

## **Chapter III**

### **A Study as a Potential Multifunctional Additive for Lubricating Oil of Poly Decyl Acrylate-Ionic Liquid Blend**

### 1.3.1 Introduction

Ionic liquids (more specifically, room temperature ionic liquids (RTIL)) have attracted great interest over the last several years. Ionic liquids (ILs) are broadly referred to as molten salts in a liquid state. Generally, ILs are a specific type of liquid salts with melting temperatures lower than 100°C (212°F). Unlike ordinary liquids such as water or alcohol, ILs are mostly composed of charged ions as opposed to electrically neutral molecules. Ionic liquids have many good features [1] such as low volatility, non-flammability, low combustibility, high ionic conductivity, high thermo-oxidative stability, eco-friendly, etc. Therefore, they should be the potential candidates for new lubricant formulations and would be suitable for use in severe conditions where conventional oils and greases or solid lubricants fail. ILs have been the subject of research and development for quite a long time. In 2001 ionic liquids (ILs) were first reported [2] as very promising high-performance lubricants and have attracted considerable attention in the field of tribology since then because of their remarkable lubrication and anti-wear capabilities as compared with lubrication oils in general use [3]. In recent times, we have seen dramatically increased interest in this topic. The choice of cation and anion in an ionic liquid (IL), and also the design of ion side chains, regulate the main functions of ionic liquids, which permits creating suitable lubricants and lubricant additives [4]. Limited results of very recent studies have shown the potential for using ionic liquids as a new class of lubricants [1]. Friction and wear reductions have been reported on metallic and ceramic surfaces lubricated by selected ionic liquids compared to conventional hydrocarbon lubricants. It was also suggested that adding a few percent of ionic liquids could improve the lubricating performance of base oils or water. Over the last 15 years, research interest in ILs has expanded into lubrication due to their potential performance as a neat lubricant or additive [5]-[11].

Regarding the use of ILs as neat lubricants, several studies have shown great potential for this purpose [8]-[10]. But at present, considering the high cost of ILs, using a small quantity of ILs as an additive, **for** engine applications seems to be an economical option. It should be noted, however, that the multiple-recycling of ILs after use could reduce the overall cost of employing ILs [1], [5], [11] in real applications. This is another cost-effective aspect for investigation by the lubricant industry. The Early works were mainly focused on ILs with imidazolium cations based [8], [11]. The interest in phosphonium [1], [2], [8], based ionic liquids has widely grown over the years in line with their increased commercial availability. They have been successfully tested for several applications. In this study, an ionic liquid with phosphonium cation and amide anion based is chosen as a lubricant additive, and studied their different performance such as PPD, VI, and anti-wear property in lube oil, as described in this article.

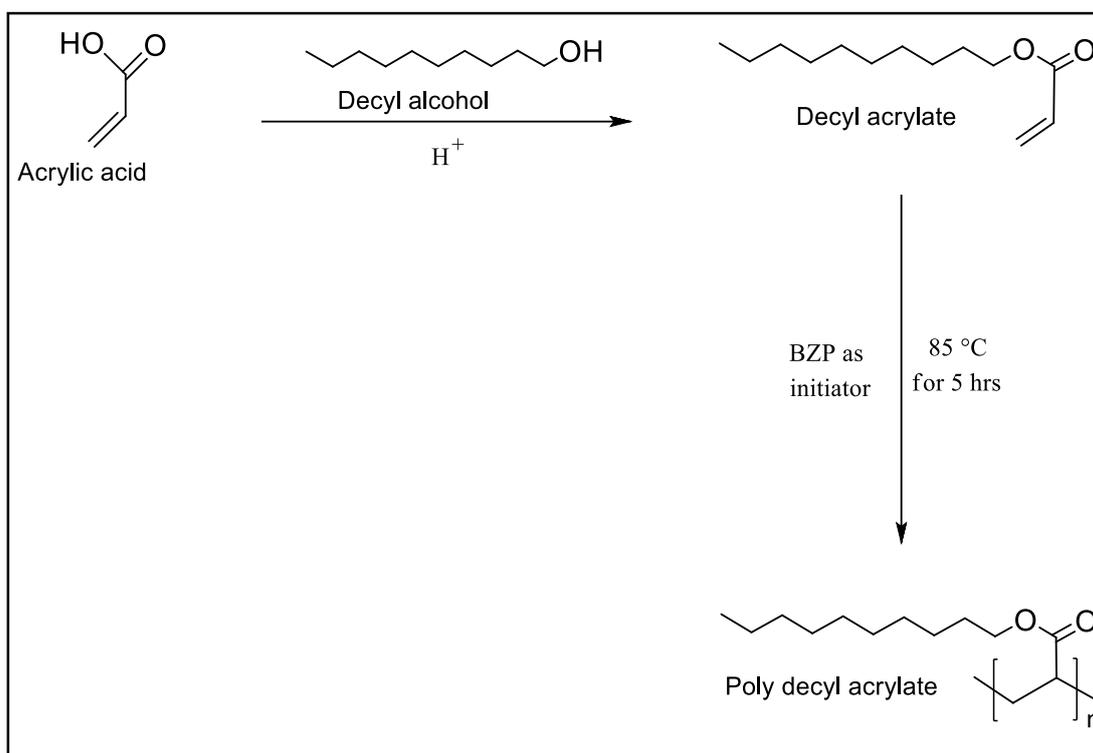
### 1.3.2 Materials and method

Toluene, hydroquinone, and H<sub>2</sub>SO<sub>4</sub> were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (GC Purity 99%) and decyl alcohol was obtained from Sisco Research Laboratories Pvt. Ltd. Ionic liquid [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>] namely Trihexyl (tetradecyl) phosphoniumbis {(trifluoromethyl) sulfonyl} amide was purchased from Sigma-Aldrich Pvt. Ltd. And CH<sub>3</sub>OH was purchased from Thomas baker Pvt. Ltd. and were used as received. Benzoyl peroxide (BZP) obtained from the LOBA chemical was recrystallized from CHCl<sub>3</sub>-MeOH before use. Specifications of the chemicals are depicted in **Table 1.3.1**. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in **Table 1.3.2**.

### 1.3.2.1 Esterification and homopolymerization of DA

Esterification of acrylic acid with decyl alcohols, purification of the prepared esters, and subsequent homopolymerization was carried out following the procedure as reported in earlier publications from our laboratory [12], [13].

#### Scheme 1.3.1 Esterification of acrylic acid with decyl alcohol followed by polymerization of ester.



### 1.3.2.2 Preparation of IL-Polymer blend

Polymer-IL blends were prepared by mixing the polymer (**P-1**) with desired amount of IL (100 ppm, 300ppm, 500ppm with respect to the polymer) in a mechanical stirrer at 60°C for one hour. The blended sample was assigned as P-2 (for 100 ppm), P-3 (for 300 ppm), P-4 (for 500 ppm). Four different concentrations (1-4% w/w) of additive (P-1 to P-4) doped base oils, namely BO1 and BO2 were prepared by the addition of a required amount of sample to the base oils.

### **1.3.3 Measurements**

#### **1.3.3.1 Spectroscopic measurements**

Perkin Elmer FT-IR 8300 spectrophotometer was used to determine IR spectra using 0.1 mm KBr cells at room temperature. The NMR spectra were recorded in a 300 MHz BrukerAvance FT-NMR spectrometer using a 5mm BBO probe. CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) was used as reference material.

#### **1.3.3.2 Thermogravetric test**

The thermograms in the air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K min<sup>-1</sup>.

#### **1.3.3.3 Molecular weight determination by GPC**

The weighted average and number average molecular weights (M<sub>w</sub> and M<sub>n</sub>) and polydispersity indices of the polymers were measured in Waters' GPC equipment using polystyrene standards for calibration in THF phase [12]. The results are tabulated in **Table 1.3.3**.

#### **1.3.3.4 Pour point determination**

The pour point of the prepared polymers in base oils was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India).

#### **1.3.3.5 Viscosity index determination**

Kinematic viscosity (KV) of the polymer was determined separately at 40°C and 100°C by counting the time of flow of polymer solution in base oil using viscometer apparatus and measuring the density of it. According to the ASTM D-7042 method and also by

using the method of viscosity index calculation [14] the viscosity index of each polymer solution was determined.

#### **1.3.3.6 Shear stability determination**

Shear stability was determined of various concentrated solutions of pure DA polymer, DA + Ionic liquid blending, and Ionic liquid in lube oil. Tests and calculations were conducted as per the ASTM D- 3945 and ASTM 6022 methods.

#### **1.3.3.7 Anti-wear property determination**

Anti-wear (AW) properties of base stocks, as well as additive doped base stocks, were studied in sliding contact using a Four-Ball wear test Machine as per the ASTM D-4172 method. The tests were carried out under the load of 20 kg and 40 kg.

### **1.3.4 Results and discussion**

#### **1.3.4.1 Spectroscopic data**

FT-IR spectrum (**Figure 1.3.1**) of poly (decyl acrylate) or homopolymer of decyl acrylate (HDA) exhibited absorption at  $1732.0\text{ cm}^{-1}$  due to ester carbonyl stretching vibration. The peak at  $1260.0$  and  $1175.0\text{ cm}^{-1}$  can be explained owing to the C–O (ester bond) stretching vibration and the absorption bands at  $975.0$ ,  $750.0$ , and  $711.0\text{ cm}^{-1}$  were due to the bending of C–H bonds. The broad peak ranging from  $2900.0$  to  $3100.0\text{ cm}^{-1}$  was due to the presence of stretching vibration (C–H bonds). In its  $^1\text{H}$ -NMR spectra (**Figure 1.3.2**), homopolymer of DA showed a multiple centered at  $3.17$  ppm due to the proton of  $-\text{OCH}_2$  group; methyl groups of decyl chain showed a broad singlet at  $0.73$  ppm. The proton decoupled  $^{13}\text{C}$ -NMR of the above sample (**Figure 1.3.3**) was in complete agreement with the homopolymer which shows the presence of

the ester carbonyl group at 170.66 ppm and the absence of any  $sp^2$  carbon in the range 130-150 ppm.

#### 1.3.4.2 Thermogravimetric analysis

The plot of TGA data in **Figure 1.3.4** presents a comparison between the thermal stability of homopolymer of DA and its blending with ionic liquid respectively. The analysis reveals that the blend is thermally less stable than the homopolymer.

#### 1.3.4.3 Performance evaluation of the prepared polymers as PPD

The pour point (PP) values of the polymers in both the base oils are tabulated in **Table 1.3.4**, which indicates that their PPD efficiency increases (up to a certain limit) with the increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is greater for DA polymers than that of the ionic liquid blend.

#### 1.3.4.4 Photo micrographic analysis

The photomicrographs of lube oil (BO2) with and without different additives are shown in **Figure 1.3.5 (a–e)**. **Figure 1.3.5a**, the photograph of the fresh lube oil showed a large number of crystalline and some needle-shaped wax crystals. But by the addition of polymers the wax crystal size [**Figure 1.3.5(b–e)**] is significantly decreased from a large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil, and the polymer which acts as better PPD (reveals by PPD data), decreases the wax size more compared to other. Therefore, a correlation between the depression of pour point and the degree of wax structure modification has been confirmed.

#### 1.3.4.5 Performance evaluation of the prepared polymers as VMs

The VI values in two base oils (measured in four different concentrations) tabulated in **Table 1.3.4** indicates that in both the base oils the values for DA homopolymer are greater than that of its ionic liquid blend but the difference is small, also the VI value

decreases with increasing ionic liquid concentration in the blending feed. This result may be explained based on the molecular weight of the polymers. Again, with the increase in the concentration of the polymers in solution, VI increases. The reason may be that although the viscosity of the lube oil gets decreased at the higher temperature, the polymer molecules may effectively offset this reduction in viscosity by thickening the oil changing its shape from a tight coil to an expanded one due to increased polymer-solvent interaction. The result is an increase in the viscosity of the solution. Again, a higher polymer concentration means an increase in the total volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.

#### **1.3.4.6 Shear stability analysis**

Shear stability determined based on PVL (permanent viscosity loss) and PSSI (percent of shear stability index), lesser the value of PVL and PSSI greater the shear stability of the sample. Shear stability determination indicates that the IL-DA blend is more shear stable than that of DA polymer and also shear stability increases with the increasing the IL concentration in the blended feed. This result is clearly explained based on the molecular weights of the sample, the higher the molecular weight greater the possibility of a loss of shear stability of the polymer.

#### **1.3.4.7 Efficiency as anti-wear (AW) additive**

Anti-wear contributions of the additives are measured with respect to wear scar diameter (WSD) under two load conditions (20 kg, 40 kg). Effect of additive concentration on the anti-wear performance is also studied. Experiments are conducted at first with pure base oils followed by the additive doped base oils. The WSD measured in all these cases is depicted in **Table 1.3.5**. As was expected, all the samples (P-1 to P-4) show better anti-wear performance compared to pure base oils and IL

blended polymers (P-2 to P-4) are found to be more efficient than pure BA homopolymer (P-1). Also, the performance increases with increasing the IL concentration in the blended feed. Irrespective of base oils or load conditions, WSD decreases (i.e. better AW properties) with increasing additive concentration. That is, both the additives are acting more efficiently at higher concentration levels. A comparison between load conditions indicates that under milder conditions (20 kg load), additives performance is better (lower WSD value).

### **1.3.5 Conclusions**

Evaluation of the performance of the additives indicates that, although the BA homopolymer showed slightly better PPD and viscosity modifier performance compared to its ionic liquid blend, but, the BA+ IL blend is more shear stable than the homopolymer, and shear stability increases with increasing the concentration of IL in blending feed. The investigation also indicates that IL blend polymers show much better anti-wear performance than that of BA homopolymer and the performance increases with increasing the concentration of IL in blending feed.

### **1.3.6 References**

References are given in *BIBLIOGRAPHY* under “Chapter III of Part I” (Page No. 139-140).

## 1.3.7 Tables and Figures

Table 1.3.1: Specification of the chemicals used

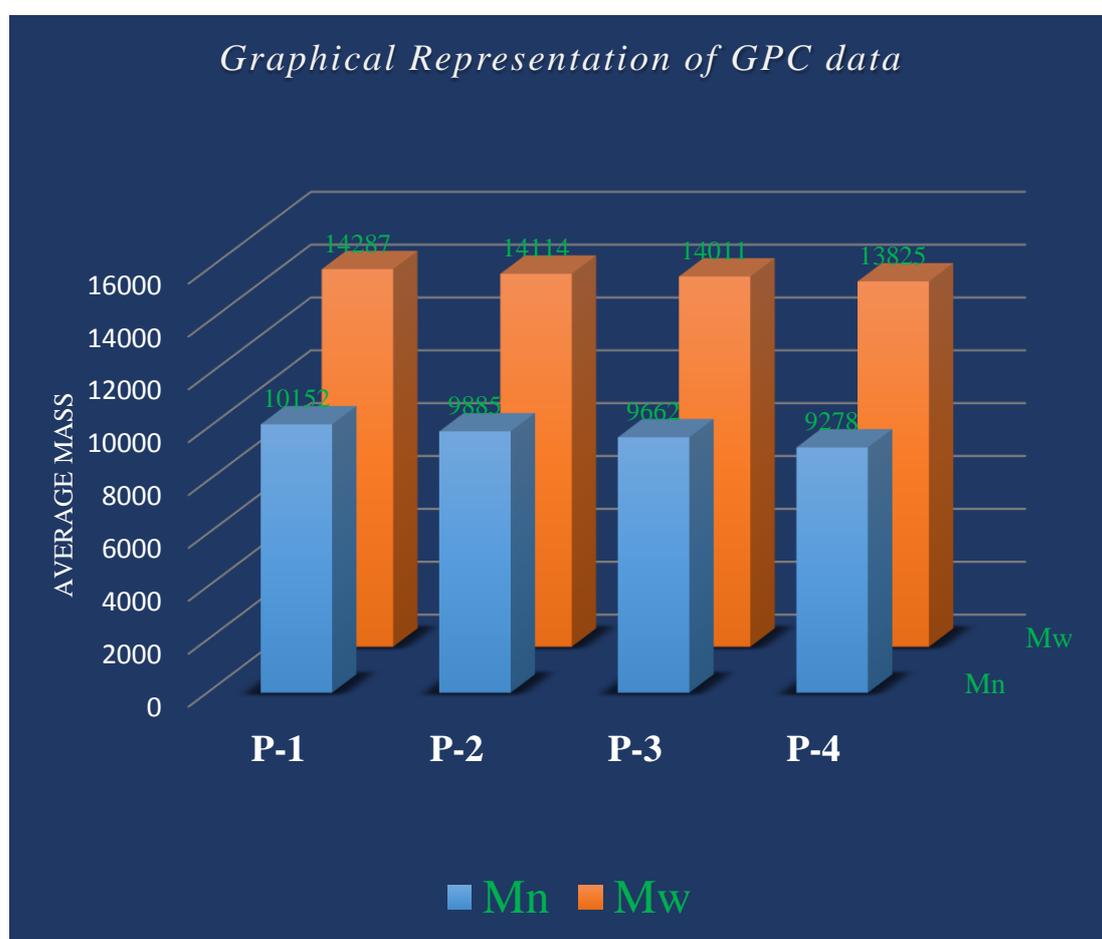
<i>Chemical name</i>	<i>Source</i>	<i>Mole fraction purity</i>
Toluene	Merck Specialities Pvt. Ltd.	0.995
Hydroquinone	Merck Specialities Pvt. Ltd.	0.990
H <sub>2</sub> SO <sub>4</sub>	Merck Specialities Pvt. Ltd.	-
Acrylic acid	SRL Pvt. Ltd.	0.990
Decanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
[P6,6,6,14][NTf <sub>2</sub> ]	Sigma-aldrichPvt. Ltd.	-

Table 1.3.2: Base oil properties

<i>Properties</i>	<i>Base oils</i>	
	<i>BO1</i>	<i>BO2</i>
Density at 313 K, kg.m <sup>-3</sup>	836.98	868.03
Viscosity at 313 K, Pa-s	5.97×10	20.31×10
Viscosity at 373 K, Pa-s	1.48×10	3.25 ×10
Cloud point, °C	-10	-8
Pour point, °C	-3	-6
Viscosity index	80	85

**Table 1.3.3: Weight average and number average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity Index of the sample and its graphical representation**

<i>Sample</i>	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>PDI</i>
P-1	10152.00	14287.00	1.40
P-2	9885.00	14114.00	1.42
P-3	9662.00	14011.00	1.45
P-4	9278.00	13825.00	1.49

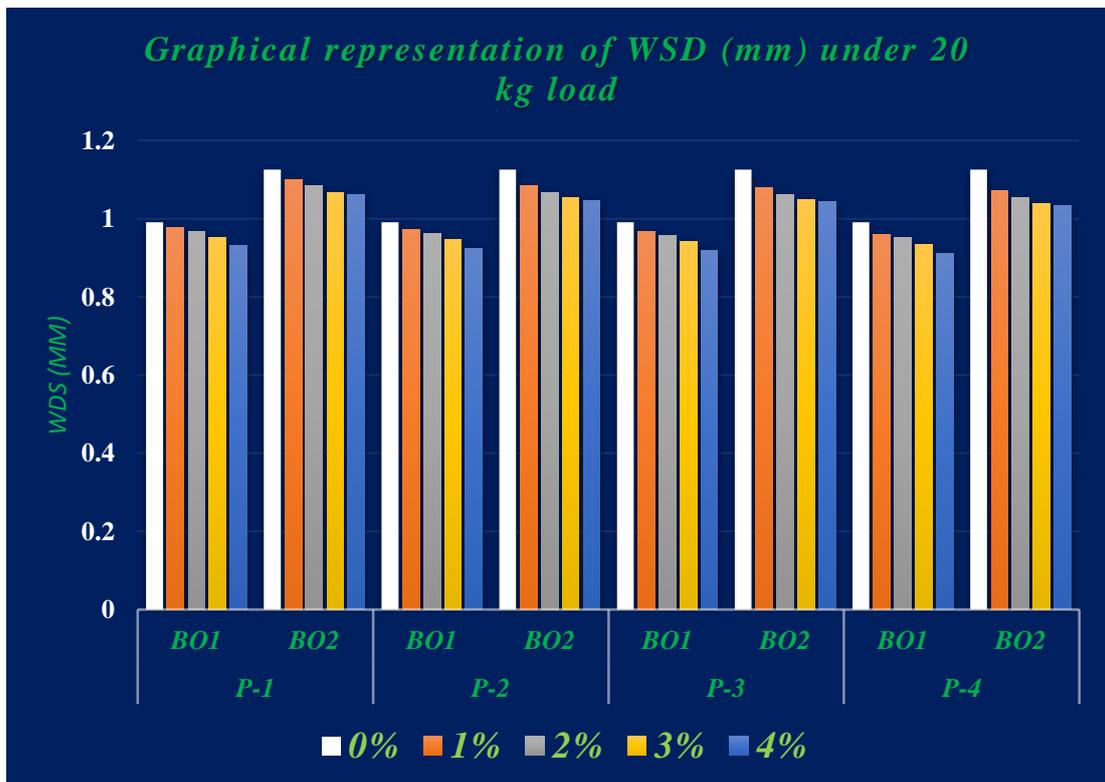


**Table 1.3.4: Tribological performance of the samples in two different base oils**

<i>Sample</i>	<i>Conc.</i> (%)	<i>BO1</i>				<i>BO2</i>			
		<i>PP</i>	<i>VI</i>	<i>PVL</i>	<i>PSSI</i>	<i>PP</i>	<i>VI</i>	<i>PVL</i>	<i>PSSI</i>
P-1	1	-6	96	0.432	8.978	-9	98	0.435	9.768
	2	-9	105	0.811	9.996	-12	110	0.832	10.778
	3	-12	115	1.353	12.411	-15	128	1.436	13.125
	4	-15	124	1.980	16.821	-18	138	2.112	17.835
P-2	1	-6	92	0.374	7.587	-9	95	0.382	8.421
	2	-6	99	0.644	8.456	-9	105	0.657	9.142
	3	-9	109	1.227	10.234	-12	121	1.259	11.247
	4	-12	119	1.590	15.527	-15	129	1.596	16.223
P-3	1	-6	91	0.298	7.214	-9	94	0.311	8.114
	2	-9	97	0.587	8.145	-12	101	0.590	8.985
	3	-9	105	1.140	9.857	-12	117	1.264	10.141
	4	-12	116	1.372	15.114	-15	123	1.415	15.784
P-4	1	-6	91	0.212	6.984	-9	93	0.242	7.128
	2	-9	95	0.478	8.11	-12	98	0.511	8.541
	3	-9	103	0.985	9.114	-12	113	1.100	9.886
	4	-12	111	1.154	14.954	-15	119	1.173	15.211
<i>PP-Pour Point, VI-Viscosity Index, PVL-Permanent Viscosity Loss, PSSI-Percent of Shear Stability Index.</i>									

**Table 1.3.5: Anti-wear Performance data of Additive Doped Base Oil and its graphical representation under 20 kg load**

Sample	Base oil	WSD(mm) of additive-base oil blends									
		20 kg load					40 kg load				
Aditives %		0%	1%	2%	3%	4%	1%	2%	3%	4%	
P-1	BO1	0.991	0.979	0.968	0.952	0.931	0.978	0.974	0.965	0.939	
	BO2	1.126	1.101	1.084	1.068	1.061	1.104	1.088	1.071	1.065	
P-2	BO1	0.991	0.973	0.963	0.948	0.925	0.974	0.967	0.959	0.929	
	BO2	1.126	1.085	1.068	1.054	1.047	1.095	1.079	1.065	1.054	
P-3	BO1	0.991	0.967	0.957	0.941	0.919	0.969	0.962	0.952	0.922	
	BO2	1.126	1.08	1.061	1.048	1.043	1.09	1.073	1.059	1.048	
P-4	BO1	0.991	0.961	0.952	0.934	0.912	0.962	0.954	0.943	0.914	
	BO2	1.126	1.072	1.054	1.04	1.033	1.081	1.064	1.05	1.041	



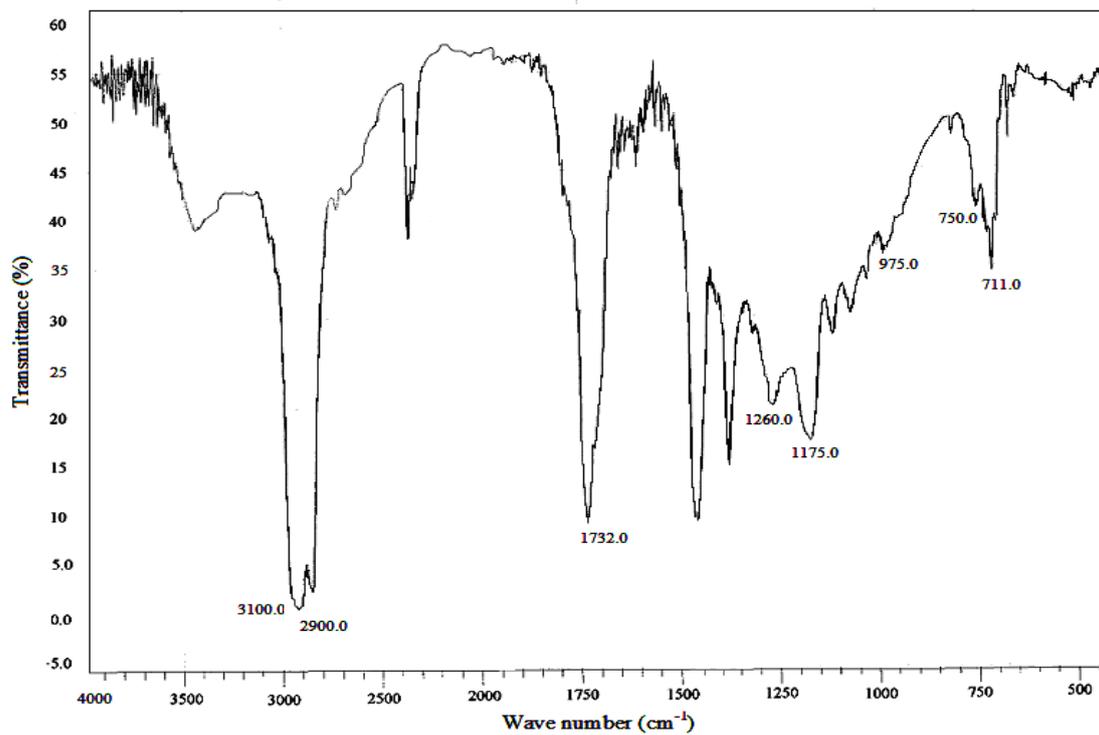


Figure 1.3.1: FT-IR spectra of polydecyl acrylate

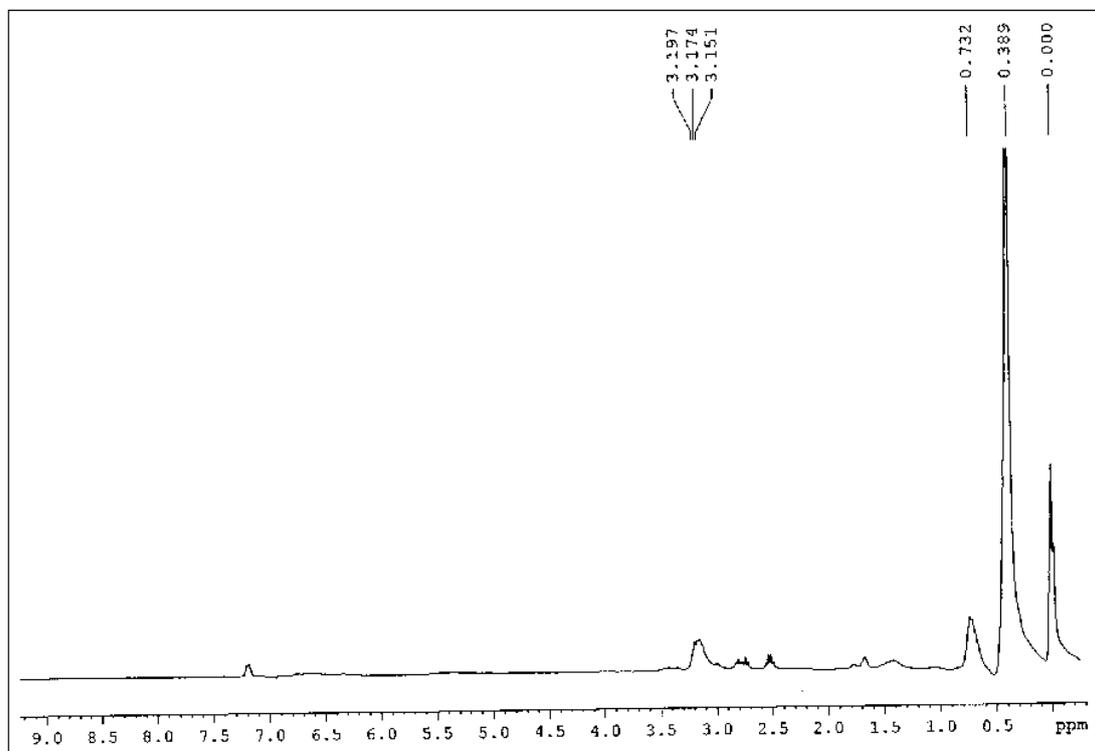


Figure 1.3.2: <sup>1</sup>H- NMR spectra of polydecyl acrylate

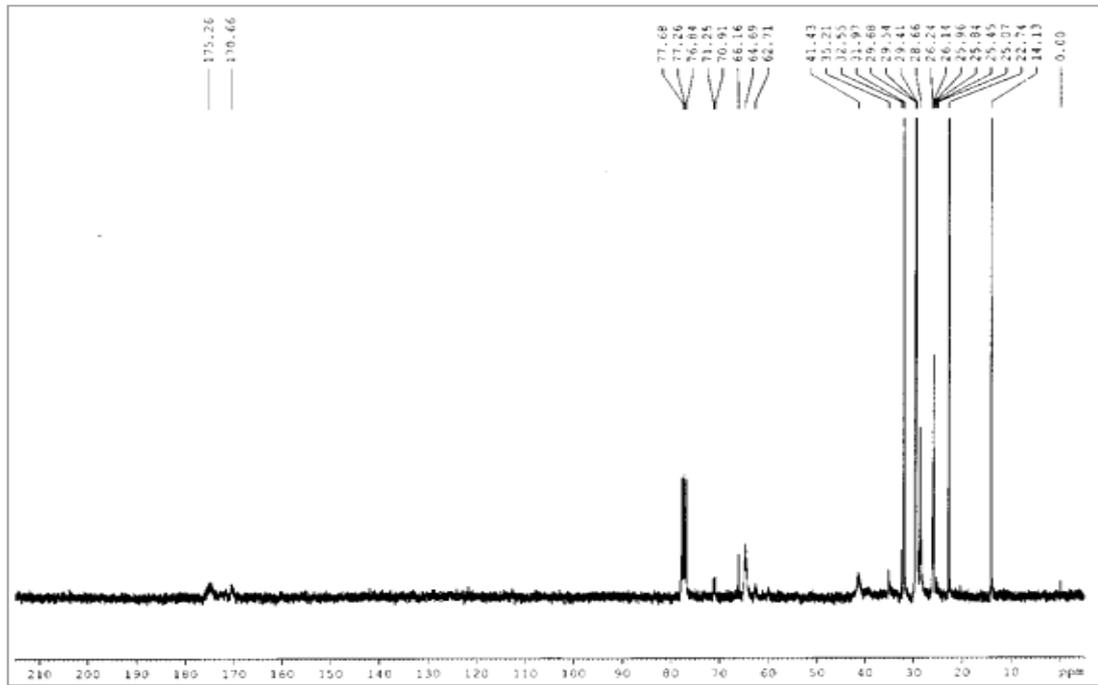


Figure 1.3.3:  $^{13}\text{C}$ - NMR spectra of poly behenyl acrylate

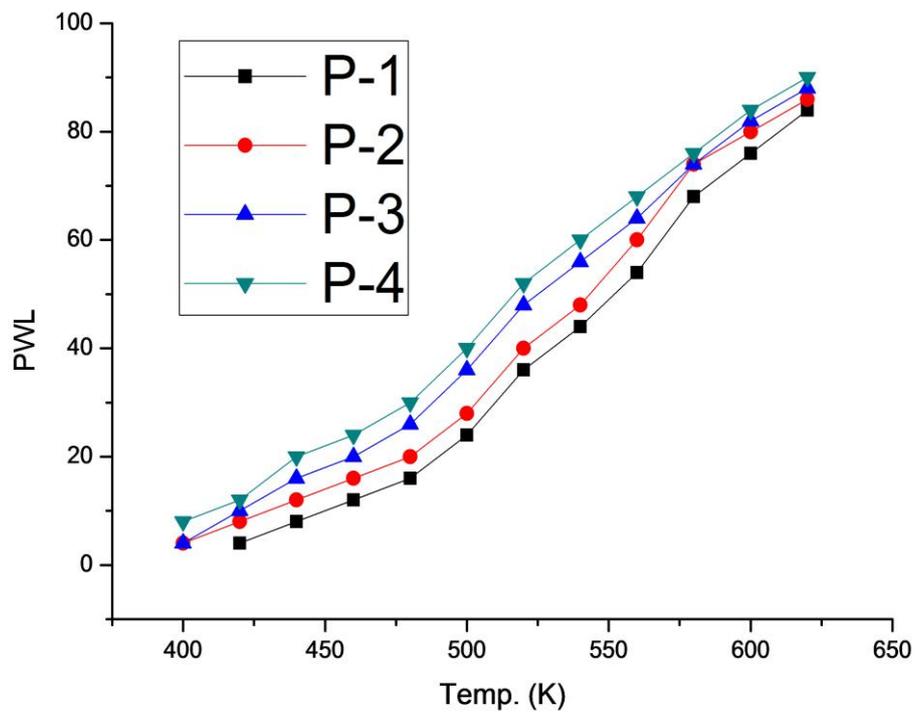


Figure 1.3.4: Plot of PWL (Percent Weight Loss) vs Temperature (in K)



5(a)

Base oil (BO2)



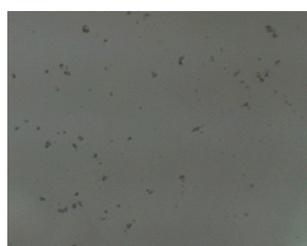
5(b)

P-1 (3%)



5(c)

P-2 (3%)



5(d)

P-3 (3%)



5(e)

P-4 (3%)

**Figure 1.3.5(a-e): Plot of photo micrographic images of base oil and additive (P-1, P-2, P-3 and P-4) doped base oil**