

**CHAPTER-II**

**SYNTHESIS AND EVALUATION OF  
GREENER ADDITIVES FOR  
LUBRICATING OIL**

### 2.1.1. Introduction

Base fluid mineral oils generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Again, the increasing environmental awareness has increased the investigation about new environmental lubricant and additive chemistry. Keeping this view in mind people has already started working in this direction to meet the above needs<sup>1,2</sup>. For the development of eco-friend polymeric additives for lube oil,  $\alpha$ -pinene has been chosen as a potential candidate to incorporate biodegradability in its acrylate backbone. Thus the present investigation comprises the synthesis, characterization, and evaluation of  $\alpha$ -pinene copolymers as a potential biodegradable additive for lubricating oil. The study includes synthesis of copolymers using different mole fractions of  $\alpha$ -pinene with dodecyl acrylate (DDA) and isodecyl acrylate (IDA), their characterization, performance evaluation, and evaluation of the biodegradable nature of the polymers. The homopolymers of DDA and IDA prepared in the previous work (Chapter-II of Part-I, Page No. 28) are taken as a reference sample for a comparison of their performance with respect to the prepared copolymers. Physical characterization of the polymers was carried out employing FT-IR, NMR techniques, and Thermogravimetric Analysis (TGA). Performance of the polymer additives was tested in respect of their Pour Point Depressant<sup>3</sup> (PPD) and Viscosity Modifier<sup>4,5</sup> (VM) properties. A comparison of all the properties and performances of the prepared copolymers with the respective homopolymers has been presented in this study.

Since viscosity is a very important property of a lubricant<sup>6-8</sup> and viscometric studies in dilute solution may give valuable information about the structure and morphology of the polymer chain in desired solvent, the present investigation also includes viscometric study of the copolymers as well as the homopolymers. In this work, intrinsic viscosity of toluene solution for samples of poly (alkyl acrylate) and copolymers

of alkyl acrylates consisting of different mole fraction of  $\alpha$ -pinene was obtained by graphic extrapolation and single point determination method. The viscosity average molecular weight, determined by using different equations, has been calculated and compared for different polymers.

## **2.1.2. Experimental procedure**

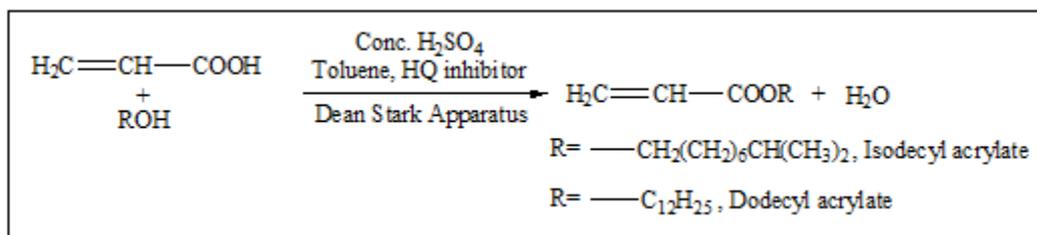
### **2.1.2.1. Materials**

Toluene, Hydroquinone, and  $H_2SO_4$  were purchased from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilised with 0.02 % Hydroquinone mono methylether) and Isodecanol were obtained from Sisco Research Laboratories Pvt. Ltd. 1-Dodecanol and Hexane were purchased from S D Fine Chem. Ltd.  $\alpha$ -pinene was obtained from Across Organics, Methanol was purchased from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl Peroxide, obtained from LOBA chemicals, was recrystallised from  $CHCl_3$ -MeOH before use. Rest of the materials was used as they were obtained without further purification. Base oils were collected from IOCL, Dhakuria, West Bengal, India and the fungal specimens were collected from Department of Microbiology, University of North Bengal, West Bengal, India.

### **2.1.2.2. Esterification**

Isodecyl acrylate (IDA) was prepared by reacting 1.1 mole of acrylic acid with 1 mole of isodecyl alcohol. The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the reactants as polymerization inhibitor and toluene as a solvent. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of

liberated water to give the ester, isodecyl acrylate. Under the same procedure dodecyl acrylate (DDA) was also prepared from acrylic acid and dodecyl alcohol.



**Scheme 2.1: Preparation of isodecyl acrylate (IDA) and dodecyl acrylate (DDA)**

### 2.1.2.3. Purification of prepared esters

The prepared esters were purified according to the following procedure: a suitable amount of charcoal was added to the ester. It was allowed to reflux for 3 h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide, the ester was then left over night on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

### 2.1.2.4. Preparation of copolymers

In the preparation of DDA +  $\alpha$ -pinene and IDA +  $\alpha$ -pinene copolymers, different concentration (mole fraction) of  $\alpha$ -pinene was used (**Table 2.1**). The thermal polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen, and a dropping funnel through which to add  $\alpha$ -pinene drop wise. In the flask, desired mass of IDA and initiator benzoyl peroxide (BZP) was placed followed by drop wise addition of desired mass of  $\alpha$ -pinene for 2 h in the presence of toluene as solvent. The reaction temperature



viscosity of the polymer solution in toluene. According to that equation, the value of intrinsic viscosity ( $[\eta]$ ) changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (1)$$

Where,  $M$  is the viscosity average molecular weight and  $K$  and  $a$  are the Mark Houwink constants. The values of  $K$  and  $a$  are specific for every polymer-solvent combination. So, to get an accurate measure of molecular weight, these constant values are to be known for appropriate polymer-solvent combination. For a new polymer, it is not possible to get the accurate molecular weight, but an idea of whether the molecular weight value is low or high can be drawn by using these values of similar types of polymers.

The most commonly used equations for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation<sup>9-13</sup> are (eqns. 2 to 5):

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

$$\text{Kraemer (K)} \quad \ln \eta_r/C = [\eta]_k - k_k [\eta]_k^2 C \quad (3)$$

$$\text{Martin (M)} \quad \ln \eta_{sp}/C = \ln [\eta]_m + k_m [\eta]_m C \quad (4)$$

$$\text{Schulz-Blaschke (SB)} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

Where,  $C$  = concentration of the solution in  $\text{g.cm}^{-3}$

$\eta_r = t/t_o$  = time of flow of the solution /time of flow of pure solvent

= relative viscosity or viscosity ratio

$\eta_{sp} = \eta_r - 1$ , specific viscosity

$[\eta]_h$  = intrinsic viscosity, respective to Huggins equation

$[\eta]_k$  = intrinsic viscosity, respective to Kraemer equation

$[\eta]_m$  = intrinsic viscosity, respective to Martin equation

$[\eta]_{sb}$  = intrinsic viscosity, respective to Schulz-Blaschke equation

$k_h$ ,  $k_k$ ,  $k_m$ , and  $k_{sb}$  are Huggins, Kraemer, Martin, and Schulz-Blaschke coefficients, respectively.

Some relations have also been proposed for determining the intrinsic viscosity in dilute polymer solution from single point determination method. This method has the advantage of being considerably faster and is better than the graphic extrapolation method when a large number of samples must be analysed in short period of time, practically in industrial laboratories. Most useful of these<sup>10-12</sup> are (eqns. 6 and 7):

$$\text{Solomon-Ciuta (SC)} \quad [\eta] = (2(\eta_{sp} - \ln \eta_r))^{1/2}/C \quad (6)$$

$$\text{Deb-Chatterjee (DC)} \quad [\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3}/C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship  $k_h + k_k = 0.5^{10}$ . The unit of intrinsic viscosity and concentration are  $\text{dL.g}^{-1}$  and  $\text{g.cm}^{-3}$ , respectively.

Viscometric properties of the polymeric samples were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow of eight different concentrations of the sample solution. The time flow of the solution was manually determined by using a chronometer. In the single point measurement, the lowest value of solution concentration was chosen for calculation. For the viscosity average molecular weight determination, the constants  $K = 0.00387 \text{ dL.g}^{-1}$  and  $a = 0.725^{14,15}$  were employed in Mark Houwink Sukurda relation.

### **2.1.3.3. Thermogravimetric analysis (TGA)**

The thermo grams in air were obtained on a mettler TA – 3000 system, at a heating rate of  $10 \text{ K.min}^{-1}$ .

### **2.1.3.4. Evaluation of prepared polymer as Pour Point Depressant (PPD) in base oils**

The prepared additives were evaluated as PPD using base oils (BO1 and BO2) through the pour point test according to the ASTM D97-09 method using Cloud and Pour

Point Tester model WIL-471(India). The effect of additive concentration on pour point was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

#### **2.1.3.5. Evaluation of Viscosity Modifier (VM) properties**

The prepared copolymers were evaluated as VM in two base oils (BO1 and BO2). The kinematic viscosity ( $\nu$ ) of the sample solutions, which is useful to calculate Viscosity Index (VI), was determined at 313 K and 373 K, from the following equation<sup>16</sup>.

$$\nu = (Kt - L/t) \rho \quad (8)$$

Where, K and L are the viscometer constants and t and  $\rho$  are time flow and density of experimental solution, respectively.

The densities were measured with a vibrating-tube density meter (Anton paar, DMA 4500M). Before measurements, the density meter was calibrated with distilled and degassed water and dry air at experimental temperature and atmospheric pressure. VI was determined from the following empirical equation<sup>16</sup>.

$$VI = 3.63 (60 - 10^n) \quad (9)$$

Where n is given by,

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2 \quad (10)$$

$\nu_1$  is the kinematic viscosity at lower temperature,  $\nu_2$  is the kinematic viscosity at higher temperature,  $k$  is a function of temperature only and n is a constant characteristic for each oil<sup>16</sup>.

Viscometric properties of the prepared samples were determined using an Ubbelohde OB viscometer, thoroughly cleaned, dried, and calibrated at the experimental temperatures (313 K and 373 K) with triply distilled, degassed water, and purified methanol<sup>17,18</sup>. It was then filled with experimental liquid and placed vertically in a glass sided thermostat. After reaching thermal equilibrium, the time flow of liquids was

recorded with a digital stopwatch. Different concentrations from 1 wt % to 6 wt % were used to study the effect of concentration on VI of the additive doped lube oil. All the experimental data as mentioned above were noted by taking an average of three experimental results under identical conditions.

#### **2.1.3.6. Biodegradability test**

Biodegradability of the polymers was tested by i) disc diffusion method against fungal pathogens and ii) soil burial degradation test of the polymer films as per ISO 846:1997 and by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

##### **2.1.3.6.1. Disc diffusion method**

The biodegradability of the prepared polymer samples (the copolymers and homopolymers) was tested against five different fungal pathogens namely *Calletotricheme camellia* (CC), *Fussarium equisitae* (FE), *Alterneria alternata* (AA), *Colletrichum gleosproides* (CG) and *Curvularia eragrostidies* (CE). All glass apparatus, culture media were autoclaved before use. Culture media for fungal strains was prepared by mixing suitable proportions of potato extract, dextrose, and agar powder. The fungal growth was confirmed by a change of yellow to blackish. All experiments were performed in Petri dishes and were incubated at 310 K for 30 days after addition of definite weight (1.50 g) of polymer samples. The whole process was carried out in incubation chamber. After 30 days polymer samples were recovered from the fungal media and washed with Chloroform, purified, and dried in an open vessel. The dried samples were weighed<sup>19,20</sup> followed by IR analysis.

##### **2.1.3.6.2. Soil burial degradation test**

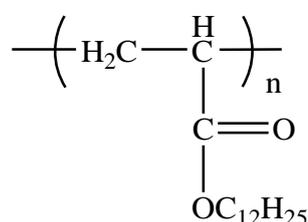
The soil burial degradation test of the polymer films was conducted as per ISO 846:1997<sup>21</sup>. The films of polymer samples were buried in soil. The soil used in this study

had been taken from University of North Bengal (West Bengal, India) campus. The soil was taken in a tray, in which the relative humidity was adjusted to 50 % to 60 % and temperature was thermostated at 303 K with the help of a humidity chamber. The buried films were removed at regular intervals of 15 days up to a span of 3 months. Recovered films were washed with chloroform, purified, and dried. The dried samples were weighed followed by IR analysis.

## 2.1.4. Results and discussions

### 2.1.4.1. Spectroscopic analysis

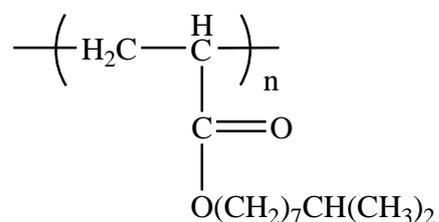
FT-IR spectra (**Figure 2.1**) of the homopolymer of dodecyl acrylate (HDDA) exhibited absorption at  $1732.0\text{ cm}^{-1}$  due to ester carbonyl stretching vibration along with other peaks at  $1456.2$ ,  $1260.0$ ,  $1164.9$ ,  $1112.9\text{ cm}^{-1}$  (CO stretching vibration), and  $1028.0$ ,  $711.7\text{ cm}^{-1}$  (bending vibration of C–H bonds).  $^1\text{H-NMR}$  spectra (**Figure 2.2**) of the homopolymer indicated the existence of  $-\text{OCH}_2$  group at 4.02 ppm (broad singlet) along with the methyl protons ranging between 0.86 and 0.90 ppm together with methylene protons ranging between 1.26 and 1.60 ppm. The proton decoupled  $^{13}\text{C-NMR}$  of the sample (**Figure 2.3**) was in complete agreement with the homopolymer in which the carbonyl carbon appears at 174.66 ppm along with other carbons and probable structure of poly (dodecyl acrylate) is given below:



The formation of the copolymer was confirmed by FT-IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  analysis. In its FT-IR spectra (**Figure 2.4**), the copolymer showed a peak at  $1732.0\text{ cm}^{-1}$  for ester carbonyl stretching vibration along with other peaks at  $2927.9$ ,  $721.9\text{ cm}^{-1}$  (stretching and bending vibration of C–H bonds), and  $1466.6\text{ cm}^{-1}$ , and a band at  $1167.8$

$\text{cm}^{-1}$  (CO stretching vibration). Absence of peak between 4 to 6 ppm in the  $^1\text{H}$ -NMR and that between 130 to 150 ppm in the  $^{13}\text{C}$ -NMR spectrum indicated the formation of copolymer of DDA with  $\alpha$ -pinene (**Figure 2.5** and **Figure 2.6**, respectively).

FT-IR spectra (**Figure 2.7**) of poly (isodecyl acrylate) or homopolymer of isodecyl acrylate (HIDA) exhibited absorption band at  $1732.0\text{ cm}^{-1}$  for the ester carbonyl stretching vibration along with other peaks at  $1456.2$ ,  $1379.0$ ,  $1260.0$ , and  $1166.9\text{ cm}^{-1}$  (CO stretching vibration), and at  $750.0$  and  $710.0\text{ cm}^{-1}$  (bending of C–H bonds). In its  $^1\text{H}$ -NMR spectra (**Figure 2.8**), HIDA showed a broad singlet centered at  $4.02\text{ ppm}$  due to the proton of  $-\text{OCH}_2$  group, another broad singlet centered at  $0.86\text{ ppm}$  was due to methyls of isodecyl chain. In the proton decoupled  $^{13}\text{C}$ -NMR of the homopolymer (**Figure 2.9**), the carbonyl carbon appears at  $174.47\text{ ppm}$  along with other carbons. Absence of peak in the range  $130\text{--}150\text{ ppm}$  indicates absence of any  $\text{sp}^2$  carbon in the homopolymer. The proton decoupled  $^{13}\text{C}$ -NMR of the above sample was in complete agreement with poly (isodecyl acrylate) and probable structure is given below:



The formation of the copolymer was confirmed by FT-IR,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR analysis. In its FT-IR spectra (**Figure 2.10**), the copolymer showed a peak at  $1731.6\text{ cm}^{-1}$  for ester carbonyl stretching vibration along with other peaks at  $2960.7\text{ cm}^{-1}$  (stretching vibration of C–H bonds) and  $1463.3\text{ cm}^{-1}$ , and a band at  $1174.3\text{ cm}^{-1}$  (CO stretching vibration). Formation of the copolymer was also indicated by the absence of  $\text{sp}^2$  hydrogen and  $\text{sp}^2$  carbon in its  $^1\text{H}$  and  $^{13}\text{C}$ -NMR (**Figure 2.11** and **Figure 2.12**), respectively.

The value of extent of incorporation of 1-decene in the copolymer composition, as determined from the FT-IR and NMR method<sup>22</sup> is tabulated in **Table 2.1**.

#### 2.1.4.2. Thermogravimetric Analysis (TGA)

**Figure 2.13** presents a comparison between the TGA data for homopolymers and copolymers. The TGA data shows that the copolymers are better in thermal stability than the homopolymers. Also with decreasing  $\alpha$ -pinene concentration in the feed, thermal stability increases. Comparison among the copolymers indicates that the copolymers of dodecyl acrylate are more stable than the copolymers made from isodecyl acrylate.

#### 2.1.4.3. Viscometric analysis

**Table 2.2** presents intrinsic viscosity i.e.  $[\eta]$  values related to all equations for the samples analysed. Taking into account the data for homo and all copolymer samples, it can be noticed that, except one or two cases values are consistent. Comparison among the copolymers indicates that there is a gradual decrease of  $[\eta]$  values with the increase of  $\alpha$ -pinene content in the monomer composition in both cases. Intrinsic viscosity values are lower for homopolymer (P-1 and P-6) compared to copolymeric sample. Although different intrinsic viscosity values may be found by graphic extrapolation method (Huggins, Kraemer, Martin and SB equation), in this work the data obtained from these four equations shows a tendency to be close for both homo and copolymers. Irrespective of the nature of the polymer, the  $[\eta]$  values obtained by single point determination method is higher than the values obtained by graphic extrapolation method.

**Table 2.3** presents the viscometric constant values obtained for all equations using graphic extrapolation method. Although,  $k_k$  values are not negative and  $k_{sb} \neq 0.28$  (for most of the cases), the values of  $k_h + k_k$  are nearly equal to 0.5 and values of  $k_h$  are less than 0.5 for the polymers of IDA, which indicates better solvation<sup>10</sup> of these polymers compared to those of DDA.

Viscometric molecular weight ( $M$ ) obtained by using Mark Houwink equation, is presented in **Table 2.4**. As is expected, the homopolymer showed lower viscometric

molecular weight ( $M$ ) compared to the copolymers. There is also a gradual decrease of  $M$  with the increase in  $\alpha$ -pinene concentration in case of the copolymers and the values are in line with the intrinsic viscosity values of the polymers.

A linear relation for the plot of  $\log \eta_{sp}$  against  $\log C[\eta]$ , obtained for all samples (**Figure 2.14**), indicates that measurements were performed in Newtonian flow<sup>9,12</sup>.

#### **2.1.4.4. Performance of the homopolymers and copolymers as PPD**

Physical properties of the base oils are tabulated in **Table 2.5**. Pour point of the different concentrations of additive doped lube oils (BO1 and BO2) were tested and tabulated in **Table 2.6** and **Table 2.7**, respectively. A graphical presentation of the PP values of the polymers in these base oils is also shown in **Figure 2.15.1** and **Figure 2.15.2**, respectively. The values indicate that the prepared copolymers of DDA with  $\alpha$ -pinene samples are more efficient as PPD than the copolymers of IDA with  $\alpha$ -pinene and the efficiency increases with the decrease in concentration of the additive in base oil. This may be explained on the basis that, when the molecular weight of the additive and its concentration increases, solvation power decreases and so as PPD<sup>23</sup>.

#### **2.1.4.5. Performance of the homopolymers and copolymers as VM**

It is clear from the VI data in these base oils (BO1 and BO2), tabulated in **Table 2.8** and **Table 2.9**, respectively (and also from **Figure 2.16.1** and **Figure 2.16.2** in these base oils, respectively) as evaluated in present investigation that irrespective of the polymer (homopolymer and copolymer) and nature of the base oil, VI values increase with the increase in additive concentration in the base oils studied. A critical observation of the VI values indicates that better performance is obtained for the copolymers of DDA with  $\alpha$ -pinene than copolymers of IDA with  $\alpha$ -pinene. It is also noticed that all copolymers show better VM property than the homopolymers (P-1 and P-6).

As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands from its coil nature due to the increase in the solvation power. This increase in coil size counterbalances the reduction of the viscosity of the lube oil with temperature and hence, decreases the changes of viscosity of the mixture. The increase in concentration of the polymer leads to an increase in the total volume of polymer coils in the oil solution and thus exerting greater thickening effect and so as to VI<sup>4</sup>.

#### **2.1.4.6. Analysis of biodegradability test result**

**Table 2.10** and **Table 2.11** presents biodegradability test results obtained by using disk diffusion method and soil burial test method, respectively. Copolymer of  $\alpha$ -pinene with isodecyl acrylate showed significant biodegradability against the fungal pathogen, *Alternaria alternata*. Result of soil burial degradation test also indicated the similar extent of biodegradability. It was further confirmed by the shift of IR frequency of the ester carbonyl after the test is over (**Figure 2.17.1** and **Figure 2.17.2**). Copolymer of  $\alpha$ -pinene with dodecyl acrylate also shows biodegradability but to a smaller extent.

#### **2.1.5. Conclusion**

A consideration of the chemical structures of DDA and IDA may be taken into consideration to explain the differences of performance between the homopolymers and copolymers of DDA and IDA. The thermal stability of the copolymers is always greater than the corresponding homopolymers, and the copolymers of dodecyl acrylate with  $\alpha$ -pinene are thermally more stable than that of the isodecyl acrylate. Both the intrinsic viscosity and viscometric molecular weight of the copolymers decrease with increase in  $\alpha$ -pinene concentration in the feed of the copolymers. The pour point of the samples is found better for the copolymers of dodecyl acrylate with  $\alpha$ -pinene than the copolymers of isodecyl acrylate with  $\alpha$ -pinene and the values decrease with increasing concentration of the polymer doped base oil. The VI values are in accordance with the molecular weight of

the polymer samples. The greater the molecular weight, greater is the VI of the polymer samples. With increasing concentration of the additive doped oil solution, VI is found to increase. The Copolymer of isodecyl acrylate with  $\alpha$ -pinene showed significant biodegradability against the fungal pathogen, *Alternaria alternata*. The copolymer of dodecyl acrylate with  $\alpha$ -pinene also shows biodegradability but to a smaller extent.

#### **2.1.6. References**

References are given in Bibliography under Chapter-II of Part-II (Page No. 203-205).

### 2.1.7. Tables and figures

**Table 2.1. Composition of the monomers in the copolymers in terms of mole fraction determined by NMR and FT-IR spectroscopic method<sup>22</sup>**

Sample	mole fraction of $\alpha$ -pinene in the feed	mole fraction of $\alpha$ -pinene in copolymer by NMR method	mole fraction of $\alpha$ -pinene in copolymer by FT-IR
P-1	0.0000	0.0000	0.0000
P-2	0.0433	0.0176	0.0261
P-3	0.0851	0.0518	0.0382
P-4	0.1251	0.0601	0.0635
P-5	0.1639	0.0685	0.0851
P-6	0.0000	0.0000	0.0000
P-7	0.0385	0.0156	0.0231
P-8	0.0759	0.0610	0.0323
P-9	0.1121	0.0579	0.0565
P-10	0.1476	0.0624	0.0743

P-1 = homopolymer of dodecyl acrylate; P-2 to P-5 = copolymer of dodecyl acrylate with different mole fractions of  $\alpha$ -pinene; P-6 = homopolymer of isodecyl acrylate; P-7 to P-10 = copolymer of isodecyl acrylate with different mole fractions of  $\alpha$ -pinene.

**Table 2.2. Intrinsic viscosity  $[\eta]$  values for all prepared polymer samples calculated by different equations**

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	4.059	4.361	4.336	4.512	4.637	4.599	4.773

P-2	5.742	6.103	6.221	6.570	6.294	6.267	6.591
P-3	4.923	5.292	5.317	5.601	5.535	5.502	5.751
P-4	4.459	4.716	4.730	4.922	4.976	4.939	5.141
P-5	4.338	4.562	4.572	4.762	4.711	4.673	4.856
P-6	3.774	3.845	3.881	3.945	4.020	3.983	4.119
P-7	6.057	6.116	6.353	6.565	6.297	6.274	6.606
P-8	5.680	5.596	5.842	5.977	5.629	5.594	5.847
P-9	5.492	5.393	5.629	5.747	5.407	5.373	5.611
P-10	5.117	5.017	5.223	5.314	4.997	4.961	5.165

a- extrapolation of graph, b- single point determination ( $k_{sb}= 0.28$ ). h, k, m, sb, sc, and dc refers Huggins, Kraemer, Martin, Schulz-Blaschke, Solomon-Ciuta, and Deb-Chatterjee, respectively.

**Table 2.3. Viscometric constants (k) obtained for all prepared polymer samples**

Sample	$k_h$	$k_k$	$k_m$	$k_{sb}$	$k_h+k_k$
P-1	0.760	0.044	0.478	0.347	0.804
P-2	0.640	0.082	0.379	0.260	0.722
P-3	0.727	0.059	0.437	0.302	0.786
P-4	0.652	0.071	0.422	0.307	0.723
P-5	0.655	0.062	0.435	0.316	0.717
P-6	0.475	0.107	0.359	0.294	0.582
P-7	0.418	0.124	0.284	0.214	0.542
P-8	0.331	0.142	0.250	0.198	0.473
P-9	0.322	0.143	0.247	0.198	0.465

P-10                    0.316                    0.145                    0.249                    0.203                    0.461

$k_h$ ,  $k_k$ ,  $k_m$ , and  $k_{sb}$  are Huggins, Kraemer, Martin, and Schulz- Blaschke coefficients respectively.

**Table 2.4. Determination of viscometric molecular weight ( $M$ ) by Mark Houwink equation**

Sample	$M_h^a$	$M_k^a$	$M_m^a$	$M_{sb}^a$	$M_{sb}^b$	$M_{sc}^b$	$M_{dc}^b$
P-1	14672	16199	16071	16977	17630	17431	18347
P-2	23674	25752	26441	28508	26870	26711	28634
P-3	19147	21154	21292	22876	22505	22320	23726
P-4	16703	18045	18119	19141	19432	19233	20326
P-5	16081	17238	17290	18288	18019	17819	18788
P-6	13270	13616	13792	14107	14478	14295	14972
P-7	25484	25827	27218	28478	26887	26752	28724
P-8	23323	22848	24245	25021	23034	22837	24274
P-9	22265	21713	23034	23703	21791	21602	22933
P-10	20195	19653	20774	21275	19545	19351	20457

**Table 2.5. Physical properties of base oils**

Base oil properties	Base oils	
	BO1	BO2
Viscosity at 313 K in cSt	7.136	23.392
Viscosity at 373 K in cSt	1.857	3.915

Cloud point, °C	-10	-8
Pour point, °C	-3	-6
Density (g.cm <sup>-3</sup> ) at 313 K	0.837	0.868

**Table 2.6. Pour Point (PP) of the additive doped base oil (BO1)**

Conc. (wt %)	PP (°C) in presence of									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
0	-3	-3	-3	-3	-3	-3	-3	-3	-3	-3
2	-9	-21	-21	-18	-18	-6	-18	-15	-15	-12
4	-6	-18	-18	-15	-15	-6	-12	-12	-12	-12
6	-6	-15	-15	-15	-12	-3	-9	-9	-12	-9

**Table 2.7. Pour Point (PP) of the additive doped base oil (BO2)**

Conc. (wt %)	PP (°C) in presence of									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
0	-6	-6	-6	-6	-6	-6	-6	-6	-6	-6
2	-12	-18	-15	-15	-12	-9	-15	-15	-15	-12
4	-9	-12	-12	-12	-12	-6	-12	-15	-12	-9
6	-6	-9	-12	-9	-9	-6	-12	-12	-9	-9

**Table 2.8. Viscosity Index (VI) values of the additive doped base oil (BO1)**

Conc. (%)	VI in presence of									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
0	85	85	85	85	85	85	85	85	85	85
1	95	105	101	99	95	92	98	95	95	91
2	98	110	112	109	107	94	103	101	96	92
3	100	120	119	116	113	95	109	107	98	94
4	103	122	120	119	122	100	114	110	100	97
5	106	125	121	125	130	102	117	112	106	99
6	109	132	126	132	137	105	122	113	109	102

**Table 2.9. Viscosity Index (VI) values of the additive doped base oil (BO2)**

Conc. (%)	VI in presence of									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
0	80	80	80	80	80	80	80	80	80	80
1	90	85	79	77	76	92	85	83	80	78
2	93	87	83	81	79	94	90	87	82	80
3	97	94	86	86	85	95	95	90	86	85
4	100	99	91	88	90	100	101	94	89	88
5	102	104	92	98	95	102	106	99	94	91
6	104	112	94	102	95	105	109	102	99	96

**Table 2.10. Result of biodegradability test by the disc diffusion method**

Pathogens used	Initial weight (g)	Weight loss (g) in the presence of									
		P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
CC		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FE		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AA	1.50	0.00	0.17	0.22	0.20	0.26	0.00	0.24	0.28	0.29	0.32
CG		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CE		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

CC, FE, AA, CG, and CE are the pathogens named *Calletotricheme camellia* (CC), *Fussarium equisitae* (FE), *Alterneria alternata* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE).

**Table 2.11. Result of biodegradability test by soil burial degradation test**

Initial weight (g)	Weight loss (g) in the presence of									
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
1.50	0.00	0.08	0.07	0.08	0.09	0.00	0.08	0.08	0.09	0.10

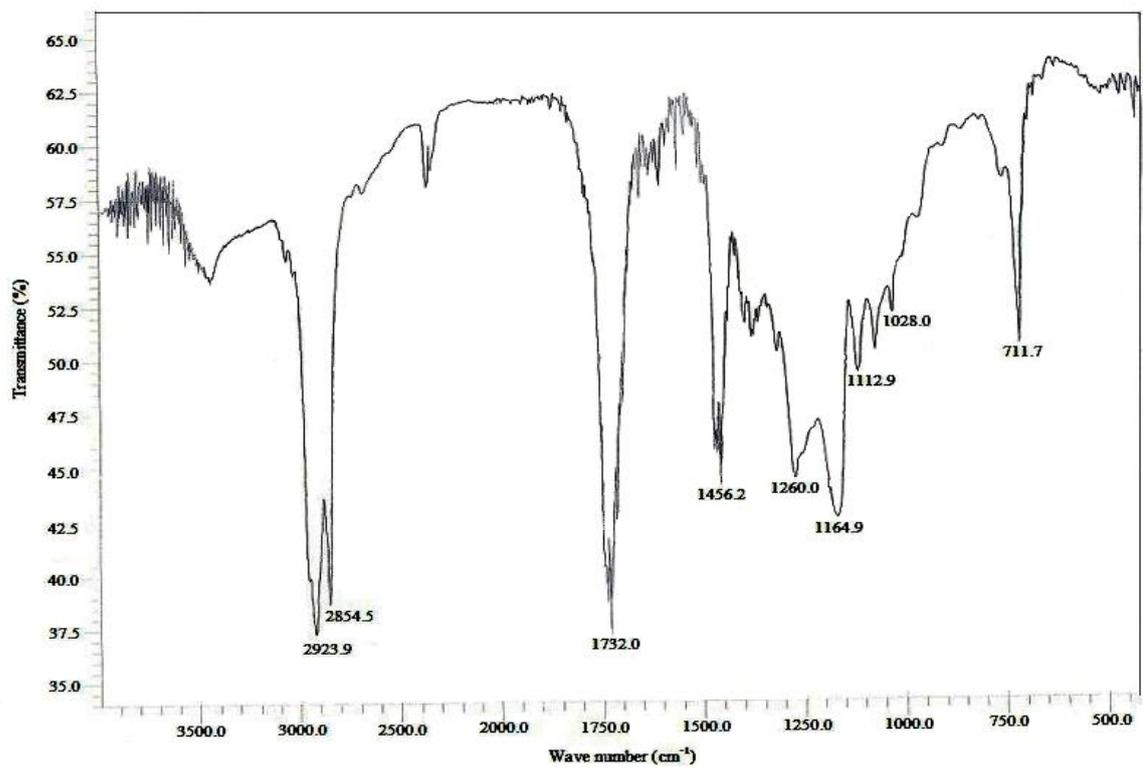


Figure 2.1. FT-IR spectra of poly (dodecyl acrylate)

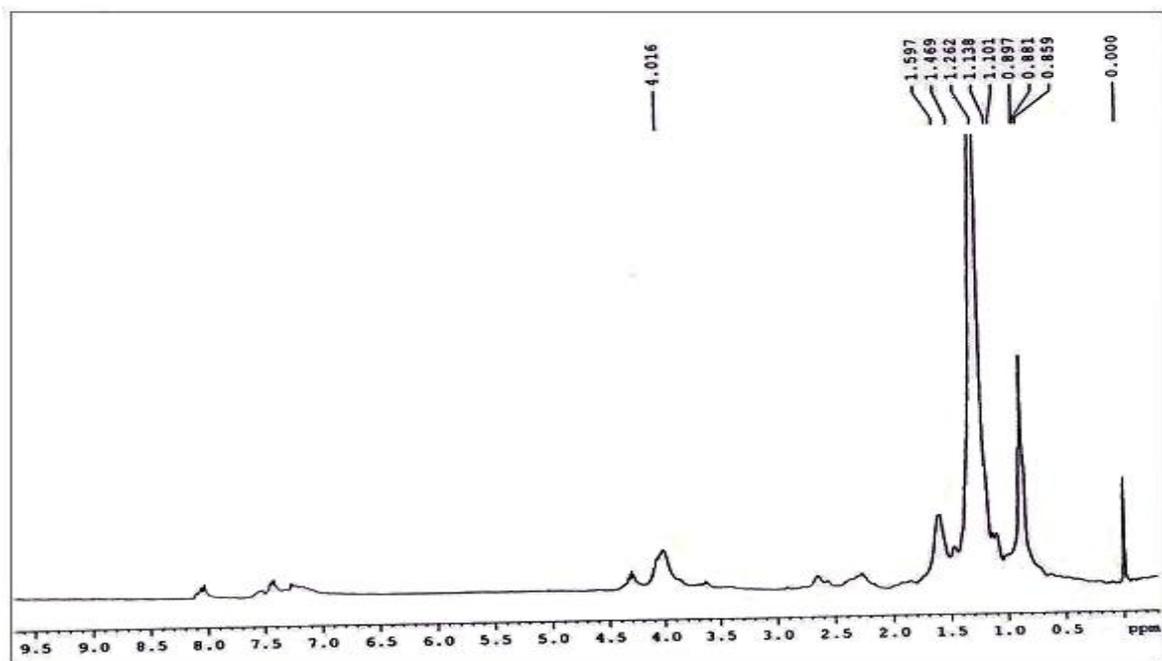


Figure 2.2. <sup>1</sup>H-NMR spectra of poly (dodecyl acrylate)

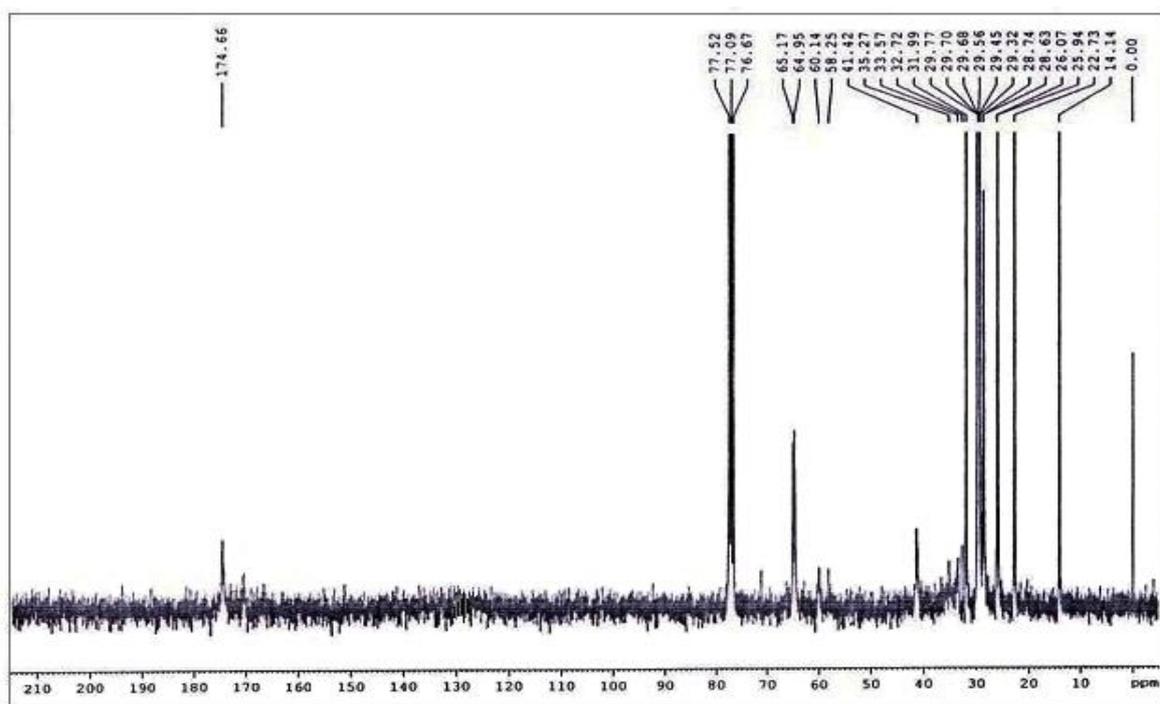


Figure 2.3.  $^{13}\text{C}$ -NMR spectra of poly (dodecyl acrylate)

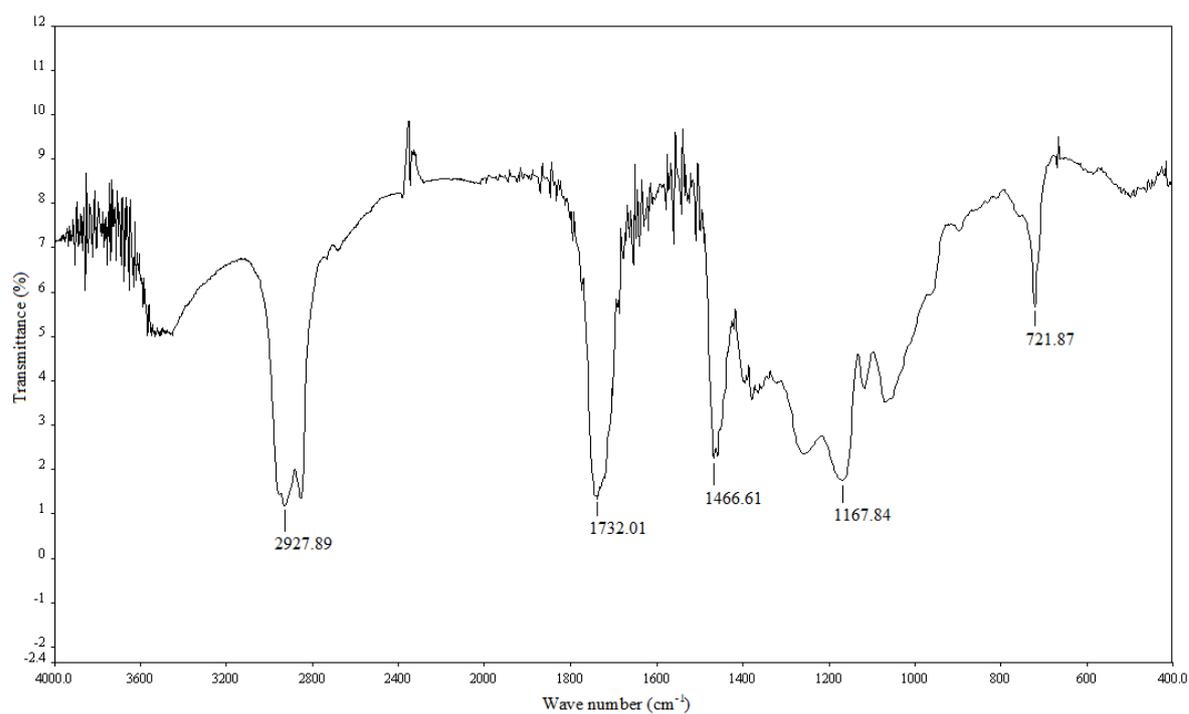
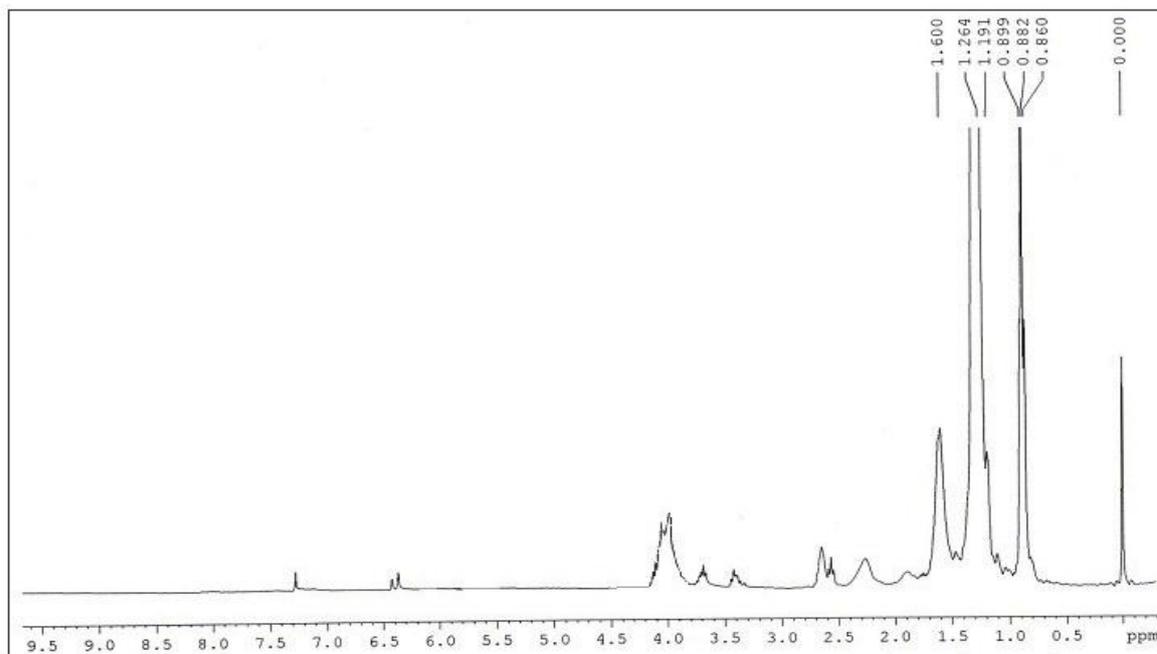
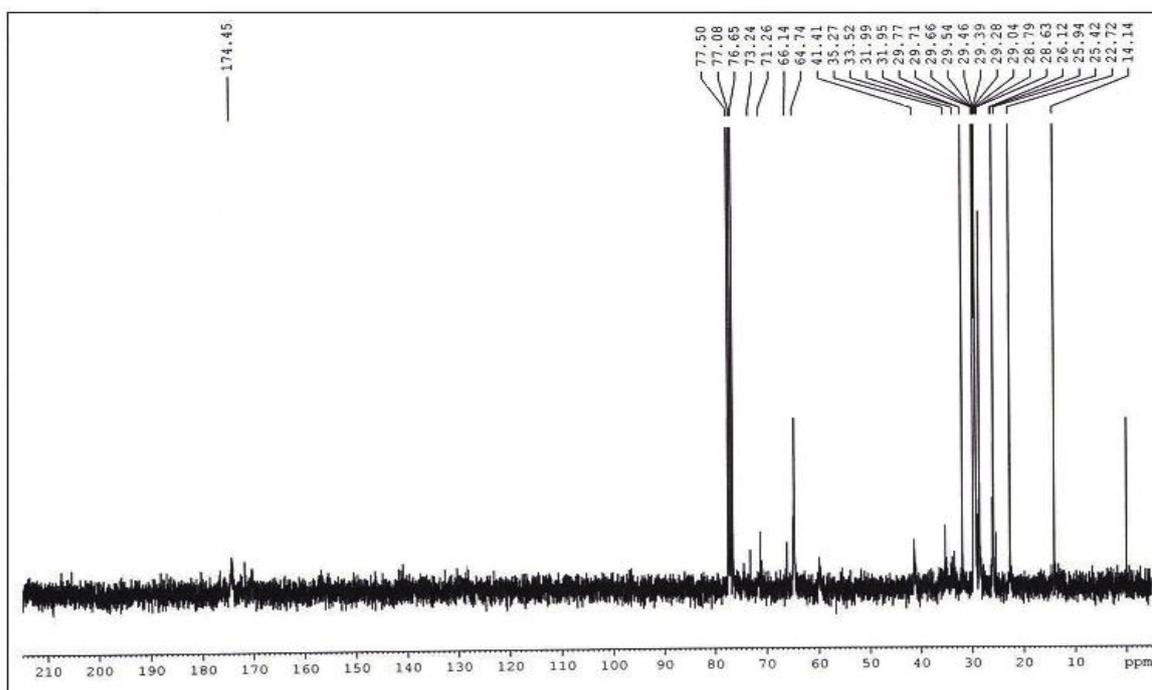


Figure 2.4. FT-IR spectra of a representative copolymer of dodecyl acrylate with  $\alpha$ -pinene



**Figure 2.5.** <sup>1</sup>H-NMR spectra of a representative copolymer of dodecyl acrylate with  $\alpha$ -pinene



**Figure 2.6.** <sup>13</sup>C-NMR spectra of a representative copolymer of dodecyl acrylate with  $\alpha$ -pinene

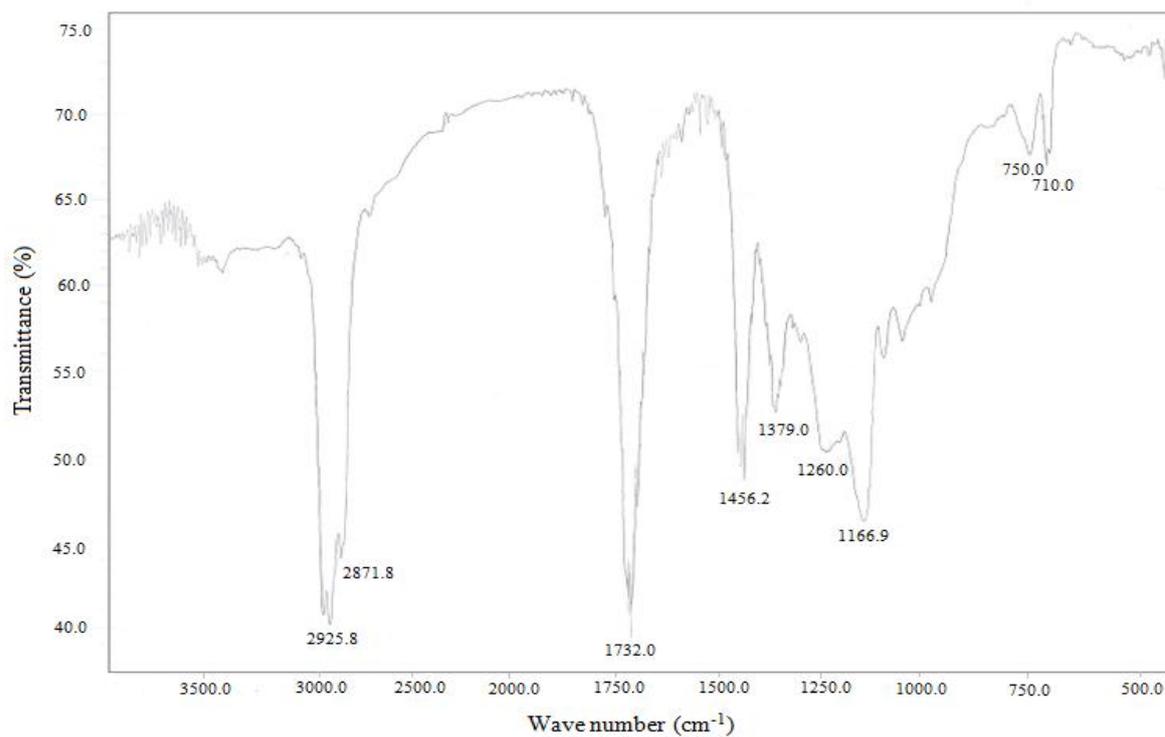


Figure 2.7. FT-IR spectra of poly (isodecyl acrylate)

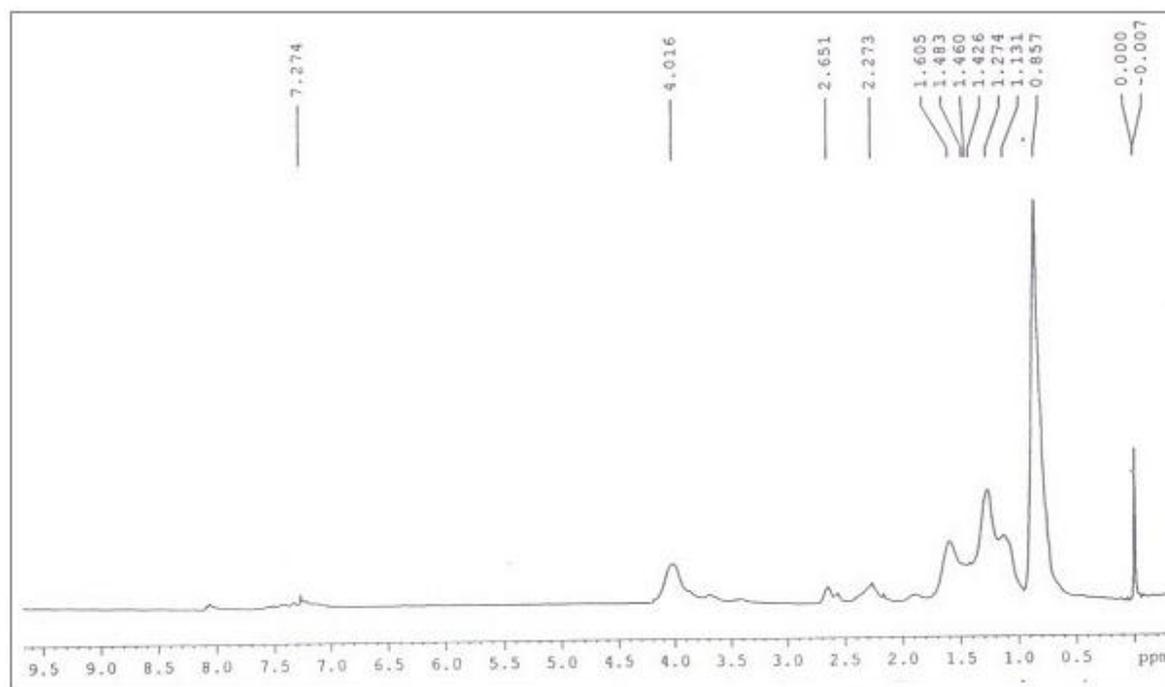


Figure 2.8. <sup>1</sup>H-NMR spectra of poly (isodecyl acrylate)

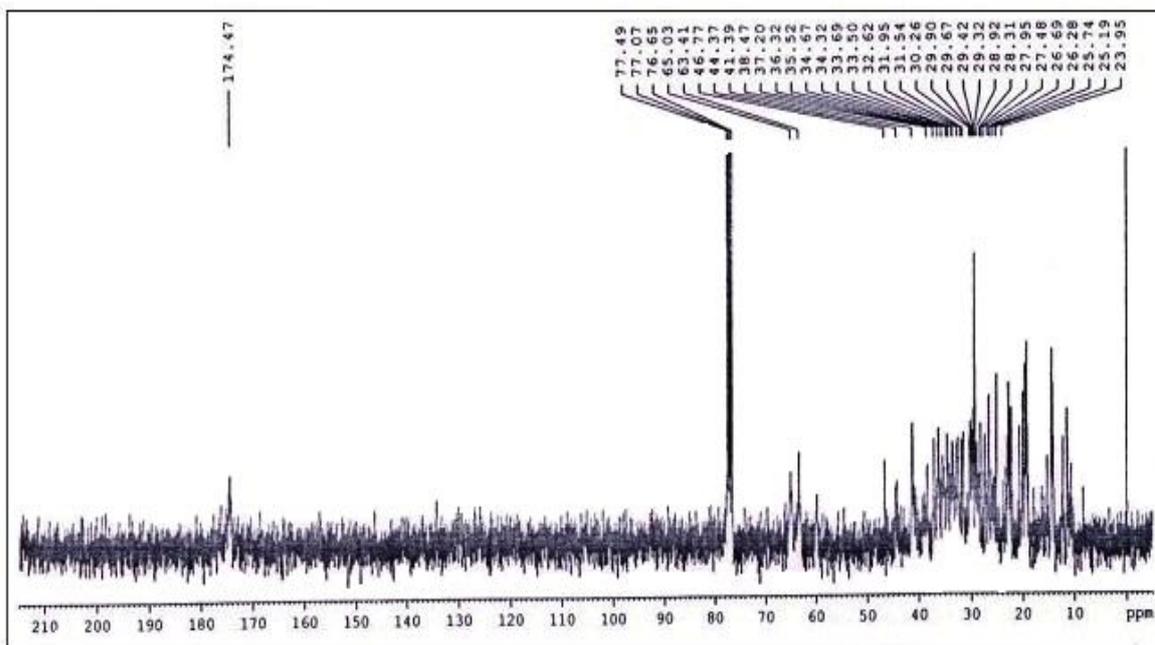


Figure 2.9.  $^{13}\text{C}$ -NMR spectra of poly (isodecyl acrylate)

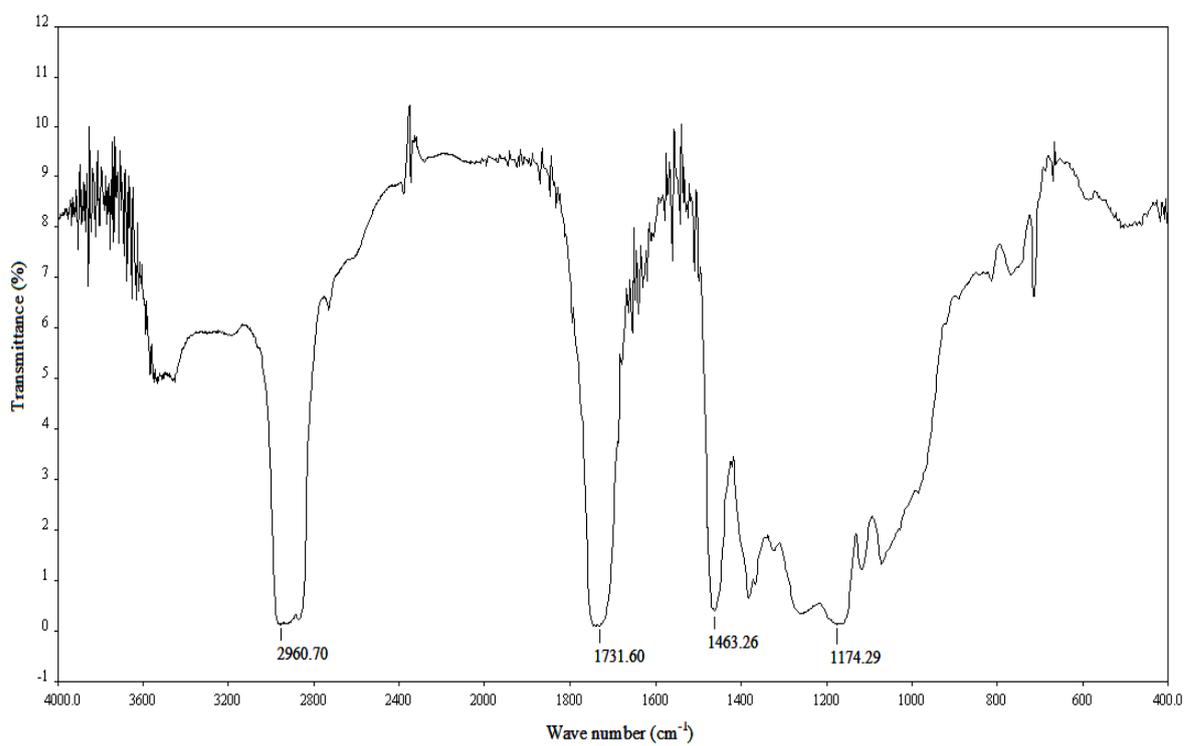


Figure 2.10. FT-IR spectra of a representative copolymer of isodecyl acrylate with  $\alpha$ -pinene

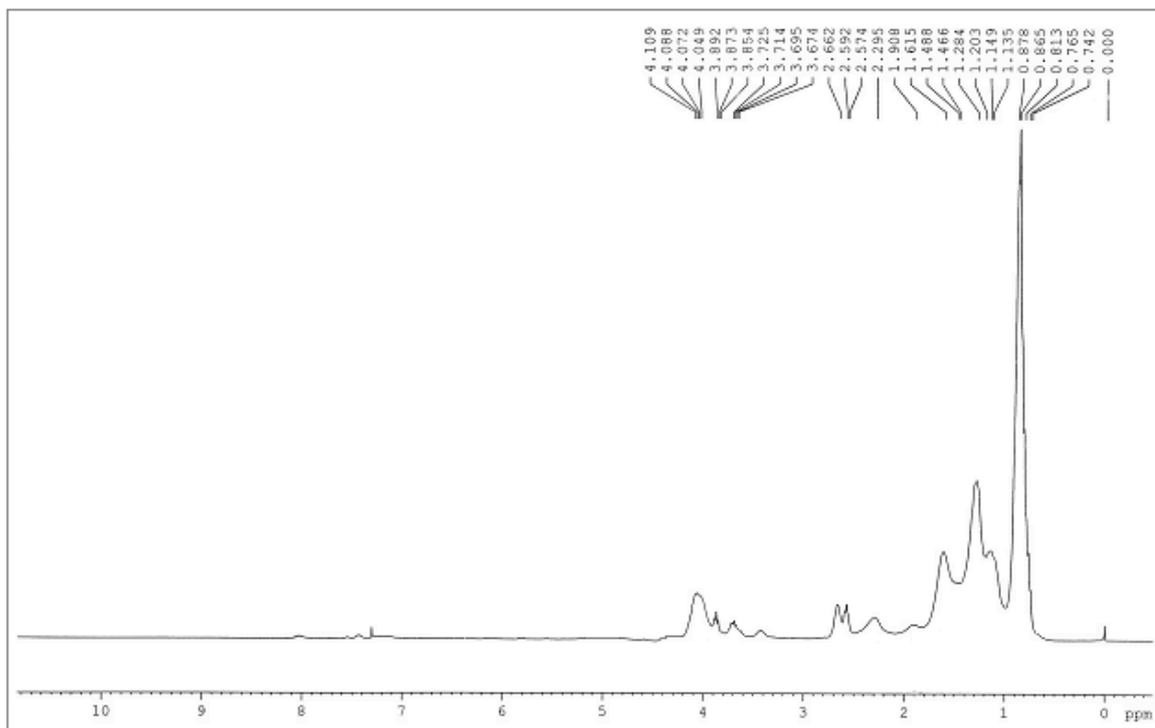


Figure 2.11.  $^1\text{H}$ -NMR spectra of a representative copolymer of isodecyl acrylate with  $\alpha$ -pinene

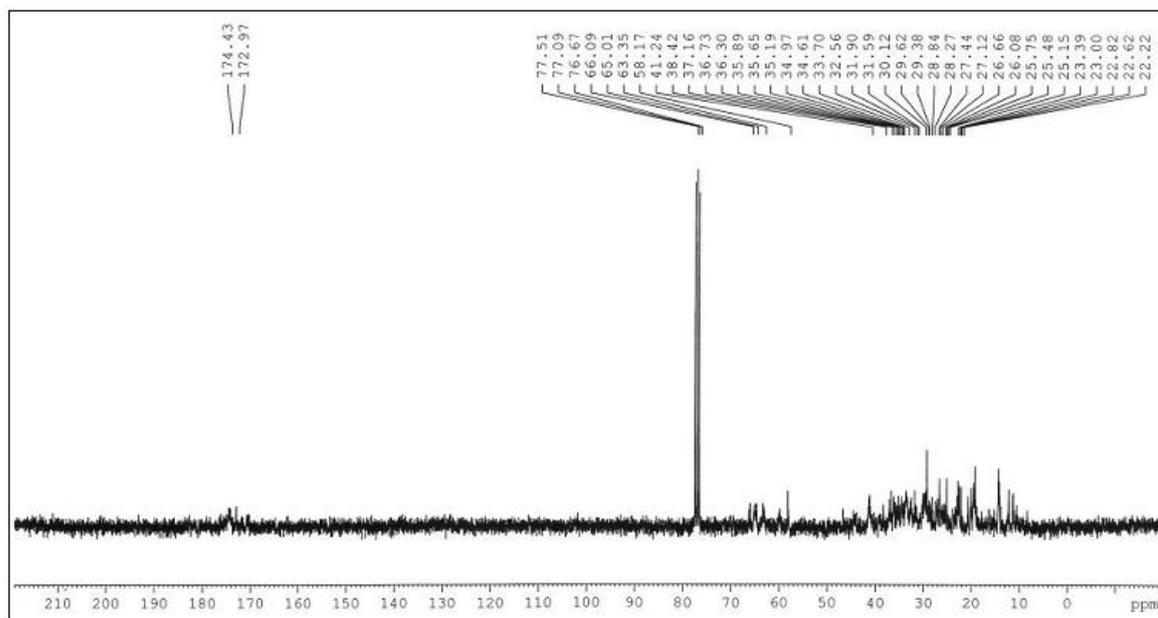
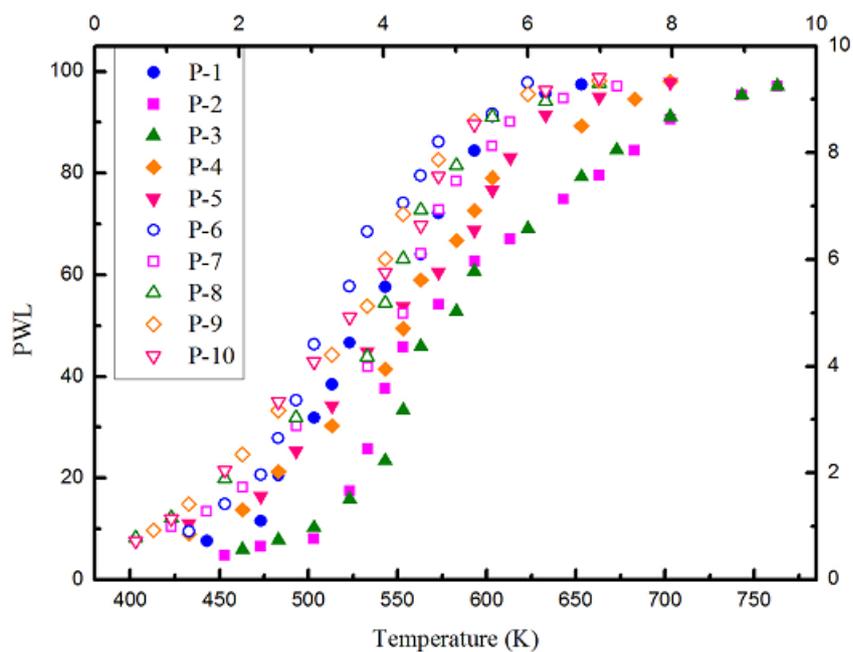
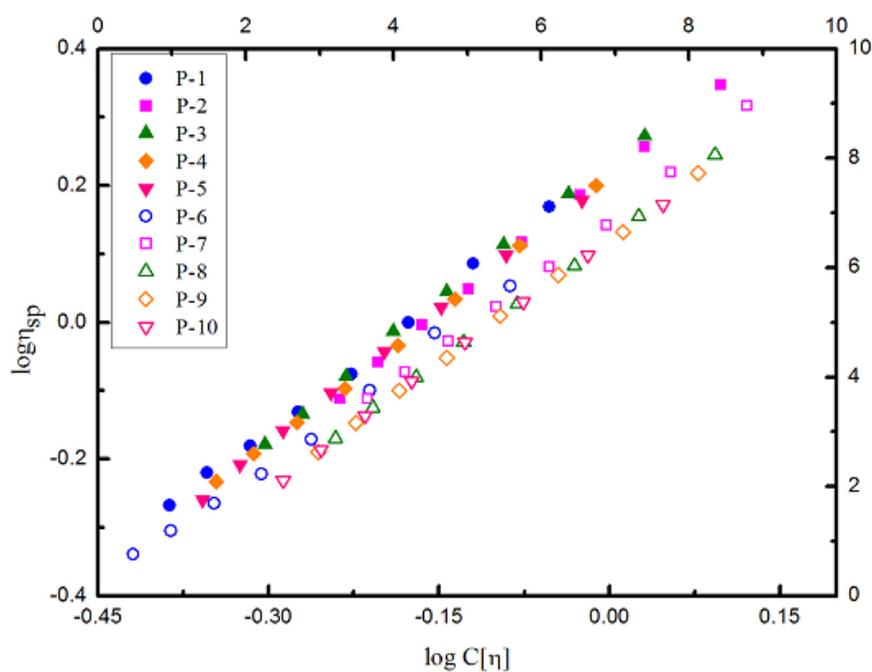


Figure 2.12.  $^{13}\text{C}$ -NMR spectra of a representative copolymer of isodecyl acrylate with  $\alpha$ -pinene



**Figure 2.13. Plot of PWL vs. Temperature. PWL is percent weight loss and temperature is measured in Kelvin.**



**Figure 2.14. Plot of  $\log \eta_{sp}$  vs.  $\log C[\eta]$ , where  $\eta_{sp}$  is the specific viscosity of the polymer solution in toluene,  $C$  is the concentration of the solution in  $\text{g}\cdot\text{cm}^{-3}$ , and  $[\eta]$  is the intrinsic viscosity of the polymer solution in toluene obtained by using Huggins equation.**

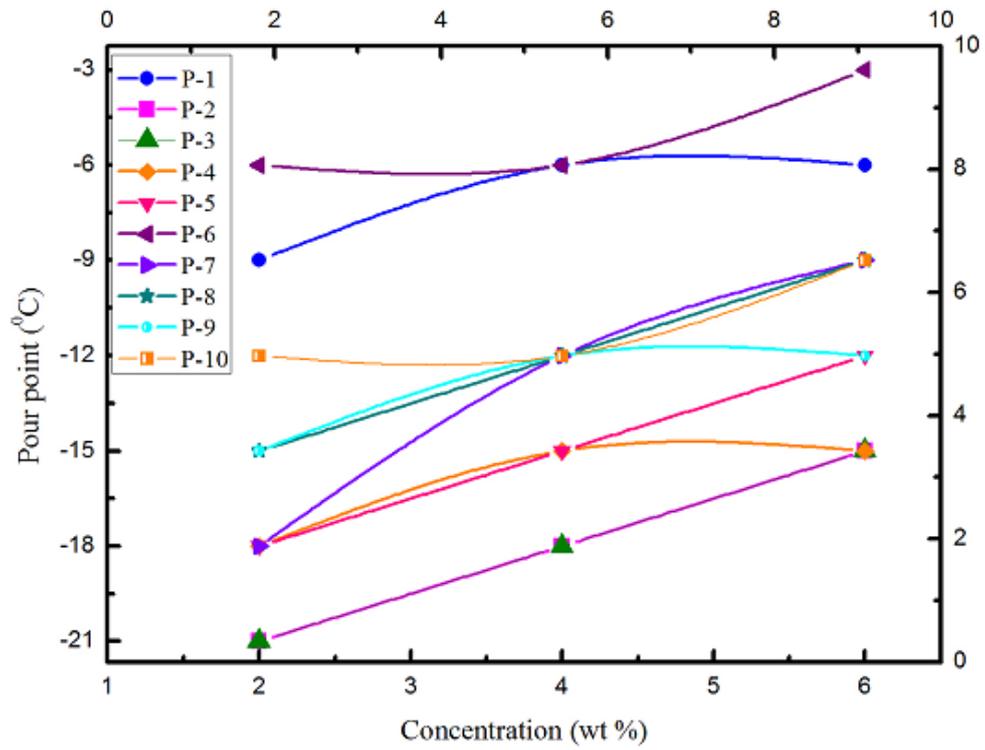


Figure 2.15.1. Plot of pour point vs. additive concentration in BO1

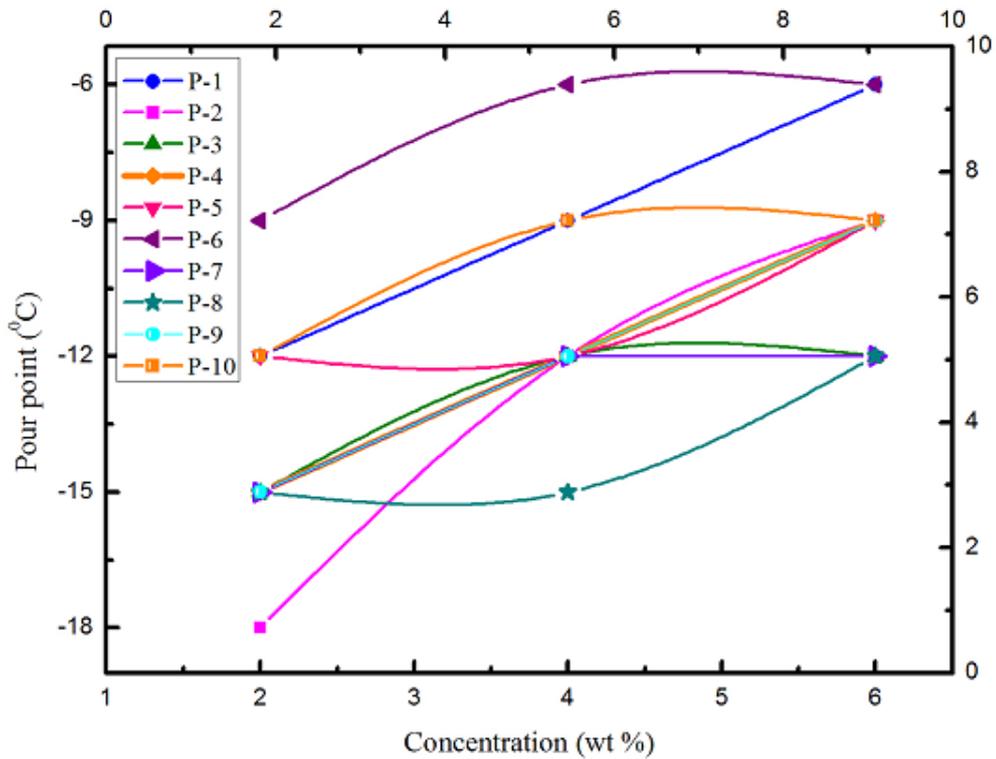


Figure 2.15.2. Plot of pour point vs. additive concentration in BO2

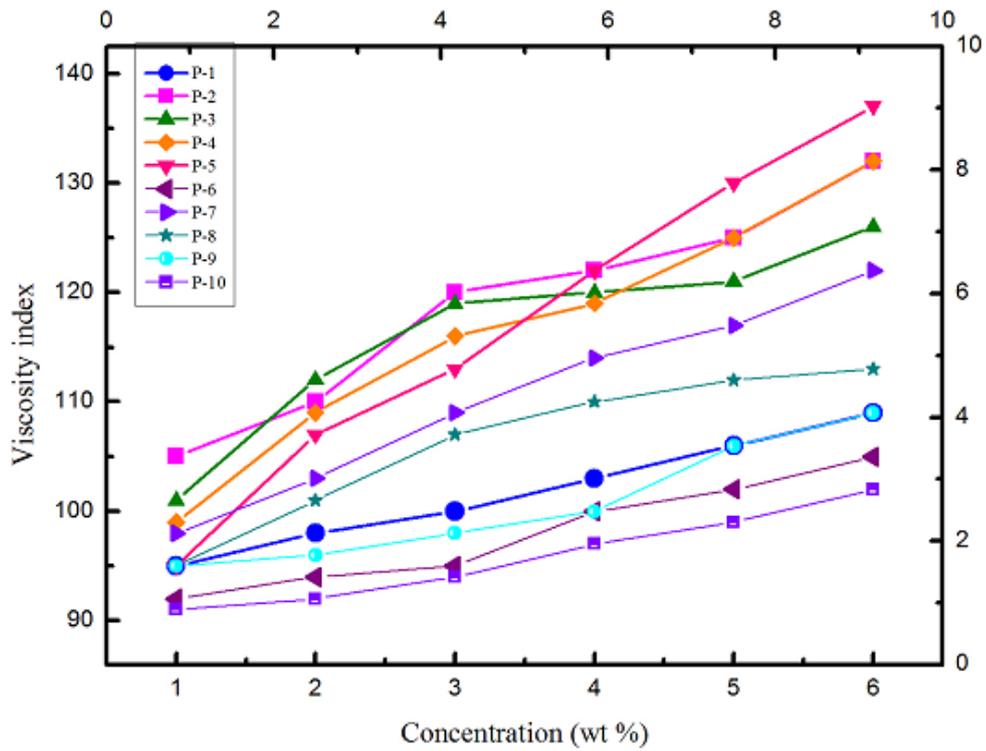


Figure 2.16.1. Plot of viscosity index vs. additive concentration in BO1

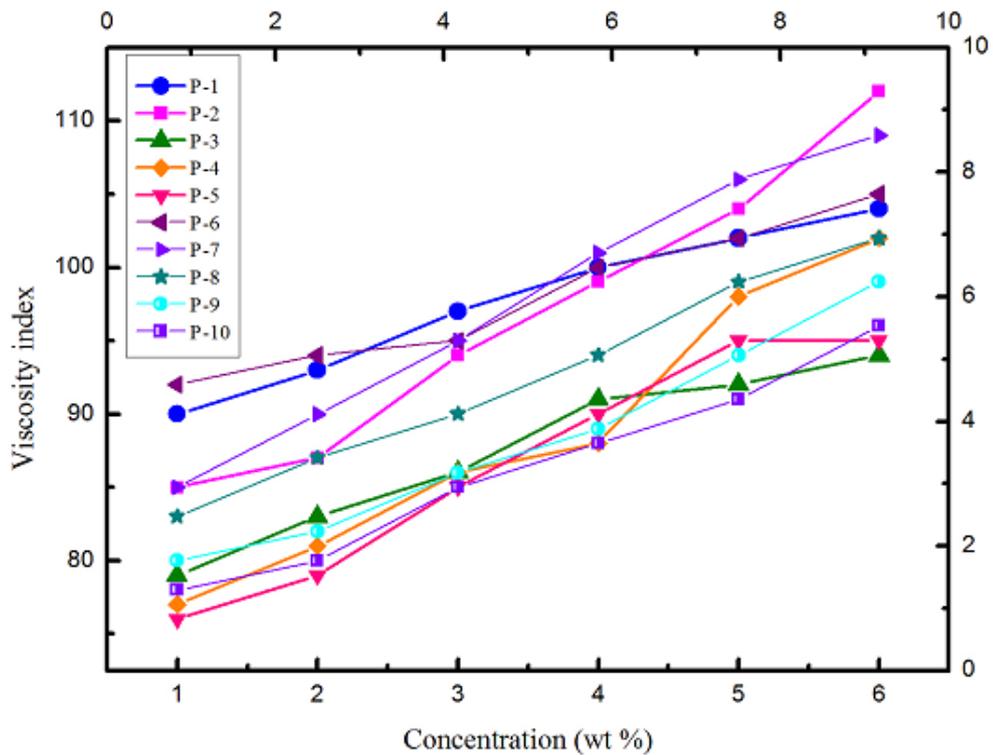
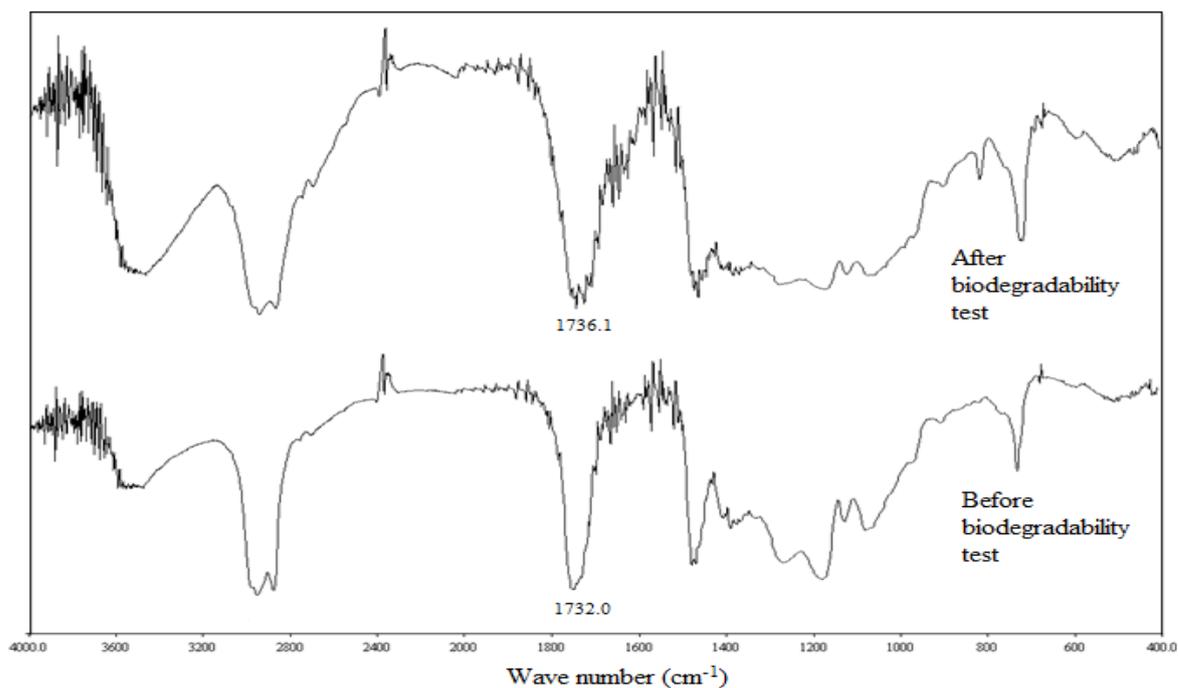
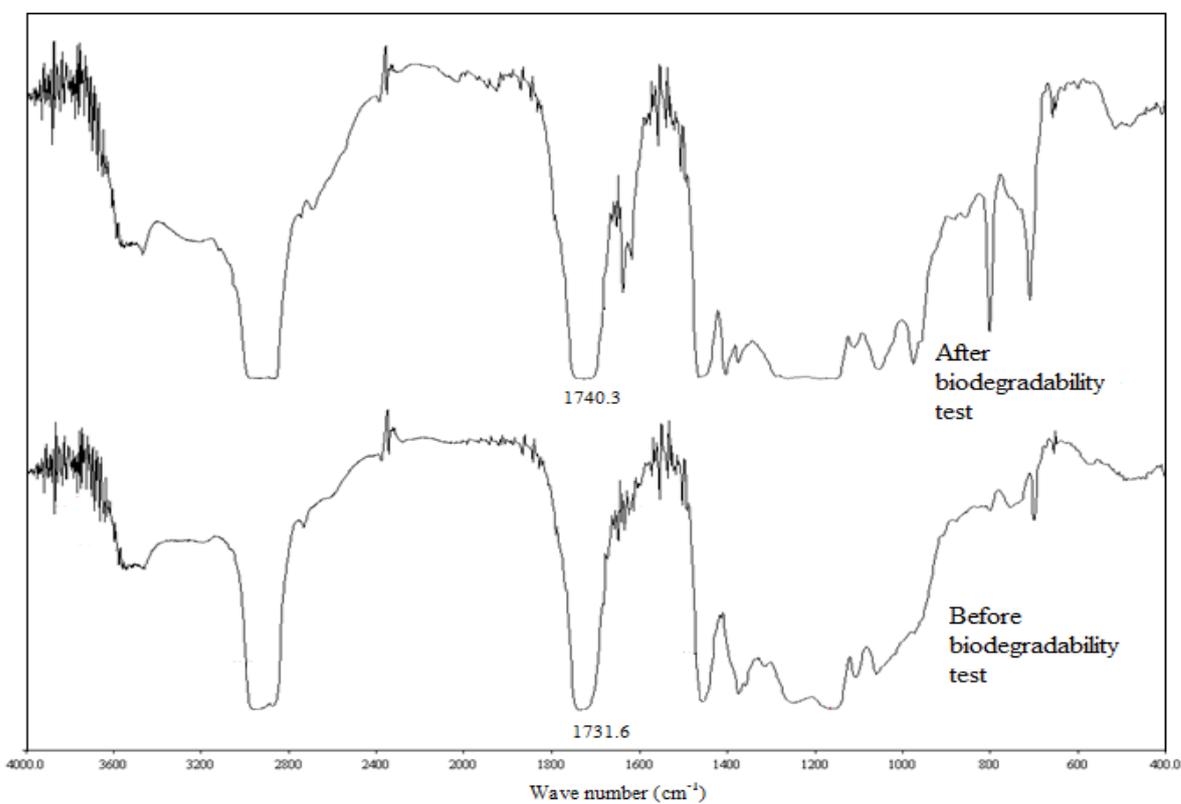


Figure 2.16.2. Plot of viscosity index vs. additive concentration in BO2



**Figure 2.17.1. Comparison of IR spectra before and after disk diffusion method for a representative copolymer sample of dodecyl acrylate with  $\alpha$ -pinene**



**Figure 2.17.2. Comparison of IR spectra before and after disk diffusion method for a representative copolymer sample of isodecyl acrylate with  $\alpha$ -pinene**