

CHAPTER-III

SYNTHESIS, CHARACTERIZATION, AND PERFORMANCE EVALUATION OF ACRYLATE BASED MULTIFUNCTIONAL LUBE OIL ADDITIVES

SECTION A: MULTIFUNCTIONAL ADDITIVE PERFORMANCE OF ISODECYL ACRYLATE + 1-DECENE AND ISOOCTYL ACRYLATE + 1-DECENE COPOLYMERS

SECTION B: MULTIFUNCTIONAL ADDITIVE PERFORMANCE OF DECYL ACRYLATE + 1-DECENE AND ISOOCTYL ACRYLATE + 1-DECENE COPOLYMERS

1.2. Section A: Multifunctional additive performance of isodecyl acrylate + 1-decene and isooctyl acrylate + 1-decene copolymers

1.2.1. Introduction

Encouraged by the result of the previous work, a new additive system based on acrylate backbone has been synthesized. In the previous work, homopolymer of isodecyl acrylate (HIDA) and its copolymers with 1-decene (IDA + 1-decene) were prepared and the analysed results were compared with homopolymer of dodecyl acrylate (HDDA) and its copolymers with 1-decene (DDA + 1-decene). In the present work, new copolymers of isodecyl acrylate (IDA) with different concentration (mole fraction) of 1-decene were prepared to optimize the concentration of 1-decene in the feed which can yield the best performance. The results were compared with isooctyl acrylate (IOA) polymers, prepared under identical conditions to check how chain length and branching in the acrylate backbone influences the different properties.

In the present work, copolymers of isodecyl acrylate with 1-decene (IDA + 1-decene), homopolymer of isooctyl acrylate or poly (isooctyl acrylate) (HIOA), and its copolymers with 1-decene (IOA + 1-decene) were synthesized. The results of our analysis toward the characterization of the polymers by spectral, thermogravimetric, and viscometric analysis and also of their evaluated performance as PPDs and VMs have been discussed in this work. Homopolymer of isodecyl acrylate, as synthesized in the previous work (Chapter-II, Page No. 29) is used for a comparative study with the respective copolymers. Comparison of different properties among the copolymers has also been presented here. 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 scanty¹ and almost nil for polymers used as lube oil additives, present work also includes viscometric study² of the copolymers as well as the homopolymers.

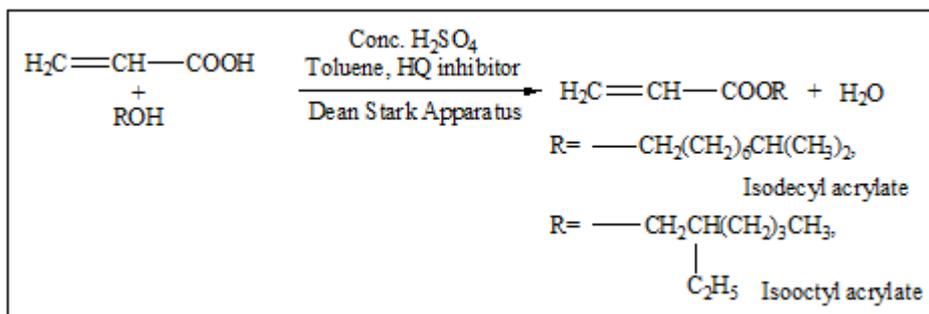
1.2.2. Experimental procedure

1.2.2.1. Materials

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd., acrylic acid (stabilized with 0.02 % hydroquinone monomethyl ether) and isodecanol from Sisco Research Laboratories Pvt. Ltd., hexane from S D Fine Chem. Ltd., 1-decene from Across Organics, methanol from Thomas Baker (Chemicals) Pvt. Ltd., and Benzoyl peroxide and 2-ethylhexanol or isooctanol from LOBA chemicals. Benzoyl peroxide (BZP) was recrystallized from CHCl₃-MeOH mixture and hydroquinone was recrystallised from hot water, before use. Rest of the materials was used after distillation. H₂SO₄ was used as received without further purification. Base oils were collected from IOCL, Dhakuria, Kolkata, West Bengal.

1.2.2.2. Esterification

Esterification of acrylic acid with isodecyl alcohol (isodecanol) and 2-ethylhexanol (isooctanol) to prepare isodecyl acrylate (IDA) and isooctyl acrylate (IOA), respectively, was carried out in toluene taking H₂SO₄ as a catalyst and hydroquinone as polymerization inhibitor and following the process as reported in the previous chapter (Chapter-II, Page No. 27).



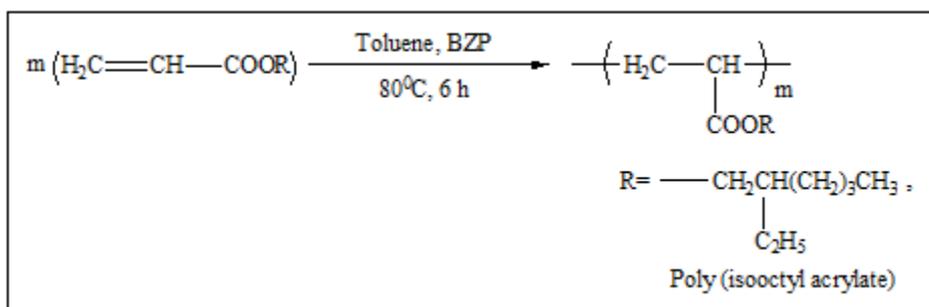
Scheme 1.4: Preparation of isodecyl acrylate (IDA) and isooctyl acrylate (IOA)

1.2.2.3. Purification of prepared esters

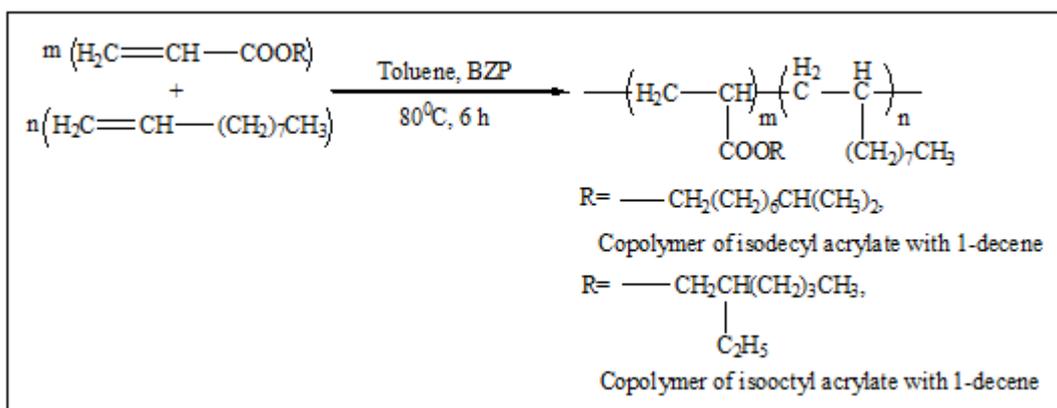
All of the prepared esters were purified by the process as reported in the previous chapter (Chapter-II, Page No. 27).

1.2.2.4. Preparation of copolymer and homopolymer

Homopolymer of IOA or poly (isooctyl acrylate) (HIOA) was prepared and in the preparation of IDA + 1-decene and IOA + 1-decene copolymers, different concentration (mole fraction) of 1-decene was used (**Table 1.12**). The thermal polymerization was carried out in toluene solvent using BZP as initiator and by following the method as reported in the previous chapter (Chapter-II, Page No. 28).



Scheme 1.5: Preparation of poly (isooctyl acrylate)



Scheme 1.6: Preparation of copolymer of isodecyl acrylate and isooctyl acrylate with 1-decene

1.2.3. Measurements

1.2.3.1. Spectroscopic measurements

Shimadzu FT-IR 8300 spectrophotometer as well as Perkin Elmer FT-IR spectrometer were used to record the IR spectra of the samples using KBr cells (0.1 mm) at room temperature within the wave number range 400-4000 cm^{-1} . ^1H and ^{13}C -NMR spectra were recorded in CDCl_3 in a 300 MHz Bruker Avance FT-NMR spectrometer using 5 mm BBO probe. Tetramethylsilane (TMS) was used as reference material.

1.2.3.2. 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 extrapolation³⁻⁷ 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 these⁴⁻⁶ 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 $k_h + k_k = 0.5^4$. The unit of intrinsic viscosity and concentration are dL.g^{-1} and g.cm^{-3} , respectively.

For the determination of viscometric properties of the polymers in toluene solution, the experiment was carried out at 313 K, using an Ubbelohde OB viscometer. Time flow of eight different concentrated solutions of each of the polymer samples was taken. A chronometer was used for manual determination of the time flow of the solution. In the single point determination method, the lowest solution concentration value was chosen for calculation. For the determination of viscosity average molecular weight (M), the Mark Houwink constants $K = 0.00387 \text{ dL.g}^{-1}$ and $a = 0.725$ were employed^{2,8} in MHS relation to get an idea of whether the molecular weight value is low or high. During the measurements adequate precautions were taken regarding the loss due to solvent evaporation.

1.2.3.3. Thermogravimetric Analysis (TGA)

TGA was carried out on a mettler TA-3000 system in air at a heating rate of 10 K.min^{-1} .

1.2.3.4. Evaluation of Pour Point (PP) of the additives in lube oil

The PP of the prepared polymers in two base oils (BO1 and BO2) was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India). Different concentrations ranging from 1 wt % to 3 wt % were used to check how the PP of lube oils varies with additive concentration. An average of three experimental data taken under identical condition was recorded.

1.2.3.5. Evaluation of Viscosity Index (VI) of the additives in lube oil

The VI of the prepared polymers was evaluated in two base oils (BO1 and BO2) by following the equations⁹ as reported in the previous chapter (Chapter-II, Page No. 32). Polymer solutions of different concentrations ranging from 1 wt % to 6 wt % were prepared to investigate the viscosity modifier properties of the polymers with the change in its concentration. The dynamic viscosity of the polymer samples was measured at 313 K and 373 K. Each measurement was repeated thrice and their average was recorded.

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^{10,11}. 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.

1.2.4. Results and discussions

1.2.4.1. Spectroscopic data

FT-IR spectra (**Figure 1.17**) 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 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 1.18**), 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 1.19**), the carbonyl carbon appears at 174.47 ppm along with other carbons. Absence of peak in the range 130-150 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 1.20**), 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 1.21**) 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 1.22**) of the copolymer, the carbonyl carbon appears at 174.47 ppm along with other carbons. Absence of peak in the range 130-150 ppm indicates absence of any sp^2 carbon in the copolymer.

IR spectrum of the poly (isooctyl acrylate) (**Figure 1.23**) exhibited absorption at 1731.0 cm^{-1} for the stretching vibration of ester carbonyl. Peaks at 1260.0 cm^{-1} and at 1164.9 cm^{-1} were due to the C–O (ester bond) stretching vibration and the absorption peaks at 961.4, 775.0 and 720.0 cm^{-1} were due to the bending vibration of C–H bond. A broad peak ranging from 2929.6 to 2950.0 cm^{-1} indicated the presence of C–H stretching vibration. ^1H and $^{13}\text{C-NMR}$ was also in complete agreement with the homopolymer. In its $^1\text{H-NMR}$ spectra (**Figure 1.24**), the homopolymer of IOA showed a broad singlet centered at 4.01 ppm for the protons of the $-\text{OCH}_2$ group; a broad singlet at 0.89 ppm was for the methyl groups of isooctyl chain. The proton decoupled $^{13}\text{C-NMR}$ of the above sample (**Figure 1.25**) showed no peak between 130 and 150 ppm which indicated the absence of any sp^2 carbon. The presence of the ester carbonyl group was indicated by the peak at 170.42 ppm.

IR spectrum of the copolymer of isooctyl acrylate with 1-decene (**Figure 1.26**) exhibited absorption at 1732.0 cm^{-1} for the stretching vibration of ester carbonyl. Peaks at

1260.0 cm^{-1} and at 1163.4 cm^{-1} were due to the C–O (ester bond) stretching vibration and the absorption peaks at 1028.0 cm^{-1} and 760.9 cm^{-1} were due to the bending vibration of C–H bond. Peaks at 2929.5 cm^{-1} and 2854.5 cm^{-1} indicated the presence of C–H stretching vibration. The formation of the copolymer was also indicated by the absence of a peak between 5 ppm and 6 ppm due to sp^2 hydrogen and that between 130 ppm and 150 ppm due to sp^2 carbon in its ^1H and ^{13}C -NMR (**Figure 1.27** and **Figure 1.28**), respectively.

The extent of incorporation of 1-decene in the copolymer composition, as determined from FT-IR and NMR methods¹², increases with increasing 1-decene concentration in the feed (**Table 1.12**).

1.2.4.2. Thermogravimetric Analysis (TGA)

Plot of Percent Weight Loss (PWL) against temperature (**Figure 1.29**) reveals that the IOA polymers are thermally more stable than the IDA polymers. Again, among all the polymers of IDA, the copolymer with maximum of 1-decene (P-4) content is the most stable while the homopolymer of IOA (P-5) is the most stable among the IOA polymers.

1.2.4.3. Viscometric analysis

By using the abovementioned six equations, viscometric data (η_r = relative viscosity, η_{sp} = specific viscosity, $[\eta]$ = intrinsic viscosity, etc.) were obtained. Plot of $\log \eta_{sp}$ versus $\log C[\eta]$, for all samples (**Figure 1.30**), shows linearity in all cases which indicates that while the experiments were performed, Newtonian flow was there in the solution^{6,13}.

In **Table 1.13**, the intrinsic viscosities ($[\eta]$) of all samples determined by using the abovementioned equations are shown. In both single point determination and the graphic extrapolation method, the SB equation is applied². For many polymer-solvent systems, k_{sb} used in SB equation is found to be very close to 0.28² and so the same value is used for the

SB single point determination method. Comparison among all the polymers of IDA indicates that, the homopolymer (HIDA, P-1) has greater intrinsic viscosity ($[\eta]$) values (corresponding to all the six equations mentioned) than the copolymers with 1-decene and for the copolymers, the $[\eta]$ values decrease with increasing concentration of 1-decene in the feed. This indicates homopolymer chains are more extended in the solution than the copolymers. For the polymers of IOA, the $[\eta]$ values for the homopolymer are lower than the copolymers and comparison among the $[\eta]$ values of the copolymers shows that the $[\eta]$ values increase with increasing concentration of 1-decene in the feed. So, there is a less extended conformation of the homopolymer chain compared to the copolymers and in the case of copolymers, stretching of the chain is more and more with increasing percentage of 1-decene in the feed. Also, comparison among the $[\eta]$ values of IOA and IDA polymers shows that the values of IOA polymers are greater than that of IDA polymers which indicates more solute-solvent interaction for IOA polymers than IDA polymers in toluene solution.

From the viscometric constant values (k_h , k_k , k_m , and k_{sb}) as obtained from the four equations (Huggins, Kraemer, Martin, and Schulz-Blaschke, respectively) of the graphic extrapolation method (**Table 1.14**), it may be concluded that there exists good solvation of the polymer in toluene and thus the extended chain orientation may also be predicted for all the polymer solutions⁴. The $k_h + k_k$ values also point toward the same conclusion⁴. Percentual difference (Δ %) of $[\eta]$ values of all the polymers (**Table 1.15**) taking Huggins equation as reference and determined through all the equations shows that the range (1.525 % - 10.691 %) for IDA polymers was narrow compared to the range (0.261 % - 18.593 %) for IOA polymers.

The viscometric molecular weight (M) values for all the polymers were calculated by measuring the $[\eta]$ values following the MHS equation and are tabulated in **Table 1.16**.

For the IDA polymers, the homopolymer has greater molecular weight value than the copolymers and comparison among the copolymers indicate that with increasing 1-decene concentration M value decreases, whereas the trend is reversed for the IOA polymers; that is, the homopolymer of IOA has lower molecular weight value than the copolymers and with increasing concentration of 1-decene content in the copolymer, molecular weight increases. Also, the IOA polymers have greater molecular weight values than the IDA polymers. The percentual difference (Δ %) of molecular weight values, taking that determined by Huggins equation as a reference shows smallest ΔM % differences for the Kraemer equation (**Table 1.17**).

1.2.4.4. Performance evaluation of the additives as Pour Point Depressant (PPD)

Physical properties of the base oils are tabulated in **Table 1.18**. PP values of polymer solutions of different concentrations ranging from 1 wt % to 3 wt % were tested and the results are tabulated in **Table 1.19** (in base oil, BO1) and **Table 1.20** (in base oil, BO2). A graphical presentation of the PP values of the polymers in these base oils is also shown in **Figure 1.31.1** and **1.31.2**, respectively. The result indicates that the prepared compounds have a low PP and they can be effectively used as a PPD. In most of the cases, the efficiency increases with decreasing concentration of additive doped solution and the trend is opposite in some cases (P-5 and P-6 in **Table 1.20**). The reason for the former is the solvation power¹⁴ of the oil. With decreasing temperature, any solvent gradually becomes less efficient in solvation and when the molecular weight of the solute and its concentration increases, solvation becomes even lesser¹⁴. Again, hydrodynamic volume of the polymer doped in oil may be considered to explain the increasing PPD properties with the increase in additive concentration¹⁵. With increase in the concentration of the polymer doped in oil, the polymer-oil interaction as well as the hydrodynamic volume of the

polymer increases. Also, both homopolymer and copolymers of IOA act as better PPD than the polymers of IDA.

1.2.4.5. Performance evaluation of the prepared additives as VM

The dynamic viscosity and VI values, of the prepared polymers in base oil (BO1) are tabulated in **Table 1.21** and **Table 1.22**, respectively. The same data of all the polymers in BO2 are recorded in **Table 1.23** and **Table 1.24**, respectively. A graphical presentation of the VI values of the polymers in these base oils is also shown in **Figure 1.32.1** and **1.32.2**, respectively. In general, dynamic viscosity of the prepared solutions increases with increasing concentration of the additives irrespective of the nature of the base oils. A similar trend is also observed in the case of calculated VI values of the respective additive doped base oils.

1.2.4.5.1. Effect of monomers on VI

The data shows that the VI for any IDA + 1-decene copolymer is lower than that for the respective IOA + 1-decene copolymer. Also, HIDA is of lower VI than HIOA; that is, longer chain length and short branching of the alcohol contribute less toward VI values than do short chain and longer branching. This result was ascribed to the lower molecular weight of the IDA polymers compared to the IOA polymers because polymerizability of IOA is greater than the polymerizability of IDA.

1.2.4.5.2. Effect of 1-decene concentration in the feed on VI

The data of VI values indicate that, for IDA + 1-decene copolymers, the values decrease with increasing content of 1-decene for the same concentration of the polymer solution in both the base oils. But, for IOA + 1-decene copolymers, the trend is reversed. This may be because of the reason relating to molecular weight.

1.2.4.5.3. Effect of additive concentration on VI

The data of **Table 1.22** and **Table 1.24** indicates that with increasing concentration of the prepared polymers in solution, VI increases. The reason for this may be, while the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively thicken the oil by changing its shape from tight coil to expanded ones due to increased polymer-solvent interaction. Increase in viscosity due to the thickening effect of the polymer molecule cancels out viscosity reduction due to a higher temperature. Again, a higher polymer concentration will show a higher viscosity index compared to a lower one as an increase of polymer concentration increases total volume of polymer micelles in the solution¹⁶.

1.2.5. Conclusion

It is observed that at higher 1-decene content the copolymer of isodecyl acrylate shows better PPD properties but at lower 1-decene content it shows better VM properties. The homopolymer and copolymers of isooctyl acrylate are better in thermal stability, have greater intrinsic viscosity and molecular weight in toluene solvent. They also show better VM and PPD properties compared to the homopolymer and copolymers of isodecyl acrylate. Thus it can be concluded that, polymers of isooctyl acrylate perform as better multifunctional lube oil additives than those of isodecyl acrylate.

1.2.6. References

References are given in Bibliography under Chapter-III; Section A of Part-I (Page No. 190-192).

1.2.7. Tables and Figures

Table 1.12. Composition of the monomers in the copolymers in terms of mole fraction determined by NMR and FT-IR spectroscopic method¹²

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	0.0154	0.0144	0.0147
P-3	0.0438	0.0427	0.0435
P-4	0.0704	0.0686	0.0698
P-5	0.0000	0.0000	0.0000
P-6	0.0130	0.0116	0.0121
P-7	0.0390	0.0364	0.0372
P-8	0.0647	0.0613	0.0622

P-1: Poly (isodecyl acrylate) (HIDA), P-2 to P-4: copolymer of IDA + different mole fractions of 1-decene, P-5: Poly (isooctyl acrylate) (HIOA), P-6 to P-8: copolymer of IOA + different mole fractions of 1-decene.

Table 1.13. 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	3.704	3.808	3.823	3.901	3.997	3.960	4.100
P-3	3.643	3.756	3.766	3.857	3.934	3.898	4.021
P-4	3.541	3.595	3.622	3.694	3.697	3.664	3.788

P-5	6.374	6.501	6.773	7.078	6.634	6.620	6.987
P-6	7.291	7.310	7.768	8.128	7.382	7.390	7.848
P-7	7.581	7.679	8.174	8.604	7.816	7.842	8.438
P-8	7.745	8.132	8.611	9.185	8.301	8.357	8.939

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 1.14. 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	0.530	0.092	0.391	0.314	0.622
P-3	0.561	0.080	0.411	0.323	0.641
P-4	0.483	0.097	0.375	0.302	0.580
P-5	0.481	0.107	0.308	0.221	0.588
P-6	0.429	0.115	0.272	0.194	0.544
P-7	0.461	0.110	0.279	0.194	0.571
P-8	0.559	0.101	0.301	0.199	0.660

Table 1.15. Percentual difference ($\Delta \% = 100([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values, Huggins equation taken as 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	2.808	3.213	5.319	7.910	6.911	10.691
P-3	3.102	3.376	5.874	7.988	7.000	10.376
P-4	1.525	2.287	4.321	4.406	3.474	6.975
P-5	1.992	6.260	11.045	4.079	3.859	9.617
P-6	0.261	6.542	11.425	1.248	1.358	7.640
P-7	1.293	7.822	13.494	3.100	3.443	11.305
P-8	4.997	11.181	18.593	7.179	7.902	15.416

Table 1.16. 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	12932	13436	13509	13890	14364	14181	14877
P-3	12639	13183	13232	13675	14053	13876	14483
P-4	12154	12410	12539	12884	12898	12740	13338
P-5	27342	28096	29730	31593	28892	28808	31034
P-6	32911	33030	35918	38234	33479	33529	36429
P-7	34731	35351	38532	41356	36224	36390	40259
P-8	35771	38260	41402	45256	39361	39727	43593

Table 1.17. Percentual difference ($\Delta \% = 100(M/M_h)-100$) obtained for molecular weight values, Huggins equation taken as 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	3.897	4.462	7.408	11.073	9.658	15.040

P-3	4.304	4.692	8.197	11.188	9.787	14.590
P-4	2.106	3.168	5.998	6.121	4.821	9.742
P-5	2.758	8.734	15.548	5.669	5.362	13.503
P-6	0.362	9.137	16.095	1.726	1.878	10.689
P-7	1.785	10.944	19.075	4.299	4.777	15.917
P-8	6.958	15.742	26.516	10.036	11.059	21.867

Table 1.18. 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 1.19. Pour Point (PP) of the additives doped in 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
0	-3	-3	-3	-3	-3	-3	-3	-3
1	-6	-10	-11	-12	-15	-12	-13	-14
2	-6	-10	-11	-11	-15	-12	-12	-13
3	-6	-10	-10	-11	-15	-9	-11	-12

Table 1.20. Pour Point (PP) of the additives doped in 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
0	-6	-6	-6	-6	-6	-6	-6	-6
1	-10	-11	-12	-12	-16	-19	-18	-15
2	-9	-11	-11	-12	-17	-19	-17	-15
3	-9	-10	-11	-11	-18	-20	-16	-14

Table 1.21. Dynamic viscosity values of the additives doped in base oil (BO1)

Conc. (wt %)	Temp. (K)	dynamic viscosity (cP) in presence of							
		P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
0	313	5.972	5.972	5.972	5.972	5.972	5.972	5.972	5.972
	373	1.481	1.481	1.481	1.481	1.481	1.481	1.481	1.481
1	313	6.150	6.128	6.074	6.055	6.108	6.039	6.015	6.114
	373	1.523	1.517	1.507	1.499	1.515	1.494	1.494	1.531
2	313	6.207	6.199	6.127	6.176	6.252	6.100	6.077	6.179
	373	1.539	1.534	1.521	1.526	1.569	1.506	1.513	1.553
3	313	6.289	6.284	6.224	6.252	6.356	6.170	6.174	6.266
	373	1.554	1.545	1.539	1.543	1.634	1.523	1.539	1.584
4	313	6.391	6.371	6.291	6.349	6.464	6.236	6.257	6.322
	373	1.582	1.577	1.560	1.567	1.678	1.537	1.569	1.605
5	313	6.444	6.458	6.380	6.417	6.567	6.311	6.319	6.392
	373	1.598	1.598	1.581	1.581	1.722	1.562	1.590	1.625
6	313	6.520	6.564	6.438	6.511	6.646	6.388	6.401	6.503
	373	1.619	1.622	1.596	1.603	1.766	1.592	1.620	1.664

Table 1.22. Viscosity Index (VI) values of the additives doped in base oil (BO1)

Conc. (wt %)	VI in 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	91	90	88	91	86	89	98
2	94	93	92	91	103	87	93	102
3	95	94	93	93	119	89	97	108
4	100	99	97	96	125	91	103	111
5	102	100	99	97	130	97	107	114
6	105	103	101	100	136	103	112	120

Table 1.23. Dynamic viscosity values of the additives doped in base oil (BO2)

Conc. (wt %)	Temp. (K)	dynamic viscosity (cP) in presence of							
		P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
0	313	20.305	20.305	20.305	20.305	20.305	20.305	20.305	20.305
	373	3.247	3.247	3.247	3.247	3.247	3.247	3.247	3.247
1	313	21.344	21.423	21.375	21.296	21.776	21.647	21.842	21.843
	373	3.418	3.423	3.413	3.401	3.498	3.452	3.538	3.596
2	313	21.446	21.493	21.500	21.400	21.948	21.786	21.982	21.973
	373	3.446	3.450	3.442	3.420	3.554	3.485	3.606	3.636
3	313	21.541	21.563	21.600	21.484	21.892	21.919	22.076	22.095
	373	3.468	3.467	3.460	3.442	3.588	3.530	3.643	3.683
4	313	21.662	21.700	21.729	21.609	22.008	22.019	22.185	22.194
	373	3.514	3.505	3.510	3.485	3.633	3.576	3.677	3.712
5	313	21.802	21.787	21.840	21.736	22.306	22.124	22.303	22.344

	373	3.580	3.561	3.556	3.537	3.842	3.614	3.726	3.772
6	313	21.919	21.904	21.944	21.860	22.553	22.225	22.401	22.493
	373	3.627	3.613	3.605	3.573	4.108	3.664	3.776	3.859

Table 1.24. Viscosity Index (VI) values of the additive doped in base oil (BO2)

Conc. (wt %)	VI in 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	87	86	86	90	87	93	98
2	89	89	88	87	94	89	98	100
3	90	89	88	88	97	92	100	102
4	93	92	92	91	100	95	101	103
5	97	96	95	94	112	97	104	106
6	100	99	98	96	124	100	106	111

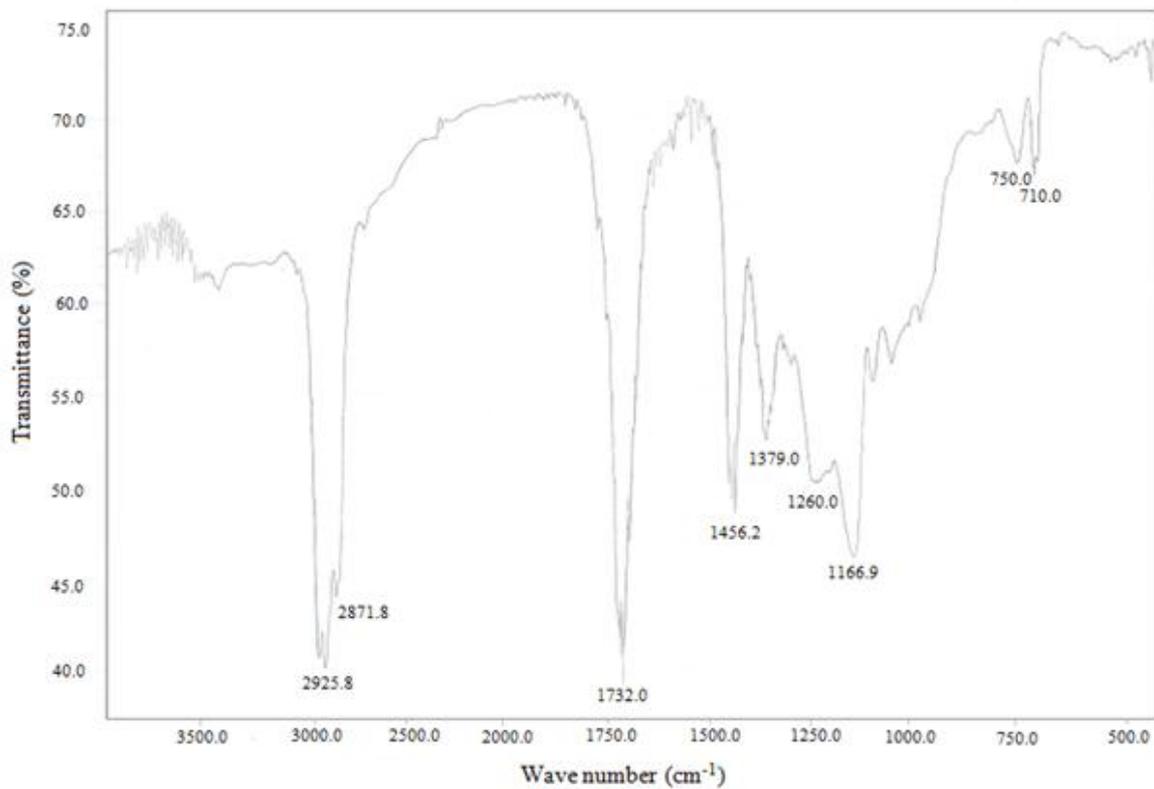


Figure 1.17. FT-IR spectra of poly (isodecyl acrylate)

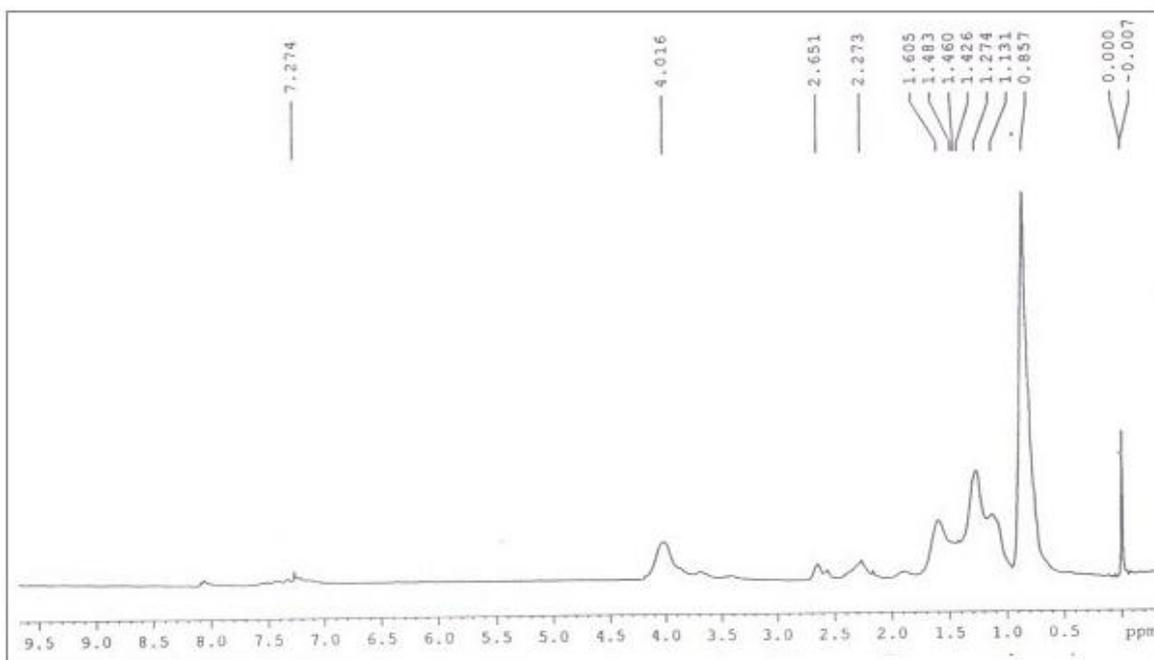


Figure 1.18. ¹H-NMR spectra of poly (isodecyl acrylate)

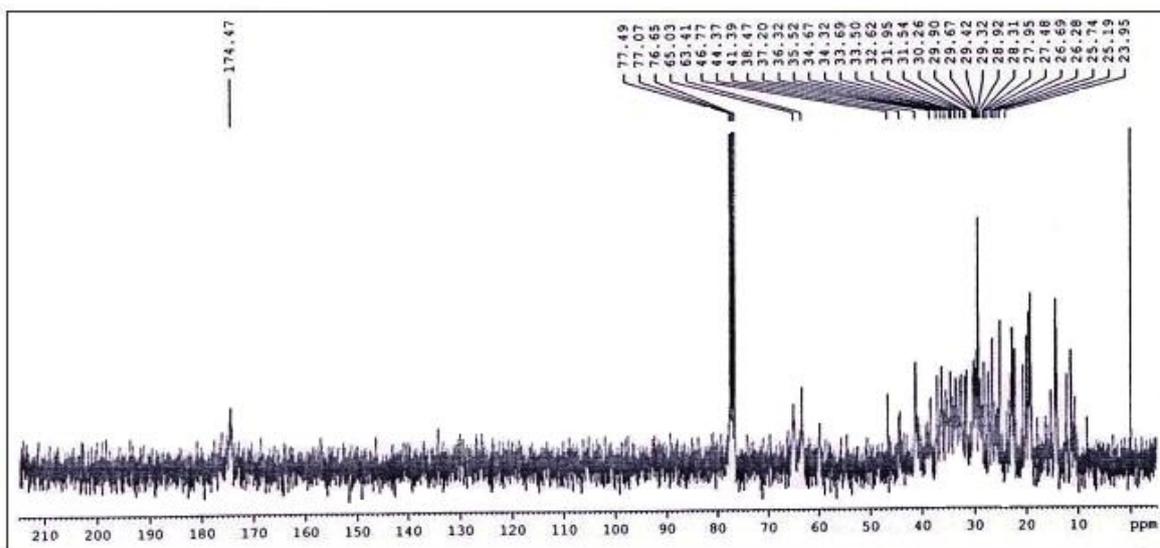


Figure 1.19. ^{13}C -NMR spectra of poly (isodecyl acrylate)

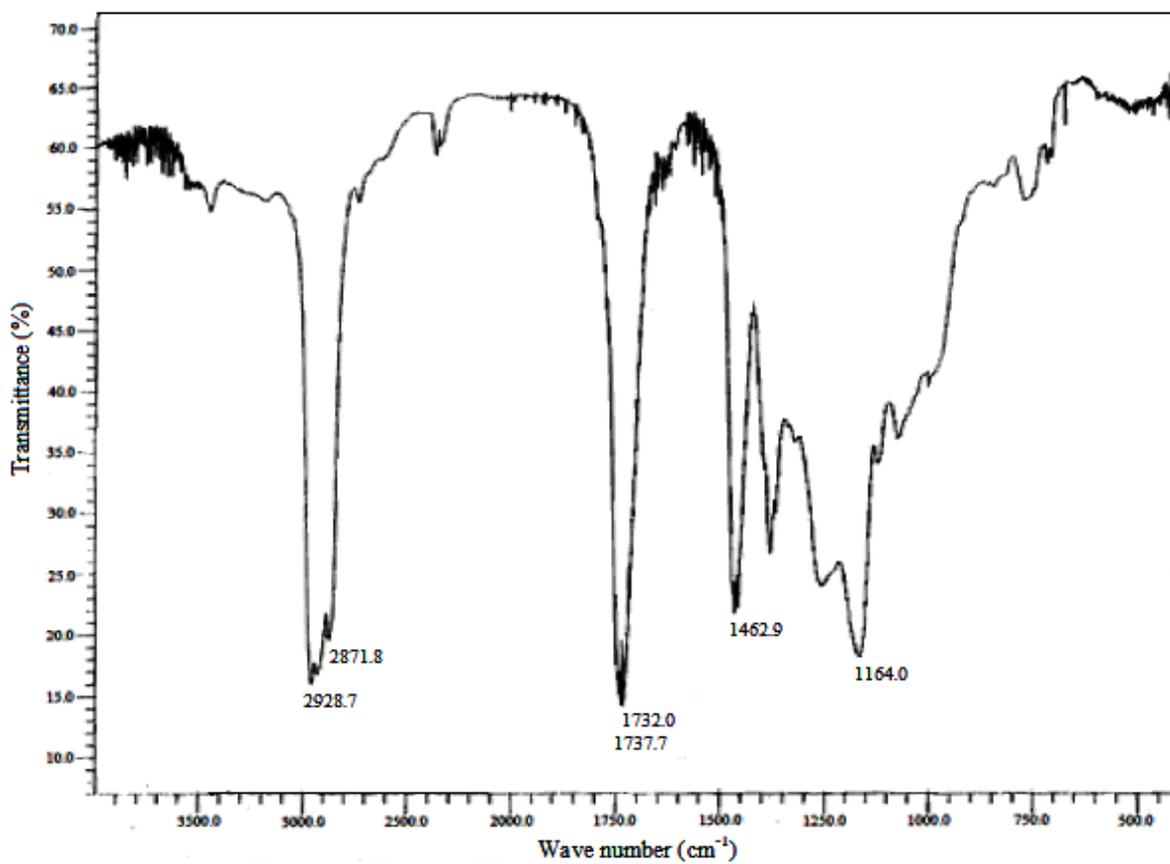


Figure 1.20. FT-IR spectra of a representative copolymer of isodecyl acrylate with 1-decene

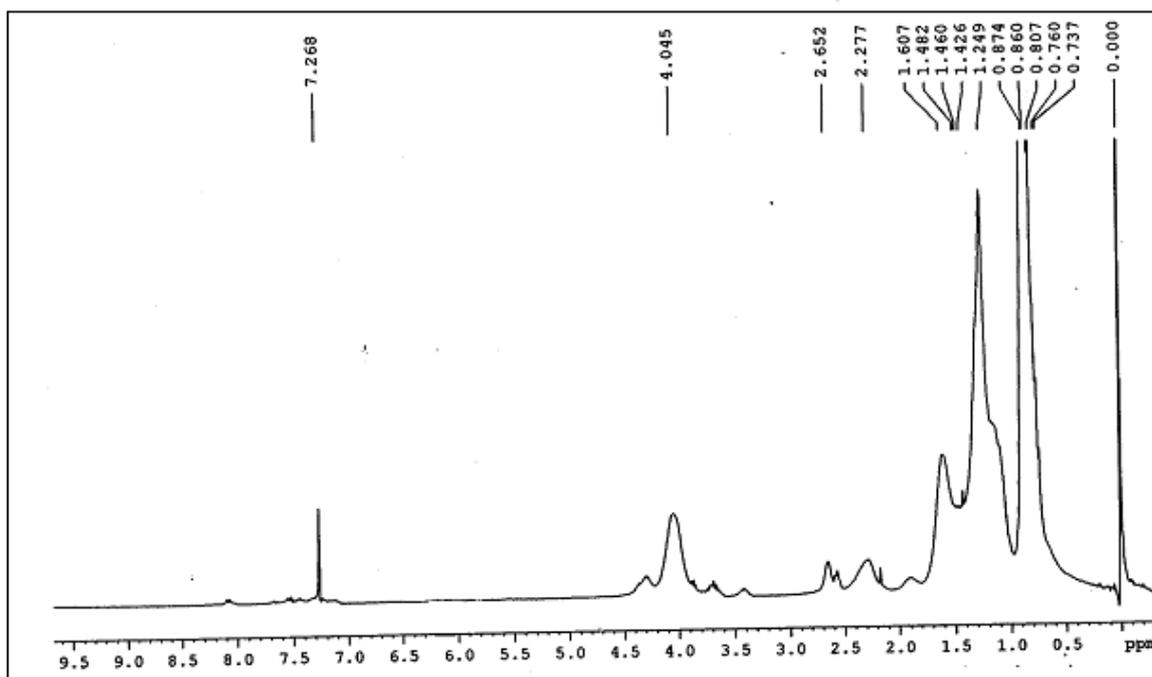


Figure 1.21. $^1\text{H-NMR}$ spectra of a representative copolymer of isodecyl acrylate with 1-decene

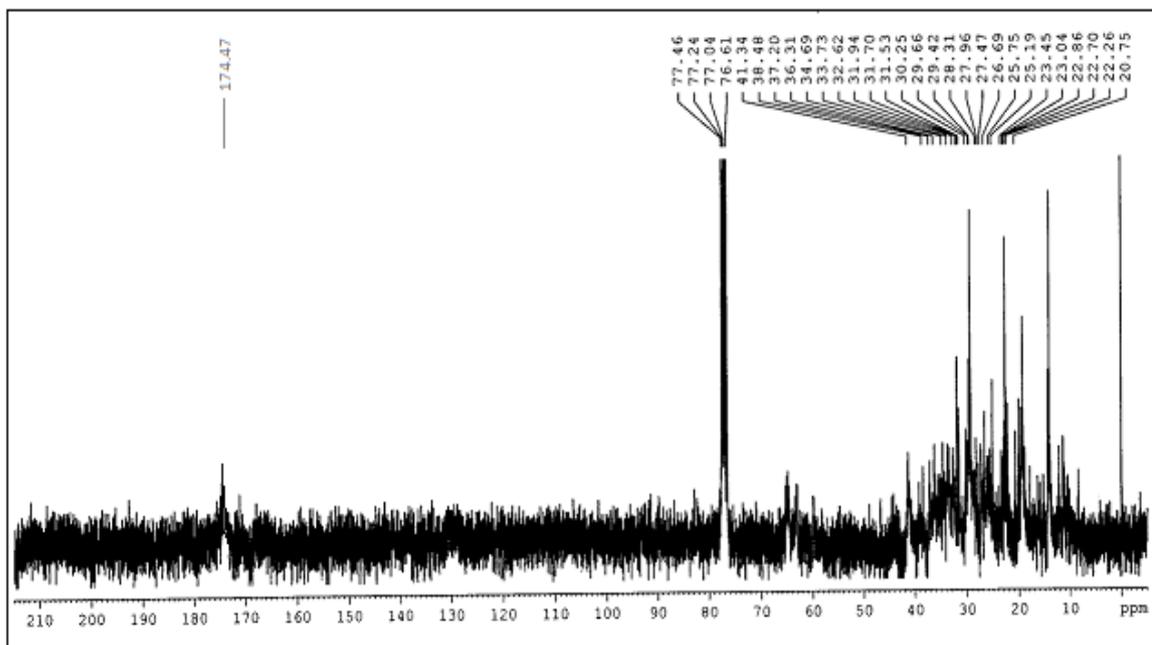


Figure 1.22. $^{13}\text{C-NMR}$ spectra of a representative copolymer of isodecyl acrylate with 1-decene

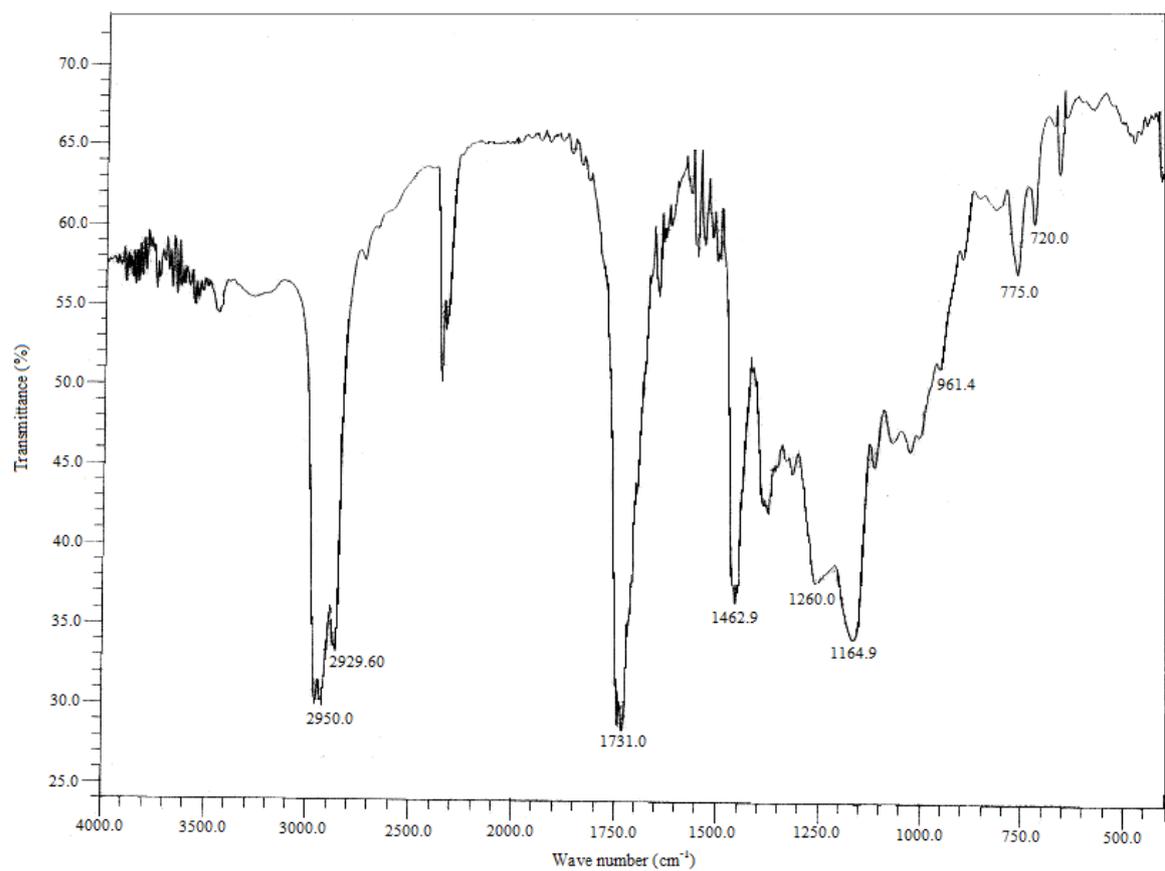


Figure 1.23. FT-IR spectra of poly (isooctyl acrylate)

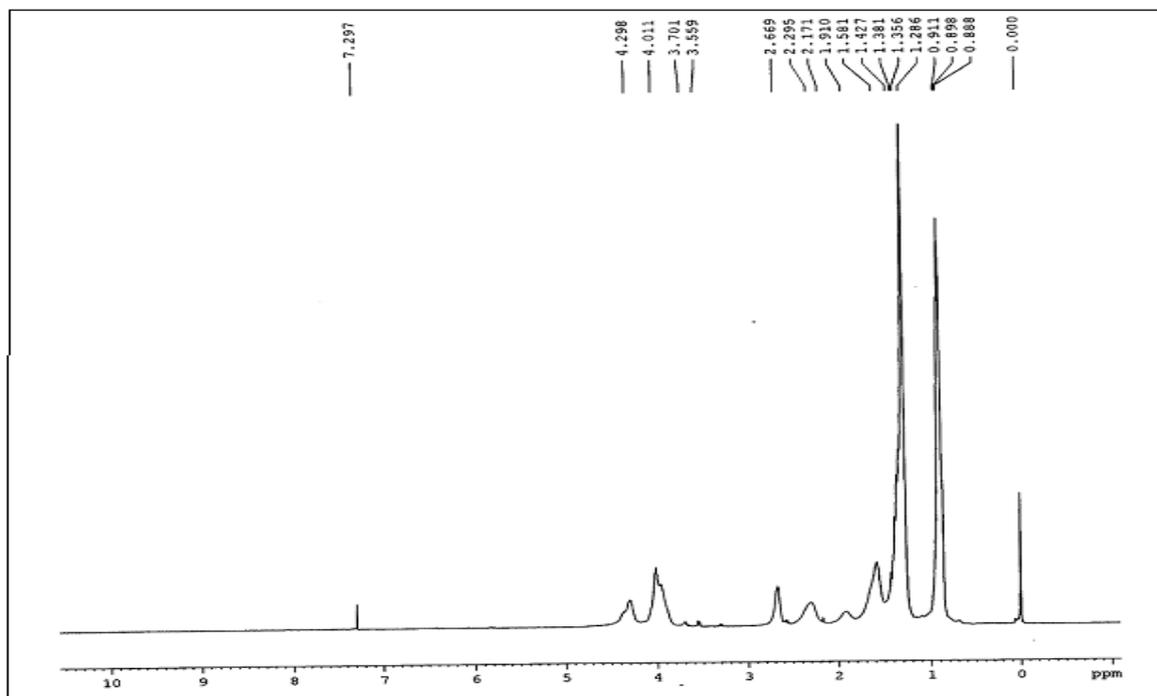


Figure 1.24. ¹H-NMR spectra of poly (isooctyl acrylate)

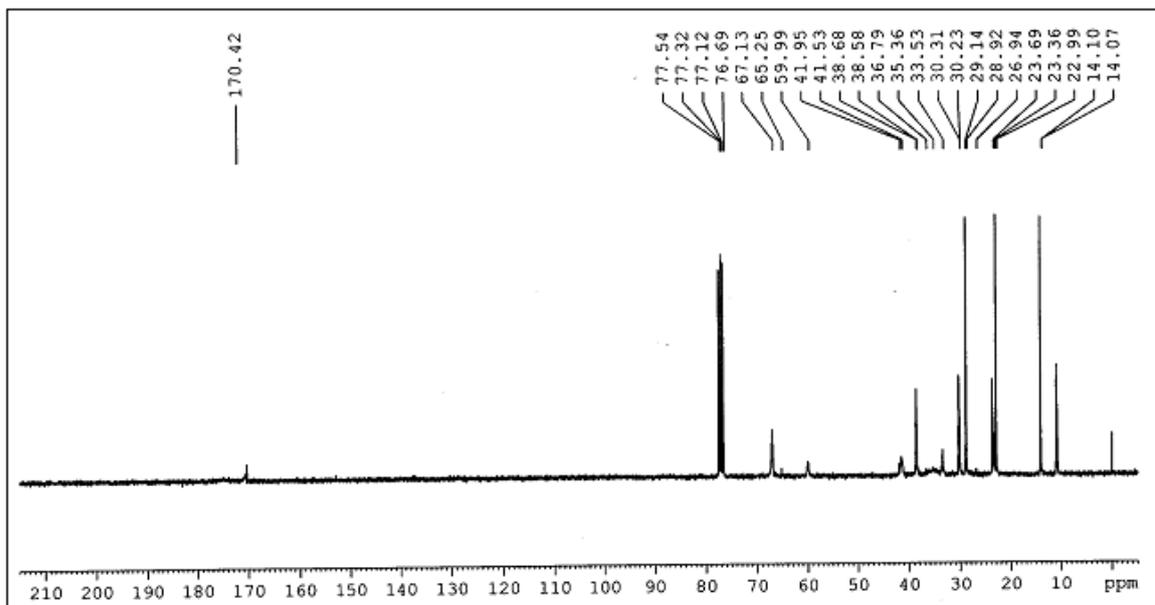


Figure 1.25. ^{13}C -NMR spectra of poly (isooctyl acrylate)

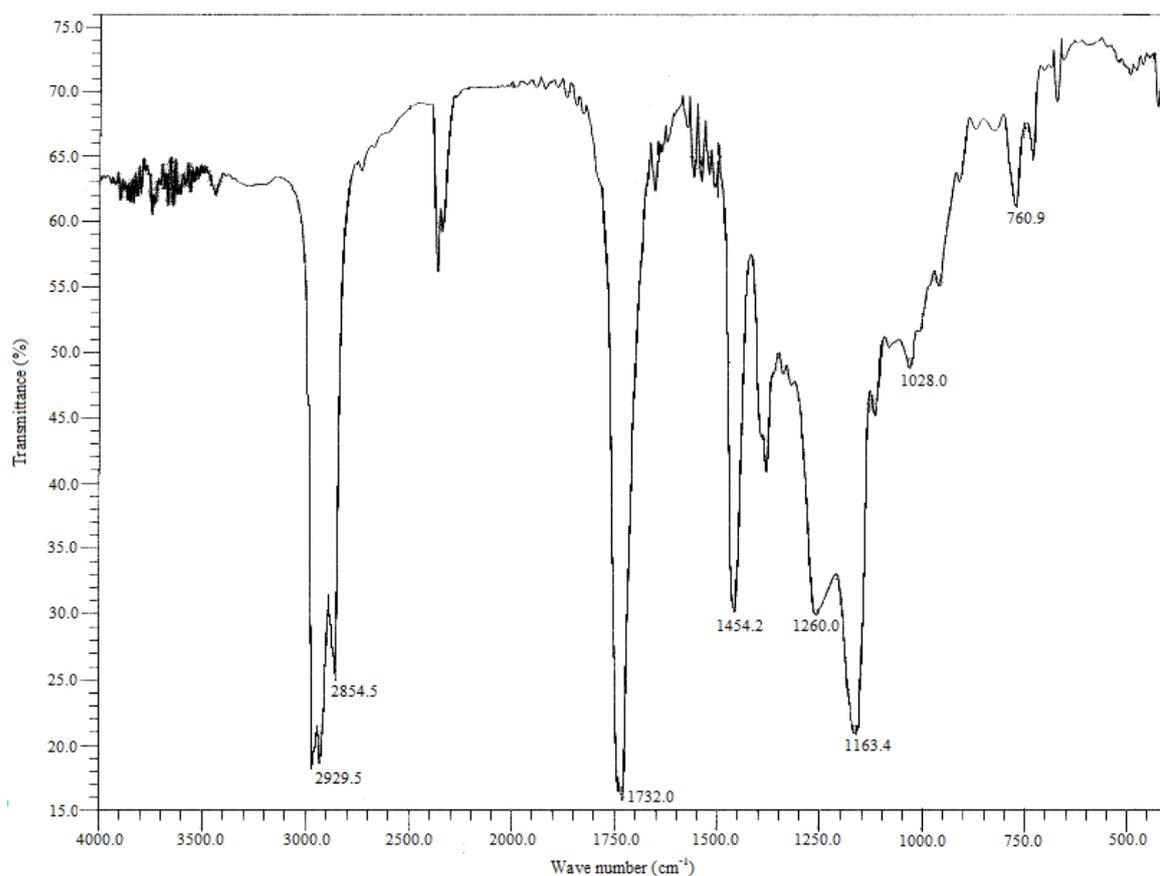


Figure 1.26. FT-IR spectra of a representative copolymer of isooctyl acrylate with 1-decene

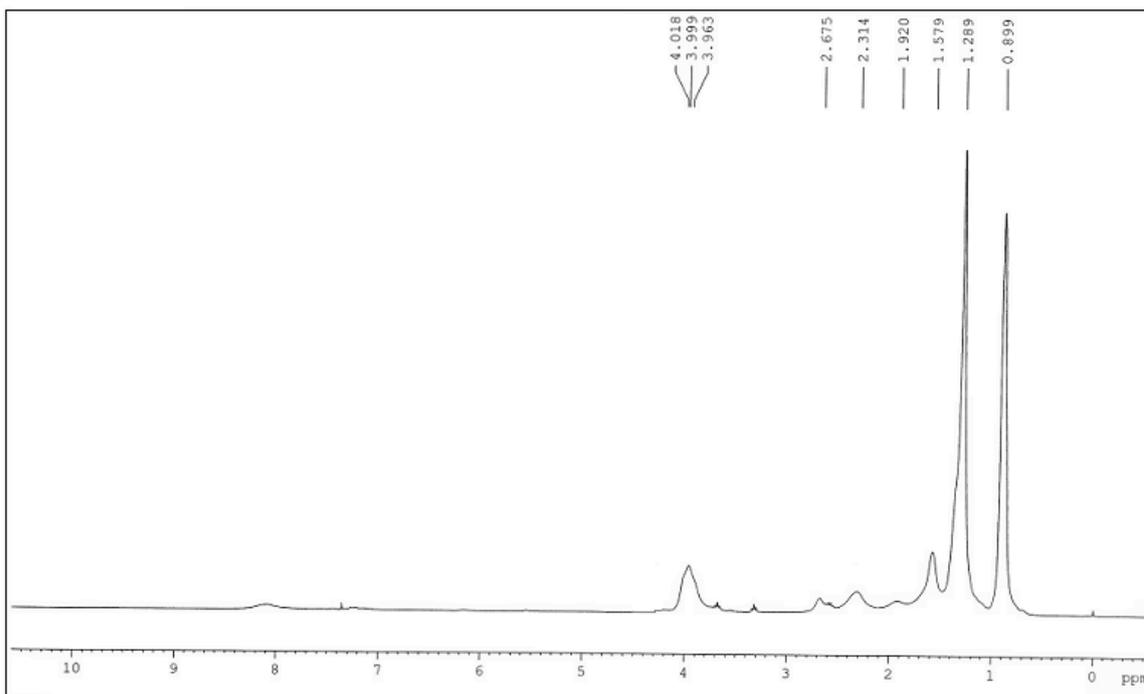


Figure 1.27. ^1H -NMR spectra of a representative copolymer of isooctyl acrylate with **1-decene**

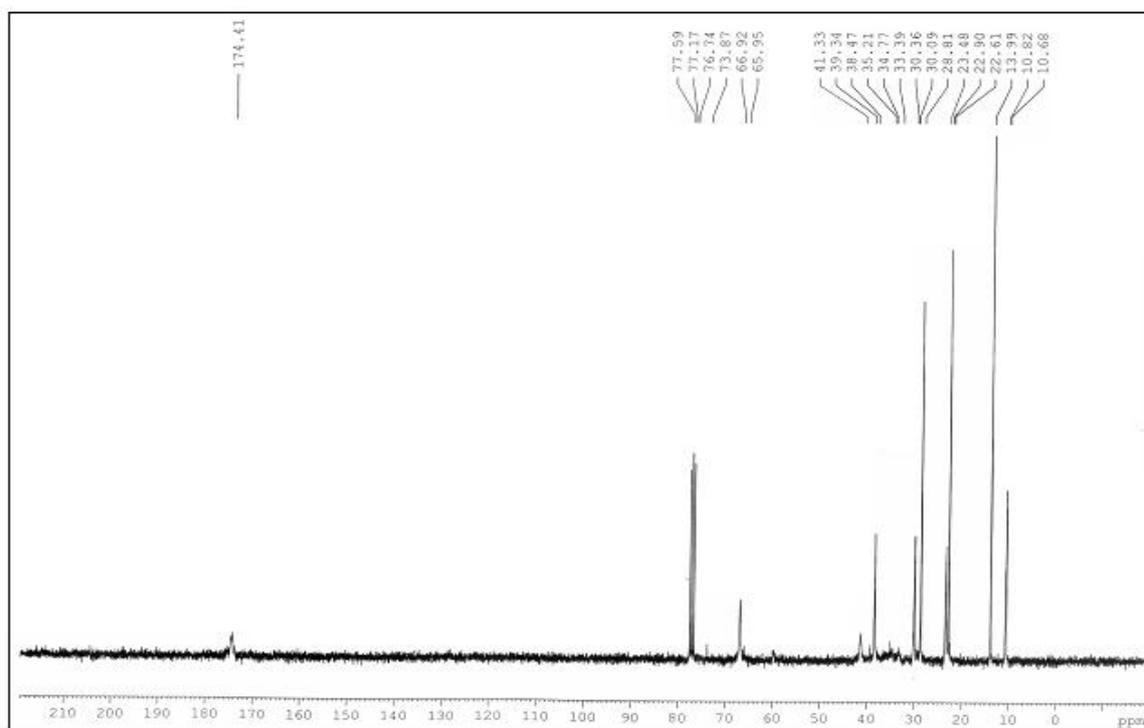


Figure 1.28. ^{13}C -NMR spectra of a representative copolymer of isooctyl acrylate with **1-decene**

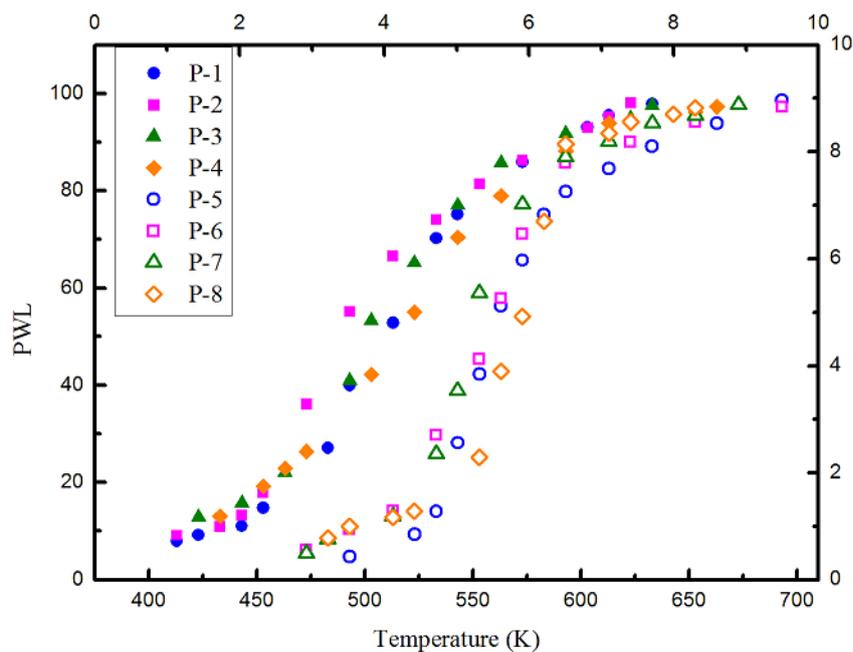


Figure 1.29. Plot of PWL vs. Temperature. PWL is Percent Weight Loss and temperature is measured in Kelvin.

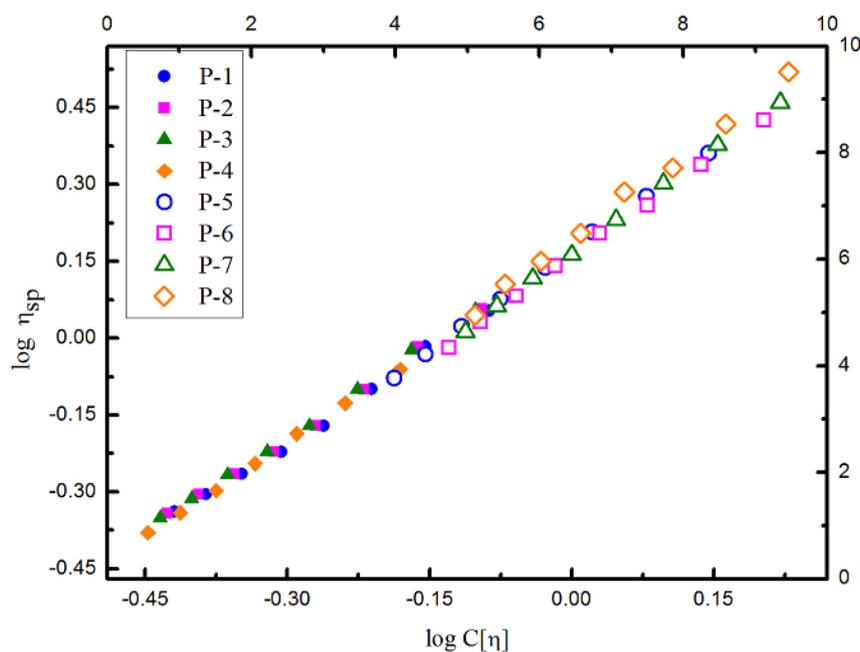


Figure 1.30. Plot of $\log \eta_{sp}$ vs. $\log C [\eta]$, where η_{sp} is the specific viscosity of the polymer solution in toluene, C is the concentration of the solution in g.cm^{-3} , and $[\eta]$ is the intrinsic viscosity of the polymer solution in toluene obtained by using Huggins equation.

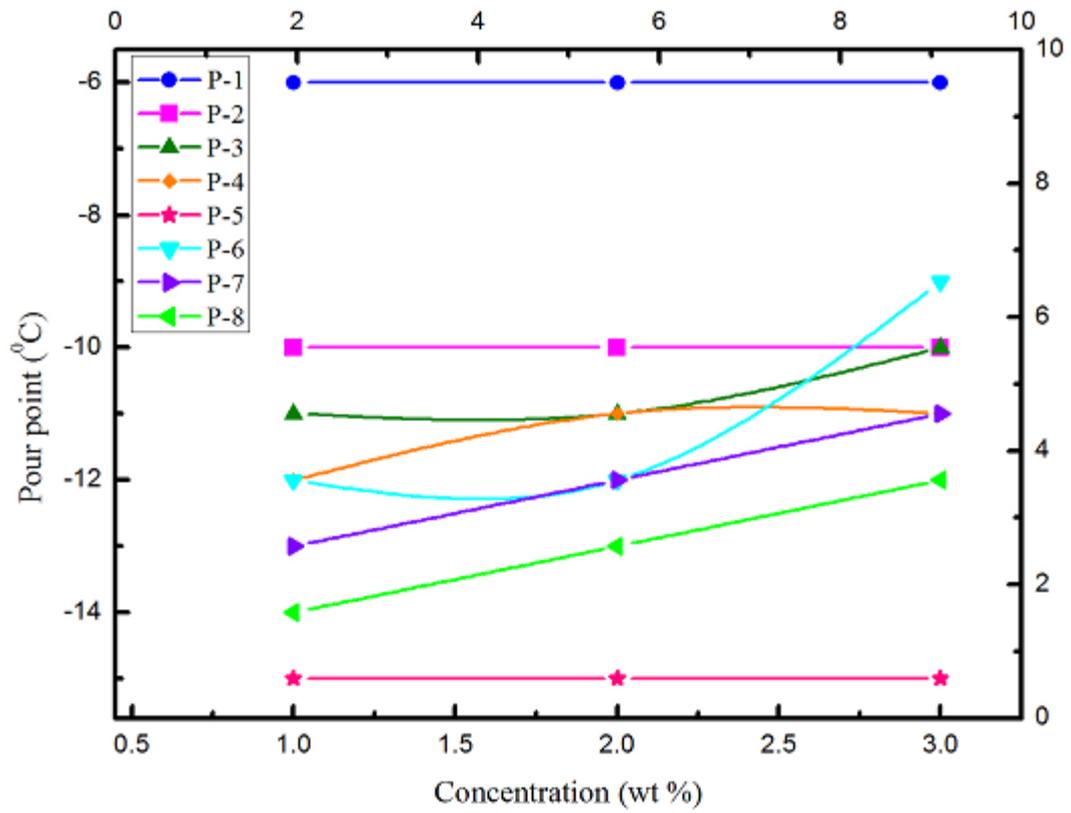


Figure 1.31.1. Plot of pour point vs. additive concentration in BO1

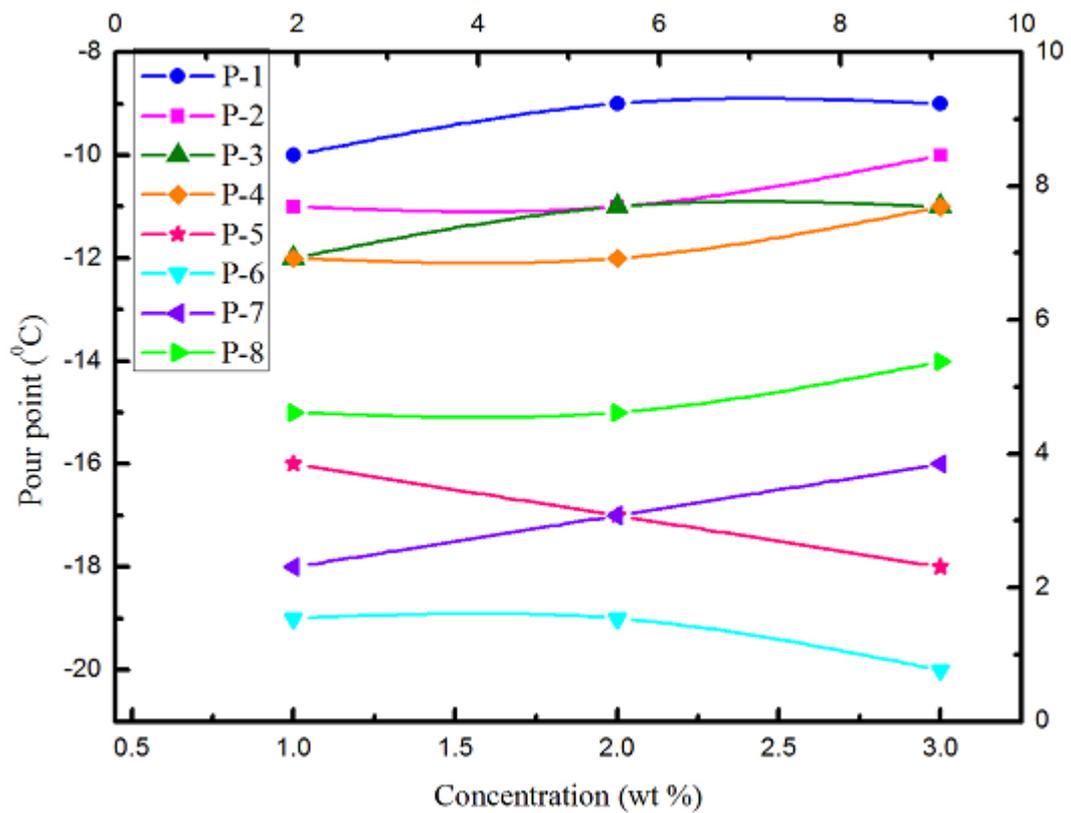


Figure 1.31.2. Plot of pour point vs. additive concentration in BO2

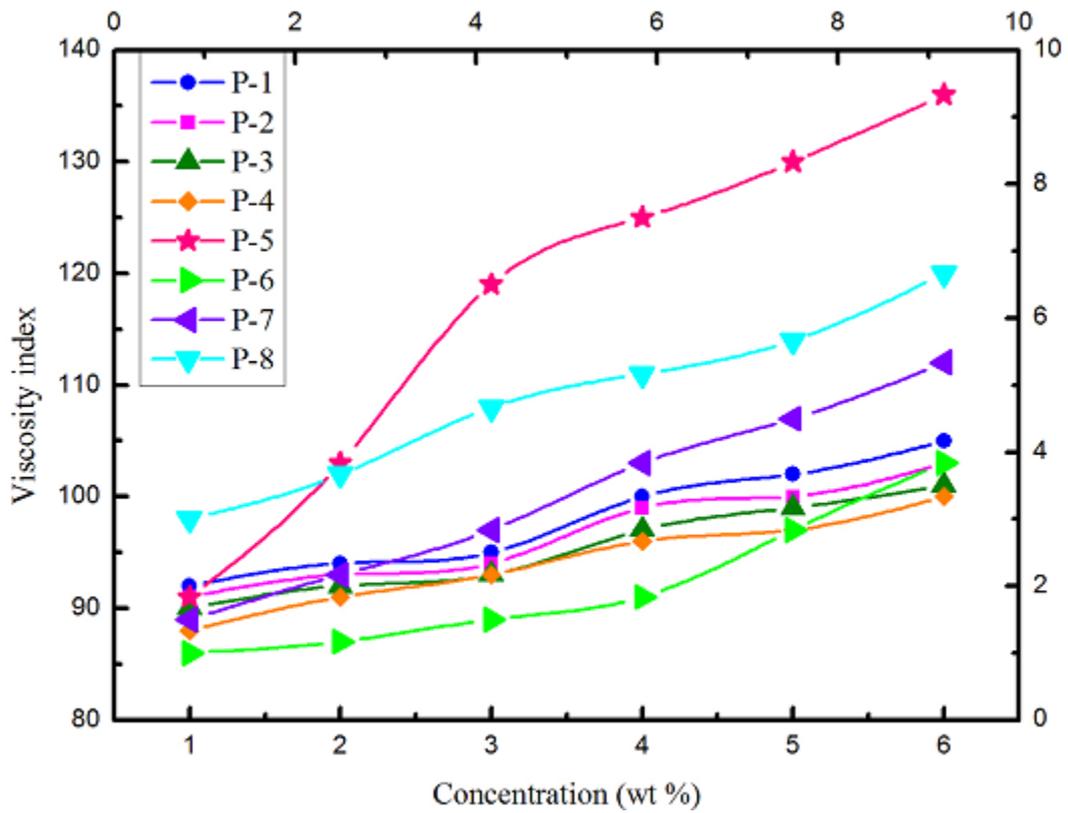


Figure 1.32.1. Plot of viscosity index vs. additive concentration in BO1

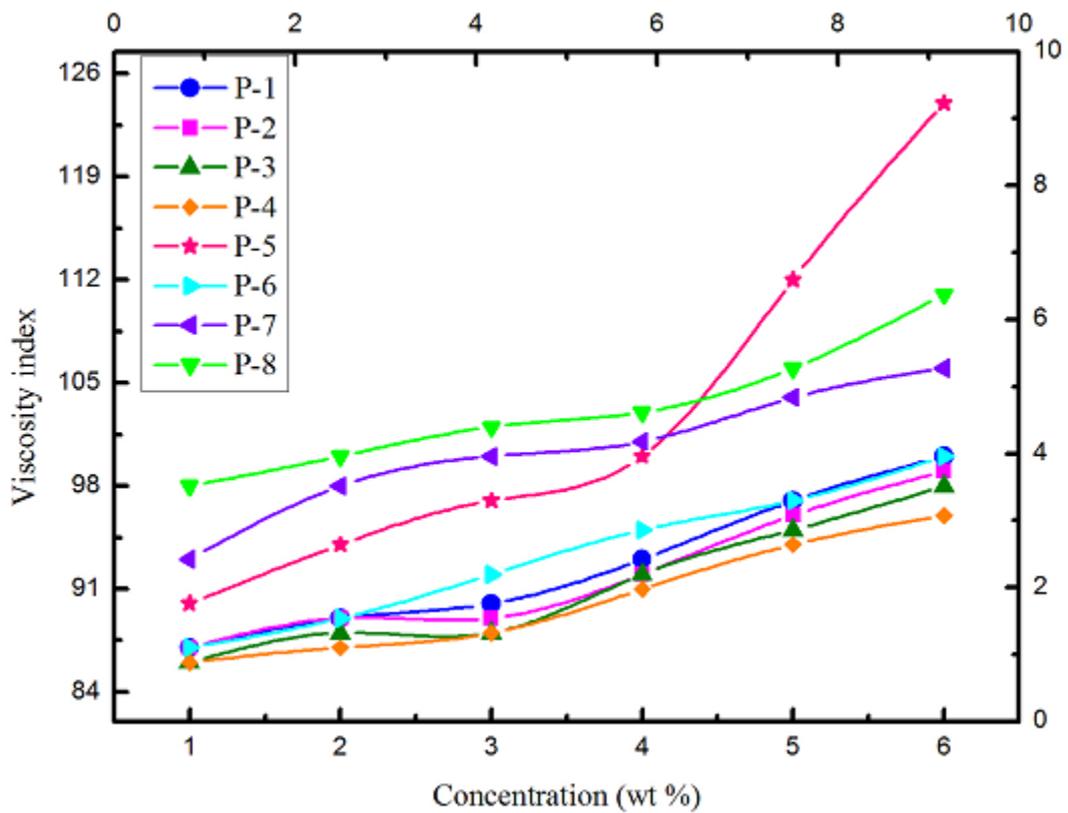


Figure 1.32.2. Plot of viscosity index vs. additive concentration in BO2

1.3. Section B: Multifunctional additive performance of decyl acrylate + 1-decene and isooctyl acrylate + 1-decene copolymers

1.3.1. Introduction

Encouraged by the result of the previous investigation, decyl acrylate (DA) was selected as a potential candidate for the synthesis of polymeric additives. Synthesis of its homopolymer (HDA) and also copolymers with 1-decene (DA + 1-decene) were carried out. All the polymers were characterized by spectral and thermogravimetric analysis. 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 scanty¹ and almost nil for polymers used as lube oil additives, present work also includes viscometric study² of the copolymers as well as the homopolymers. Performance evaluation of the prepared polymeric additives as Pour Point Depressant (PPD) and Viscosity Modifier (VM) was also carried out. The results of this analysis were compared with the results of isooctyl acrylate (IOA) polymers i.e. poly (isooctyl acrylate) (HIOA) and its copolymers with 1-decene (IOA + 1-decene) as reported in the previous work (Chapter-III, Section A).

1.3.2. Experimental procedure

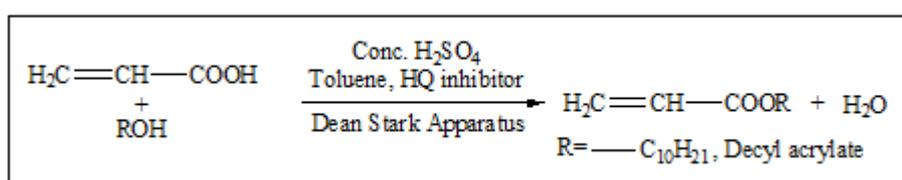
1.3.2.1. Materials

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd., acrylic acid (stabilized with 0.02 % hydroquinone monomethyl ether) from Sisco Research Laboratories Pvt. Ltd., decyl alcohol (decanol) and hexane from S D Fine Chem. Ltd., 1-decene from Across Organics, methanol from Thomas Baker (Chemicals) Pvt. Ltd., benzoyl peroxide (BZP) from LOBA chemicals. BZP was recrystallized from

CHCl₃-MeOH mixture before use. All other were used as they obtained without further purification. Base oils were collected from IOCL, Dhakuria, Kolkata, West Bengal.

1.3.2.2. Esterification

Esterification of acrylic acid with decyl alcohol to prepare decyl acrylate (DA) was carried out in toluene taking H₂SO₄ as a catalyst and hydroquinone as polymerization inhibitor and following the process as reported in the previous chapter (Chapter-II, Page No. 27).



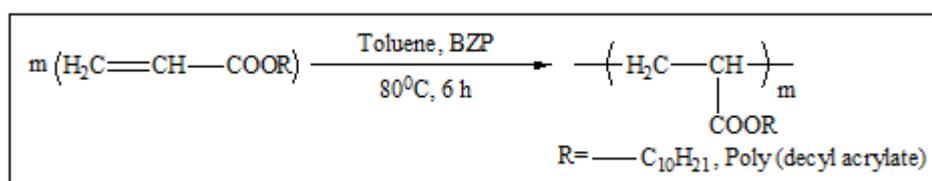
Scheme 1.7: Preparation of decyl acrylate (DA)

1.3.2.3. Purification of prepared esters

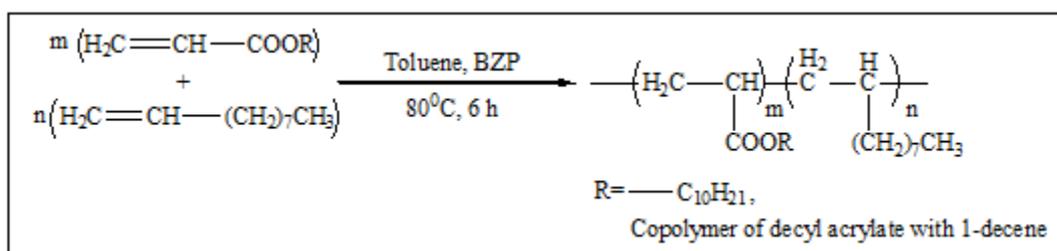
All of the prepared esters were purified by the process as reported in the previous chapter (Chapter-II, Page No. 27).

1.3.2.4. Preparation of copolymer and homopolymer

Homopolymer of DA (HDA) was prepared and in the preparation of DA + 1-decene copolymers, different concentration (mole fractions) of 1-decene was used (**Table 1.25**). The thermal polymerization was carried out in toluene solvent using BZP as initiator and by following the method as reported in the previous chapter (Chapter-II, Page No. 28).



Scheme 1.8: Preparation of poly (decyl acrylate)



Scheme 1.9: Preparation of copolymer of decyl acrylate with 1-decene

1.3.3. Measurements

1.3.3.1. Spectroscopic measurements

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

1.3.3.2. Viscometric measurements

Viscometric measurements were carried out using graphic extrapolation as well as by the single point determination method³⁻⁷. The later method has the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in short period of time, practically in industrial laboratories.

Among the graphic extrapolation method, the most commonly used equations are:

$$\text{Huggins (H)} \quad \eta_{\text{sp}}/C = [\eta]_h + k_h [\eta]_h^2 C \quad (1)$$

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

$$\text{Martin (M)} \quad \ln (\eta_{\text{sp}}/C) = \ln [\eta]_m + k_m [\eta]_m C \quad (3)$$

$$\text{Schulz-Blaschke (SB)} \quad \eta_{\text{sp}}/C = [\eta]_{\text{sb}} + k_{\text{sb}} [\eta]_{\text{sb}} \eta_{\text{sp}} \quad (4)$$

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

$\eta_r = t/t_0$, 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.

For single point determination method, the equations used are:

$$\text{Solomon-Ciuta (SC)} \quad [\eta] = (2(\eta_{sp} - \ln \eta_r))^{1/2}/C \quad (5)$$

$$\text{Deb-Chatterjee (DC)} \quad [\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3}/C \quad (6)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5^4$. 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 of flow of eight different concentrations of the sample solution. The time of flow of the solutions was manually determined by using a chronometer. In the single point measurement, the lowest value of solution concentration was chosen for calculation. For the determination of viscosity-average molecular weight (M), the Mark Houwink constants $K = 0.00387 \text{ dL.g}^{-1}$ and $a = 0.725$ were employed^{2,8} in Mark Houwink Sukurda (MHS) equation (eqn. 7). 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. In this investigation, the values $K = 0.00387 \text{ dL.g}^{-1}$ and $a = 0.725$ were employed to get an idea of whether the molecular

weight value is low or high. During the measurements adequate precautions were taken regarding the loss due to solvent evaporation.

$$[\eta] = KM^a \quad (7)$$

1.3.3.3. Thermogravimetric Analysis (TGA)

The thermograms in air were obtained on a mettler TA-3000 system, at a heating rate of 10 K.min⁻¹ at room temperature under atmospheric pressure taking 0.2 g of each polymer sample in a platinum crucible.

1.3.3.4. Evaluation of Pour Point Depressant (PPD) properties of the additives in lube oil

The prepared compounds were evaluated as PPDs 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. An average of three experimental data taken under identical condition was recorded.

1.3.3.5. Evaluation of the prepared additives as Viscosity Modifier (VM) in lube oil

The prepared polymers were evaluated as VMs in two base oils (BO1 and BO2). The viscosity index values of the polymeric oil solutions have been determined by using the following equations⁹.

$$VI = 3.63(60 - 10^n) \quad (8)$$

where,
$$n = (\ln v_1 - \ln k) / \ln v_2 \quad (9)$$

v_1 and v_2 are the kinematic viscosities (cSt) of the solution at lower and higher temperature, respectively. The kinematic viscosity (v) of the sample solutions was determined at 313 K and 373 K, from the following equation⁹.

$$v = (Kt - L/t) \rho \quad (10)$$

Where, K and L are the viscometer constants and t and ρ are time flow and density of experimental solution, respectively. k is a function of temperature only and is equal to 2.714 for the temperature range performed. n is a constant characteristic for each oil⁹.

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. 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^{10,11}. 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 copolymer concentration on the VI.

1.3.4. Results and discussions

1.3.4.1. Spectroscopic analysis

FT-IR spectrum (**Figure 1.33**) of poly (decyl acrylate) or homo polymer of decyl acrylate (HDA) exhibited absorption at 1732.0 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260.0 and at 1175.0 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 cm^{-1} were due to the bending of C–H bonds. The broad peak ranging from 2900.0 to 3100.0 cm^{-1} was due to the presence of stretching vibration (C–H bonds). In its $^1\text{H-NMR}$ spectra (**Figure 1.34**), homo polymer of DA showed a multiplet centered at 3.17 ppm due to the proton of $-\text{OCH}_2$ group; a broad singlet at 0.73 ppm was due to methyl groups of decyl

chain. The proton decoupled ^{13}C -NMR of the above sample (**Figure 1.35**) was in complete agreement with the homopolymer which shows the presence of ester carbonyl group at 170.66 ppm and absence of any sp^2 carbon in the range 130-150 ppm.

IR spectrum of the copolymer of decyl acrylate with 1-decene (**Figure 1.36**) exhibited absorption at 1729.7 cm^{-1} for the stretching vibration of ester carbonyl. Peaks at 1272.4 cm^{-1} and at 1149.2 cm^{-1} were due to the C–O (ester bond) stretching vibration and the absorption peaks at 2995.6 , 2950.3 , 732.6 and 696.2 cm^{-1} were due to the stretching and bending vibration of C–H bonds. The formation of the copolymer was also indicated by the absence of peak between 5 ppm and 6 ppm due to sp^2 hydrogen and that between 130 ppm and 150 ppm due to sp^2 carbon in its ^1H and ^{13}C -NMR (**Figure 1.37** and **Figure 1.38**), respectively.

IR spectrum of the poly (isooctyl acrylate) (**Figure 1.39**) exhibited absorption at 1731.0 cm^{-1} for the stretching vibration of ester carbonyl. Peaks at 1260.0 cm^{-1} and at 1164.9 cm^{-1} were due to the C–O (ester bond) stretching vibration and the absorption peaks at 961.4 , 775.0 and 720.0 cm^{-1} were due to the bending vibration of C–H bonds. A broad peak ranging from 2929.6 to 2950.0 cm^{-1} indicated the presence of C–H stretching vibration. ^1H and ^{13}C -NMR was also in complete agreement with the homopolymer. In its ^1H -NMR spectra (**Figure 1.40**), the homopolymer of IOA showed a broad singlet centered at 4.01 ppm for the protons of the $-\text{OCH}_2$ group; a broad singlet at 0.89 ppm was for the methyl groups of isooctyl chain. The proton decoupled ^{13}C -NMR of the above sample (**Figure 1.41**) shows no peak between 130 and 150 ppm which indicated the absence of any sp^2 carbon. The presence of the ester carbonyl group was indicated by the peak at 170.42 ppm.

IR spectrum of the copolymer of isooctyl acrylate with 1-decene (**Figure 1.42**) exhibited absorption at 1732.0 cm^{-1} for the stretching vibration of ester carbonyl. Peaks at

1260.0 cm^{-1} and at 1163.4 cm^{-1} were due to the C–O (ester bond) stretching vibration and the absorption peaks at 1028.0 cm^{-1} and 760.9 cm^{-1} were due to the bending vibration of C–H bonds. Peaks at 2929.5 cm^{-1} and 2854.5 cm^{-1} indicated the presence of C–H stretching vibration. The formation of the copolymer was also indicated by the absence of a peak between 5 ppm and 6 ppm due to sp^2 hydrogen and that between 130 ppm and 150 ppm due to sp^2 carbon in its ^1H and ^{13}C -NMR (**Figure 1.43** and **Figure 1.44**), respectively.

The value of extent of incorporation of 1-decene in the copolymer composition, as determined from FT-IR and NMR method¹² is tabulated in **Table 1.25**.

1.3.4.2. Thermogravimetric analysis

A graphical presentation (**Figure 1.45**) presents a comparison between the TGA data for homo and copolymers. The TGA data shows that in case of DA polymers, the copolymers are better in thermal stability than the homopolymer and with increasing concentration of 1-decene in the feed, the stability increases. But the trend is reversed for the polymers of IOA. The homopolymer is thermally more stable than the copolymers and with increasing concentration of 1-decene, thermal stability decreases. Also, comparison among the TGA values indicates that DA polymers are thermally more stable than the IOA polymers.

1.3.4.3. Viscometric analysis

Viscometric data were obtained using the six equations mentioned. A linear relation for the plot of $\log \eta_{\text{sp}}$ vs. $\log C[\eta]$, obtained for all samples (**Figure 1.46**), indicated that measurements were performed in Newtonian flow^{6,13} (η_{sp} , C , $[\eta]$ represents specific viscosity, concentration and intrinsic viscosity of the polymer solutions corresponding to the Huggins equation, respectively).

Using the graphic extrapolation method, respective intrinsic viscosities and constants were evaluated (**Table 1.26** and **Table 1.27**). In single point determinations, Schulz-Blaschke (SB), Solomon-Ciuta (SC), and Deb-Chatterjee (DC) equations were employed to determine the intrinsic viscosity (**Table 1.26**). 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 systems². The same is used here also.

Table 1.26 presents intrinsic viscosity values related to all equations for the studied samples. Taking into account the data for homopolymers and all copolymer samples, it can be noticed that the values are consistent. Comparison among the homopolymer and copolymers of DA indicated that, the homopolymer has greater $[\eta]$ values than the copolymers with 1-decene and for the copolymers, the $[\eta]$ values decrease with increasing concentration of 1-decene in the feed. This indicates a more extended conformation of the homopolymer chain compared to the copolymers. For the polymers of IOA, the $[\eta]$ values for the homopolymer are lower than the copolymers and comparison among the $[\eta]$ values of the copolymers showed that the $[\eta]$ values increase with increasing concentration of 1-decene in the feed. So, there is a more extended conformation of the copolymer chain compared to the homopolymer and in the case of copolymers, stretching of the chain is more and more with increasing percentage of 1-decene in the feed.

Both homopolymer and copolymer viscosities in toluene medium indicate poor solvation (**Table 1.27**), as is evident from the respective viscometric constant values, and thus points to the formation of spherical structures as discussed earlier⁵. This conclusion is further supported by the positive values of the Kraemer coefficient for all the systems analysed. The maximum deviation for both of the homopolymers may be attributed to the

more coiled nature of the homopolymers and comparatively poor solubility of these polymers in toluene. However, it is interesting to note that for most of the polymers in toluene, the k_{sb} values were close to 0.28. Thus it can be concluded that the relation $k_h + k_k \neq 0.5$ did not restrict application of the SB equation. The relation $k_h + k_k = 0.5$ was not found for most of the samples analysed (**Table 1.27**), but the present findings are similar to those reported elsewhere².

The viscometric molecular weight (M) values for all the polymers were calculated by measuring the $[\eta]$ values following the MHS equation and are tabulated in **Table 1.28**. For the DA polymers, the homopolymer has greater molecular weight value than the copolymers and comparison among the copolymers indicate that with increasing 1-decene concentration M value decreases, whereas the trend is reversed for the IOA polymers; that is, the homopolymer of IOA has lower molecular weight value than the copolymers and with increasing concentration of 1-decene content in the copolymer, molecular weight increases. Also, the IOA polymers have greater molecular weight values than the DA polymers.

1.3.4.4. Efficiency of the prepared compounds as pour point depressant

The base oil properties are tabulated in **Table 1.29**. The efficiency of the prepared polymers as pour point depressant was tested by using 0.1 wt % to 3 wt % polymer doped base oils and the experimental data are grouped in **Table 1.30** (in base oil, BO1) and **Table 1.31** (in base oil, BO2). A graphical presentation of the PP values of the polymers in these base oils is also shown in **Figure 1.47.1** and **Figure 1.47.2**, respectively. The data indicate that the prepared compounds may be considered as efficient pour point depressants. The results for most of the polymers indicate that their efficiency as PPD goes on increasing from 0.1 wt % to 0.5 wt %, beyond that there is a gradual decrease of their PPD performance. Thus it can be concluded that the pour point depression efficiency of

the investigated polymers, initially increases and then gradually decreases with the increasing additive concentration. However, in few cases the trend is found opposite (P1, P5 and P6 in **Table 1.31**). The case where the pour point depression efficiency increases by decreasing additive concentration may be explained by considering the solvation power of the oil¹⁴. The reduction in solvation power becomes more obvious when the concentration of the polymer increases. Again, increase of PPD efficiency with increase in additive concentration may be explained by the hydrodynamic volume of the polymer doped in oil¹⁵. Also, homopolymer of isooctyl acrylate acts as a better PPD than homopolymer of decyl acrylate.

1.3.4.5. Efficiency of the prepared compounds as viscosity modifier

Table 1.32 and **Table 1.33** present the viscosity index values of the prepared homo and copolymers in two base oils BO1 and BO2, respectively. A graphical presentation of the VI values of the polymers in these base oils is also shown in **Figure 1.48.1** and **Figure 1.48.2**, respectively. The data obtained clearly shows that the homopolymer of decyl acrylate is of having lower VI values than the respective copolymers and with the increase of 1-decene content in the feed, the VI is found to decrease. Again, homopolymer of isooctyl acrylate is of having higher VI values than the respective copolymers and with the increase of 1-decene content in the feed, the VI is found to increase. The data reveal that the VI values of the isooctyl acrylate polymers are higher in comparison to the respective decyl acrylate polymers in both the base oils. Again, with increasing concentration of the polymer solution, VI is found to increase in all cases. 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 molecule¹⁶. 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 in concentration of the polymer also leads to an increase in total volume of polymer coils in the oil solutions as was reported elsewhere^{17,18}. Consequently, a high concentration of polymer will impart a high viscosity index rather than a low concentration of the same polymer⁷.

1.3.5. Conclusion

Decyl acrylate polymers are thermally more stable than the isooctyl acrylate polymers. In general the PPD properties of the additives, doped in the base oils, initially increase and then gradually decrease with the increasing additive concentration in most of the polymer-oil blends. Homopolymer of decyl acrylate showed lower VM properties than the DA + 1-decene copolymers but homopolymer of isooctyl acrylate exhibit higher VM properties than the corresponding copolymers with 1-decene. Also, isooctyl acrylate polymers have higher VI values than the respective decyl acrylate polymers. Again, with increasing concentration of the polymer doped in oil, VM properties increase in all the cases. So, it can be concluded that the prepared polymers can effectively be used as multifunctional lube oil additives.

1.3.6. References

References are given in Bibliography under Chapter-III; Section B of Part-I (Page No. 192-194).

1.3.7. Tables and figures

Table 1.25. Composition of the monomers in the copolymers in terms of mole fraction determined by NMR and FT-IR spectroscopic method¹²

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	0.0146	0.0138	0.0143
P-3	0.0421	0.0411	0.0415
P-4	0.0717	0.0695	0.0702
P-5	0.0000	0.0000	0.0000
P-6	0.0130	0.0116	0.0121
P-7	0.0390	0.0364	0.0372
P-8	0.0647	0.0613	0.0622

P-1 = homopolymer of decyl acrylate; P-2 to P-4 = copolymer of decyl acrylate + different mole fractions of 1-decene; P-5 = homopolymer of isooctyl acrylate; P-6 to P-8 = copolymer of isooctyl acrylate + different mole fractions of 1-decene.

Table 1.26. 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	4.335	5.004	4.180	5.368	6.490	6.697	7.340
P-2	4.303	4.441	4.482	4.607	4.637	4.599	4.773
P-3	3.805	3.894	3.924	4.010	4.043	4.007	4.138
P-4	3.414	3.559	3.547	3.654	3.673	3.640	3.742

P-5	6.374	6.501	6.773	7.078	6.634	6.620	6.987
P-6	7.291	7.310	7.768	8.128	7.382	7.390	7.848
P-7	7.581	7.679	8.174	8.604	7.816	7.842	8.438
P-8	7.745	8.132	8.611	9.185	8.301	8.357	8.939

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 equations, respectively.

Table 1.27. Viscometric constants (k) obtained for all prepared homopolymer and copolymer samples

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	1.572	-0.134	2.079	0.462	1.438
P-2	0.533	0.095	0.374	0.289	0.628
P-3	0.505	0.098	0.375	0.298	0.603
P-4	0.678	0.036	0.484	0.369	0.714
P-5	0.481	0.107	0.308	0.221	0.588
P-6	0.429	0.115	0.272	0.194	0.544
P-7	0.461	0.110	0.279	0.194	0.571
P-8	0.559	0.101	0.301	0.199	0.660

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

Table 1.28. 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	16066	19583	15279	21574	28031	29271	33217
P-2	15902	16601	16822	17472	17630	17431	18347
P-3	13421	13856	14003	14428	14592	14414	15067
P-4	11557	12239	12182	12692	12783	12625	13115
P-5	27342	28096	29730	31593	28892	28808	31034
P-6	32911	33030	35918	38208	33479	33529	36429
P-7	34731	35351	38532	41356	36224	36390	40259
P-8	35771	38260	41402	45256	39361	39727	43593

Table 1.29. 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, $^{\circ}\text{C}$	-10	-8
Pour point, $^{\circ}\text{C}$	-3	-6

Table 1.30. Dependence of Pour Point (PP) on the concentration of additives in base oil (BO1)

Conc. (wt %)	PP ($^{\circ}$ C) in 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
0.1	-6	-8	-9	-12	-15	-12	-13	-14
0.25	-6	-8	-9	-12	-15	-12	-13	-14
0.5	-7	-9	-10	-13	-16	-13	-13	-14
1	-7	-8	-9	-12	-15	-12	-13	-14
2	-6	-8	-9	-12	-15	-12	-12	-13
3	-6	-6	-9	-11	-15	-9	-11	-12

Table 1.31. Dependence of Pour Point (PP) on the concentration of additives in base oil (BO2)

Conc. (wt %)	PP ($^{\circ}$ C) in 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
0.1	-8	-13	-13	-13	-16	-18	-17	-15
0.25	-9	-14	-14	-14	-17	-19	-19	-15
0.5	-8	-15	-14	-15	-17	-19	-18	-16
1	-8	-15	-14	-14	-16	-19	-18	-15
2	-9	-14	-13	-13	-17	-19	-17	-15
3	-10	-13	-12	-12	-18	-20	-16	-14

Table 1.32. Dependence of Viscosity Index (VI) on the concentration of additives in base oil (BO1)

Conc. (wt %)	VI in 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	90	92	88	86	91	86	89	98
2	92	95	90	88	103	87	93	102
3	94	99	93	90	119	89	97	108
4	95	101	95	94	125	91	103	111
5	99	105	101	97	130	97	107	114
6	102	109	103	100	136	103	112	120

Table 1.33. Dependence of Viscosity Index (VI) on the concentration of additives in base oil (BO2)

Conc. (wt %)	VI in 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	85	98	97	95	90	87	93	98
2	88	100	99	98	94	89	98	100
3	89	103	101	100	97	92	100	102
4	93	105	102	101	100	95	101	103
5	95	106	103	102	112	97	104	106
6	98	108	106	104	124	100	106	111

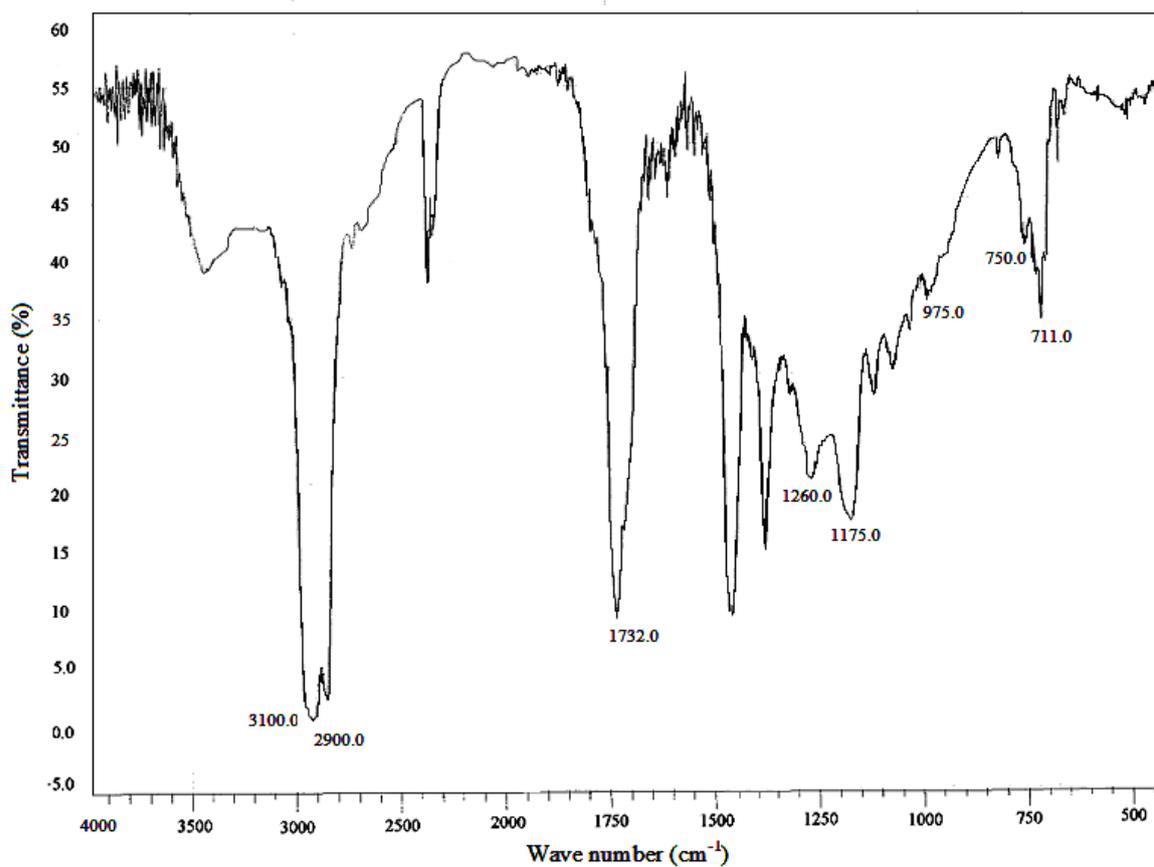


Figure 1.33. FT-IR spectra of poly (decyl acrylate)

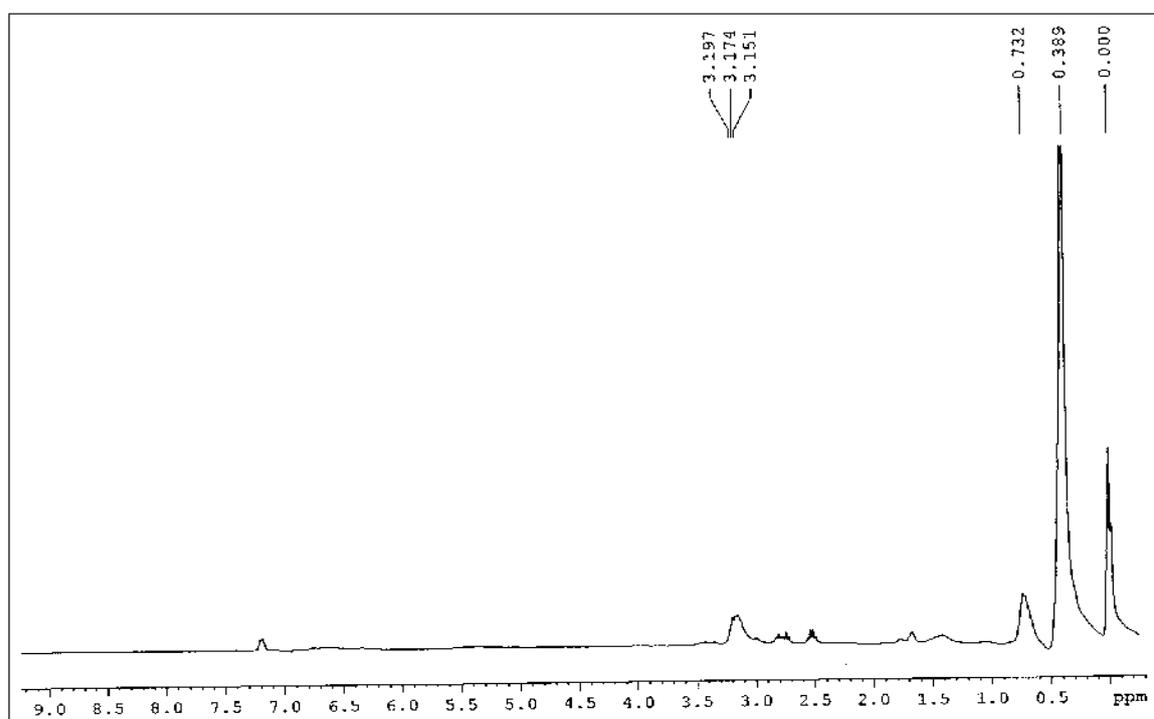


Figure 1.34. ¹H- NMR spectra of poly (decyl acrylate)

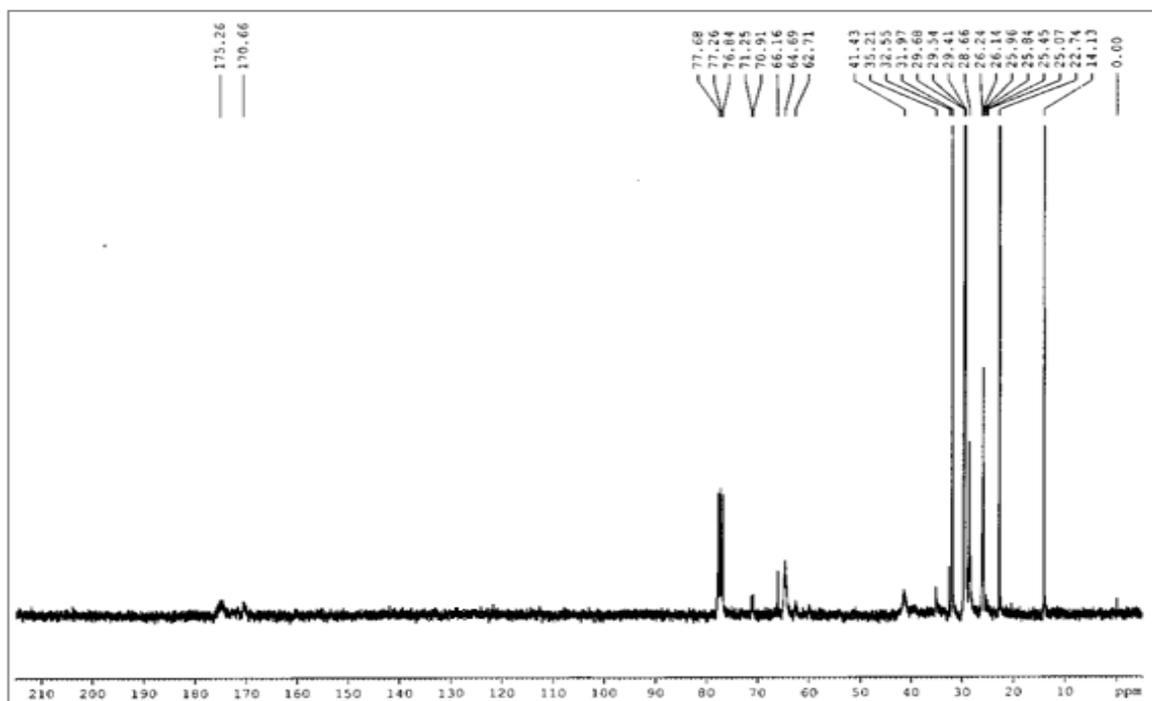


Figure 1.35. ^{13}C - NMR spectra of poly (decyl acrylate)

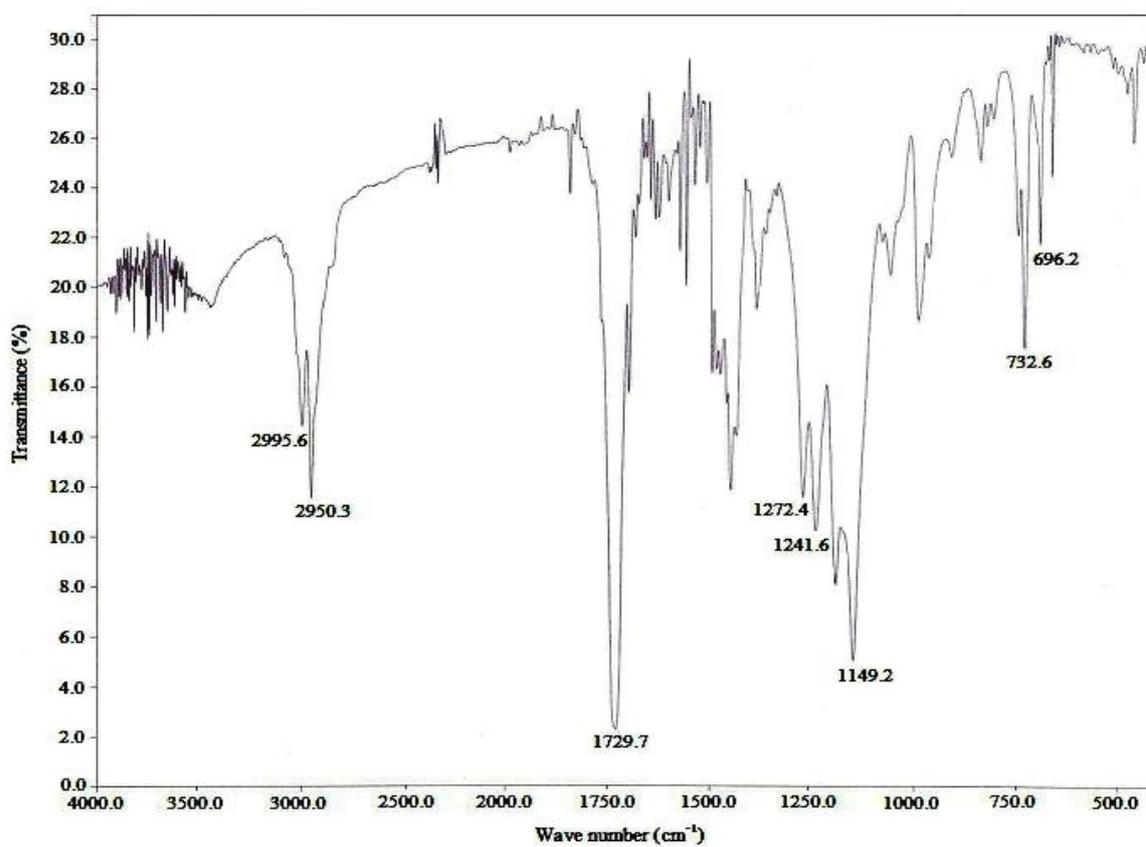


Figure 1.36. FT-IR spectra of a representative copolymer of decyl acrylate with 1-decene

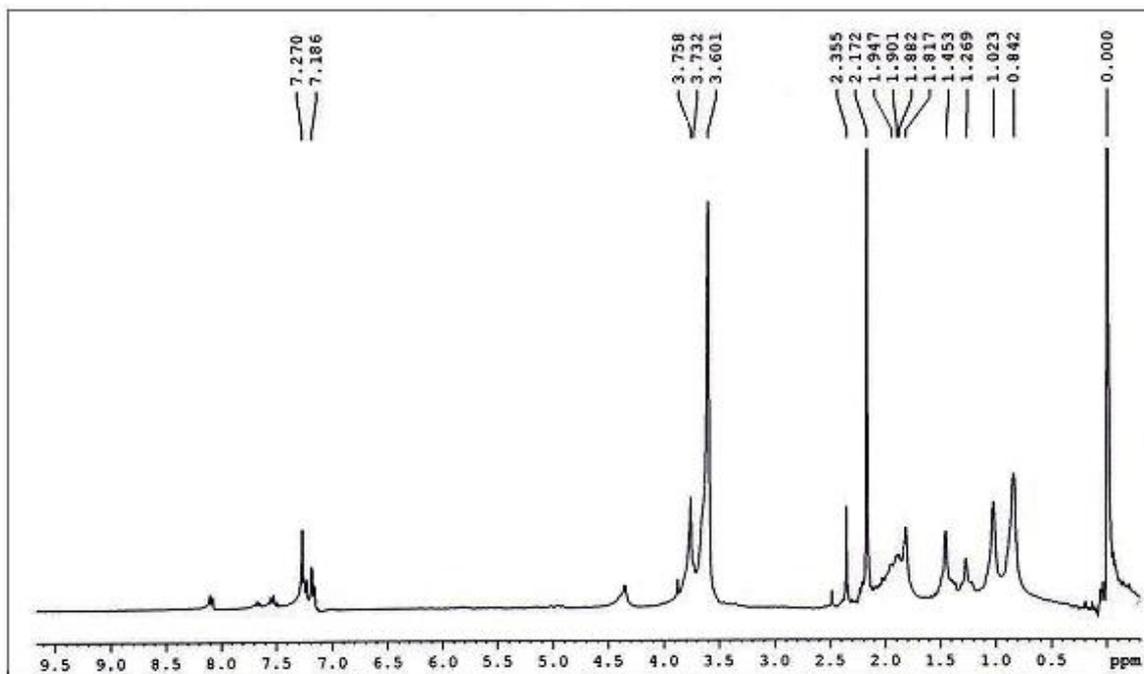


Figure 1.37. ^1H - NMR spectra of a representative copolymer of decyl acrylate with 1-decene

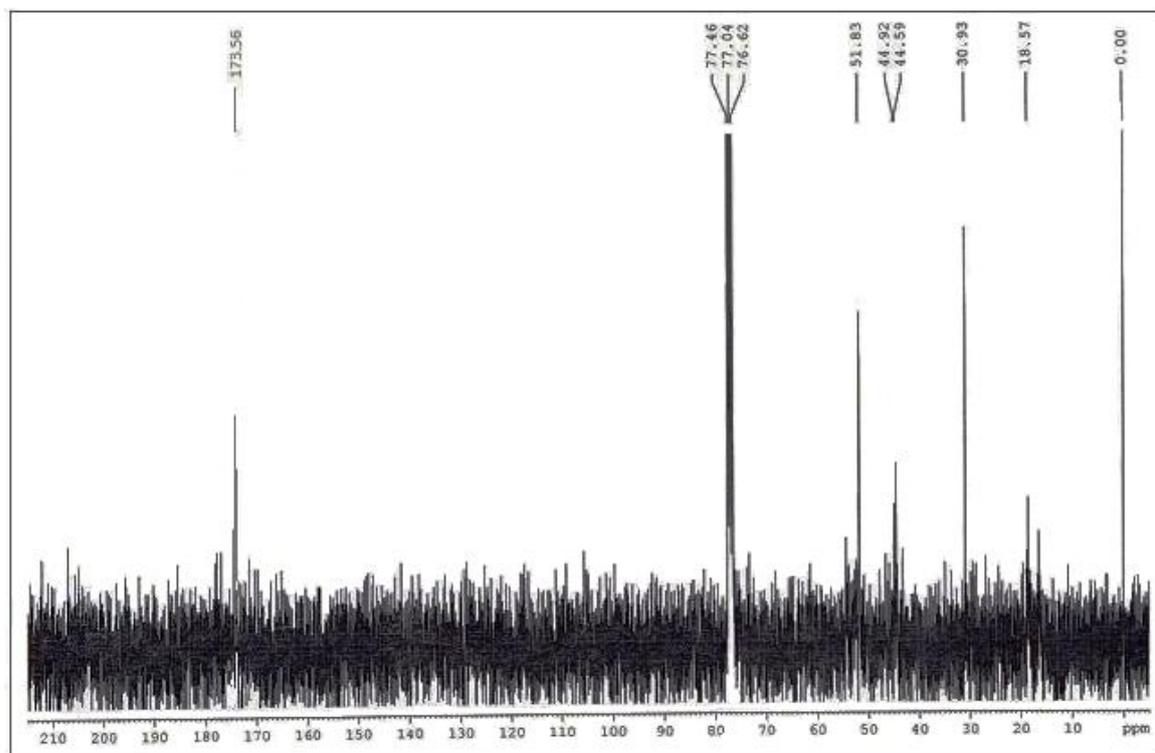


Figure 1.38. ^{13}C - NMR spectra of a representative copolymer of decyl acrylate with 1-decene

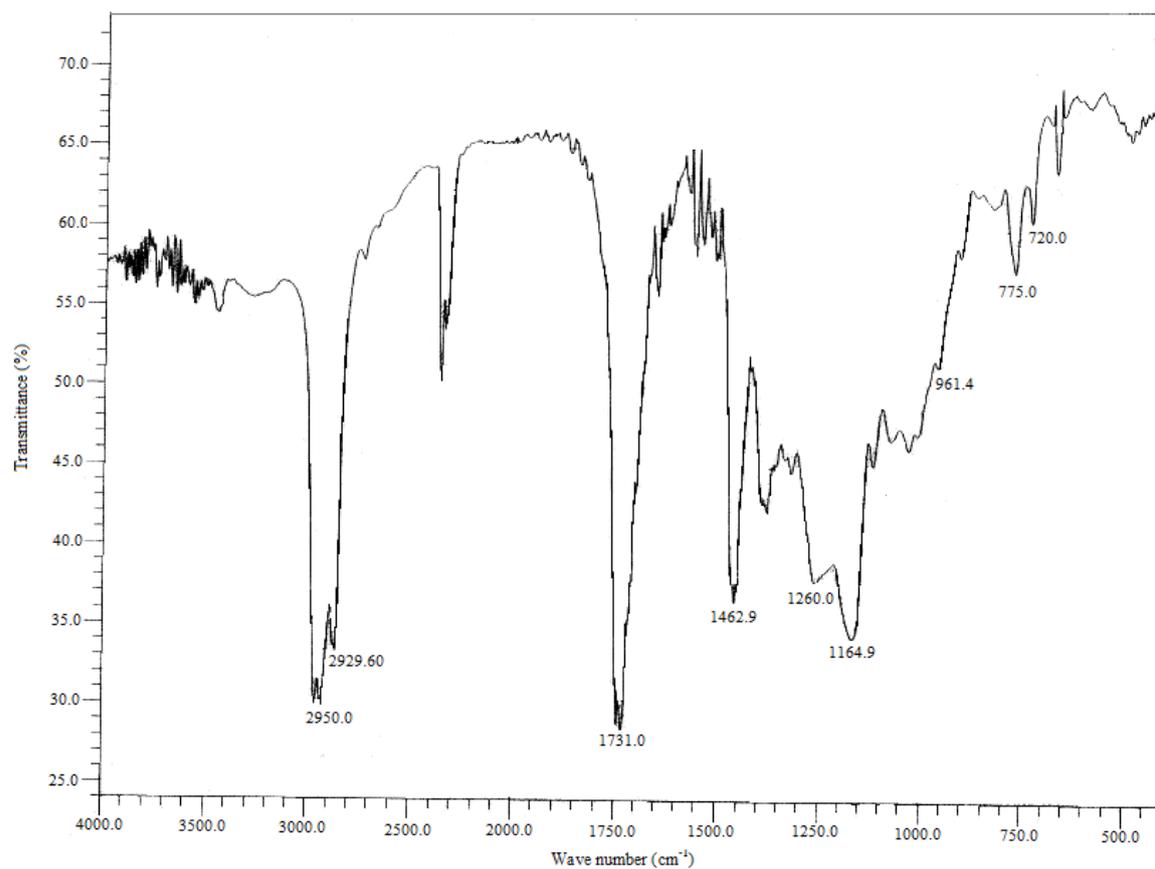


Figure 1.39. FT-IR spectra of poly (isooctyl acrylate)

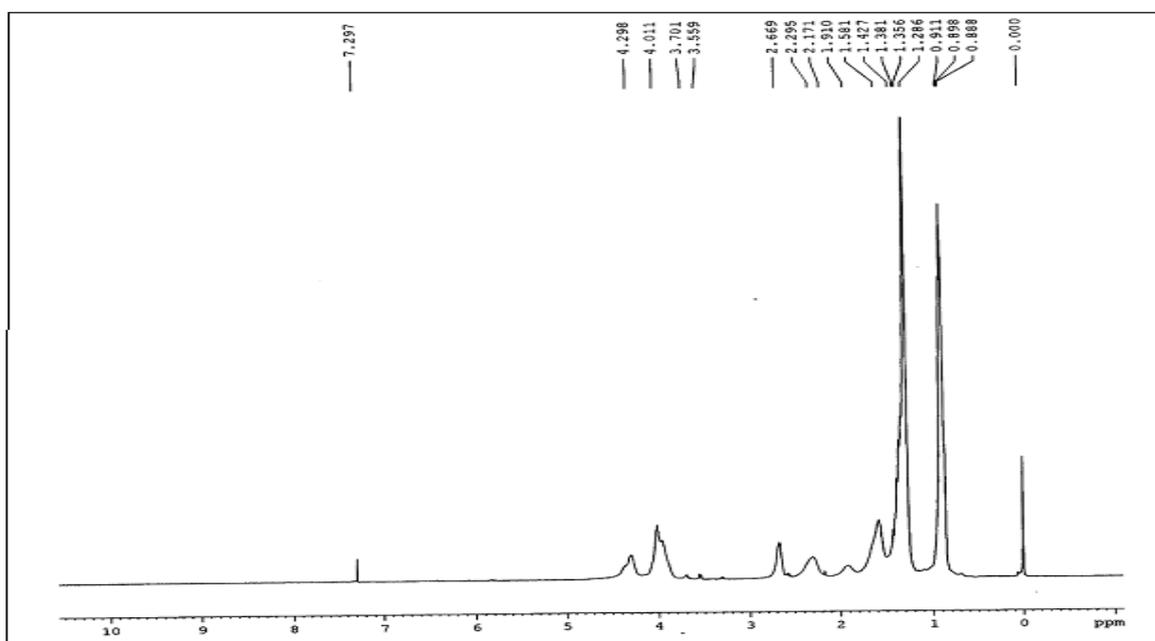


Figure 1.40. ¹H-NMR spectra of poly (isooctyl acrylate)

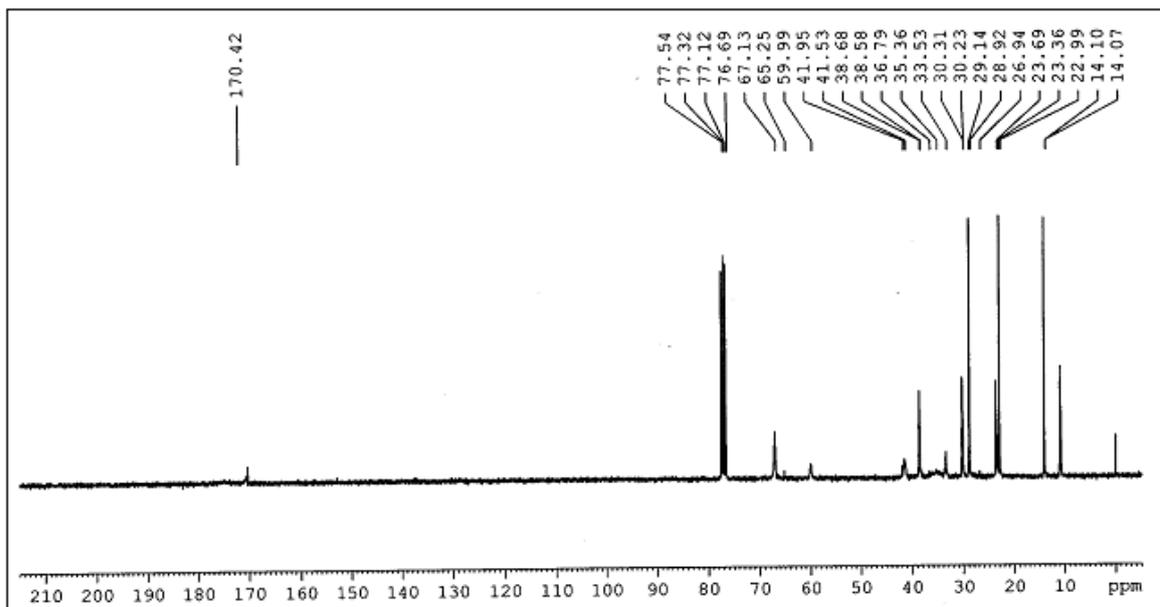


Figure 1.41. ^{13}C -NMR spectra of poly (isooctyl acrylate)

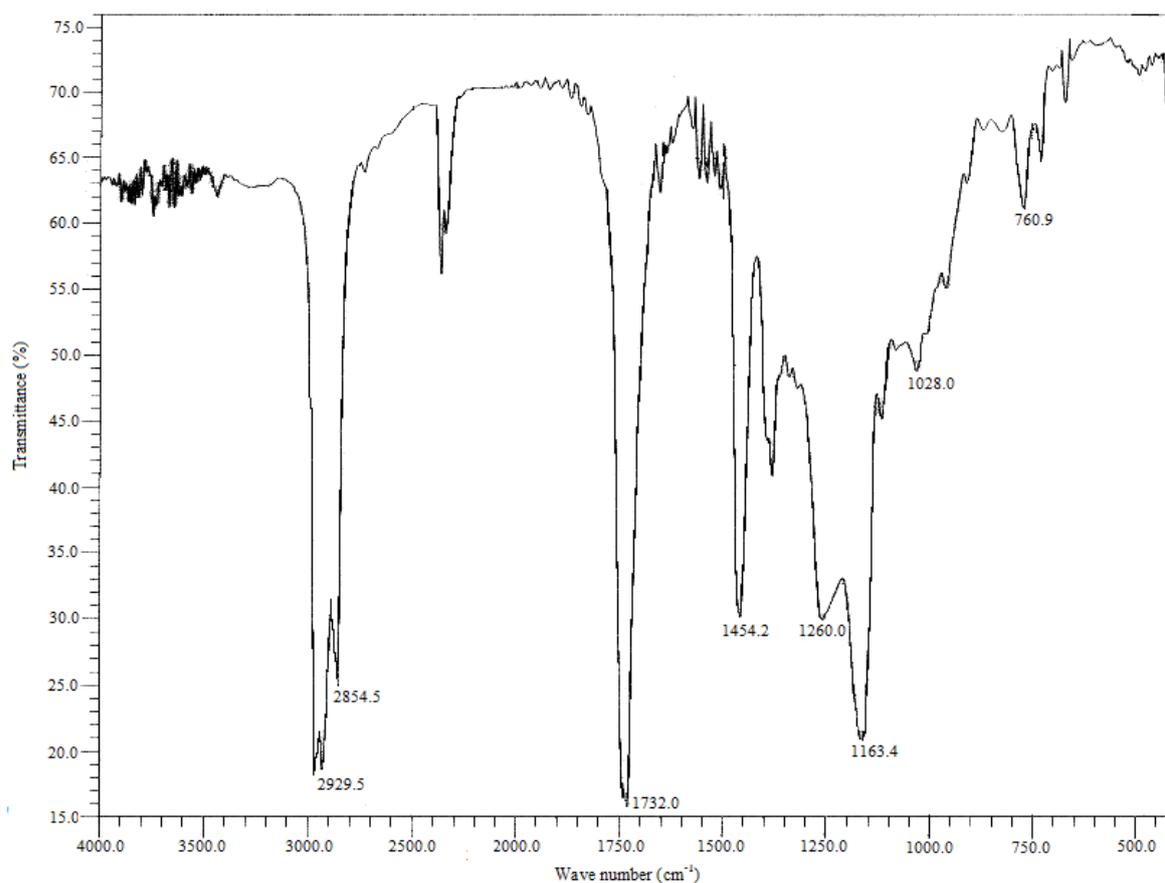


Figure 1.42. FT-IR spectra of a representative copolymer of isooctyl acrylate with 1-decene

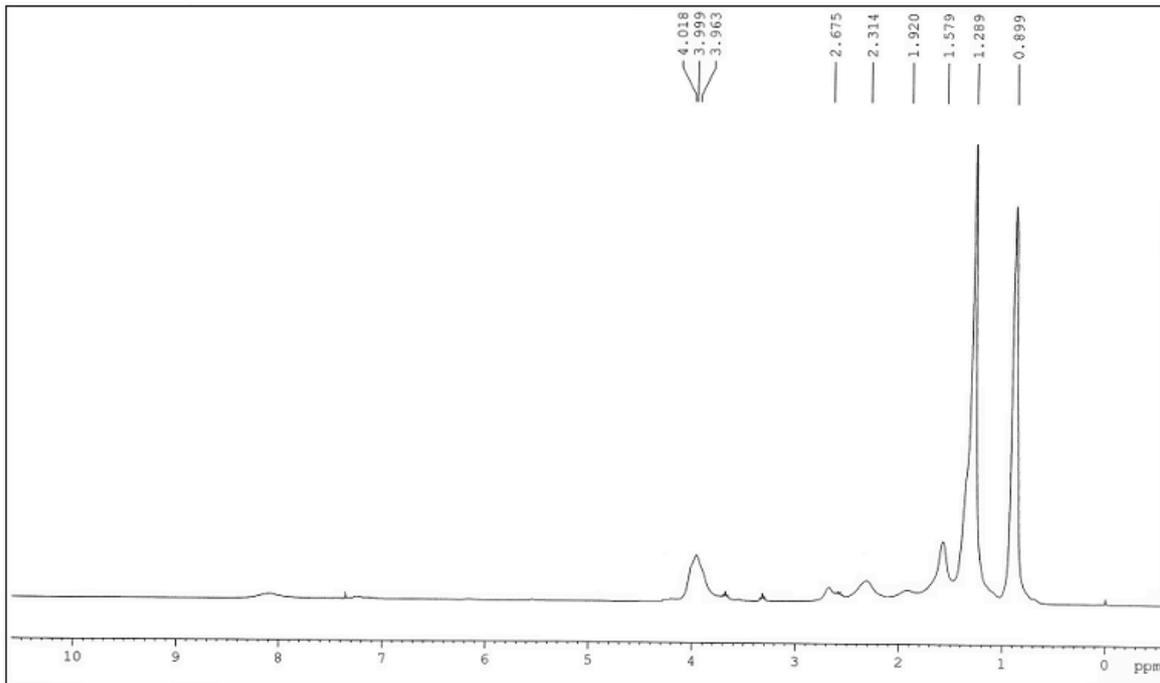


Figure 1.43. ^1H -NMR spectra of a representative copolymer of isooctyl acrylate with 1-decene

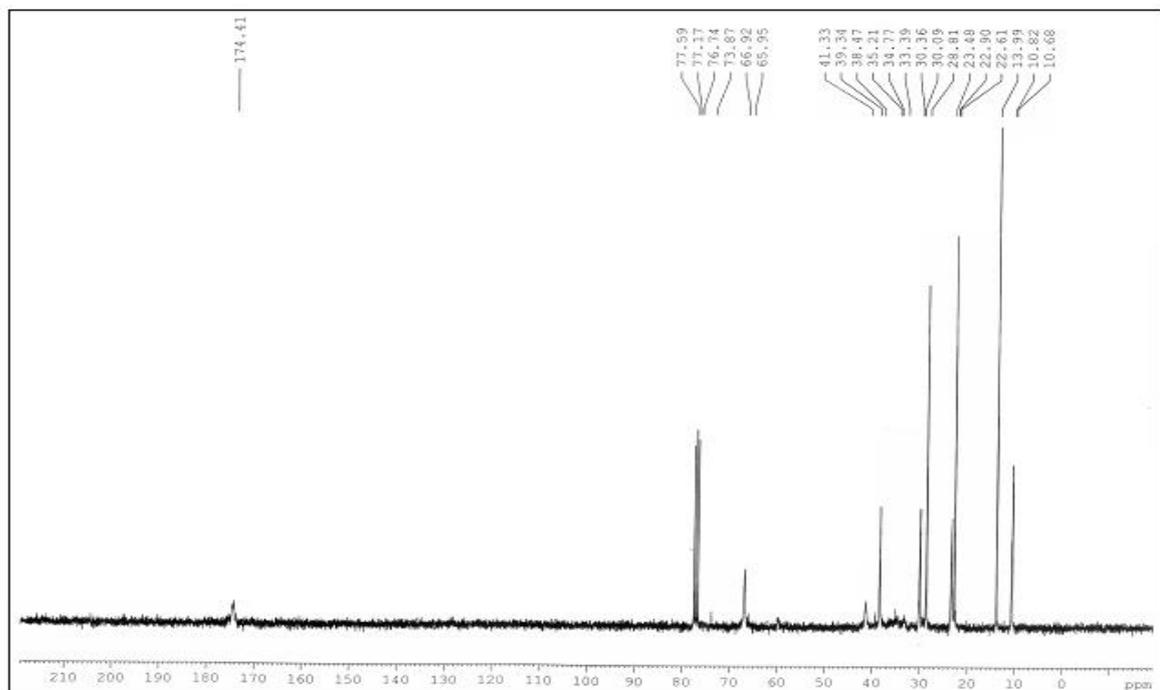


Figure 1.44. ^{13}C -NMR spectra of a representative copolymer of isooctyl acrylate with 1-decene

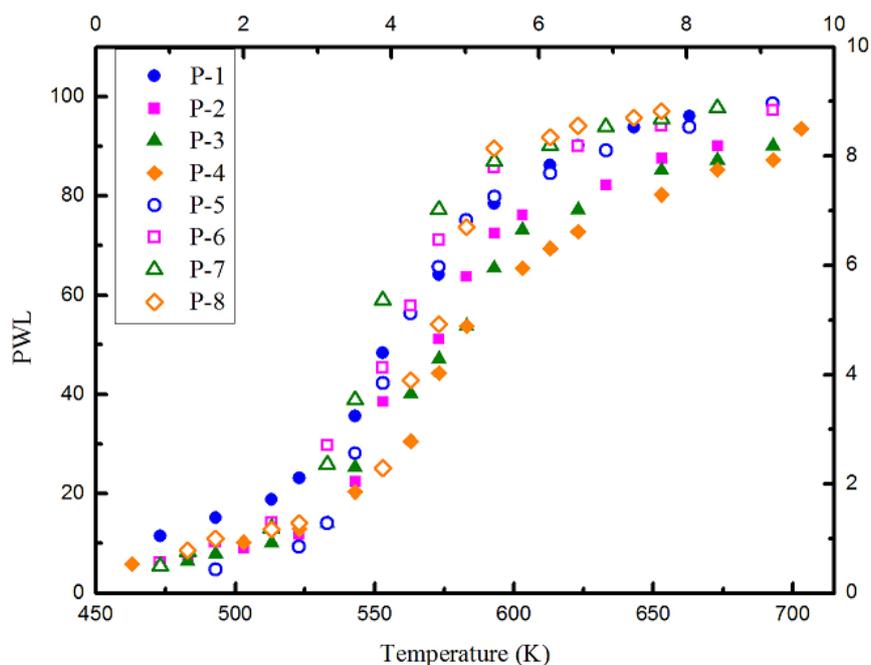


Figure 1.45. Plot of PWL vs. Temperature. PWL is percent weight loss and temperature is measured in Kelvin

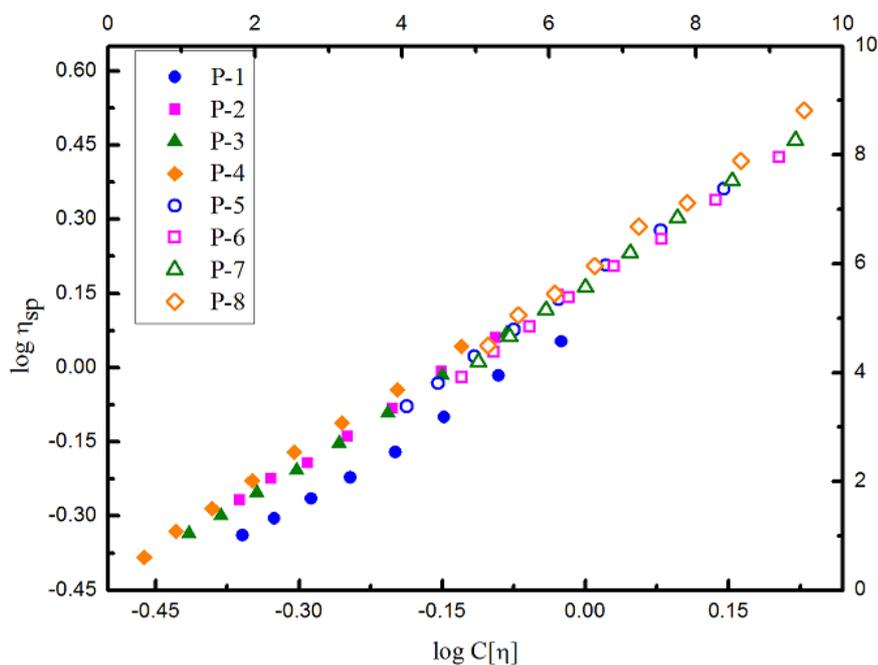


Figure 1.46. Plot of $\log \eta_{sp}$ vs. $\log C[\eta]$, where η_{sp} is the specific viscosity of the polymer solution in toluene, C is the concentration of the solution in $\text{g}\cdot\text{cm}^{-3}$, and $[\eta]$ is the intrinsic viscosity of the polymer solution in toluene obtained by using Huggins equation

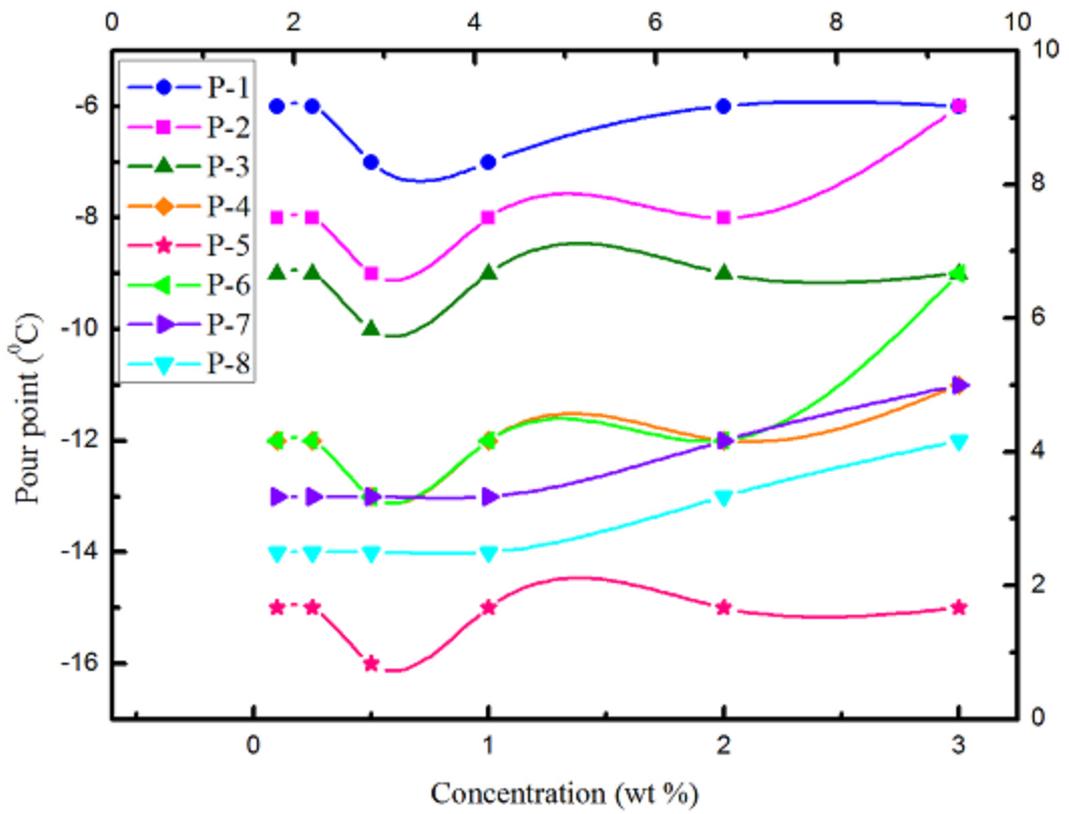


Figure 1.47.1. Plot of pour point vs. additive concentration in BO1

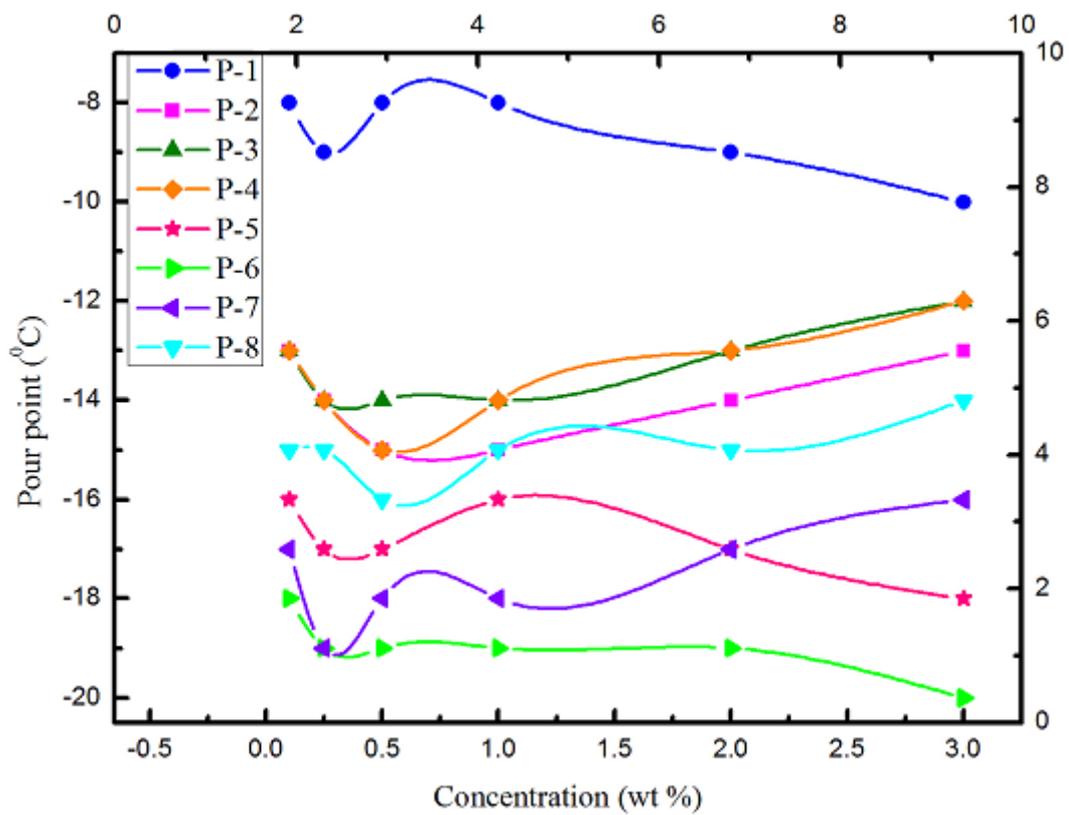


Figure 1.47.2. Plot of pour point vs. additive concentration in BO2

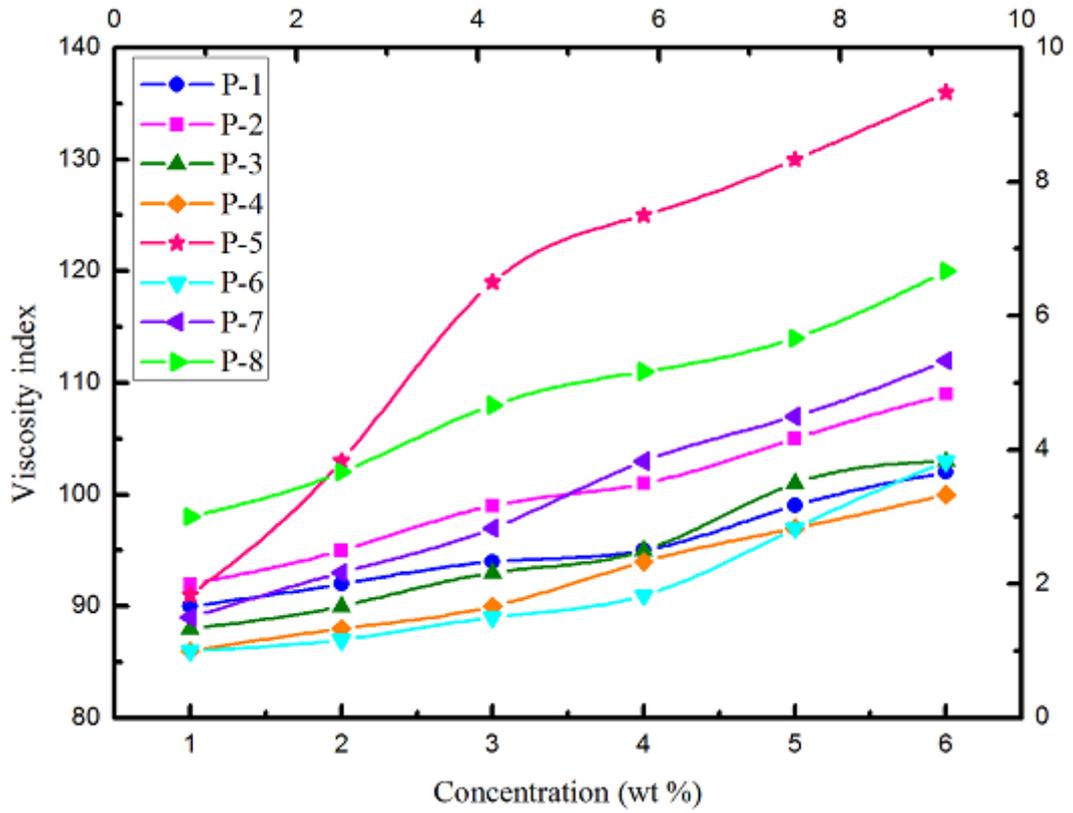


Figure 1.48.1. Plot of viscosity index vs. additive concentration in BO1

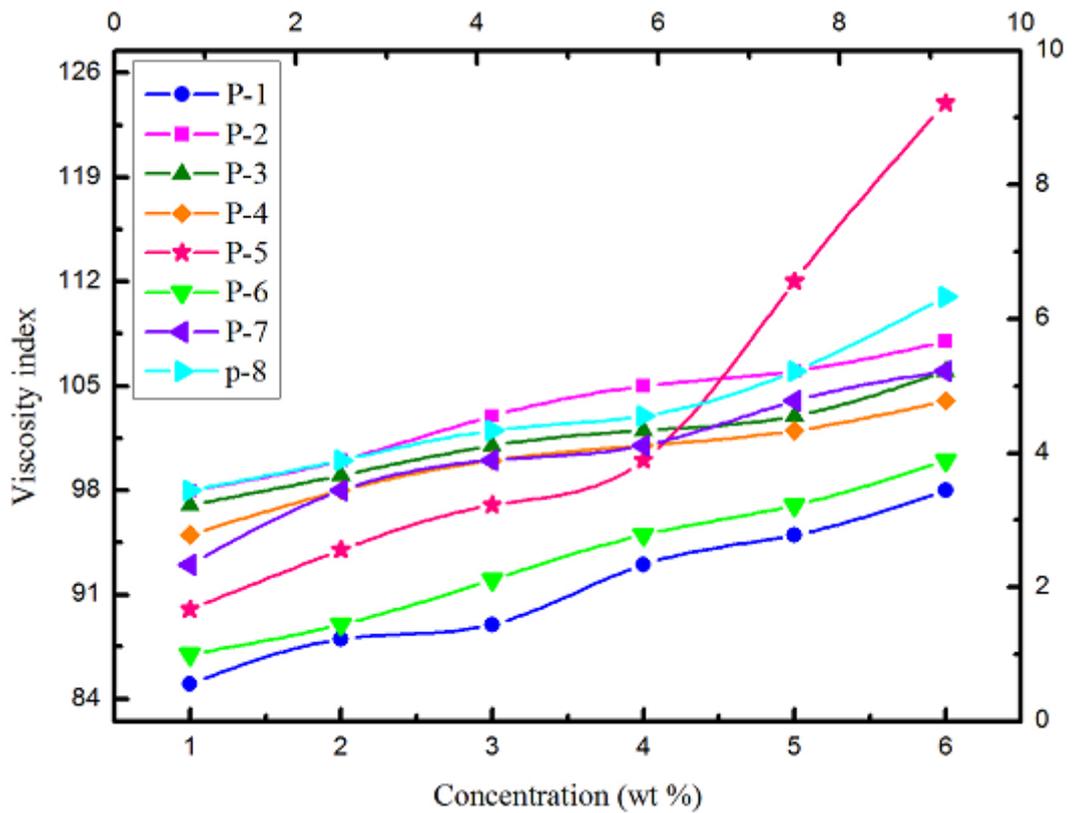


Figure 1.48.2. Plot of viscosity index vs. additive concentration in BO2