

Chapter IV

Synthesis and a Comparative Study on Their Performances as Multifunctional Lube Oil Additives of Behenyl and Isodecyl Acrylate Based Polymers

1.4.1 Introduction

Modern lubricants consist of the base oil as a major constituent along with some additives required for providing some specific characteristics or sometimes enhancing the existing properties [1]. Antioxidant, detergents, dispersants, corrosion inhibitors, viscosity index improvers (VIIs), pour point depressants (PPDs), anti-wear and antifriction additives are some of the important types of these additives. Out of these, VIIs and PPDs are added in large quantities because the viscosity and fluidity variation with temperature determines the applicability of a lubricant formulation in low and high temperature operational conditions with effective and efficient performance [2]. Utilization of polymeric additives as chemical treatment is considered the most valuable and economic method to inhibit wax precipitation at low temperatures. Basically, these polymeric wax inhibitors consist of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms in addition to a polar segment typically acrylates or acetates. The polar head group is responsible for the modification of wax crystals morphology and the non-polar long hydrocarbon chain renders the interaction between the additives and paraffin [3], [4]. A considerable number of polymeric additives have been created and utilized as PPDs to modify the growing pattern of wax crystals [5]-[7]. Normally, a linear polymer of alkyl methacrylate or acrylate having a pendent alkyl side chain of specific length is used as pour point depressants (PPDs) or flow improvers (FIs) [8]-[11]. PPDs do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates, rather they co-crystallize along with the wax species present in the oil at lower temperature and modify the growing pattern of wax crystal structures. Additionally, the PPD backbone kept the wax crystals apart from each other and because of this steric hindrance, the wax crystals are no longer able to form 3-D matrix which entraps the oil and inhibits

the flow at a lower temperature. Recent studies on the structure–reactivity relationship for the polymers of higher alkyl acrylates and methacrylates [12], [13], promoted the research towards improving processes for the polymerization of *n*-alkyl acrylates with narrow molecular weight distribution (MWD) [14]. Some commercially available properly designed polymeric flow improvers are poly (ethylene–co–vinyl acetate) (EVA) [15], poly (ethylene-butene) (PEB) [16], polymethacrylates [17], and modified maleic anhydride copolymers [4]. Recently Chen et al. reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax crystal precipitation and improve low-temperature fluidity [18]. Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups [19]. Again, some investigations indicated that molecular weight (MW) and molecular weight distribution (MWD) should also play an important role in the performance as a flow improver [20]. Homopolymers of alkyl methacrylates and acrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour point depressants and flow improvers in high waxy crude oils, lubricating oils, and fuel oils. These types of polymer contain an alkyl length of more than 14 carbons. Behenyl acrylate (BA) consists of a mixture of C₂₂, C₂₀, and C₁₈ acrylates and is used extensively in the preparation of these additives [13]. Recently development of the novel additives based on copolymers containing *n*-alkyl acrylates has gained huge attention due to their multifunctional nature and the fact that the comb-shaped polymeric additives can be more effective as PPD in lube oil by providing different nucleation sites for the precipitation of wax [21]. Dao in 2017 has reported that copolymers formed by stearyl methacrylate and behenyl acrylate with vinyl acetate using AIBN as initiator give high efficiency to reduce pour point temperature [22]. R.

K. Singh et al. have reported the successful synthesis, characterization, and performance evaluation of two homopolymers of C₁₈ alkyl acrylate and N,N-dimethylacrylamide and their three copolymers as synthesized by using 1:1, 1:2, and 2:1 monomer ratios as VII and PPDs in polyol base oil taking the homopolymers as reference [2]. B. Subrahmanyam et al. had presented a thorough study on the effect of initiator concentration and monomer concentration on the molecular weight and molecular weight distribution in behenyl acrylate polymerization. They found that at a higher concentration of initiator and monomer, the branching reactions led to gel formation in behenyl acrylate polymerization. They reported that viscosity of the polymerizing medium also influenced the high conversion polymerization in alkyl acrylate polymerization [13].

Thus growing demand for the requirement of high performance characteristics and increasing environment related concerns have forced the researchers to develop new multifunctional polymeric additives so that maximum activity can be achieved with a minimum dosage. In this present context, we have prepared homopolymers of behenyl acrylate and isodecyl acrylate and further their copolymers with 1-Decene at variable percentage. All the prepared polymers have been characterized by FT-IR and NMR spectroscopy. Their thermal stability and molecular weight were determined and then they were evaluated as VII and PPD in lube oil.

1.4.2 Experimental section

1.4.2.1 Materials

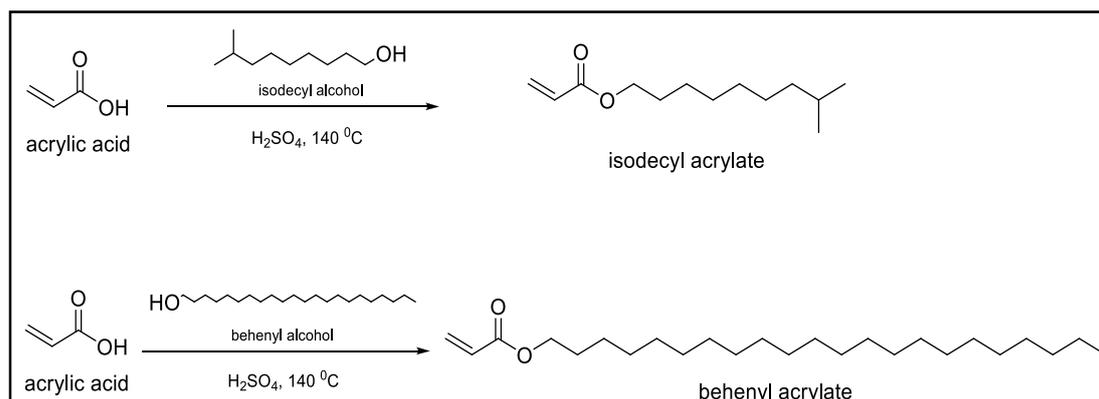
Isodecyl alcohol (98%, SRL Pvt. Ltd.), behenyl alcohol (Merck Specialties Pvt. Ltd.), 1-decene (95%, Acros organics), and acrylic acid (Merck Specialties Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Chem Ltd.), and Methanol (98%, Thomas Baker Pvt. Ltd.) were

used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H_2SO_4 (98%, Merck Specialties Pvt. Ltd.) was used as received. The properties of the used base oils are tabulated in **Table 1.4.1**.

1.4.2.2 Preparation of esters

The ester (Isodecyl acrylate, IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isodecyl alcohol. The reactants were mixed with toluene along with few drops of concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as a polymerization inhibitor in a resin kettle, and heated gradually from room temperature to 140°C using a well-controlled thermostat under a slow stream of deoxygenated nitrogen. The extent of esterification was monitored by the amount of liberated water. Another ester (Behenyl acrylate, BA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of behenyl alcohol following the same procedure.

Scheme 1.4.1 Reaction for the preparation of isodecyl acrylate and behenyl acrylate



1.4.2.3 Purification of prepared esters

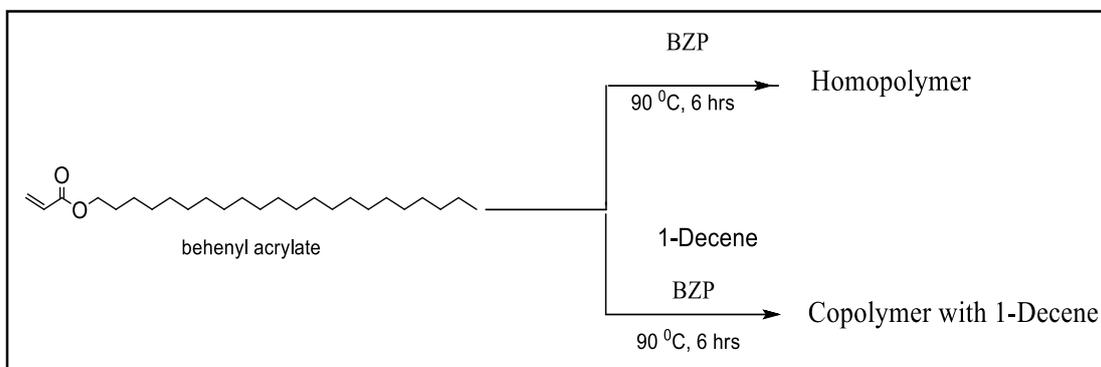
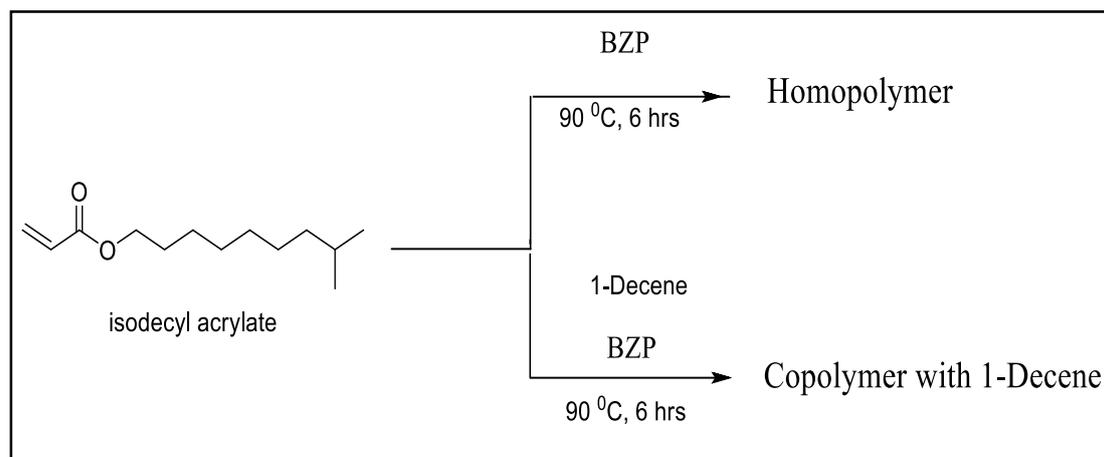
The prepared esters were refluxed for 3 hours with a suitable amount of charcoal and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separatory funnel several times to ensure the complete removal of untreated acid. The ester was

then washed repeatedly with distilled water to remove any traces of sodium hydroxide. The purified ester was then left overnight on calcium chloride. It was then removed by distillation under reduced pressure. Then the ester was ready to be used in the polymerization process.

1.4.2.4 Preparation of the polymers

The polymers (homo and copolymers) were prepared by free radical polymerization at different percentage compositions of monomers (**Table 1.4.2**) in presence of BZP as an initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of the polymer was carried out by the procedure as reported in our earlier publication [23].

Scheme 1.4.2 Reaction for the preparation of homopolymer of isodecyl and behenyl acrylate and copolymer with 1-Decene



1.4.3 Measurements

1.4.3.1 Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35°C temperature at a flow rate of 1mL/min. The values are given in **Table 1.4.2**.

1.4.3.2 Spectroscopic Measurements

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

1.4.3.3 Performance evaluation as pour point depressants in base oil

The effect of additive concentration on the pour point of two base oils (BO1 and BO2) was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for each of the prepared polymers. According to the ASTM D 97-09 method, the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India) given in **Tables 1.4.3 & Table 1.4.4**.

1.4.3.4 Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the base oils containing the polymers determined at 40°C and 100°C. Different concentrations of the polymers in the base oil (% w/w) from 1% to 6% was used to study the effect of concentration on VI of the additive-doped lube oil. All of the experimental data given in **Table 1.4.5 & Table 1.4.6** were noted by taking an average of three experimental results under identical conditions in each case.

1.4.3.5 Determination of thermogravimetric analysis (TGA) data

TGA data (Table 1.4.7) was measured on Mettler TA-3000 system, at a heating rate of 10K min^{-1} . The variation of temperature within the range was $\pm 10^{\circ}\text{C}$ during the experiment. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.5\%$.

1.4.4 Results and discussion

1.4.4.1 Molecular Weight Analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w), and polydispersity index data (PDI) of the prepared polymers are given in Table 1.4.2.

Analyzing the experimental data, it was found that the homopolymer of behenyl acrylate (P_1) had a higher number average and weight average molecular weight than the others. Again in terms of polydispersity index (PDI), this polymer is less polydispersed which indicates better uniformity. With an increasing concentration of 1-Decene, the polymers (P_2 , P_3 & P_4) exhibited a higher polydispersity index. Among the polymers of IDA (P_5 to

P_8), the copolymer of 95% IDA and 5% 1-Decene (P_8) showed the highest number average and weight average molecular weight and lowest polydispersity index.

1.4.4.2 Spectroscopic analysis

In FT-IR spectroscopy almost all the polymers being acrylate produced similar spectra. Peaks around $1733\text{--}1738\text{ cm}^{-1}$ clearly indicated the presence of the ester carbonyl group in each case. Absence of peaks above 3000 cm^{-1} indicates the absence of C=C unsaturation which supports complete polymerization in all the cases. In ^1H NMR spectra, peaks appeared in the range of $3.93\text{--}4.32\text{ ppm}$ clearly indicated the presence of $-\text{OCH}_2-$ protons. Here again, the absence of peaks around 6 ppm indicated

the absence of C=C unsaturation and hence supported total polymerization. In ^{13}C NMR spectra, peaks at 170.34–177.8 ppm indicated the presence of ester carbonyl carbon. The peaks at 59.78–65.99 ppm corresponded to the $-\text{OCH}_2-$ carbons, peaks ranging from 13.95–45.22 ppm for all other sp^3 carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization.

1.4.4.3 Performance evaluation as pour point depressant

The pour point data are given in **Tables 1.4.3** & **Table 1.4.4** clearly prove that the prepared polymers are good pour point depressants for both the base oils except the homopolymer of behenyl acrylate (P_1) which exhibited very little depletion in pour point in both cases (BO1 & BO2). The very high molecular weight of this polymer might be the reason for its low solubility in the base oils which discards its effectiveness as PPD. But the copolymers of behenyl acrylate and 1-Decene have been proved to be effective PPDs in both the base oils. Comparing all the pour point data, it can be said that the homopolymer of IDA (P_5) and its copolymers (P_6 to P_8) are better pour point depressants and among them all, P_5 polymer gave the best result. Branching in the alkyl chain of these polymers might be the reason behind this observation. Almost in all the cases the pour point depression curves get flattened above 4% concentration since at higher concentration the polymers suffer lower solubility and hence their effectiveness as PPD also diminishes.

1.4.4.4 Performance evaluation as viscosity index improver

Solubility of the polymer, its molecular weight, and composition play an important role in its performance as a viscosity index improver [24]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases the solubility of the polymer increases and it unfolds itself to an open configuration of higher volume and

hence overall higher viscosity is exhibited at higher temperature by polymer-doped base oil. This activity offsets the normal trend of a decrease in viscosity with an increase in temperature [25]. It is seen from **Tables 1.4.5 & Table 1.4.6** that all the prepared polymers are effective viscosity index improvers for both the base oils. Here again, due to very high molecular weight and hence lower solubility, the homopolymer of behenyl acrylate (P₁) is least effective as VII among all. On the other hand, the homopolymer of IDA (P₅) has been proved to be the best viscosity index improver in both the base oils. The rests are almost comparable VIIs. With increasing concentration of the polymer in the base oil, the total volume of the polymer micelle increases, and hence the viscosity index data also increases [26].

1.4.4.5 Analysis of TGA data

The thermal studies confirmed that all the prepared polymers are thermally stable (**Table 1.4.7**). Lower the percent weight loss (PWL) higher will be the thermal stability. Therefore, among the prepared polymers, the copolymer of behenyl acrylate and 1% 1-Decene (P₂) is thermally most stable while the homopolymer of behenyl acrylate (P₁) is thermally least stable. Higher thermal stability of the additives indicated their suitability as lubricant additives.

1.4.5 Conclusion

The above study may be summarized as follows. All the prepared polymers have been evaluated as effective multifunctional and thermally stable additives for lube oil. In terms of molecular weight, the homopolymer of behenyl acrylate exhibited the highest number average and weight average molecular weight. Further, the PDI value accounts for better uniformity in this polymer than others. But this polymer is very much less effective as PPD as well as VII which may be attributed to its solubility problem. All the other polymers have been proved to be good flow improvers in both the base oils.

Especially the homopolymer of isodecyl acrylate resulted the highest depression in pour point in both cases. This polymer was also proved to be the best VII among all the prepared ones.

1.4.6 References

References are given in *BIBLIOGRAPHY* under “Chapter IV of Part I” (Page No. 140-143).

1.4.7 Tables and Figures

Table 1.4.1: Base Oil (BO) Properties

<i>Physical Property</i>	<i>BO1</i>	<i>BO2</i>
Density (gcm^{-3} at 40 °C)	0.837	0.868
Viscosity at 40 °C in cSt	7.136	23.392
Viscosity at 100 °C in cSt	1.856	3.915
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8
<i>BO1, BO2 collected from IOCL, Dhakuria, West Bengal</i>		

Table 1.4.2: Weight percentage (%) composition, M_n , M_w , and PDI values of polymers (P₁ to P₈)

<i>Polymer</i>	<i>% of BA</i>	<i>% of IDA</i>	<i>% of 1-D</i>	M_n	M_w	<i>PDI</i>
P ₁	100	–	–	22574	333217	1.50
P ₂	99	–	1	117472	218347	1.86
P ₃	97	–	3	114428	215067	1.88
P ₄	95	–	5	112692	213115	1.89
P ₅	–	100	–	131593	231034	1.76
P ₆	–	99	1	138208	236429	1.71
P ₇	–	97	3	141356	240259	1.70
P ₈	–	95	5	145256	243593	1.68
<i>BA = Behenyl acrylate, IDA = Isodecyl acrylate, 1-D = 1-Decene, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index</i>						

Table 1.4.3: Pour point (°C) data with respect to the different concentrations of the additives in BO1 and its graphical representation

Additive	1%	2%	3%	4%	5%	6%
P ₁	-4.9	-5.4	-6.0	-6.0	-5.8	-5.1
P ₂	-6.0	-6.5	-7.2	-7.8	-8.1	-8.0
P ₃	-8.1	-8.6	-9.2	-9.4	-9.4	-9.1
P ₄	-10.9	-11.2	-11.6	-12.1	-12.0	-12.0
P ₅	-14.0	-14.6	-15.0	-15.2	-15.1	-15.0
P ₆	-9.4	-10.8	-11.6	-12.4	-12.3	-12.3
P ₇	-11.1	-11.8	-12.2	-12.9	-12.9	-12.4
P ₈	-11.9	-12.5	-13.4	-13.6	-13.6	-13.3

Concⁿ represents concentration in % w/w

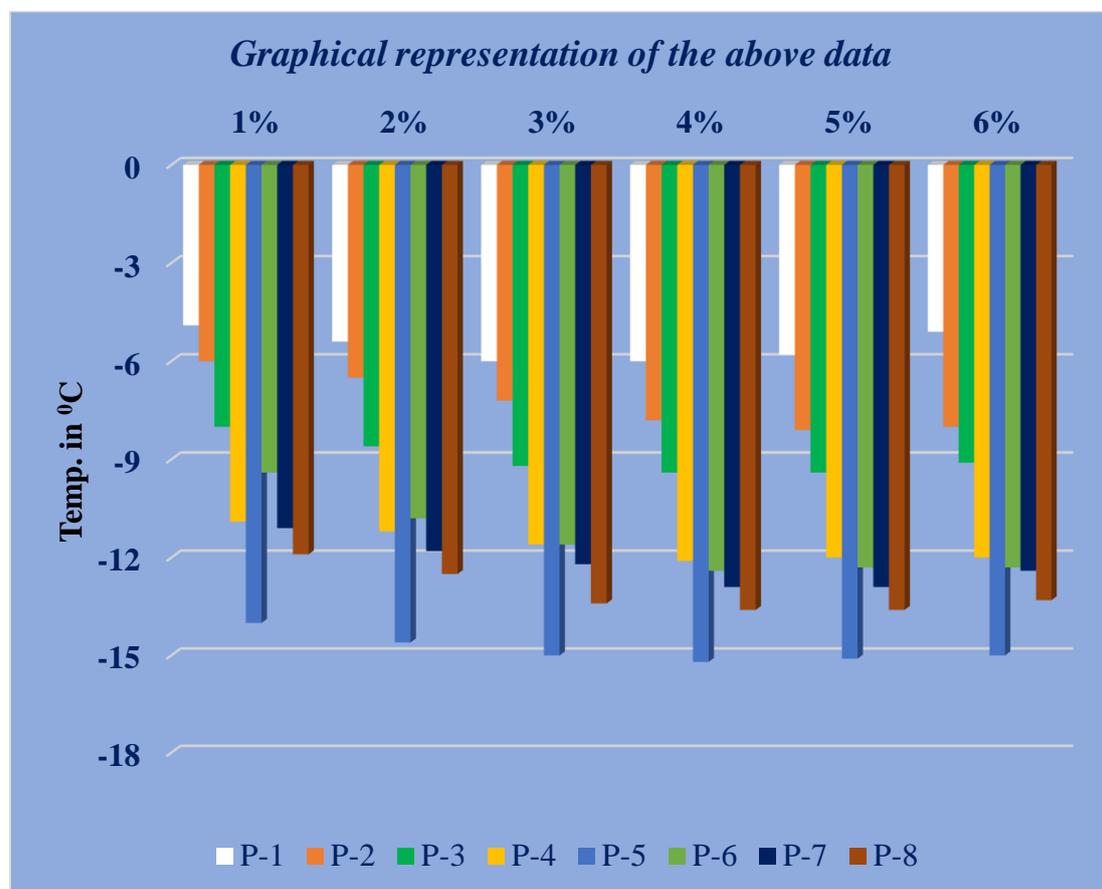


Table 1.4.4: Pour point (°C) data with respect to the different concentrations of the additives in BO2 and its graphical representation

<i>Additive</i>	<i>1%</i>	<i>2%</i>	<i>3%</i>	<i>4%</i>	<i>5%</i>	<i>6%</i>
P₁	-8.4	-9.0	-9.4	-9.8	-9.8	-9.6
P₂	-12.5	-13.1	-13.5	-14.1	-14.6	-14.6
P₃	-12.4	-12.9	-13.2	-13.8	13.8	-13.7
P₄	-12.0	-12.6	-13.2	-13.8	-14.2	-14.2
P₅	-18.0	-18.5	-19.4	-19.8	-20.0	-20.0
P₆	-15.8	-16.4	-17.0	-17.3	-17.7	-17.7
P₇	-16.1	-16.8	-17.2	-17.6	-17.9	-17.4
P₈	-14.0	-14.3	-14.8	-15.1	-15.4	-15.0

Concⁿ represents concentration in % w/w

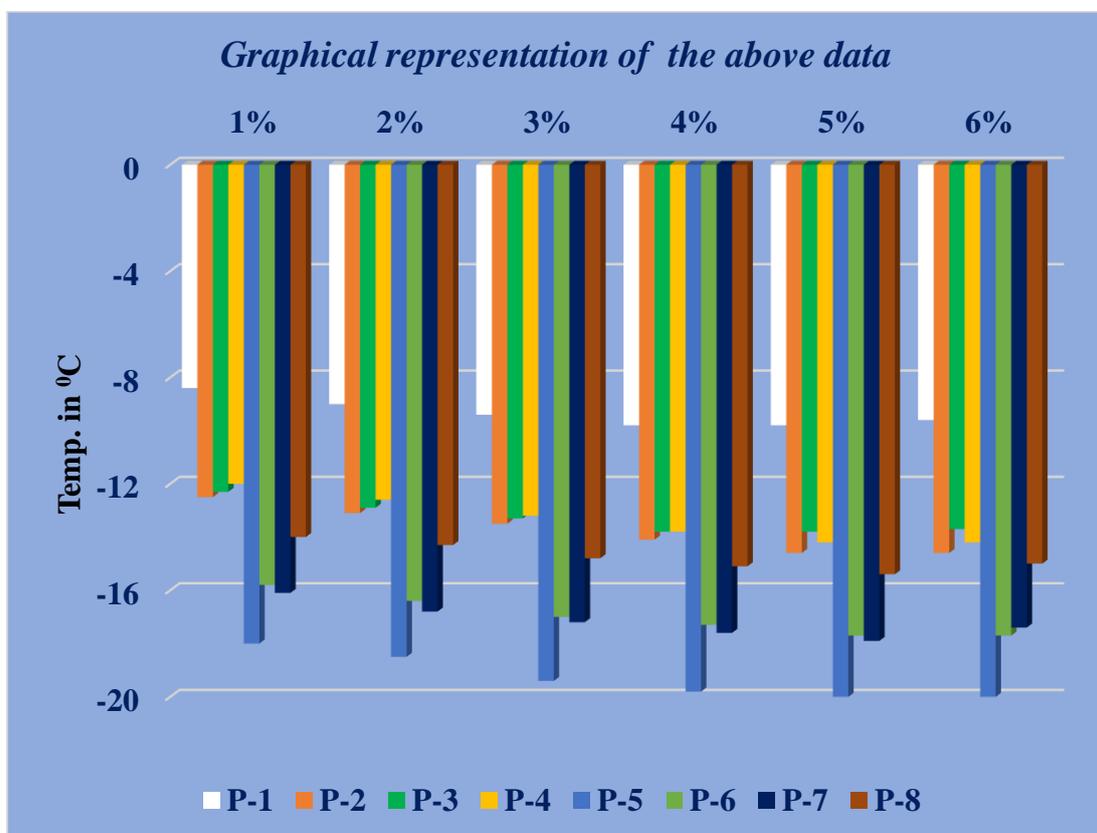


Table 1.4.5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO1 and its graphical representation

Additive	0%	1%	2%	3%	4%	5%	6%
P ₁	85	90	92	94	95	99	102
P ₂	85	92	95	99	101	105	109
P ₃	85	88	90	93	95	101	103
P ₄	85	86	88	90	94	97	100
P ₅	85	91	103	119	125	130	136
P ₆	85	86	87	89	91	97	103
P ₇	85	89	93	97	103	107	112
P ₈	85	98	102	108	111	114	120

Concⁿ represents concentration in % w/w

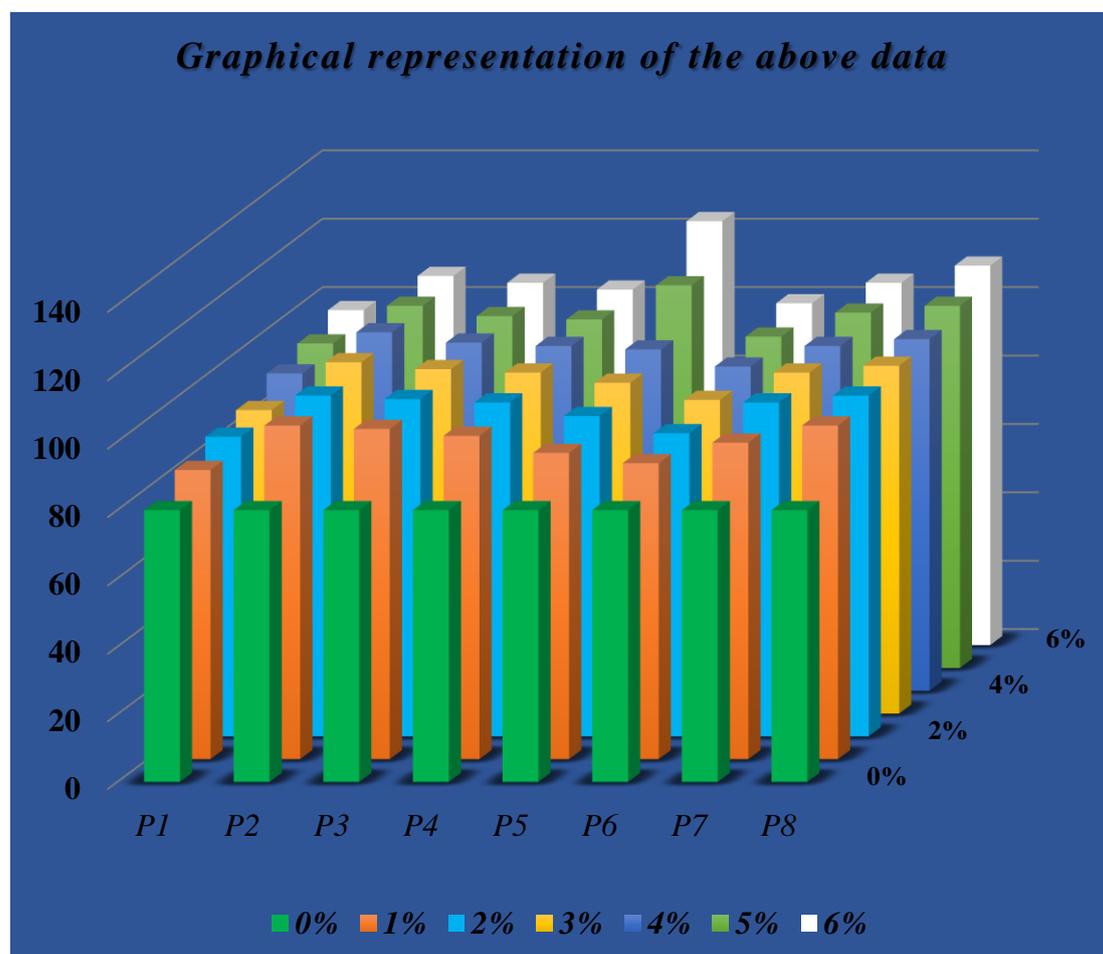


Table 1.4.6: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO2

<i>Additive</i>	<i>0%</i>	<i>1%</i>	<i>2%</i>	<i>3%</i>	<i>4%</i>	<i>5%</i>	<i>6%</i>
P₁	80	85	88	89	93	95	98
P₂	80	98	100	103	105	106	108
P₃	80	97	99	101	102	103	106
P₄	80	95	98	100	101	102	104
P₅	80	90	94	97	100	112	124
P₆	80	87	89	92	95	97	100
P₇	80	93	98	100	101	104	106
P₈	80	98	100	102	103	106	111
<i>Concⁿ represents concentration in % w/w</i>							

Table 1.4.7: TGA data of the polymers

<i>Polymer</i>	<i>Decomposition temperature</i>	<i>Percent weight loss (PWL)</i>
P₁	250/340	23/86
P₂	250/360	12/82
P₃	260/380	14/85
P₄	250/380	13/80
P₅	260/320	14/80
P₆	240/320	14/86
P₇	240/320	13/87
P₈	250/320	14/90

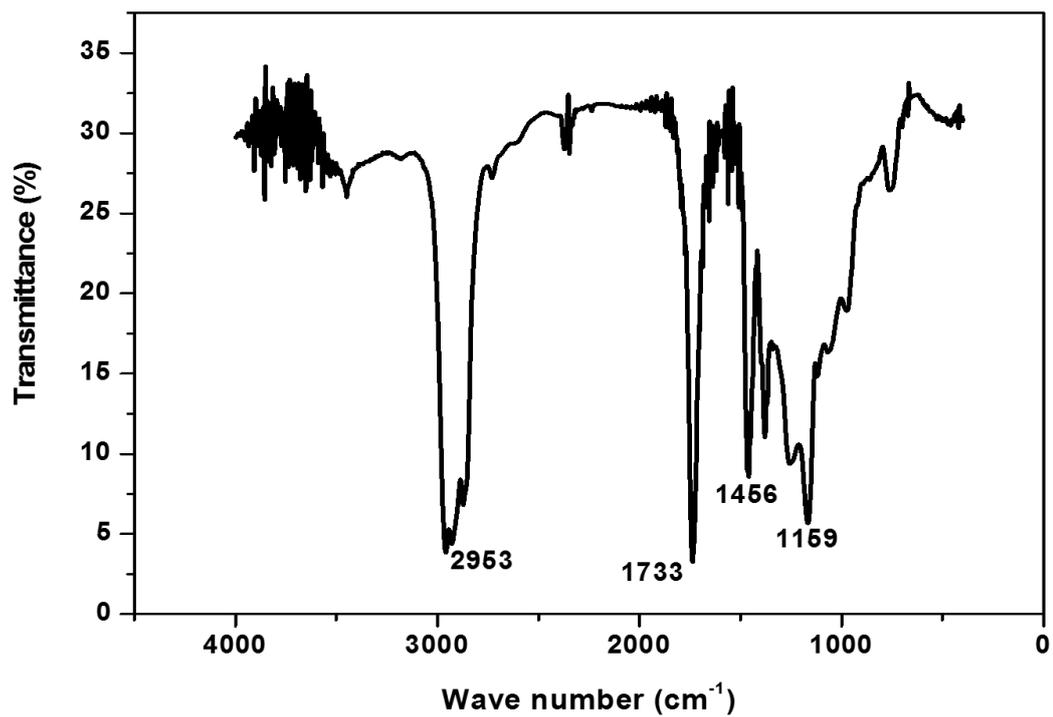


Figure 1.4.1: FT-IR spectrum of co-polymer of BA- 1-Decene (P3)

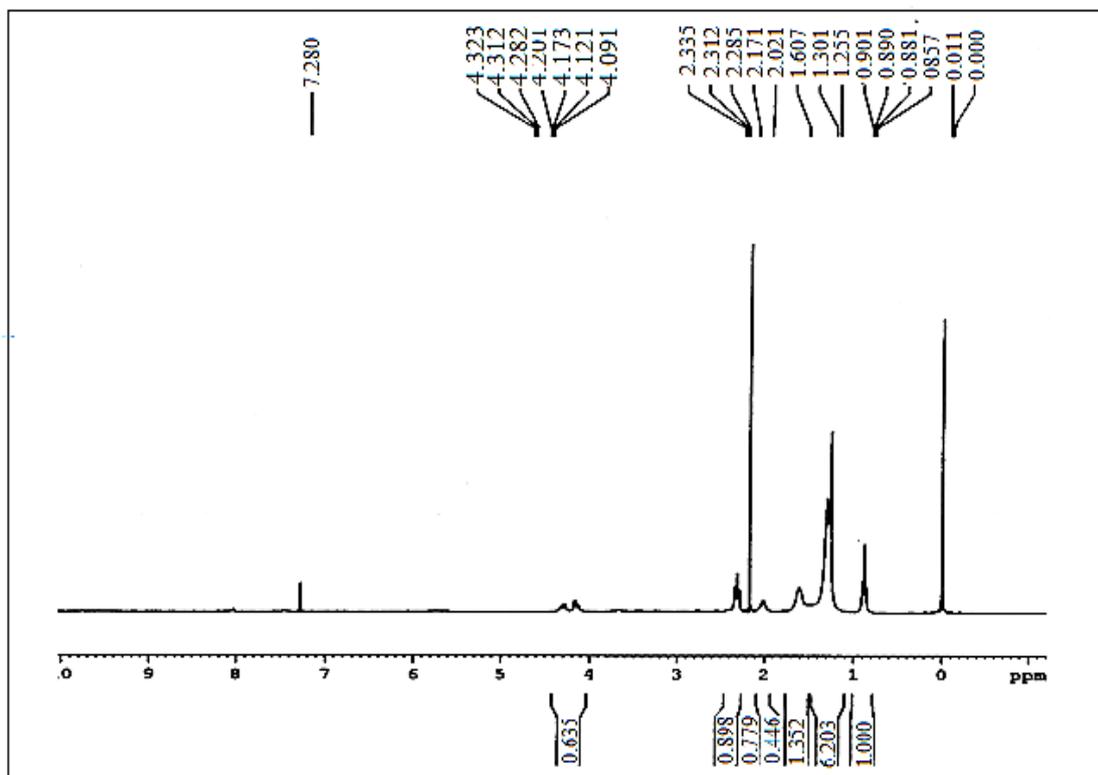


Figure 1.4.2: ¹H NMR spectrum of co-polymer of BA- 1-Decene (P3)

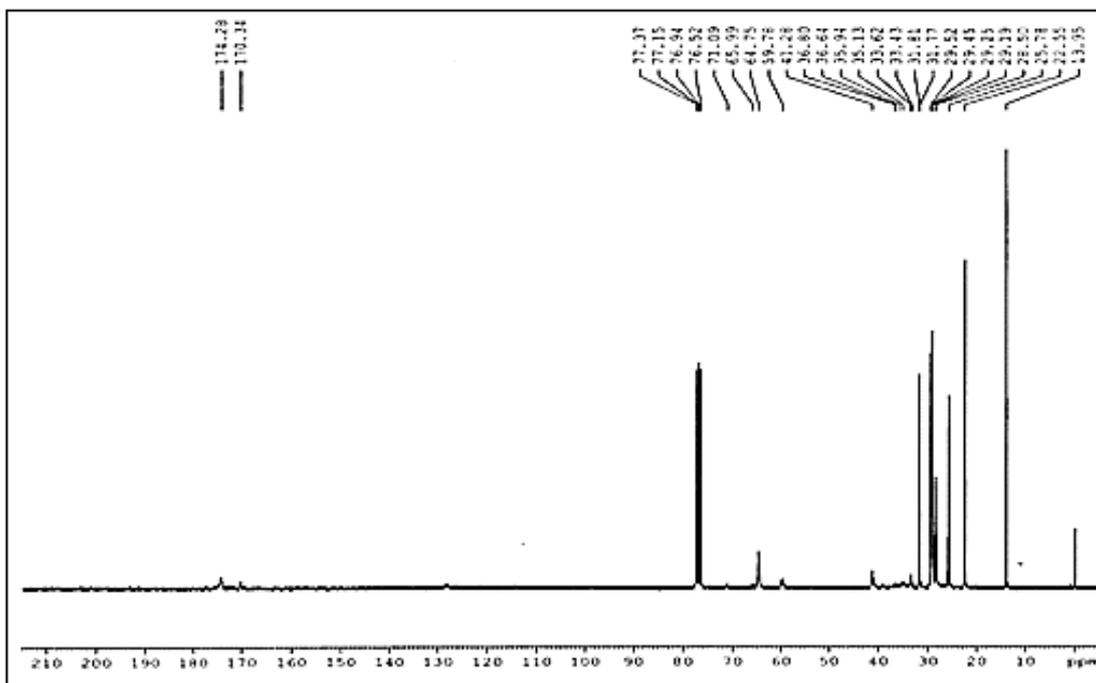


Figure 1.4.3: ^{13}C - NMR spectrum of co-polymer of BA - 1-Decene (P3)

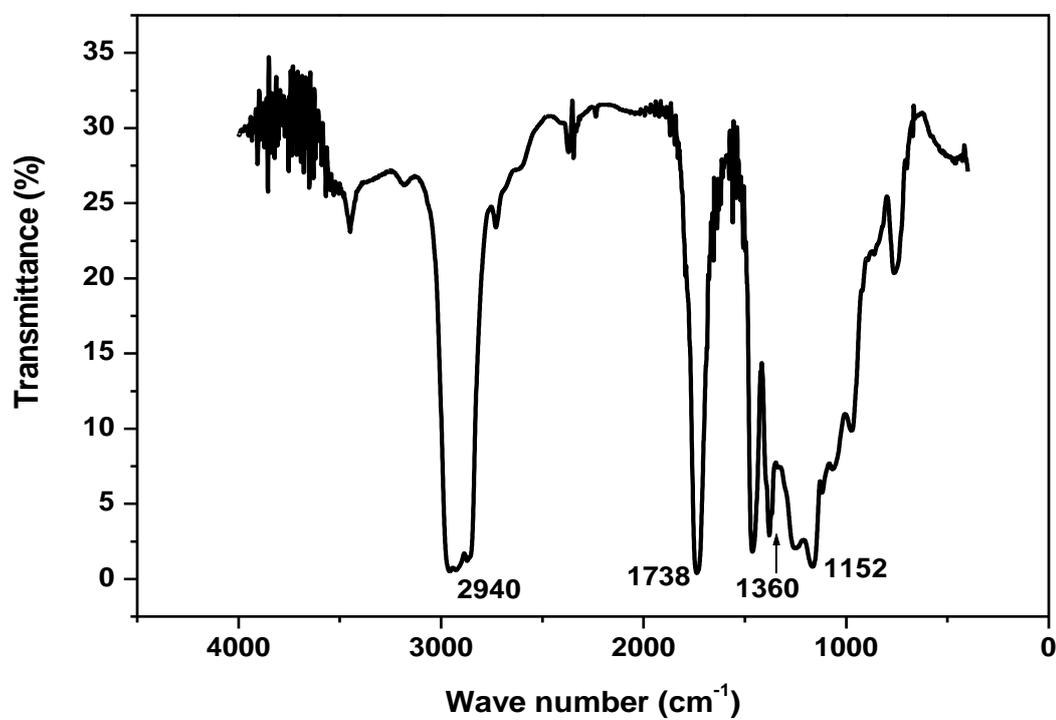


Figure 1.4.4: FT-IR spectrum of co-polymer of IDA- 1-Decene (P7)

