

CHAPTER-II

SYNTHESIS, CHARACTERIZATION, AND PERFORMANCE EVALUATION OF POLY (ACRYLATES) AND ACRYLATE- α -OLEFIN COPOLYMERS IN LUBE OIL

1.1.1. Introduction

Polymers of alkyl acrylate are used as additives in lubricant composition for improving the viscometric and rheological properties of the lubricant^{1,2}. Copolymers of styrene as additive for Pour Point Depressant (PPD) and Viscosity Modifier (VM) are well known³⁻⁵. In order to investigate the influence of incorporation of aliphatic long chain, in the present study 1-decene unit has been incorporated into the acrylate backbone to study the performance of the respective copolymers as PPD and VM.

In this work, the results of the investigation toward the synthesis, characterization and viscometric measurements of an additive, based on long chain acrylate + 1-decene copolymer and evaluation of their performance as PPD and VM in comparison to the respective homopolymers, prepared under identical condition, has been discussed. The acrylates used in this work are isodecyl acrylate (IDA) and dodecyl acrylate (DDA).

Physical characterization of the copolymers and homopolymers was carried out employing FT-IR, NMR and Thermogravimetric Analysis (TGA). However, as performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent, viscometric studies in dilute solution may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solutions are concerned. Since reports regarding such information is scanty⁶ and almost nil for polymers used as lube oil additives, present research also include viscometric study⁷ of the copolymers as well as the homopolymers.

1.1.2. Experimental Procedure

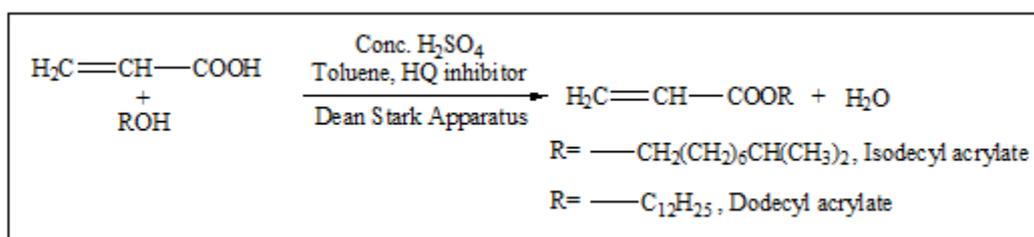
1.1.2.1. Materials

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd., acrylic acid (stabilized with 0.02 % hydroquinone monomethyl ether) and isodecyl

alcohol from Sisco Research Laboratories Pvt. Ltd., dodecyl alcohol and hexane from S D Fine Chem. Ltd., 1-decene from Across Organics, and methanol from Thomas Baker (Chemicals) Pvt. Ltd. All were used as they obtained without further purification. Benzoyl peroxide (BZP), obtained from LOBA chemicals, was recrystallized from CHCl₃-MeOH mixture before use. Base oils were collected from IOCL, Dhakuria, Kolkata, West Bengal.

1.1.2.2. 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 1.1: Preparation of isodecyl acrylate (IDA) and dodecyl acrylate (DDA)

1.1.2.3. Purification of prepared esters

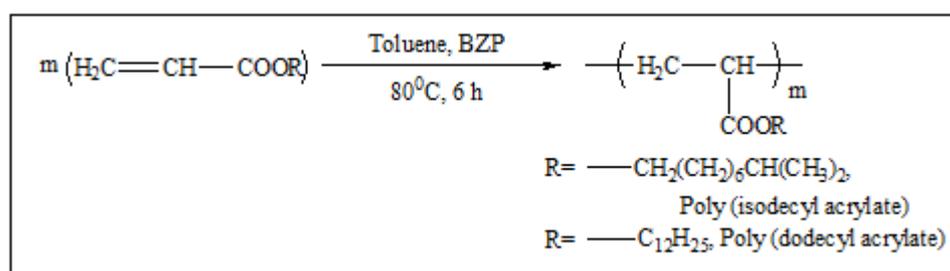
The prepared esters were purified according to the following procedure: a suitable amount of charcoal was added to the ester. It was allowed to reflux for 3 h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separating funnel

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.

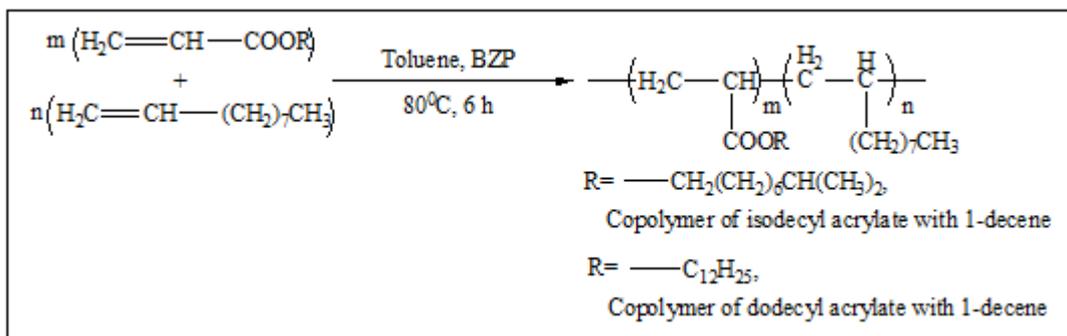
1.1.2.4. Preparation of copolymer and homopolymer

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 1-decene 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 1-decene for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the copolymer of IDA with 1-decene. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K.

In the preparation of copolymers, different mole fraction of 1-decene was used in the feed.



Scheme 1.2: Preparation of poly (isodecyl acrylate) and poly (dodecyl acrylate)



Scheme 1.3: Preparation of copolymer of isodecyl acrylate and dodecyl acrylate with 1-decene

Homopolymers of IDA and DDA i.e., poly (isodecyl acrylate) and poly (dodecyl acrylate) (HIDA and HDDA, respectively), and also copolymers of DDA with different mole fraction of 1-decene were similarly prepared and purified under identical condition for use in reference experiments.

1.1.3. Measurements

1.1.3.1. Spectroscopic measurements

Spectroscopic IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer as well as in Perkin Elmer FT-IR spectrometer by using 0.1 mm KBr cells at room temperature within the wave number range 400-4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl₃ was used as solvent and TMS as reference material.

1.1.3.2. Viscometric measurements

The viscometric molecular weight of the polymers in solution can be determined by using Mark Houwink Sukurda (MHS) equation (eqn. 1), measuring the intrinsic 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 extrapolation⁸⁻¹² method 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 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 these⁹⁻¹¹ 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 $k_h + k_k = 0.5$ ⁹. The unit of intrinsic viscosity and concentration are dL.g^{-1} and g.cm^{-3} , respectively.

Viscometric properties 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. Precautions regarding the prevention of evaporation of the solvent were taken in all of the cases. For the viscosity average molecular weight determination, the constants $K = 0.00387 \text{ dL.g}^{-1}$ and $a = 0.725$ ^{7,13} were employed in MHS relation to get an idea of whether the molecular weight value is low or high. In the single point measurement, the lowest value of solution concentration was chosen for calculation.

1.1.3.3. Thermogravimetric Analysis (TGA)

The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K.min^{-1} .

1.1.3.4. Evaluation of Pour Point Depressant (PPD) properties

The prepared compounds were evaluated as PPD using two different base oils (BO1 and BO2) through the pour point test according to the ASTM D97-09 on a 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.

1.1.3.5. Evaluation of Viscosity Modifier (VM) properties

The prepared copolymers were evaluated as viscosity modifiers in two base oils (BO1 and BO2). The kinematic viscosity (ν) of the sample solutions, useful to calculate viscosity index (VI), was determined at 313 K and 373 K, from the following equation¹⁴.

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

Where, K and L are the viscometer constants and t and ρ 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 equation¹⁴.

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

Where n is given by,

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

ν_1 is the kinematic viscosity (cSt) at lower temperature, ν_2 is the kinematic viscosity (cSt) at higher temperature, k is a function of temperature only and is equal to 2.714 for the temperature range performed and n is a constant characteristic for each oil¹⁴.

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^{15,16}. 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. In all determinations, an average of three measurements

was taken into account and precautions were taken to minimize losses due to evaporation. Different concentrations ranging between 1 wt % to 6 wt % were used to study the effect of polymer concentration on VI.

1.1.4. Results and discussions

1.1.4.1. Spectroscopic analysis

FT-IR spectra (**Figure 1.1**) of poly (isodecyl acrylate) or homopolymer of isodecyl acrylate (HIDA) exhibited absorption band at 1732.0 cm^{-1} for the ester carbonyl stretching vibration along with other peaks appeared at 1456.2 , 1379.0 , 1260.0 , and 1166.9 cm^{-1} (CO stretching vibration), and at 750.0 , 710.0 cm^{-1} (bending of C–H bonds). In its $^1\text{H-NMR}$ spectra (**Figure 1.2**), HIDA showed a broad singlet centered at 4.02 ppm due to the proton of $-\text{OCH}_2$ group, another broad singlet centered at 0.86 ppm was due to methyls of isodecyl chain. In the proton decoupled $^{13}\text{C-NMR}$ of the homopolymer (**Figure 1.3**), the carbonyl carbon appears at 174.47 ppm along with other carbons. Absence of peak in the range $130\text{-}150\text{ ppm}$ indicates absence of any sp^2 carbon in the homopolymer.

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 1.4**), the copolymer showed a broad peak ranging from 1732.0 to 1737.7 cm^{-1} for ester carbonyl along with other peaks at 2928.7 , 2871.8 cm^{-1} (stretching vibration of C–H bonds), and 1462.9 cm^{-1} , and a band at 1164.0 cm^{-1} (CO stretching vibration). In the $^1\text{H-NMR}$ spectra (**Figure 1.5**) of the copolymer, a broad singlet at 4.05 ppm was due to the protons of $-\text{OCH}_2$ group. Methyls of the isodecyl chain appeared between 0.81 and 0.87 ppm and the absence of singlets between 5 and 6 ppm indicated the absence of any sp^2 proton in the copolymer. In the $^{13}\text{C-NMR}$ spectrum (**Figure 1.6**) of the copolymer, the carbonyl carbon appears at 174.47 ppm along with other carbons. Absence of peak in the range $130\text{-}150\text{ ppm}$ indicates absence of any sp^2 carbon in the copolymer.

FT-IR spectra (**Figure 1.7**) of poly (dodecyl acrylate) or homopolymer of dodecyl acrylate (HDDA) exhibited absorption at 1732.0 cm^{-1} due to ester carbonyl stretching vibration along with other peaks appeared 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 1.8**) 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 1.9**) was in complete agreement with the homopolymer.

The existence of the copolymer of dodecyl acrylate with 1-decene was confirmed by the analysis of FT-IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra of the copolymer. FT-IR spectra of the copolymer (**Figure 1.10**) showed sharp peak at 1732.9 cm^{-1} for the ester carbonyl along with other peaks at $2923.9, 2853.5\text{ cm}^{-1}$ (stretching vibration of C–H bonds), and 1463.9 cm^{-1} and a band at 1162.0 cm^{-1} (CO stretching vibration). $^1\text{H-NMR}$ spectra of the copolymer (**Figure 1.11**) showed broad singlet at 4.02 ppm due to $-\text{OCH}_2$ protons. The absence of singlet between 5 and 6 ppm indicated the absence of sp^2 protons in the copolymer. $^{13}\text{C-NMR}$ spectrum (**Figure 1.12**) of the above sample showed the presence of ester carbonyl at 173 ppm.

The value of extent of incorporation of 1-decene in the copolymer composition, as determined from the FT-IR and NMR method¹⁷ is tabulated in **Table 1.1**.

1.1.4.2. Thermogravimetric Analysis (TGA)

Plot of Percent Weight Loss (PWL) against Temperature (**Figure 1.13**) presents a comparison between the TGA data for homopolymers and copolymers. It shows that the copolymers are better in thermal stability than the homopolymers.

1.1.4.3. Viscometric analysis

Viscometric data were obtained using the six equations mentioned. A linear relation for the plot of $\log \eta_{sp}$ versus $\log C[\eta]$, obtained for all samples (**Figure 1.14**), indicates that measurements were performed in Newtonian flow^{11,18}.

Using the graphic extrapolation method, respective intrinsic viscosities ($[\eta]$) (**Table 1.2**) and viscometric constants were evaluated (**Table 1.3**). In single point determinations, Schulz-Blaschke (SB), Solomon-Ciuta (SC), and Deb-Chatterjee (DC) equations were employed to determine the intrinsic viscosity (**Table 1.2**). Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent systems⁷. The same is used here also.

Intrinsic viscosity ($[\eta]$) values related to all equations for the samples analyzed are presented in **Table 1.2**. Comparison among the copolymers indicates that there is a gradual decrease of $[\eta]$ values with the increase of 1-decene content in the monomer composition in case of both set of copolymers (P-2 to P-4) and (P-6 to P-8). Except P-6, all copolymers show lower intrinsic viscosity compared to their respective homopolymers. This indicates that in most of the cases the polymer chain is extended more in the homopolymer than in the copolymers.

Although different intrinsic viscosity values ($[\eta]$) may be observed by graphic extrapolation of Huggins, Kraemer, Martin, and SB equation, in this work the data ($[\eta]$) obtained from these four equations shows a tendency to be close for homopolymer and copolymers. For the homopolymer and copolymers, $[\eta]$ values obtained by Huggins and Kraemer's equations were similar (**Table 1.2**). Both homopolymers and copolymers in toluene medium indicate poor solvation as is evident from the respective Huggins constant (k_h) values (**Table 1.3**). This conclusion is further supported by k_{sb} values, which are not close to 0.28. But negative values of Kraemer coefficient (k_k) indicate good salvation of

most of the systems analyzed. Thus it can be concluded that the relation $k_h + k_k \neq 0.5$ and $k_{sb} \neq 0.28$ did not put any restriction for the application of Kraemer equation. By comparing the percentage difference ($\Delta \% = 100([\eta]/[\eta]_h) - 100$) values (taking $[\eta]$ determined by Huggins equation as a reference) of HDDA and the copolymers determined through graphic extrapolation and single point determination (**Table 1.4**), it can be noticed that the range (1.881 % - 20.016 %) was narrow when compared to the values obtained from HDDA and its copolymers (11.021 % - 36.386 %).

Table 1.5 presents a comparison between the values of molecular weight (M) obtained by viscometric methods for homopolymers and copolymers analyzed. The general trend observed is a gradual decrease in molecular weight with the increase in 1-decene content in the monomer composition (P-1 to P-4) and same trend is also followed from P-5 to P-8 except P-6. The percentage differences ($\Delta \% = 100(M/M_h) - 100$) obtained for viscometric molecular weight values, are shown in **Table 1.6**. These values were calculated taking molecular weight determined by Huggins equation as a reference. Martin equation shows the smallest Δ % differences for viscometric molecular weight.

1.1.4.4. Efficiency of the prepared compounds as pour point depressant

Physical properties of the base oils are tabulated in **Table 1.7**. PP values of the polymers evaluated in two different base stocks (BO1 and BO2) are presented in **Table 1.8** and **Table 1.9**, respectively. A graphical presentation of the PP values of the polymers in these base oils is also shown in **Figure 1.15.1** and **1.15.2**, respectively. It has been observed that, in both the base oils copolymers showed better performances than the respective homopolymers and the values were always better for the copolymers of DDA than that of IDA. Also, the efficiency increases by decreasing the concentration of additive in the base oil. This can be explained by the solvation power of the oil. Solvation power of

any solvent decreases with decreasing temperature and vice versa⁵. Also, with increase in molecular weight of the solute and its concentration, solvation power decreases⁵.

1.1.4.5. Efficiency of the prepared compounds as viscosity modifier

Table 1.10 and **Table 1.11** present the VI values of the prepared homopolymer and copolymers in two base oils, BO1 and BO2, respectively. **Figure 1.16.1** and **Figure 1.16.2** also depict the VI data in these base oils, respectively. The data obtained clearly shows that the homopolymers are of having greater VI values than the respective copolymers and the copolymers of DDA showed better performance over the IDA copolymers. Also, with the increase of 1-decene content in the feed, the VI is found to decrease for both DDA and IDA copolymers. Again, with increasing concentration of the polymer solution, VI is found to increase. This may be because of the fact that, at a higher temperature, while the lube oil viscosity gets decreased, the polymer molecules change from tight coil to expanded ones as a result of increase in the interaction between the polymer chain and the solvent molecule. This increase in volume causes an increase in the viscosity of the mixture and offsets the normal reduction in viscosity of the oil with increasing temperature. The increase of concentration of the polymer also leads to an increase in total volume of polymer micelles in the oil solutions. Consequently, a high concentration of polymer will impart a high viscosity index rather than a low concentration of the same polymer⁴.

1.1.5. Conclusion

Thermal stability of the copolymers is found better than the corresponding homopolymers. There is a gradual decrease of intrinsic viscosity values of the copolymers (except P-6) with the increase of 1-decene content in the feed. Negative values of Kraemer coefficient indicate good solvation for some of the polymers analyzed, although $k_h + k_k \neq 0.5$ and $k_{sb} \neq 0.28$ for them. In general, there is a gradual decrease in molecular weight

with the increase of 1-decene concentration in the copolymer (except P-6). Copolymers showed better PPD performance than the homopolymers and best results are obtained with DDA + 1-decene copolymers. PPD properties decrease with increasing concentration of the additive in the base stocks. In terms of VI properties, homopolymers are found better than the respective copolymers. Irrespective of the polymers, VI values are found directly proportional to the molecular weight of the polymer (with only one exception) as well as with the concentration of the additive in base oil.

1.1.6. References

References are given in Bibliography under Chapter-II of Part-I (Page No. 188-190).

1.1.7. Tables and figures

Table 1.1. Composition of the monomers in the copolymers in terms of mole fraction determined by NMR and FT-IR spectroscopic method¹⁷

Sample	mole fraction of 1-decene in the feed	mole fraction of 1-decene in copolymer by NMR method	mole fraction of 1-decene in copolymer by FT-IR
P-1	0.0000	0.0000	0.0000
P-2	0.1440	0.0896	0.0766
P-3	0.2108	0.1265	0.1146
P-4	0.2746	0.2185	0.1968
P-5	0.0000	0.0000	0.0000
P-6	0.1599	0.1162	0.1021
P-7	0.2322	0.1347	0.1178
P-8	0.3001	0.2334	0.2122

P-1: Poly (isodecyl acrylate) (HIDA); P-2 to P-4: copolymers of isodecyl acrylate with different mole fraction of 1-decene; P-5: Poly (dodecyl acrylate) (HDDA); P-6 to P-8: copolymers of dodecyl acrylate with different mole fraction of 1-decene.

Table 1.2. Intrinsic viscosity ($[\eta]$) values calculated by using 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	3.774	3.845	3.881	3.945	4.020	3.983	4.119
P-2	3.390	3.680	3.626	3.765	3.971	3.937	4.061
P-3	3.177	3.427	3.374	3.509	3.714	3.679	3.788
P-4	2.804	3.148	3.053	3.241	3.214	3.184	3.269

P-5	4.058	4.361	4.332	4.512	4.637	4.599	4.773
P-6	4.358	4.476	4.531	4.649	4.646	4.606	4.778
P-7	3.606	3.886	3.842	4.011	4.137	4.099	4.248
P-8	3.562	3.869	3.815	3.985	4.088	4.053	4.194

h, k, m, sb, sc, and dc refer to the Huggins, Kraemer, Martin, Schulz- Blaschke, Solomon-Ciuta, and Deb-Chatterjee equations, respectively. a- Extrapolation of graph; b- Single point determination ($k_{sb} = 0.28$).

Table 1.3. Viscometric constants (k) obtained for all homopolymer and copolymer samples

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	0.475	0.107	0.359	0.294	0.582
P-2	0.897	-0.002	0.562	0.412	0.895
P-3	0.924	-0.026	0.596	0.434	0.898
P-4	1.461	-0.194	0.849	0.571	1.267
P-5	0.760	0.044	0.479	0.347	0.804
P-6	0.505	0.102	0.359	0.279	0.607
P-7	0.873	-0.003	0.555	0.398	0.870
P-8	0.897	-0.0003	0.559	0.399	0.897

Table 1.4. Percentual differences ($\Delta \% = (100[\eta]/[\eta]_h)-100$) obtained for intrinsic viscosity values, Huggins equation taken as a reference

Sample	$(\Delta_{[\eta]})_k^a$	$(\Delta_{[\eta]})_m^a$	$(\Delta_{[\eta]})_{sb}^a$	$(\Delta_{[\eta]})_{sb}^b$	$(\Delta_{[\eta]})_{sc}^b$	$(\Delta_{[\eta]})_{dc}^b$
P-1	1.881	2.835	4.531	6.518	5.538	9.141
P-2	6.006	5.212	8.782	12.493	11.530	15.042
P-3	7.655	6.546	10.765	17.095	16.040	20.016
P-4	12.267	8.880	15.584	14.622	13.552	16.583
P-5	14.172	11.690	17.324	22.760	21.866	26.682
P-6	19.369	16.450	26.156	31.123	30.326	36.386
P-7	13.651	11.021	18.595	25.145	24.093	28.800
P-8	14.359	11.713	28.050	25.239	24.788	29.823

Table 1.5. Viscometric molecular weight (M) values calculated by using different equations

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	13270	13616	13792	14107	14478	14295	14972
P-2	11445	12817	12558	13227	14235	14067	14682
P-3	10465	11617	11370	12003	12980	12812	13338
P-4	8809	10333	9906	10757	10633	10497	10885
P-5	14667	16199	16050	16977	17630	17431	18347
P-6	16183	16791	17076	17693	17676	17467	18373
P-7	12463	13817	13601	14433	15062	14872	15623
P-8	12253	13733	13470	14304	14817	14642	15349

Table 1.6. Percentual differences obtained for viscometric molecular weight values (Δ % = (100[M/M_h]- 100), Huggins equation taken as a reference

Sample	$(\Delta M)_k^a$	$(\Delta M)_m^a$	$(\Delta M)_{sb}^a$	$(\Delta M)_{sb}^b$	$(\Delta M)_{sc}^b$	$(\Delta M)_{dc}^b$
P-1	2.607	3.934	6.307	9.103	7.724	12.826
P-2	11.900	9.725	15.570	24.377	22.910	28.283
P-3	11.008	8.648	14.697	24.032	22.427	27.453
P-4	17.300	12.453	22.114	20.706	19.162	23.567
P-5	10.408	9.540	15.710	20.161	18.805	25.048
P-6	3.757	5.518	9.331	9.201	7.934	13.533
P-7	10.864	9.131	15.807	20.854	19.329	25.355
P-8	12.079	9.932	16.739	20.925	19.497	25.267

Table 1.7. Base oil properties

Properties	Base oils	
	BO1	BO2
Density (g.cm ⁻³) at 313 K	0.837	0.868
Viscosity at 313 K in cSt	7.136	23.392
Viscosity at 373 K in cSt	1.856	3.915
Cloud Point, °C	-10	-8
Pour Point, °C	-3	-6

Table 1.8. Dependence of Pour Point (PP) on the concentration of additives in base oil (BO1)

Conc. (wt %)	PP (°C) in the presence of							
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8

0	-3	-3	-3	-3	-3	-3	-3	-3
2	-6	-12	-12	-15	-9	-9	-15	-15
4	-6	-9	-12	-12	-6	-9	-12	-12
6	-3	-9	-9	-12	-6	-6	-9	-12

Table 1.9. Dependence of Pour Point (PP) on the concentration of additives in base oil (BO2)

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

Table 1.10. Dependence of Viscosity Index (VI) on the concentration of additives in base oil (BO1)

Conc. (wt %)	VI in the presence of							
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
0	85	85	85	85	85	85	85	85
1	92	87	87	86	95	88	87	87
2	94	90	89	88	98	91	89	88
3	95	92	90	91	100	93	92	90
4	100	94	91	91	103	97	94	94
5	102	96	94	94	106	105	101	97

6	105	97	95	95	109	110	103	100
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Table 1.11. Dependence of Viscosity Index (VI) on the concentration of additives in base oil (BO2)

Conc. (wt %)	VI in the presence of							
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
0	80	80	80	80	80	80	80	80
1	87	86	85	84	90	87	87	86
2	89	88	86	86	93	90	89	88
3	90	90	88	87	97	91	89	89
4	93	91	90	89	100	93	92	90
5	97	93	92	91	102	95	94	91
6	100	95	94	92	104	98	96	94

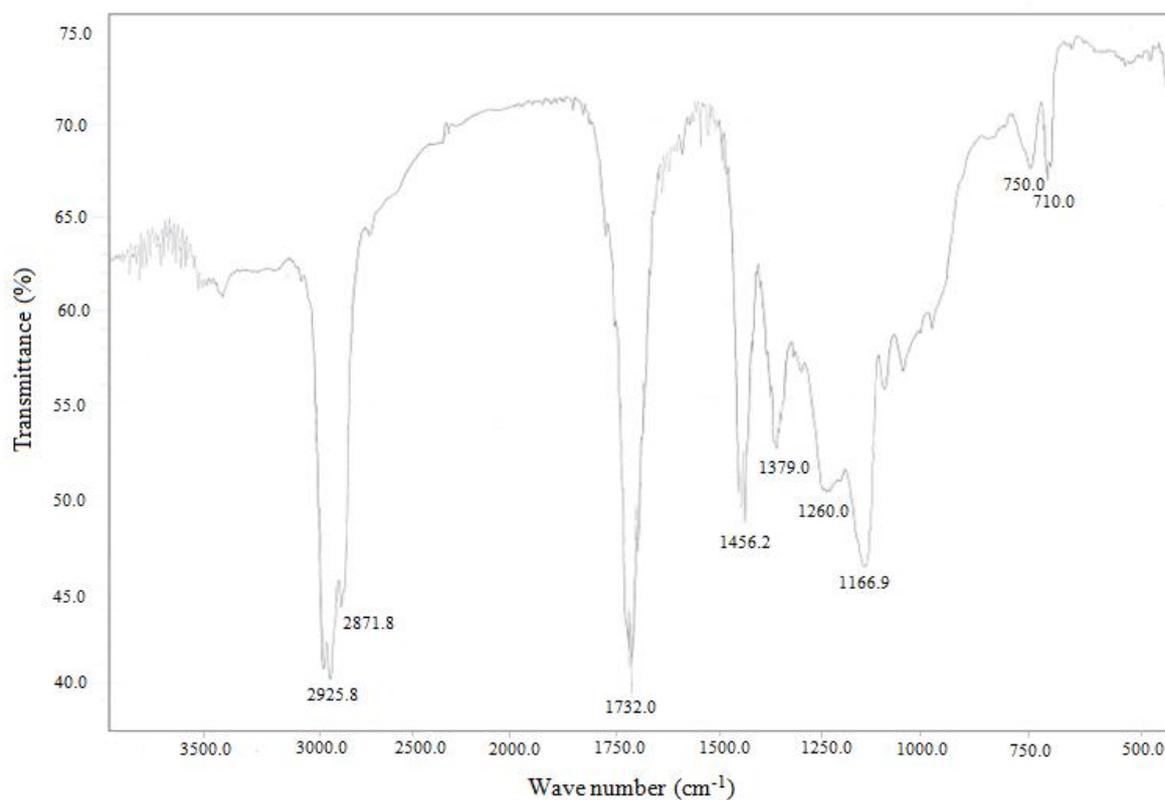


Figure 1.1. FT-IR spectra of poly (isodecyl acrylate)

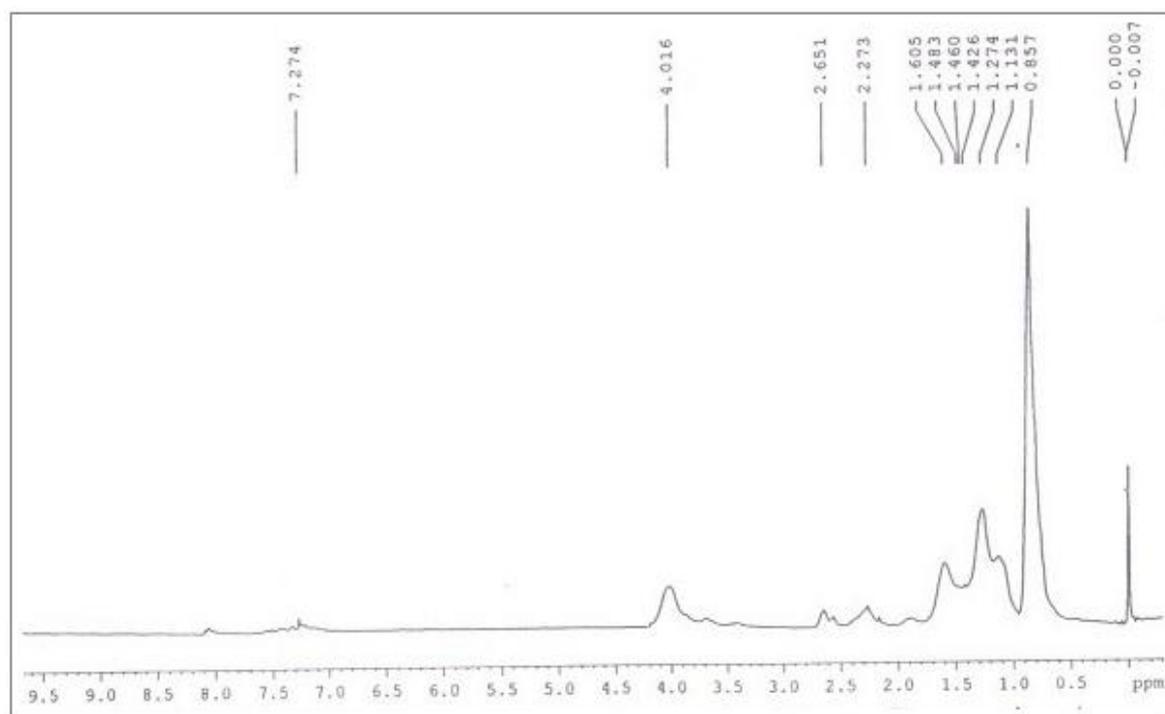


Figure 1.2. ¹H-NMR spectra of poly (isodecyl acrylate)

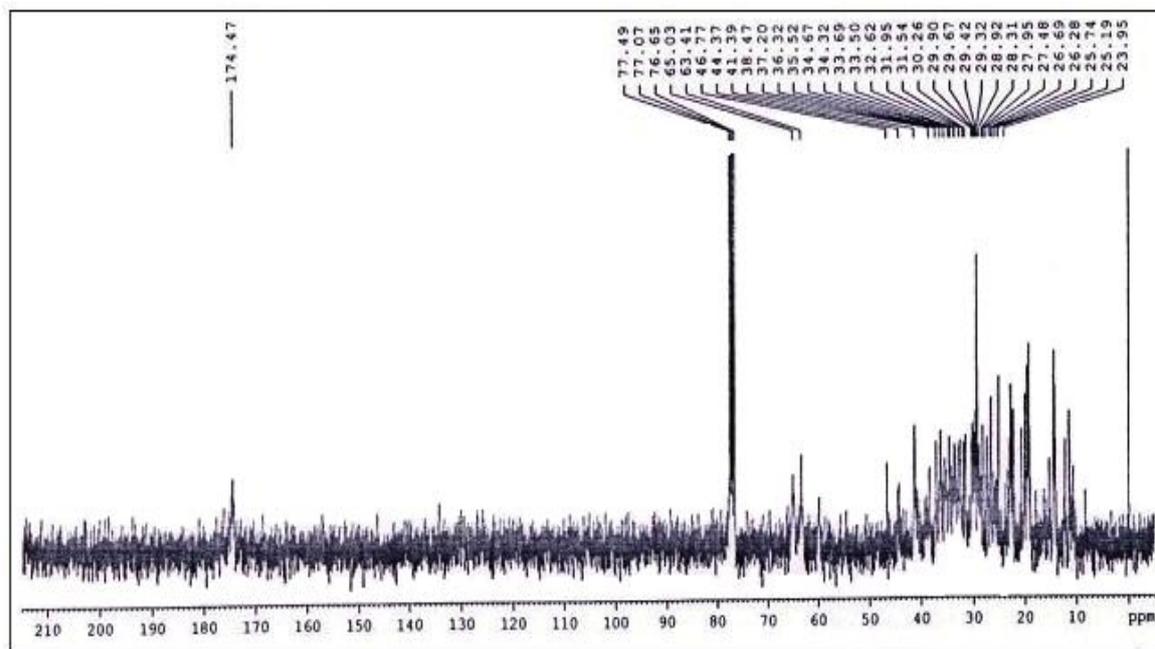


Figure 1.3. ^{13}C -NMR spectra of poly (isodecyl acrylate)

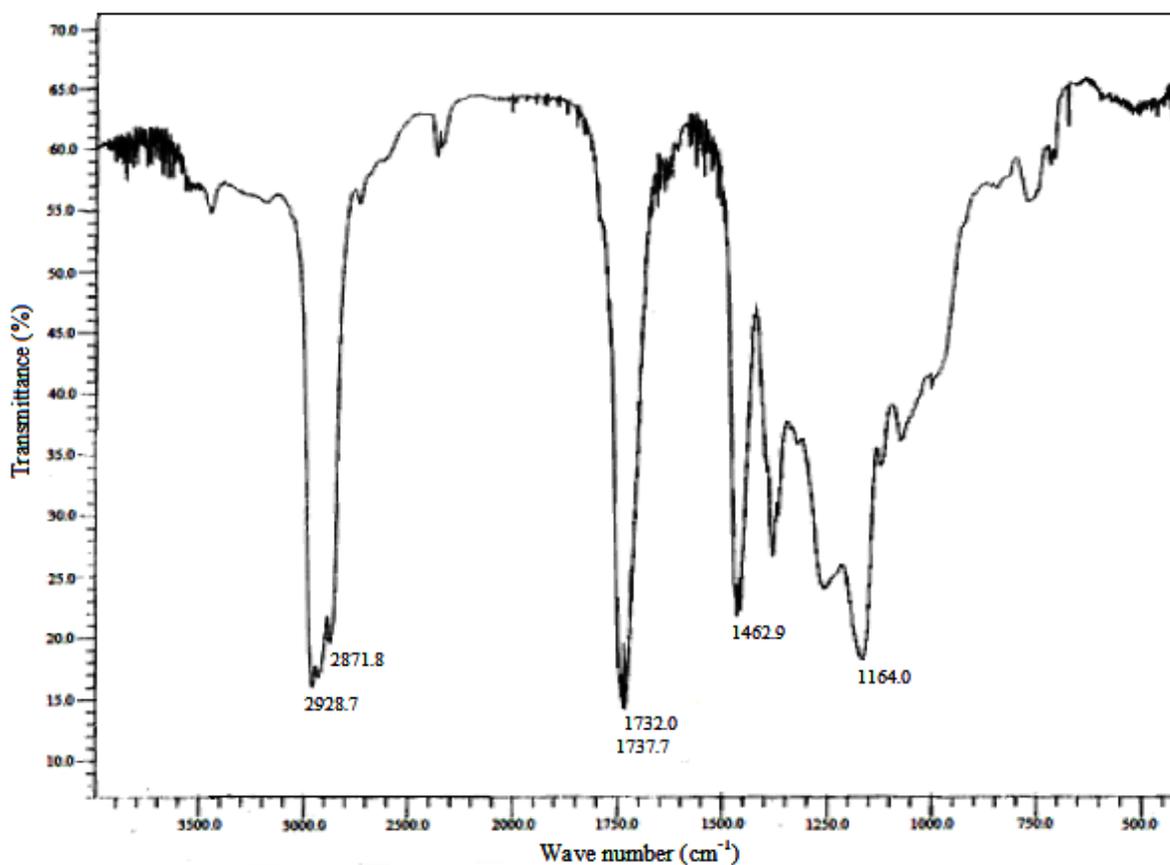


Figure 1.4. FT-IR spectra of a representative copolymer of isodecyl acrylate with 1-decene

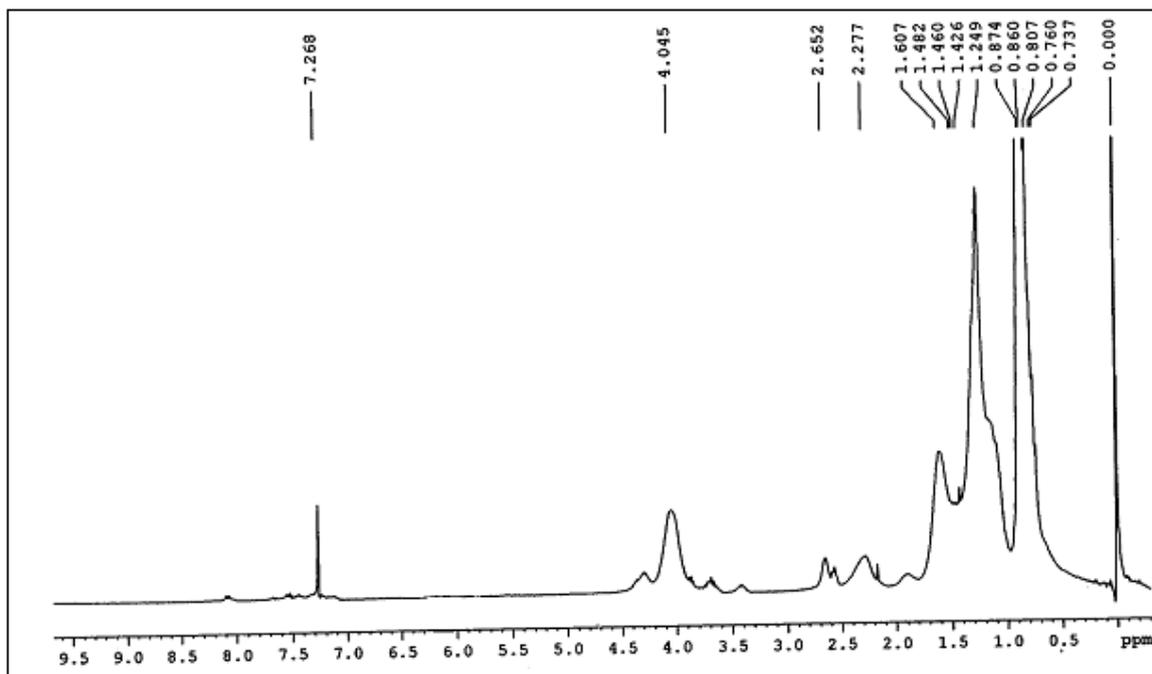


Figure 1.5. ¹H-NMR spectra of a representative copolymer of isodecyl acrylate with 1-decene

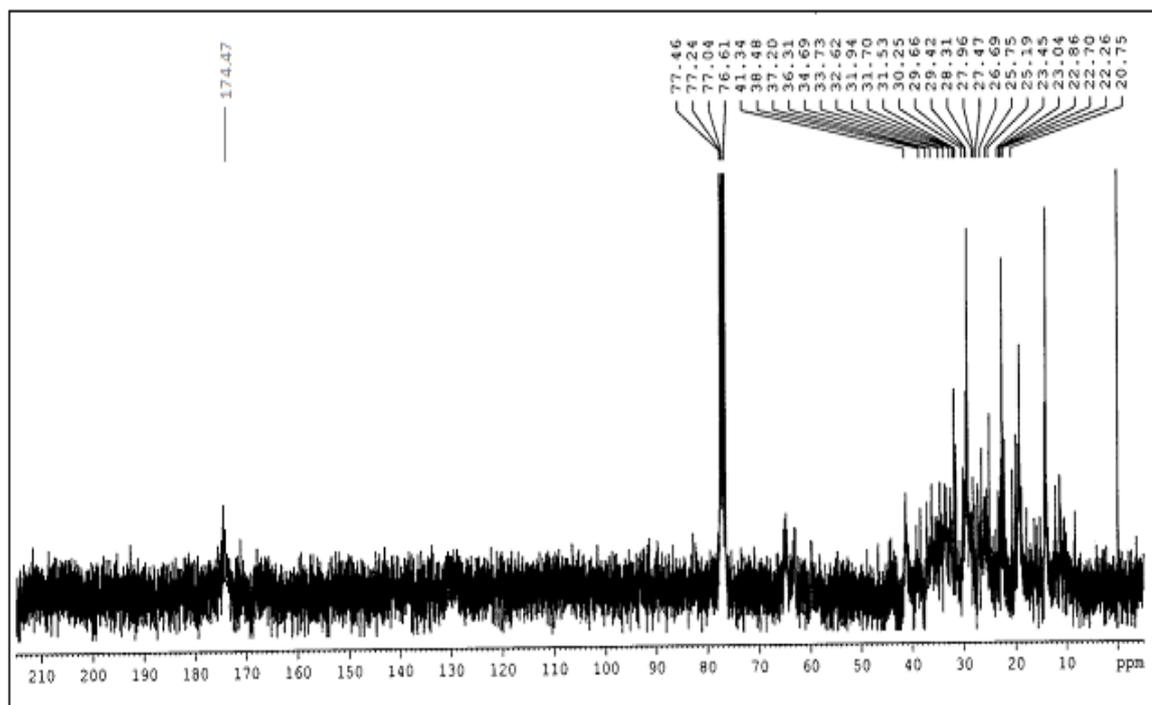


Figure 1.6. ¹³C-NMR spectra of a representative copolymer of isodecyl acrylate with 1-decene

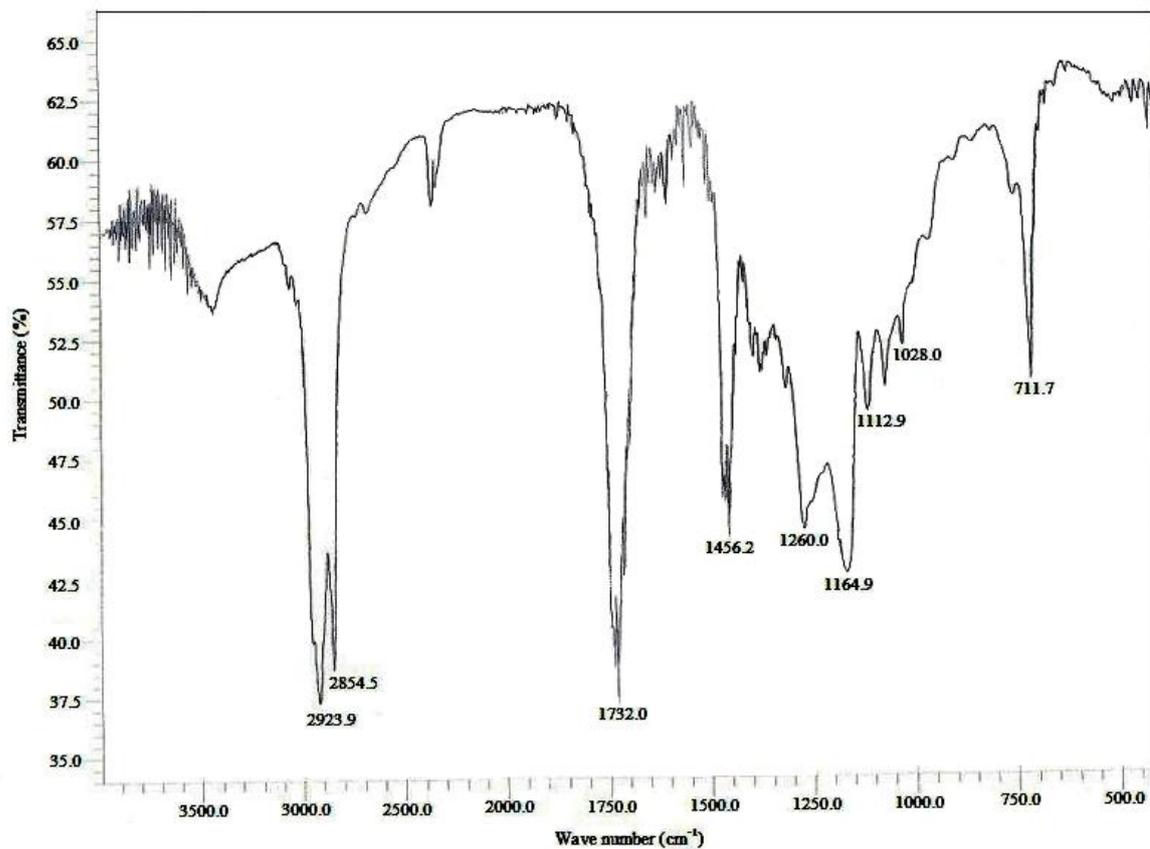


Figure 1.7. FT-IR spectra of poly (dodecyl acrylate)

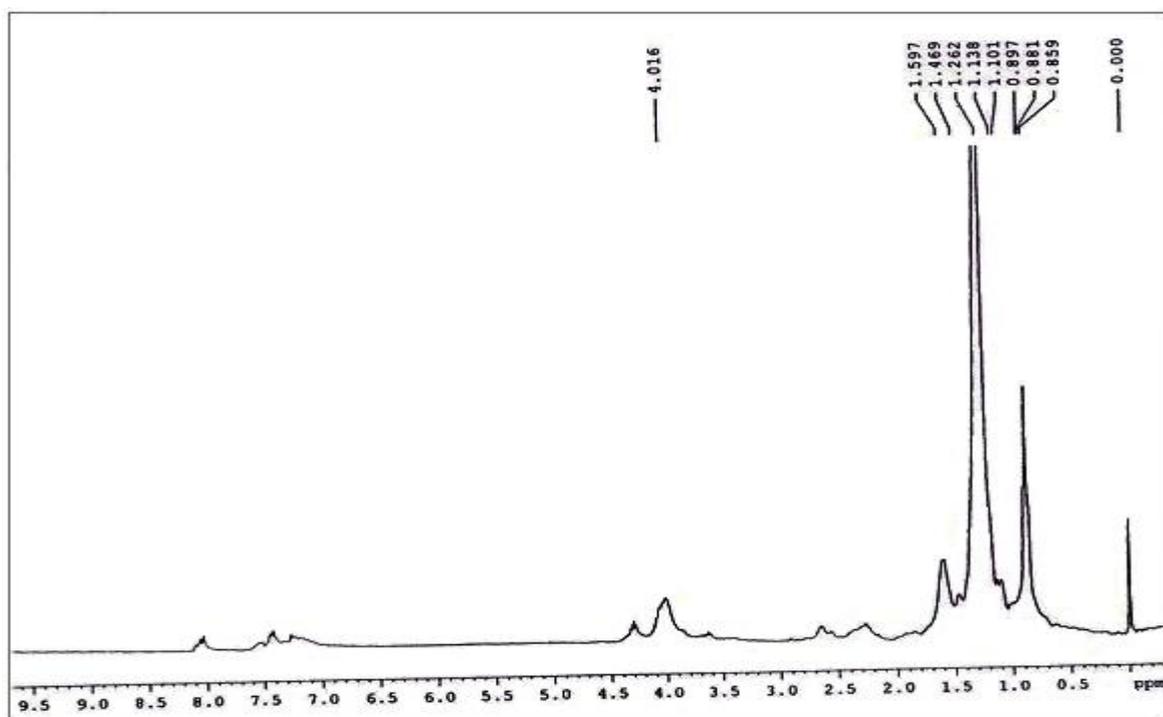


Figure 1.8. ¹H-NMR spectra of poly (dodecyl acrylate)

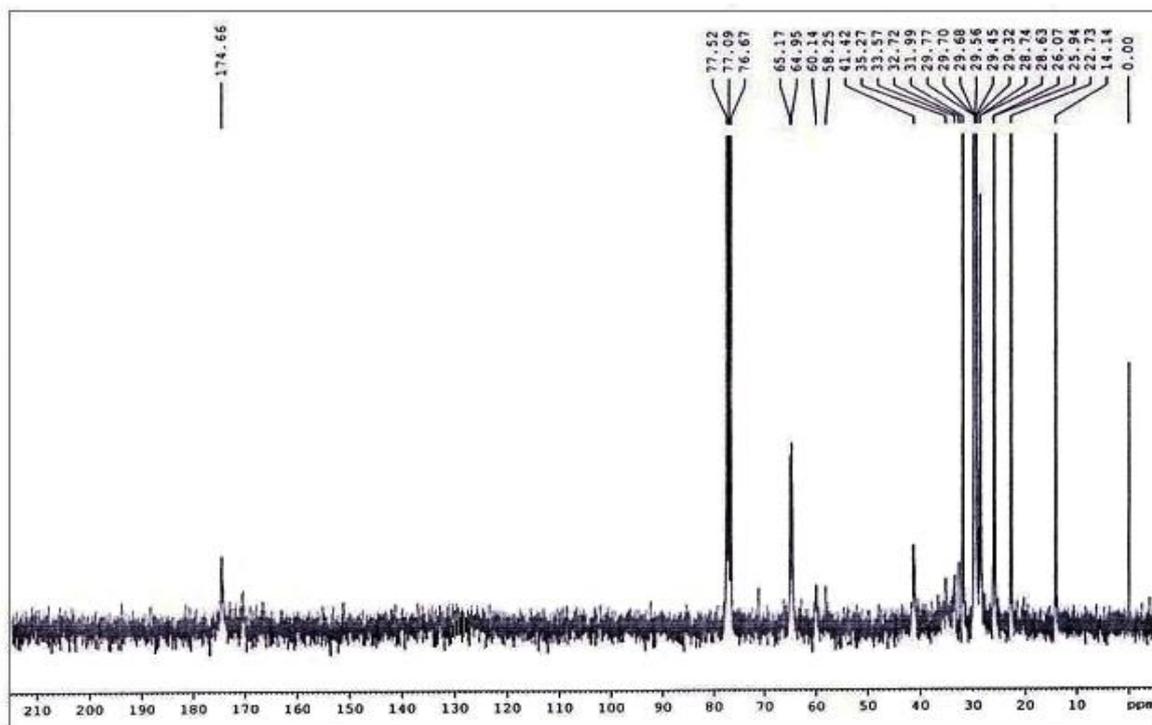


Figure 1.9. ¹³C-NMR spectra of poly (dodecyl acrylate)

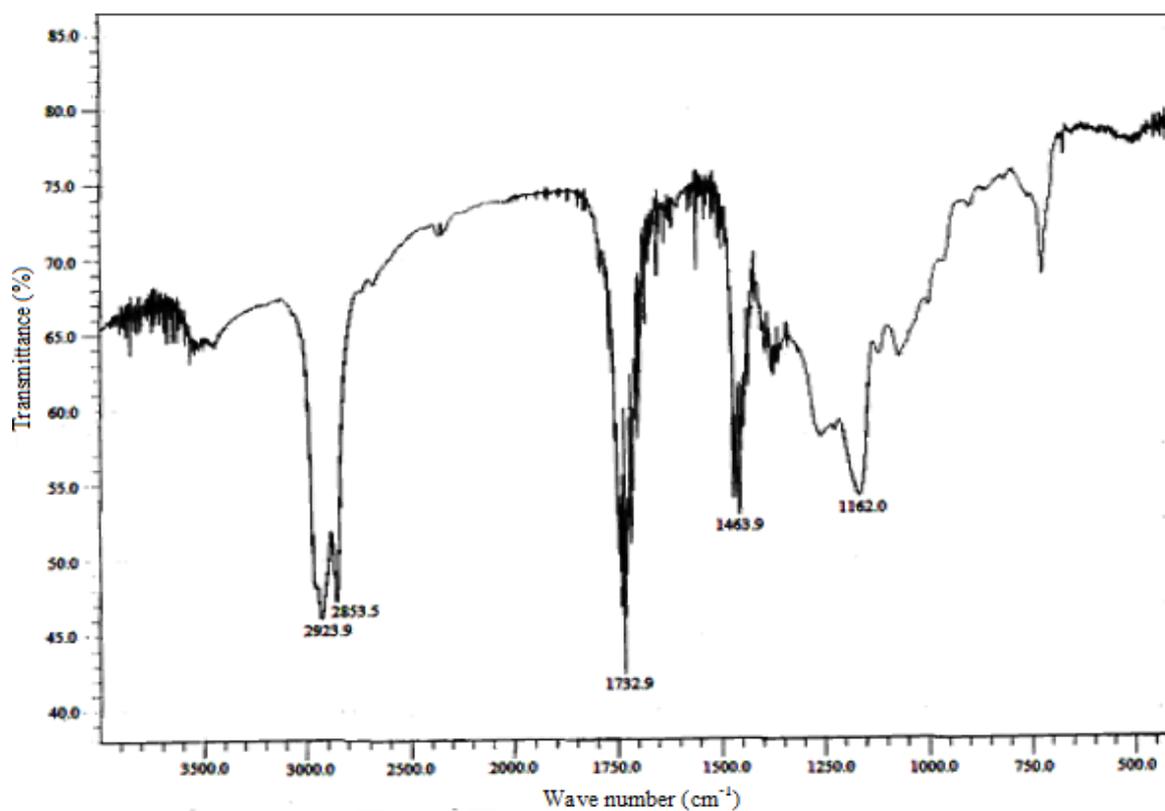


Figure 1.10. FT-IR spectra of a representative copolymer of dodecyl acrylate with 1-decene

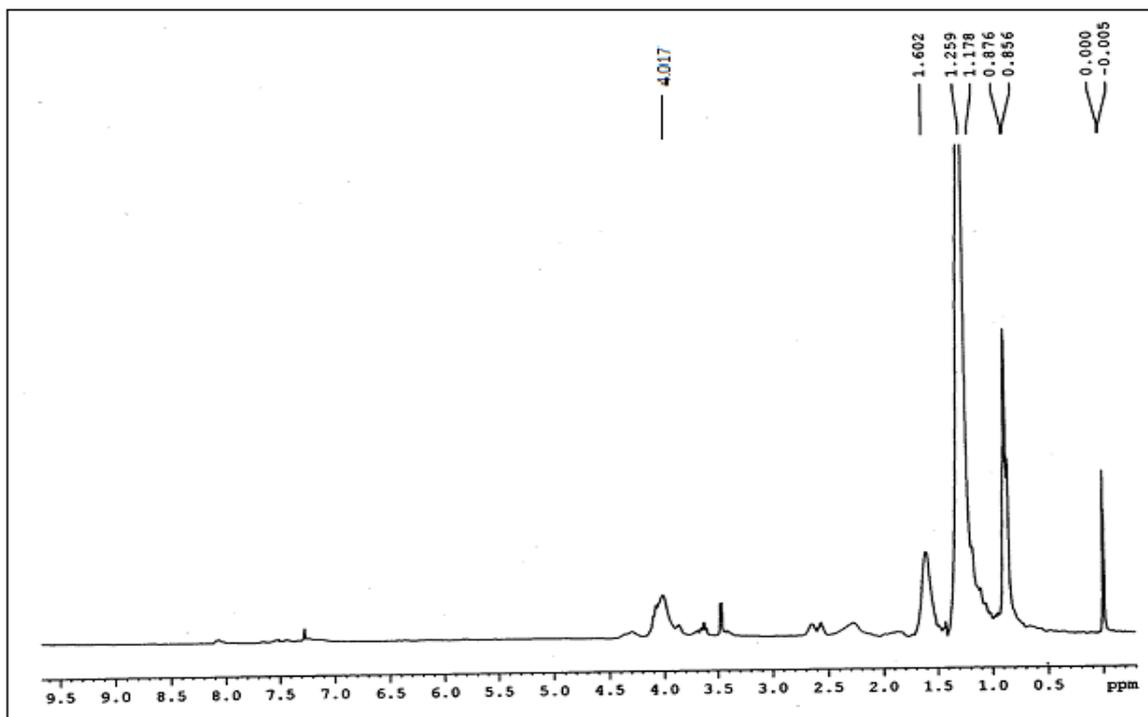


Figure 1.11. $^1\text{H-NMR}$ spectra of a representative copolymer of dodecyl acrylate with
1-decene

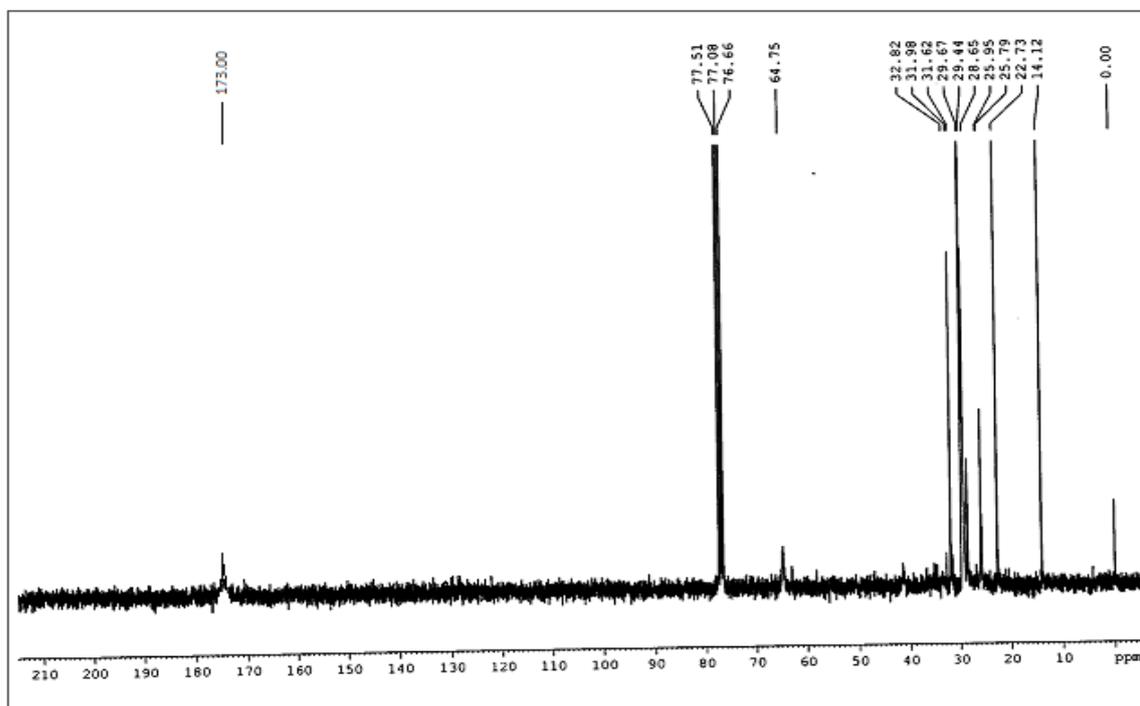


Figure 1.12. $^{13}\text{C-NMR}$ spectra of a representative copolymer of dodecyl acrylate with
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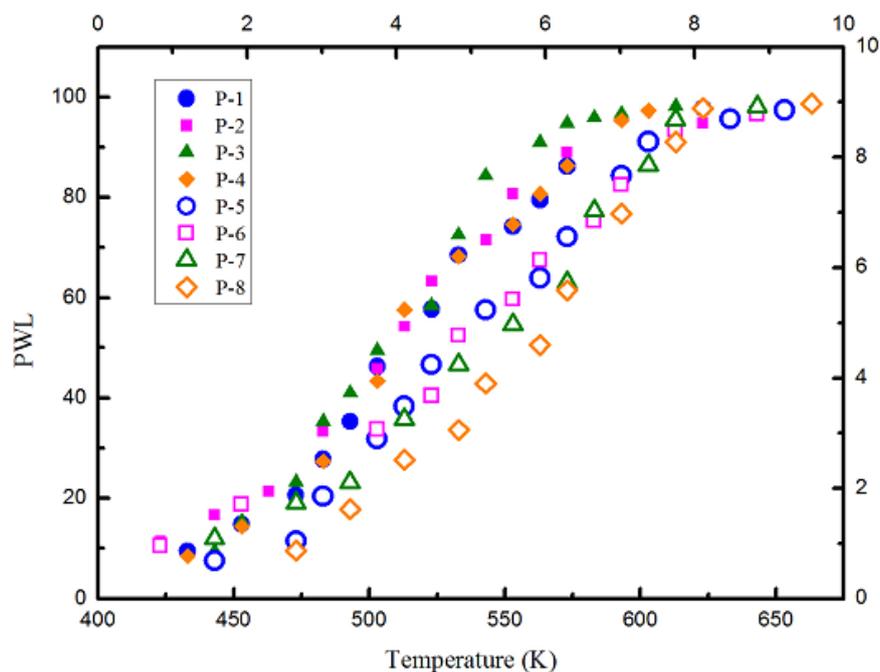


Figure 1.13. Plot of PWL vs. Temperature. PWL is Percent Weight Loss and temperature is measured in Kelvin

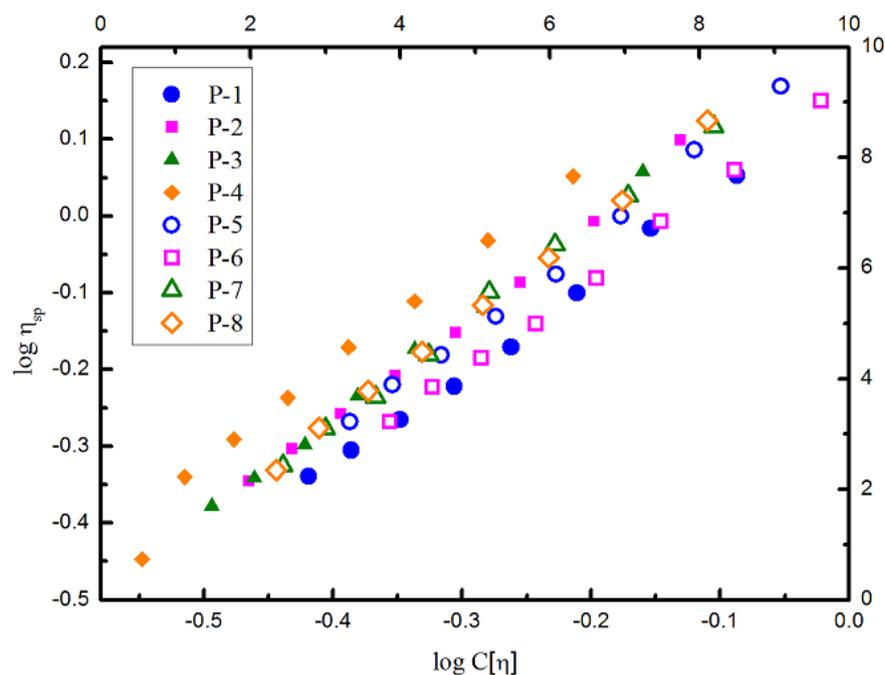


Figure 1.14. Plot of $\log \eta_{sp}$ vs. $\log C[\eta]$, where η_{sp} is the specific viscosity of the polymer solution in toluene, C is the concentration of the solution in $\text{g}\cdot\text{cm}^{-3}$, and $[\eta]$ is the intrinsic viscosity of the polymer solution in toluene obtained by using Huggins equation

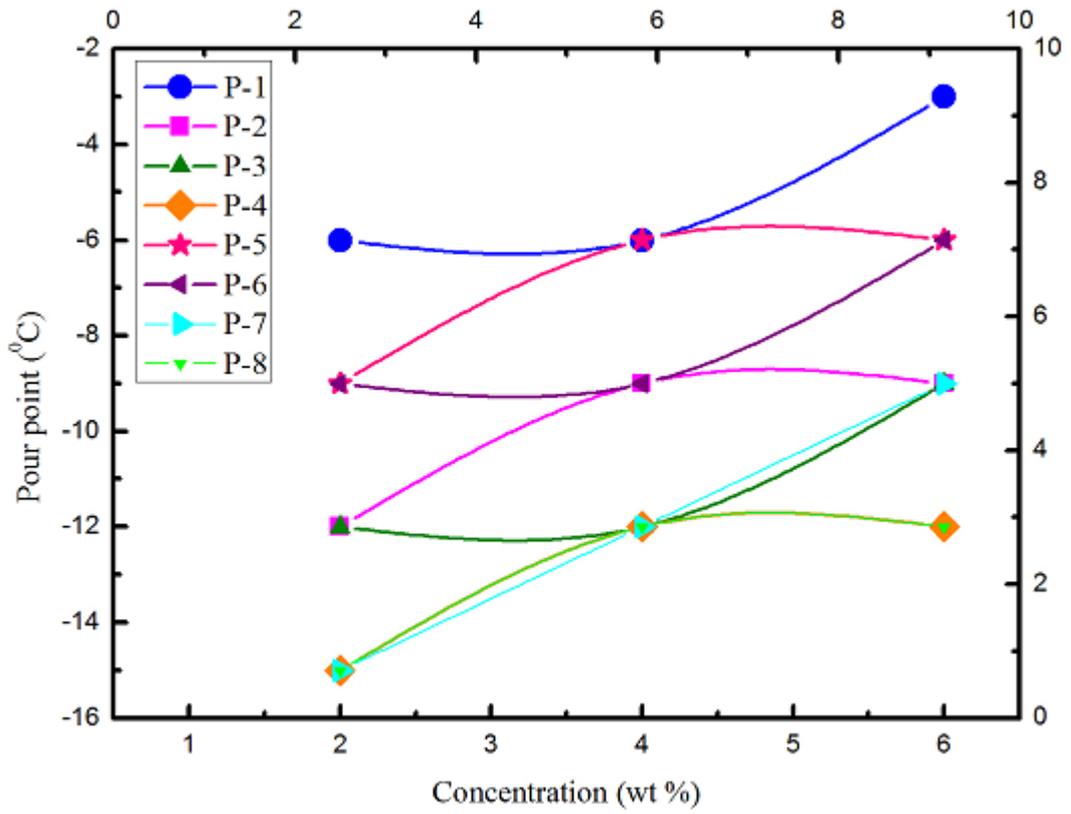


Figure 1.15.1. Plot of pour point vs. additive concentration in BO1

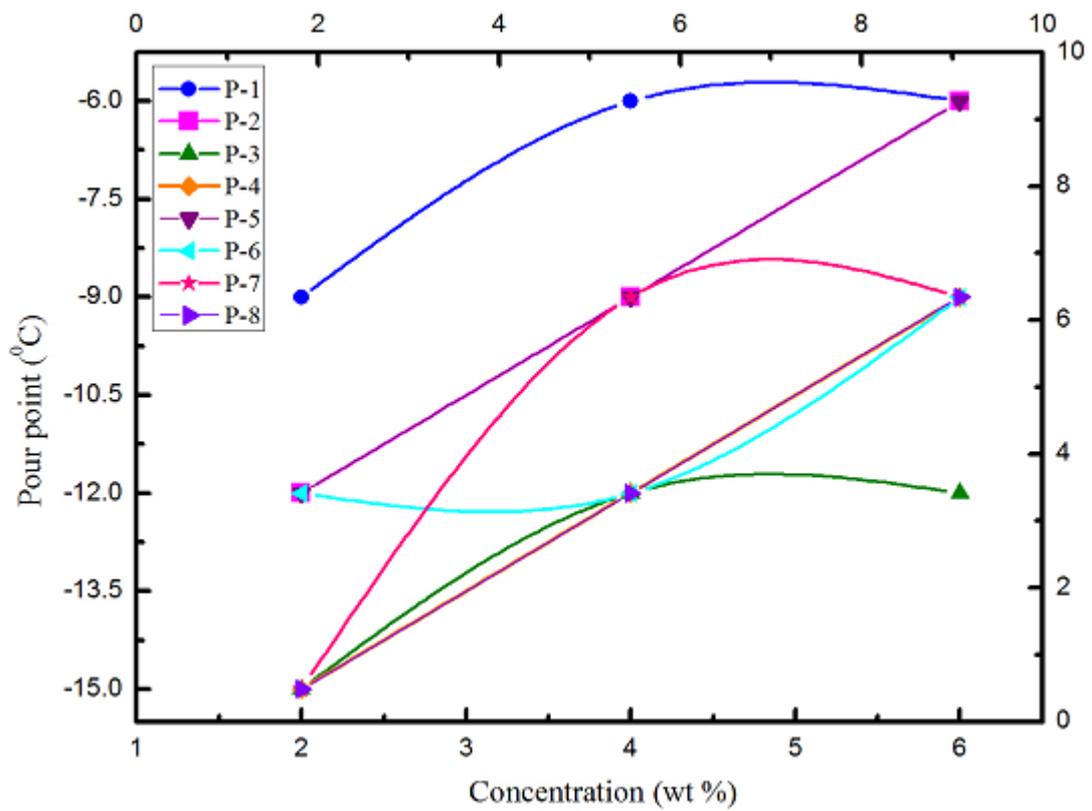


Figure 1.15.2. Plot of pour point vs. additive concentration in BO2

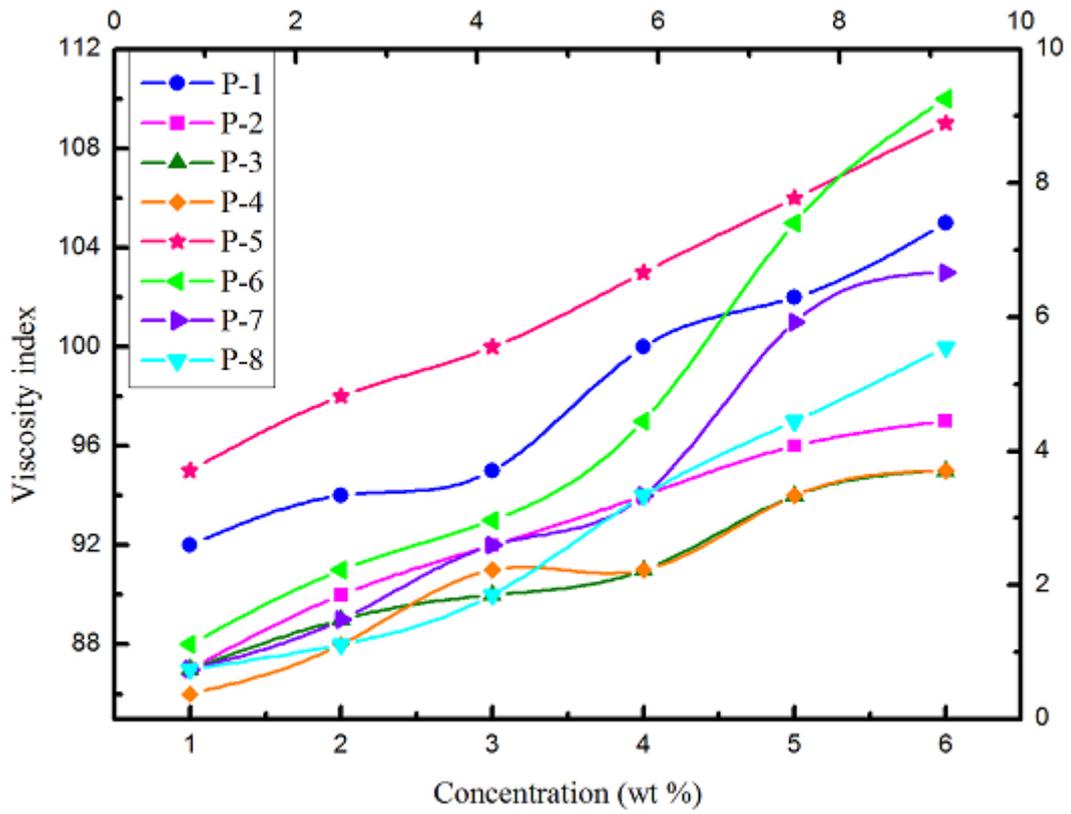


Figure 1.16.1. Plot of viscosity index vs. additive concentration in BO1

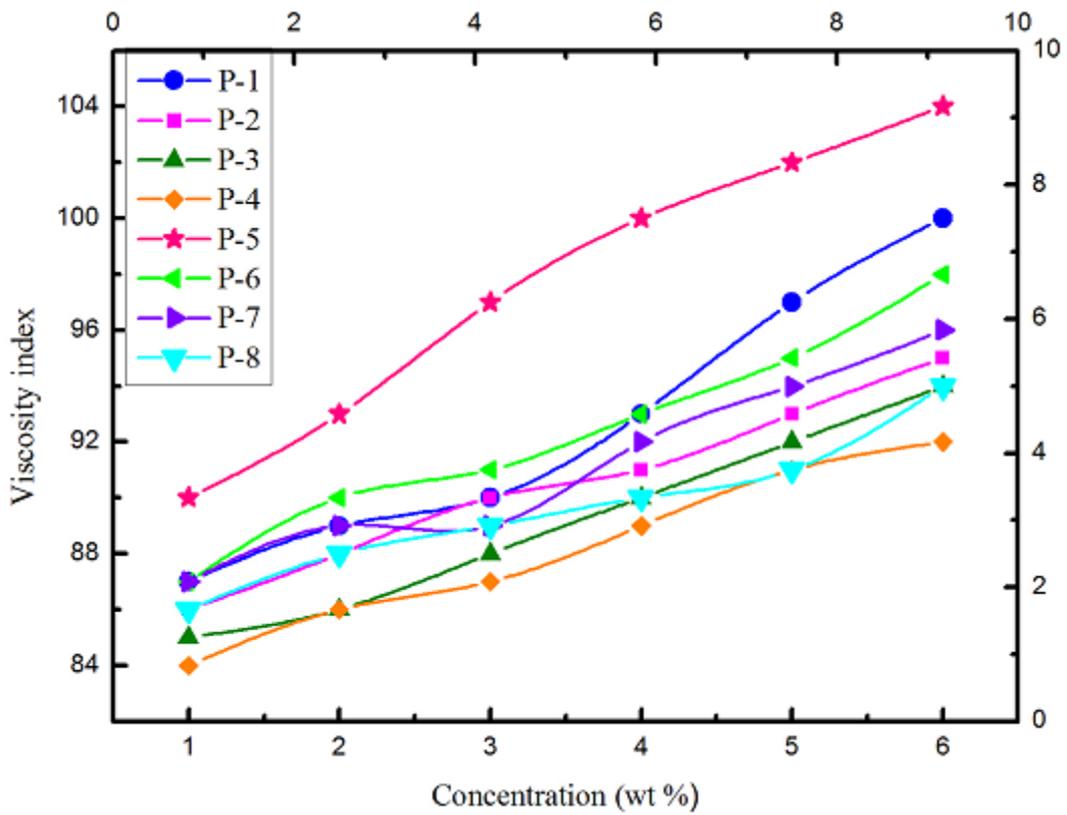


Figure 1.16.2. Plot of viscosity index vs. additive concentration in BO2