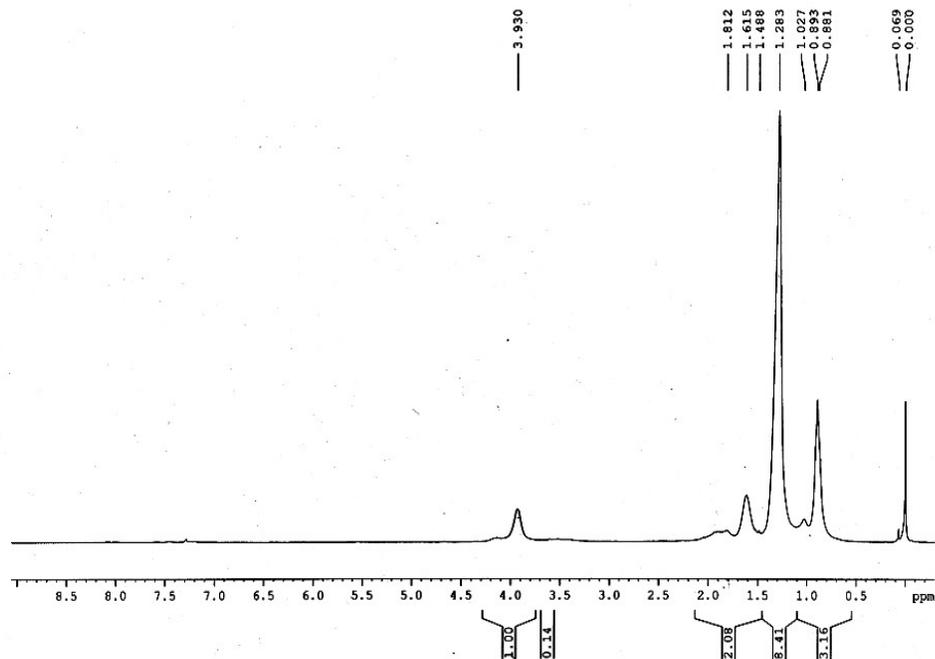


FIGURE 1.2.7.4

¹³C NMR SPECTRA OF A HOMOPOLYMER OF DDMA(P-1)

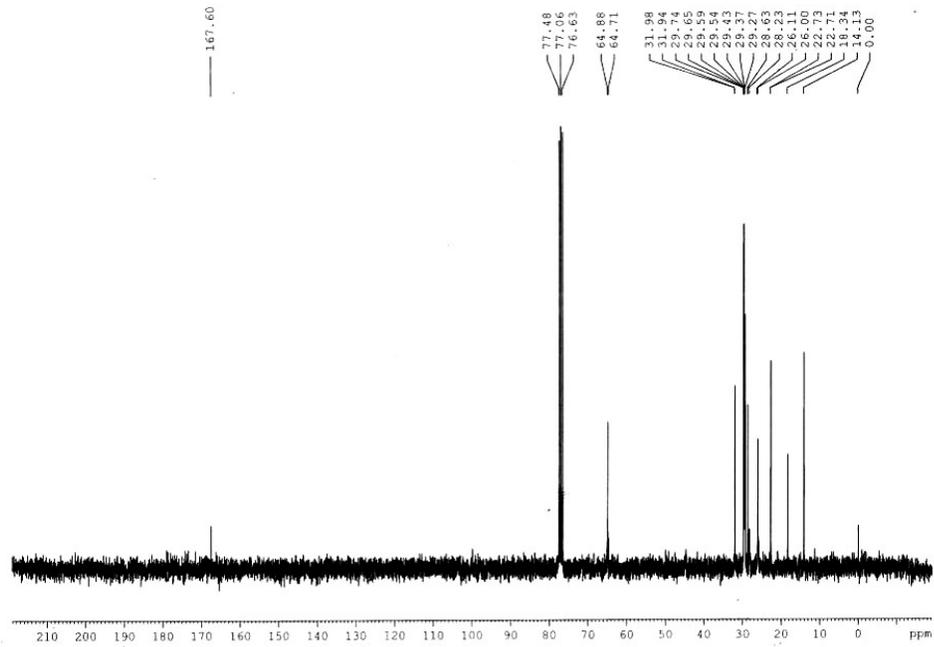


FIGURE 1.2.7.5

FT-IR SPECTRA OF COPOLYMERS (P-2 TO P-5)

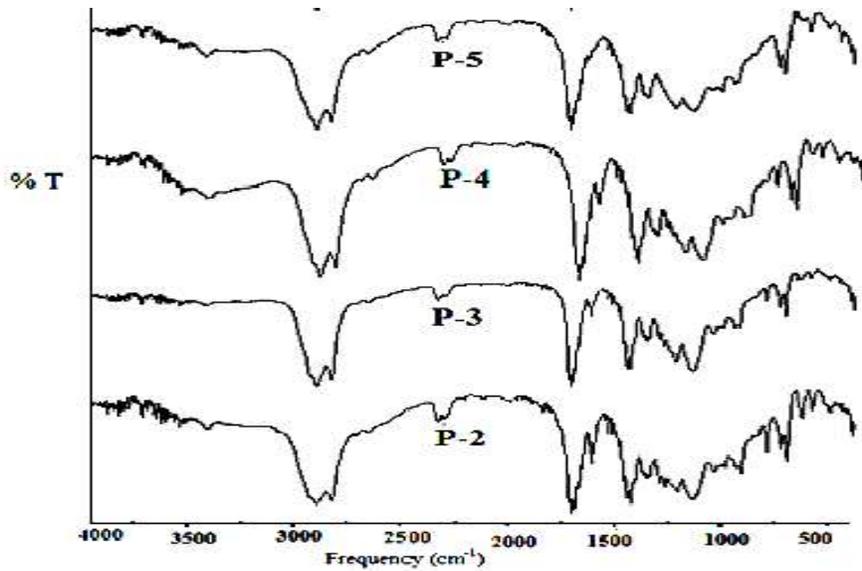


FIGURE 1.2.7.6
 ^1H NMR SPECTRA OF COPOLYMER (P-2)

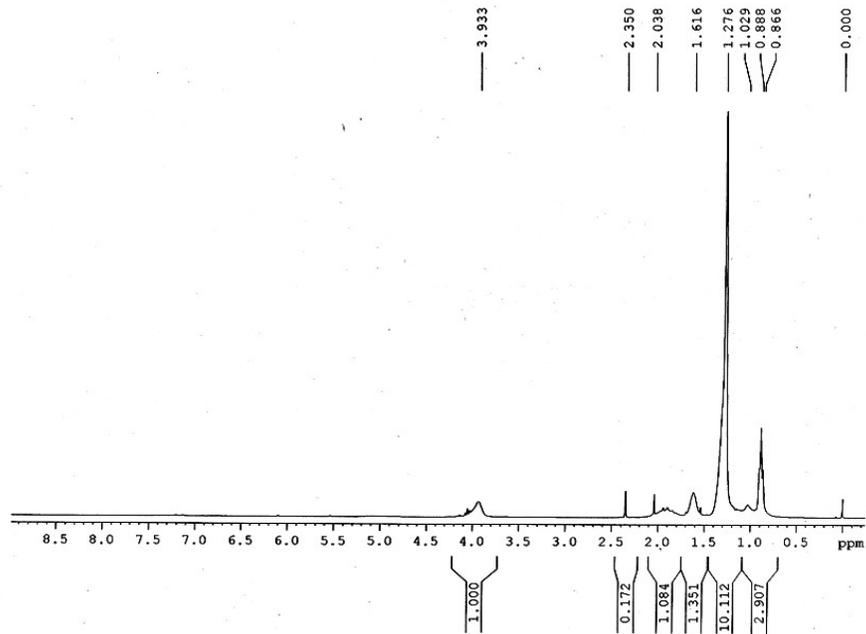


FIGURE 1.2.7.7
 ^{13}C NMR SPECTRA OF COPOLYMER (P-2)

