

## **CHAPTER II**

### **Additives for lubricating (lube) oil**

## **CHAPTER II.A**

### **Synthesis of polymeric blend of vinyl acetate and acrylate–based copolymers and its performance evaluation in lubricating oil**

#### **II.A.1. INTRODUCTION**

Polymer blending is a kind of polymer modification process that has attracted much attention as an easy, cost–effective and less time–consuming method for developing new polymeric materials enriched with versatile application at commercial sector. A polymer blend is analogous to metal alloys. It is a mixture of two or more polymers, blended together to form a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends. In general, preparation of polymers by traditional method using some suitable raw materials which are easy to polymerise and then commercialization of new polymer requires many years and the whole process is very expensive too. But polymer blending process may reduce both cost and time for the development and commercialization of new polymeric material to perhaps two to three years [1]. A study revealed that the production of polymer blends replacing traditional polymers represents half of all plastics produced in 2010 [2].

The most important and interesting thing about polymer blends is that the properties of the blends can be manipulated as per its requirement, by suitable selection of the component polymers [3]. Today’s highly sophisticated polymer industry is equipped with ultra–high–performance injection moulding machines and extruders which easily allow phase–separations and via which viscosity changes also can be effectively detected or manipulated during the processing stages [4]. Although such modern and sophisticated blending technology has greatly enhanced the performance capabilities of polymer blends, it has to face a huge challenge every now and then to come up to the increasing market expectation. To satisfy market pressure, for specific applications polymer blends must perform under some specified mechanical, chemical, thermal or electrical condition. Hence thorough study of the properties and performance of polymer blends is essential to determine the maximum limit of performance of a particular blend.

Recently a data-based approach to the development of industrial polymer blends with specified final properties was presented by John F. MacGregor et al [5].

The performance of polymer blends depends on the properties of each polymer in the blend, their content and morphology. The cost of the blend depends on the material, compounding method and blend morphology. Most blends have been developed for the improvement of a specific property such as impact strength and the process or recycling facility. Polymer blends can be classified as:

1. Immiscible Polymer Blends: These blends have large size domains of dispersed phase and poor adhesion between them. If the blend is formed by two polymers, two glass transition temperatures will be observed. Poly(propylene)-poly(styrene) and poly(propylene)-poly(ethylene) are immiscible blends.
2. Miscible Polymer Blends: These are homogeneous blends with a single-phase structure. In this case, one glass transition temperature will be observed. For example, poly(styrene)-poly(phenylene oxide) and poly(styrene-acrylonitrile)-poly (methyl methacrylate) are miscible blends.
3. Compatible Polymer Blends: These are immiscible polymer blends but exhibit uniform physical properties due to strong interface interactions between the polymer blend components.
4. Compatibilized Polymer Blends: These are also immiscible blends whose physical properties can be stabilized by adding surface-active species called compatibilizers. These compatibilizers influence various morphological processes.

The properties of a polymer blend depend on the final morphology. Hence various research groups have recently undertaken extensive studies of the miscibility and phase behaviour of polymer blends. In practice, the physical properties of interest are found either by miscible pairs or by a heterogeneous system, depending on the type of application. The mixing is exothermic only when strong specific interactions occur between the blend components. The most common specific interactions found in polymer blends are hydrogen bonding [6].

## II.A.2. BACKGROUND & OBJECTIVES

Various studies have been performed with polymer blends which establish its effectiveness. Blends of polystyrene (PS) and Acrylonitrile–Butadiene–Styrene (ABS) were prepared in different ratios by melt blending technique by Buthaina A. et al. and the results from their work showed that the mechanical properties for blend system were better than those of pure polymers [7].

Rajendran et al. Successfully Prepared polymer electrolyte membranes comprising of poly(ethyl methacrylate)/ poly(vinyl chloride) with propylene carbonate as plasticizer and  $\text{LiClO}_4$  as salt by solvent casting technique [8].

The green blends of an ionic liquid, 1–ethyl–3–propylimidazolium bis(trifluoromethanesulfonyl)imide {[EPrI][TFSI]} and a biodegradable polymer, poly(3–hydroxybutyrate), were investigated by Li–Ting Lee and Chun–Ting Yang to explore the effect of ILs on the crystallization behaviours of the biodegradable polymers [9].

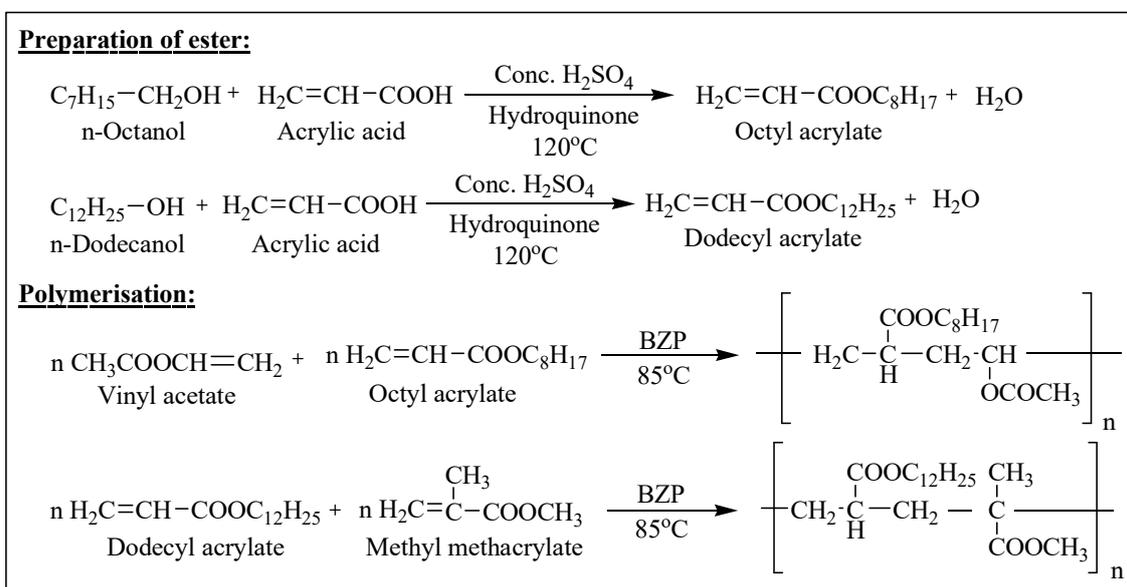
The effect of soybean lecithin and acrylated epoxidized soybean oil as biomass–based compatibilizer agents was studied successfully by Eksiler et al. for the purpose of enhancing the compatibility of environmentally friendly thermoplastic blend of poly (lactic acid) and synthetic rubber [10].

In the area of drug delivery systems, chitosan blends have been widely used for drugs control because of their various advantages such as non–toxicity, biocompatibility, biodegradability and availability of terminal functional groups [11].

The versatility and unique characteristics, such as hydrophilicity, film–forming ability, biodegradability, biocompatibility, antibacterial activity and non–toxicity of chitosan has contributed to the successful development of various blends for medical, pharmaceutical, agricultural and environmental applications [12]. Biodegradable compatibilized polymer blends

have acquired widespread application in packaging industry replacing non-biodegradable materials to satisfy the demands in environmental safety and sustainability [13].

In view of the versatility of polymer blends we have prepared two copolymers—one P<sub>1</sub> of vinyl acetate (VA) and octyl acrylate (OA) and another P<sub>2</sub> of dodecyl acrylate (DDA) and methyl methacrylate (MMA) and then prepared their blend. We characterised them via FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. We further evaluated their performance as flow improver for lubricating oil and also investigated their mechanical strength in terms of shear stability index.



**Scheme II.A: Preparation of octyl acrylate and its subsequent polymerization with vinyl acetate; Preparation of dodecyl acrylate and its subsequent polymerization with methyl methacrylate**

### II.A.3. EXPERIMENTAL SECTION

#### II.A.3.a. Materials

Dodecyl alcohol, octyl alcohol, methyl methacrylate (MMA), Acrylic acid, Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. Conc. H<sub>2</sub>SO<sub>4</sub> (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are tabulated in **Table II.A.1**.

**Table II.A.1: Base Oil (BO) Properties**

<b>Physical Property</b>	<b>BO1</b>	<b>BO2</b>
<b>Density (gcm<sup>-3</sup> at 40°C)</b>	0.83	0.95
<b>Viscosity at 40°C in cSt</b>	6.698	24.211
<b>Viscosity at 100°C in cSt</b>	2.02	4.47
<b>Viscosity Index (VI)</b>	81.13	89.87
<b>Pour Point (PP in °C)</b>	-3	-6
<b>Cloud Point (°C)</b>	-10	-8

**BO1, BO2 collected from IOCL, Dhakuria, West Bengal**

### **II.A.3.b. Preparation of esters and their purification**

The ester (dodecyl acrylate, DDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. Another ester (octyl acrylate, OA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of octyl alcohol. The process was carried out in a resin kettle which was heated gradually from room temperature to 130°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 [14].

The prepared esters were refluxed for 3 hours with 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 complete removal of untreated acid. The esters were then washed repeatedly with

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

### **II.A.3.c. Preparation of copolymers and blend**

The copolymers were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). We have prepared two copolymers – one of vinyl acetate (VA) and octyl acrylate (OA) designated as P<sub>1</sub> and another of dodecyl acrylate (DDA) and methyl methacrylate (MMA) designated as P<sub>2</sub>.

The polymerization process was carried out in a four-necked round bottom flask fitted with stirrer, condenser, thermometer and an inlet for the introduction of nitrogen along with a dropping funnel. The monomers were taken in equimolar amount and the initiator BZP was added in 0.5% amount of the total mass. Toluene was added as solvent. The reaction temperature was fixed at 85°C for 6h. At the end of the reaction, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40°C. The two prepared and purified copolymers were further mixed together via mechanical blending process at a magnetic stirrer at 60°C to get a homogeneous blend.

## **II.A.4. MEASUREMENTS**

### **II.A.4.a. Molecular weight determination**

The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) were measured by GPC (Gel Permeation Chromatography) 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 II.A.2**.

#### **II.A.4.b. Spectroscopic Measurements**

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range (400 to 4000  $\text{cm}^{-1}$ ). NMR spectra were recorded in Bruker Avance 300 MHz NMR spectrometer using a 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and tetramethylsilane (TMS) as reference material.

#### **II.A.4.c. Performance evaluation as pour point depressants in lube oil**

The effect of additive concentration on pour point of the crude oil was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared polymer. 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 **Table II.A.3**.

#### **II.A.4.d. Performance evaluation as viscosity index improver (VII)**

Viscometric properties were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at six different concentrations of the sample solutions. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Kinematic viscosity (KV) data at 40°C, 100°C and viscosity index (VI) data are given in **Table II.A.4 and II.A.5**.

#### **II.A.4.e. Shear stability measurement**

Shear stability of a polymer is a measurement of its ability to sustain its viscosity under shearing conditions. Viscosity loss under shearing conditions may be of two kind's viz. Temporary Viscosity Loss (TVL) and Permanent Viscosity Loss (PVL) [15]. The latter occurs due to mechanical degradation of polymer molecules and is often expressed in terms of Permanent Shear Stability Index (PSSI). PSSI data is obtained following the equations expressed in chapter I (**I.A.1.b**). The PVL and PSSI values are measured here preparing 1%–6% solutions of the

prepared copolymers and their blend in BO1 and BO2 as per ASTM D-3945 method and are given in **Table II.A.6**.

## II.A.5. RESULTS AND DISCUSSION

### II.A.5.a. 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 ( $P_1$ ,  $P_2$ ) and their blend are given in **Table II.A.2**. From the experimental data, it was found that blend had higher number average and weight average molecular weight than the copolymers. This result also indicates a fine blending of  $P_1$  and  $P_2$ . Again in terms of polydispersity index (PDI) the polymer blend is less poly-dispersed than the copolymers ( $P_1$  and  $P_2$ ) which indicates better uniformity in the blend. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the  $M_w$  values decrease but PDI value increases.

**Table II.A.2: Molecular weight and polydispersity index data**

Additive	$M_n$	$M_w$	PDI
$P_1$	25339	53374	2.11
$P_2$	13644	31166	2.28
Blend	34110	58693	1.72

### II.A.5.b. Spectroscopic analysis

IR spectrum for copolymer  $P_1$  (**Figure II.A.1**) showed clear peak around  $1739\text{ cm}^{-1}$  and  $1685\text{ cm}^{-1}$  indicating the presence of ester carbonyl group. Strong peak around  $1107\text{ cm}^{-1}$  accounted for the presence of C–O stretching frequency for ester group. Similar IR spectrum is obtained for the polymer  $P_2$  (**Figure II.A.2**). Here peak at  $1732\text{ cm}^{-1}$  indicates the presence of ester carbonyl group and peak around  $1165\text{ cm}^{-1}$  appeared for the carbonyl C–O stretching. In both cases no

peak has been observed around  $3100\text{ cm}^{-1}$  associated with alkenyl C–H stretching. This observation actually supported the complete polymerization in both the polymers.

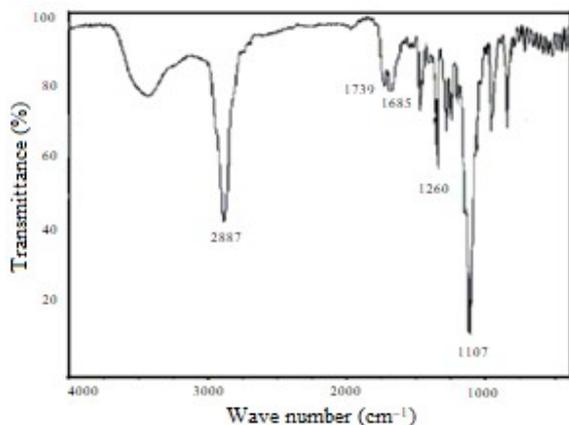


Figure II.A.1: FT-IR spectrum of polymer P<sub>1</sub>

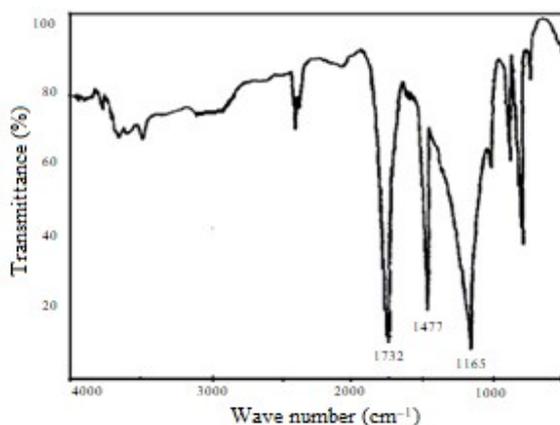


Figure II.A.2: FT-IR spectrum of polymer P<sub>2</sub>

<sup>1</sup>H NMR spectroscopy for the polymer P<sub>1</sub> produced the following result (Figure II.A.3). Here, peaks in the range of 3.36–3.58 ppm indicated the presence of –OCH<sub>2</sub>– protons and peaks in the range of 1.53–1.69 ppm accounted for the presence of –CH<sub>2</sub>– and –CH<sub>3</sub> protons attached with carbonyl carbon. Peaks in the range of 0.90–1.27 ppm indicated the presence of other methyl or methylene protons. Absence of peaks around 6 ppm indicated absence of unsaturation and hence supports total polymerisation.

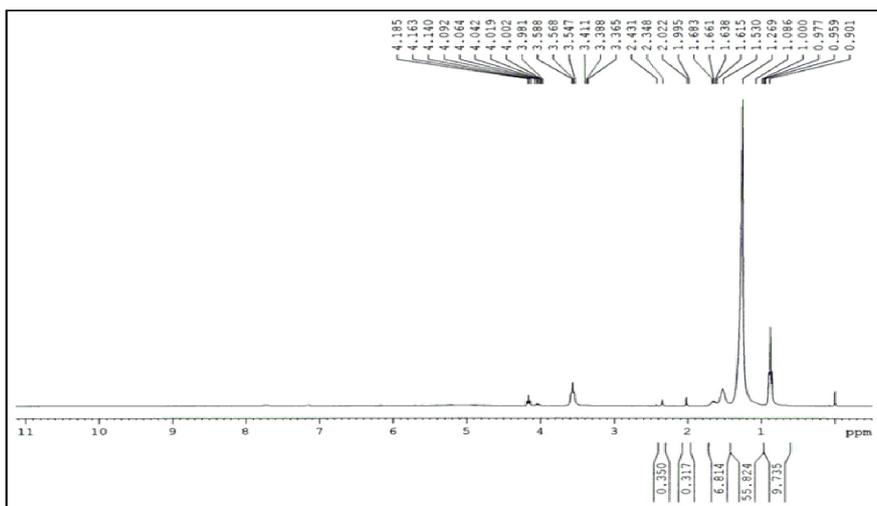
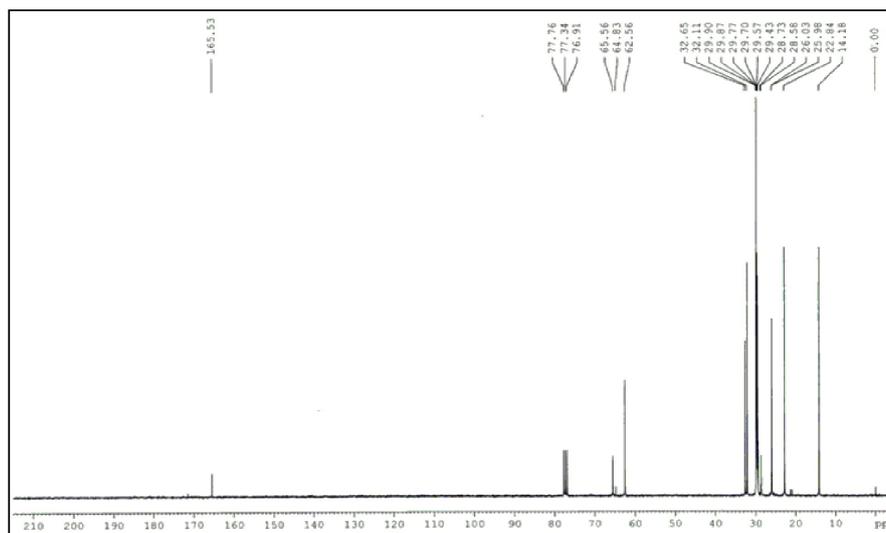
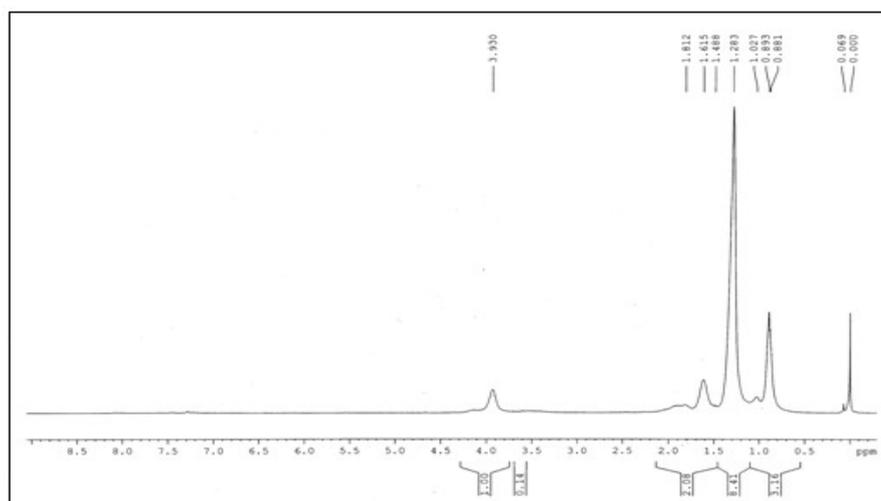


Figure II.A.3: <sup>1</sup>H NMR spectrum of P<sub>1</sub>

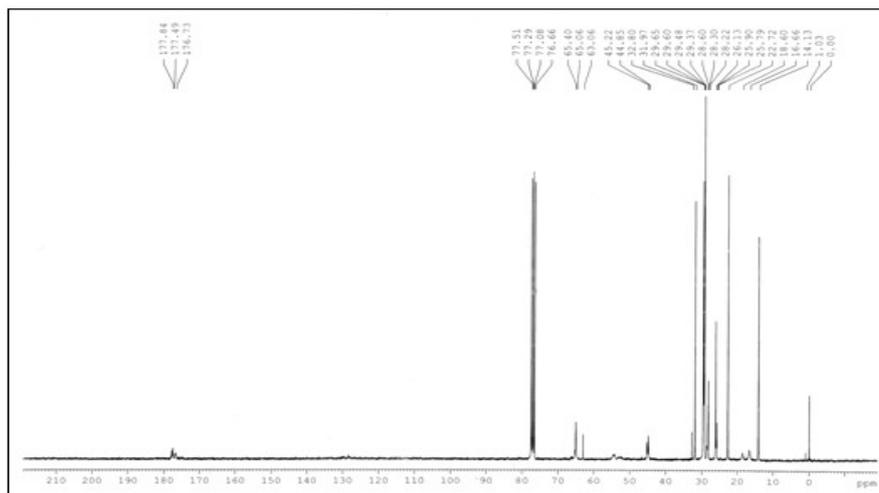


**Figure II.A.4:**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_1$

In  $^{13}\text{C}$  NMR of the polymer  $\text{P}_1$  (**Figure II.A.4**), the peak around 165.5 ppm indicated the presence of ester carbonyl carbon. The peaks at 62.6–65.6 ppm corresponded to the  $-\text{OCH}_2-$  carbons and peaks ranging from 14.2–32.4 ppm for all other  $\text{sp}^3$  carbons. Again no peak in the range of 120–150 ppm indicated the absence of  $\text{sp}^2$  carbons and confirmed the successful polymerization.



**Figure II.A.5:**  $^1\text{H}$  NMR spectrum of  $\text{P}_2$



**Figure II.A.6:**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_2$

$^1\text{H}$  NMR spectroscopy for the polymer  $\text{P}_2$  (**Figure II.A.5**) also showed almost similar values. Here peaks around 3.93 ppm indicated the presence of  $-\text{OCH}_2-$  protons and peaks in the range 0.88–1.61 ppm appeared for other methyl and methylene protons. In  $^{13}\text{C}$  NMR of the polymer  $\text{P}_2$ , (**Figure II.A.6**) ester carbonyl peak appeared at 174.7–177.8 ppm and  $-\text{OCH}_2-$  carbons appeared in the range of 63.06–65.40 ppm. Here also no peak appeared around 120–150 ppm corresponding to unsaturated carbons.

#### **II.A.5.c. Performance evaluation as pour point depressant**

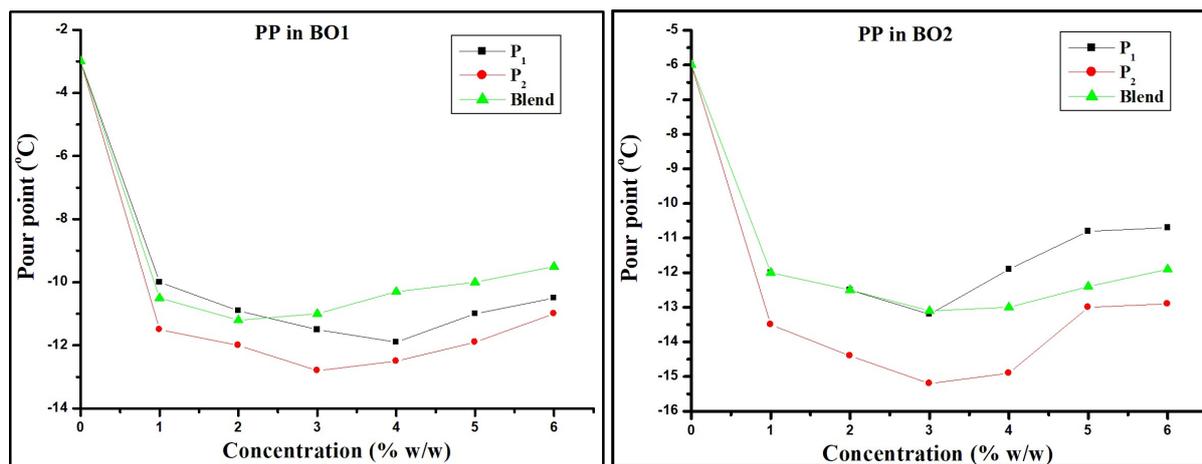
Analysing the pour point data given in **Table II.A.3**, it may be said that both the prepared copolymers and their blend acted as good flow improvers and among them all the copolymer  $\text{P}_2$  i.e. copolymer of methyl methacrylate and dodecyl acrylate was proved to be the best one. The graphical representation of the pour point data (**Figure II.A.7**) makes the comparison clearer.

The pour point depression at higher concentrations nearly reaches to constant or almost no change is observed at higher concentration which may be due to lower solubility of the polymers at higher concentration. The longer alkyl chain length of the ester in  $\text{P}_2$  actually accounts for its better effectiveness as PPD which was supported by earlier reports [16]. In case of the blend lower solubility in the base oil might retard its property as flow improver at higher

concentration. The best result was obtained for the copolymer P<sub>2</sub> at 3% concentration in the base oil 2 (BO2).

**Table II.A.3: Pour point data with respect to the different concentrations of the additives in base oil (BO)**

Additive	BO	PP (°C) at different concentrations (% w/w) of additive						
		0%	1%	2%	3%	4%	5%	6%
P <sub>1</sub>	BO1	-3	-10.0	-10.9	-11.5	-11.9	-11.0	-10.5
	BO2	-6	-12.0	-12.5	-13.2	-11.9	-10.8	-10.7
P <sub>2</sub>	BO1	-3	-11.5	-12.0	-12.8	-12.5	-11.9	-11.0
	BO2	-6	-13.5	-14.4	-15.2	-14.9	-13.0	-12.9
Blend	BO1	-3	-10.5	-11.2	-11.0	-10.3	-10.0	-9.5
	BO2	-6	-12.0	-12.5	-13.1	-13.0	-12.4	-11.9



**Figure II.A.7: PP (°C) at different concentrations (% w/w) of additive**

#### II.A.5.d. Performance evaluation as viscosity index improver

Among the copolymers, P<sub>1</sub> i.e. copolymer of vinyl acetate and octyl acrylate showed better result (Table II.A.4 and II.A.5) as viscosity index improver which may be attributed to its lower alkyl chain length in the ester and also its higher molecular weight than P<sub>2</sub>.

**Table II.A.4: Viscosity Index (VI) data with respect to the different concentrations of the additives in base oil 1 (BO1)**

Conc <sup>n</sup>	P <sub>1</sub>			P <sub>2</sub>			Blend		
	KV <sub>1</sub>	KV <sub>2</sub>	VI	KV <sub>1</sub>	KV <sub>2</sub>	VI	KV <sub>1</sub>	KV <sub>2</sub>	VI
1	6.705	2.120	113	6.701	2.100	106	6.710	2.160	128
2	6.714	2.160	127	6.709	2.130	111	6.724	2.190	135
3	6.727	2.200	141	6.717	2.180	132	6.740	2.240	153
4	6.750	2.250	157	6.123	2.210	144	6.770	2.280	164
5	6.780	2.300	170	6.741	2.250	155	6.800	2.310	172
6	6.810	2.340	184	6.760	2.290	171	6.830	2.350	185

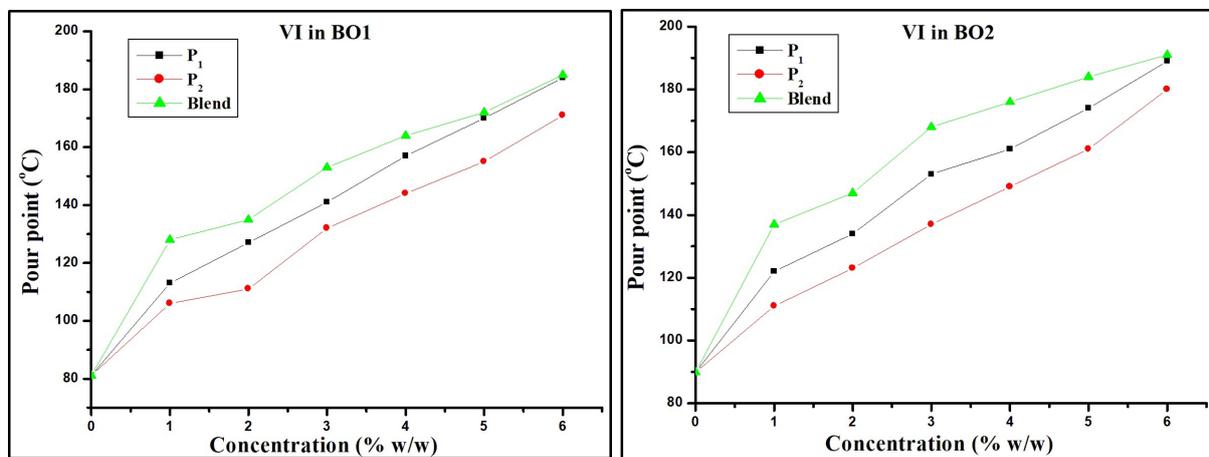
Conc<sup>n</sup> represents concentration in % w/w; KV<sub>1</sub> & KV<sub>2</sub> represent kinematic viscosity at 40°C & 100°C respectively.

Interestingly here blend of P<sub>1</sub> and P<sub>2</sub> acted as the best viscosity index improver may be due to its higher molecular weight. Irrespective of all the polymers and base oil, viscosity index gradually increased with increasing concentration (Figure II.A.8) of the added polymers which may be due to an increase in the total volume of the polymer micelles in the oil solutions [17].

**Table II.A.5: Viscosity Index data with respect to the different concentrations of the additives in base oil 2 (BO2)**

Conc <sup>n</sup>	P <sub>1</sub>			P <sub>2</sub>			Blend		
	KV <sub>1</sub>	KV <sub>2</sub>	VI	KV <sub>1</sub>	KV <sub>2</sub>	VI	KV <sub>1</sub>	KV <sub>2</sub>	VI
1	24.320	4.850	122	24.250	4.710	111	24.380	5.050	137
2	24.340	5.000	134	24.280	4.860	123	24.430	5.180	147
3	24.390	5.250	153	24.330	5.040	137	24.550	5.470	168
4	24.480	5.370	161	24.410	5.200	149	24.590	5.590	176
5	24.570	5.560	174	24.490	5.370	161	24.640	5.710	184
6	24.650	5.780	189	24.560	5.640	180	24.700	5.820	191

Conc<sup>n</sup> represents concentration in % w/w; KV<sub>1</sub> & KV<sub>2</sub> represent kinematic viscosity at 40°C & 100°C respectively.



**Figure II.A.8: Variation of viscosity index with respect to the different concentrations of the additives**

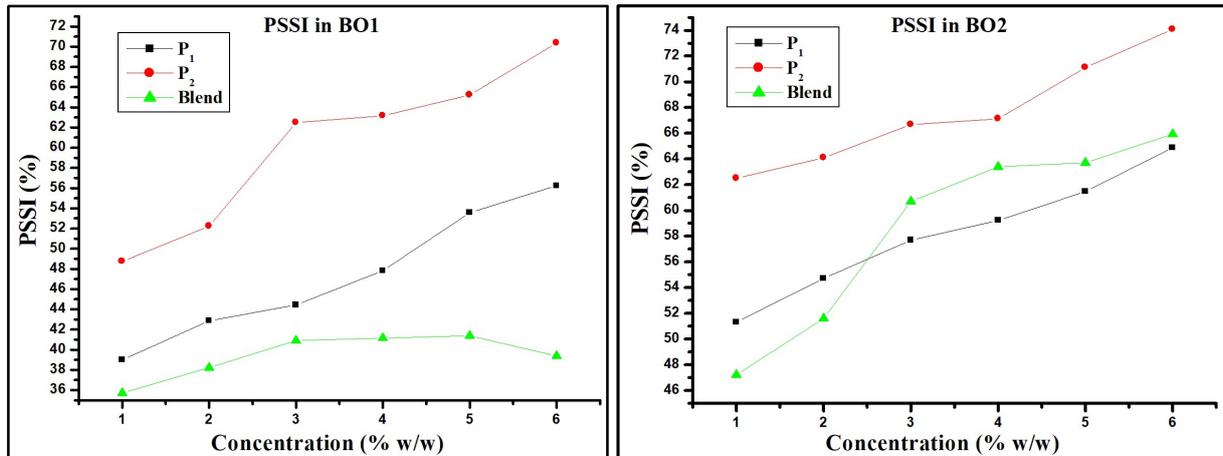
### II.A.5.e. Shear stability index analysis

As expected polymer blend of the prepared copolymers showed highest stability against mechanical shear at all concentrations, which clearly supports its better mechanical and thermal property in both the base oils (**Table II.A.6**).

**Table II.A.6: PVL & PSSI data with respect to the different concentrations of the additives in base oil (BO)**

Base Oil	Conc <sup>n</sup>	KV <sub>2</sub> after shear			PVL (%)			PSSI (%)		
		P <sub>1</sub>	P <sub>2</sub>	Blend	P <sub>1</sub>	P <sub>2</sub>	Blend	P <sub>1</sub>	P <sub>2</sub>	Blend
BO1	1	2.081	2.016	2.110	1.84	1.86	2.32	39.00	48.75	35.71
	2	2.100	2.083	2.125	2.78	2.21	2.97	42.86	52.22	38.23
	3	2.120	2.080	2.150	3.64	4.59	4.02	44.44	62.50	40.91
	4	2.140	2.090	2.173	4.89	5.43	4.69	47.83	63.16	41.15
	5	2.150	2.100	2.190	6.52	6.67	5.19	53.57	65.22	41.38
	6	2.160	2.100	2.220	7.69	8.29	5.53	56.25	70.37	39.39
BO2	1	4.655	4.560	4.965	4.02	3.18	1.68	51.32	62.50	47.22
	2	4.710	4.610	5.020	5.80	5.14	3.09	54.72	64.10	51.61
	3	4.800	4.660	5.493	8.57	7.54	1.11	57.69	66.67	60.70
	4	4.837	4.710	4.880	9.93	9.42	12.70	59.22	67.12	63.39
	5	4.890	4.730	4.920	12.05	11.92	13.83	61.47	71.11	63.71
	6	4.930	4.820	4.930	14.71	14.54	15.29	64.89	74.07	65.93

Conc<sup>n</sup> represents concentration in % w/w; KV<sub>2</sub> represents kinematic viscosity at 100°C.



**Figure II.A.9: Variation of PSSI with respect to the different concentrations of the additives**

Another important observation was that irrespective of both the copolymers and their blend, moderately higher PSSI value was obtained in case of the base oil with higher viscosity (BO2). It is believed that polymer molecules are more tightly bound in high viscous base oil and hence the mobility of the polymer chain is reduced which makes the polymer molecule more susceptible to bond rupture i.e. mechanical degradation. Hence in base oil with higher viscosity, shear stability of the additives decreases [18] which was evident from our result more clearly shown in **Figure II.A.9**. Higher the concentration of the additive higher was the PVL and hence PSSI value. But the relationship between the concentration of the polymer and shear stability index was not linear since various other factors like molecular weight of the polymer, composition of the base oil might play different role on shear stability.

## II.A.6. CONCLUSION

Thus it may be concluded that all the prepared polymers including the blend were proved to be a good flow improver for lubricating oil. When it comes to mechanical stability the polymer blend of the prepared copolymers excels. It may be because of its higher molecular weight and lower polydispersity index. The blend was also proved to a better viscosity modifier at all concentrations in the base oil.

## II.A.7. REFERENCES

References for chapter II.A are given in bibliography section (page 125–126).

## **CHAPTER II.B**

### **Effect of percentage of initiator used in the polymerisation process on the performance of the prepared additives: A comparative study**

#### **II.B.1. INTRODUCTION**

High performance lubricating oil is a major exploring area in automotive industry. It is the lubricant which keeps the moving surfaces away from each other and protects them from corrosion and rust and thus enhances engine's durability and performance [1]. Modern lubricants are formulated from wide variety of mineral base oils blended together with some appropriate chemical additives [2]. The additives play very important role to optimize the properties of lubricants such as pour point depressants [3, 4], viscosity index improvers [5, 6], extreme pressure additives [7] etc. Polymers have conquered a special and major place in this aspect to be explored as additives. A number of research groups have been engaged in this field to synthesize multifunctional polymeric additive. But still there is a quest to find out the most suitable cost effective additive with minimum dosage but maximum effect.

Free radical polymerisation has been considered to be one of the most favourite processes for the production of polymers. Free radical polymerisation process proceeds via three steps; mainly initiation, propagation and termination. Free radical polymerisation processes are really very hard to control. But today some advanced techniques have made it possible to control free radical polymerization reactions especially by suppressing termination and transfer processes which has gained enough attention, even if their share in the total polymer production is still rather small [8].

Peroxy compounds may be the oldest initiating agents in technical polymerization processes since about 100 years. Either singly or in combination with other promoting agent, benzoyl peroxide (BZP) has been utilised vastly in free radical polymerisation processes. Berger et al. delivered a kinetic study on BZP initiated polymerisation of styrene in bulk at 30 to 80°C [9]. The rates and degrees of polymerisation of styrene using various concentration of BZP initiator at 60°C was determined by Mayo et al where contribution to the average degree of

polymerisation of chain transfer of the polymer radical with the monomer and peroxide was evaluated [10]. They reported that chain transfer with the initiator, the efficiency of benzoyl peroxide in initiating chains in styrene and the relative importance of disproportionation and coupling in the termination reaction are closely related. Kinetic study of polymerisation of styrene in benzene at 60°C initiated by BZP was reported by P.C. Deb and G. Meyerhoff [11].

On the other hand, azobisisobutyronitrile (AIBN) is the first and up to now mostly used aliphatic azo initiator. It was discovered by Thiele and Heuser in 1896 [12]. Several studies proved that AIBN yields initiating radicals at the same rate irrespective of different series of solvents [13, 14]. But presence of cyano group makes it susceptible to cause toxic side products during thermal decomposition which is a drawback of this initiator.

## **II.B.2. BACKGROUND & OBJECTIVES**

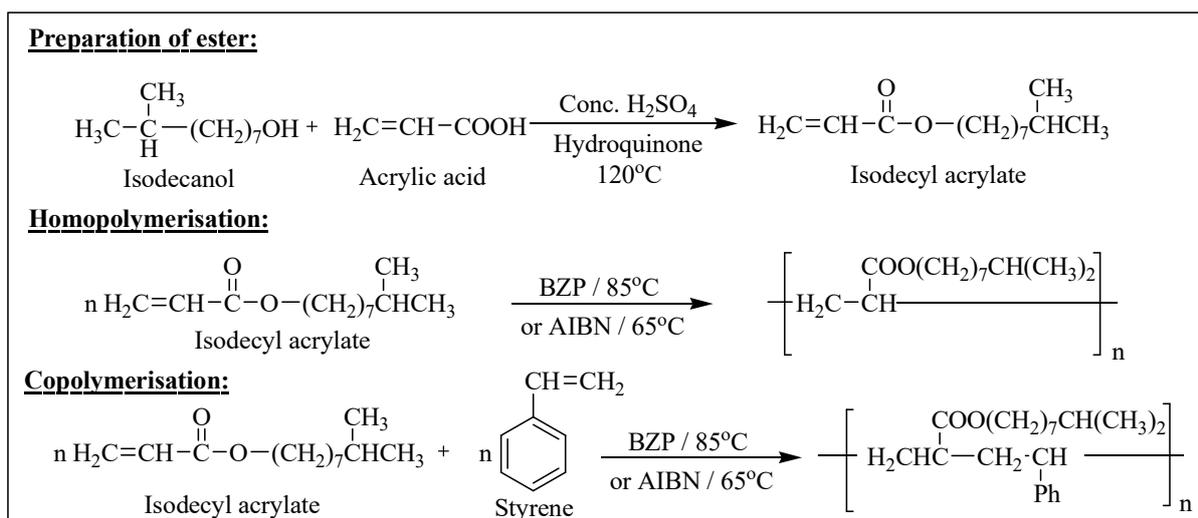
Several kinetic investigations of polymerisation under binary initiator system like BZP–amine system have been reported [15]. S. N. Trubitsyna et al. delivered a report on the interaction of benzoyl peroxide with the polymeric emulsifier, aminated polystyrene [16]. Cationic emulsifiers of the quaternary ammonium salt form an efficient initiating system with benzoyl peroxide. In alkaline conditions, the quaternary ammonium salt isomerises to a carbinolbase which interacts with the peroxide via peroxide–amine mechanism leading to formation of the benzoate radical, which initiates polymerization. The free radical homopolymerization of bis–phenol–A–bis(glycidyl methacrylate), a urethane dimethacrylate and triethylene glycol dimethacrylate induced by a benzoyl peroxide–amine redox couple was studied by Sideridou et al using differential scanning calorimetry [17]. This study revealed that amines with electron donating para–substituents are efficient co–initiators for polymerization at 37°C whereas amines with the electron–withdrawing para–substituent could not initiate polymerization at 37°C, but only at higher temperatures. Polymerization of methyl methacrylate in the presence of binary systems containing benzoylperoxide and activators 4–(4–dimethylaminostyryl)pyridine, 4–(4–dimethylaminostyryl)pyridine–N–oxide in chlorobenzene at 30°C was studied by N. A. Turovskii et al. The rate constants of decomposition of benzoyl peroxide in the presence of

activators, initial polymerization rates, initiation rates, and initiation efficiencies at 30°C were determined [18].

Different kinetic studies have been reported on AIBN-initiated polymerisation. The kinetic rate constants of AIBN initiated polymerisation of styrene at 60°C were determined by Braks and Huang [19]. Burnett and Loan observed that the rate of polymerization of methyl methacrylate, methyl acrylate, and vinyl acetate in benzene decreases with the increase in solvent concentration [20]. The AIBN-initiated polymerization of methylmethacrylate in pyridine at 50°C proceeds to higher conversion than that carried out in bulk. The increased values of the overall rate constant are due to the increased values of the initiation rate constant. Another report showed that polymerization of vinyl acetate in benzene experienced low polymerisation rate which was explained by the formation of a complex between the growing radical and benzene [21]. This complex remains comparatively inactive in the propagation reaction. Same case of retardation was observed also in the AIBN-initiated polymerization of styrene in carbon tetrabromide [22]. Burnett and co-workers found that the polymerization rate of methylmethacrylate in halogenated benzenes and in naphthalene at 60°C in presence of AIBN was higher than in cases when the solvent acts as an inert diluents. They suggested that three macroradical species might contribute to propagation in methylmethacrylate polymerization: an uncomplexed species, a species complexed with solvent, and a species complexed with monomer [20]. Recently AIBN in combination with (SiMes)Ru(PPh<sub>3</sub>)IndCl<sub>2</sub> catalytic system was investigated for controlled radical polymerisation of methylmethacrylate in solution and various factors such as aging time of the initiator, concentration of the monomer, polymerisation time, temperature and nature of solvent were examined [23]. Kinetic study of AIBN initiated polymerisation of methylmethacrylate in pyridine at 50°C, done by Kaloforov revealed that the overall rate constant increases with increasing initiation rate constant [24]. Another investigation estimated the retarding effect of acetophenone in the polymerization of methylmethacrylate initiated by AIBN in the temperature range of 50 to 80°C where the effects of varying concentrations of substrate, monomer, initiator, and salts were also investigated by Manjushree Senapati et al [25]. A comparative study between homopolymer of decyl methacrylate and its copolymer with different concentration of styrene using AIBN and BZP initiator was presented

by Ghosh et al. [26]. Another comparative study between homogeneous reverse atom transfer radical polymerisation (ATRP) of styrene using BZP in presence of CuBr/ CuBr<sub>2</sub> complexed by 4,4'-di(5-nonyl)-2,2'-bipyridine and the same polymerisation using AIBN and CuBr<sub>2</sub>/2dNbpy was reported [27].

As we can see lot of studies have done on the kinetic investigations of the AIBN or BZP-initiated polymerisation processes. But few studies have reported providing their proper comparison. In this present context, we have delivered a comparative study over the effect of percentage of the initiator either BZP or AIBN, used during the homopolymerisation of isodecyl acrylate and its copolymerisation with styrene, on the molecular weights of the prepared polymers and on their performance as PPDs, VIIs and extreme pressure additives.



**Scheme II.B: Preparation of isodecyl acrylate; its subsequent homopolymerisation and copolymerization with styrene**

## II.B.3. EXPERIMENTAL SECTION

### II.B.3.a. Materials

Isodecyl alcohol, acrylic acid and styrene (99%, Sigma–Aldrich) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme 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 re-crystallization before use. AIBN (GC 98%), obtained from Spectrochem Pvt. Ltd. Mumbai (India) was recrystallized from  $\text{CHCl}_3$ -MeOH before use. Conc.  $\text{H}_2\text{SO}_4$  (98%, Merck Specialties Pvt. Ltd.) was used as received. Properties of the mineral base oils used are previously mentioned in Chapter II.A.

### **II.B.3.b. Preparation of esters and their purification**

The ester (isodecylacrylate, IDA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isodecyl alcohol in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in Chapter II.A [28].

### **II.B.3.c. Preparation of polymers**

The homo polymer of isodecylacrylate and its copolymer with styrene were prepared via free radical polymerisation using varied percentage of either BZP or AIBN. Homopolymers  $P_1$  to  $P_5$  and copolymers  $P_{11}$  to  $P_{15}$  were prepared using BZP whereas homopolymers  $P_6$  to  $P_{10}$  and copolymers  $P_{16}$  to  $P_{20}$  were prepared using AIBN. The percentages of the added initiator with respect to total weight of monomer during polymerisation are mentioned in **Table II.B.1**. The process of polymerization and purification of polymer was carried out by the procedure as reported in Chapter II.A [28].

## **II.B.4. MEASUREMENTS**

### **II.B.4.a. Molecular weight determination**

The average molecular weights of the prepared polymers were measured by 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 number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) data are given in **Table II.B.1**.

#### **II.B.4.b. Spectroscopic Measurements**

IR spectrum of the prepared polymers were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range (400 to 4000  $\text{cm}^{-1}$ ). NMR spectrum were also recorded for the polymers in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe in  $\text{CDCl}_3$  solvent and tetramethylsilane (TMS) as reference material.

#### **II.B.4.c. Performance evaluation as pour point depressants in lube oil**

The lowest temperature at which movement of the oil sample can be noticed when the sample container is tilted, is called pour point of that oil [29]. To achieve high performance lube oil its pour point must be lowered with perfect dosage of perfect additives called pour point depressants. The performance of our prepared polymers as ppds in the mineral base oils (BO1 and BO2) was tested according to the ASTM D 97-09 method. Solutions were prepared using different doping concentrations ranging from 1% to 5% (w/w) for each of the prepared polymer and the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India). The values are given in **Table II.B.2**.

#### **II.B.4.d. Performance evaluation as viscosity index improver (VII)**

Viscometric properties of the prepared polymers were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. For each polymer five solutions were prepared from 1% to 5% (w/w) concentration in both the base oils. The time of flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2%. Precautions regarding prevention of evaporation of solvent were taken in all the cases. Kinematic viscosity (KV) data at 40°C, 100°C and viscosity index (VI) data in BO1 and BO2 are given in **Table II.B.3**, **II.B.4** and **II.B.5**.

#### II.B.4.e. Shear stability measurement

Shear stability of a polymer is one of the most important parameters to judge its acceptability as a chemical additive. It is a measurement of ability to sustain viscosity under shearing conditions. The required equations for shear stability measurement are discussed in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here preparing 1%–5% solutions of the prepared polymers in BO1 and BO2 as per ASTM D-3945 method and are given in **Table II.B.6**, **II.B.7** and **II.B.8**.

### II.B.5. RESULTS AND DISCUSSION

#### II.B.5.a. 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 ( $P_1$  to  $P_{20}$ ) are given in **Table II.B.1**. It is evident from the molecular weight data that the homopolymers have higher molecular weight than the copolymers irrespective of the initiators used during polymerisation. But the homopolymers prepared using BZP initiator, have higher molecular weight than those prepared using AIBN initiator. On the other hand copolymers prepared using AIBN initiator, have higher molecular weight than those prepared using BZP initiator. But PDI values are more or less same in all the cases. Comparing all the molecular weight data it may be said that the homopolymer  $P_2$  prepared using 0.5% BZP showed highest molecular weight among all whereas polymerisation using 1.0% AIBN showed better result among polymers prepared using AIBN initiator.

**Table II.B.1: Percentage of initiator used during polymerisation and molecular weight data**

Polymer	BZP (%)	AIBN (%)	$M_n$	$M_w$	PDI
$P_1$	0.1	–	14059	32540	2.31
$P_2$	0.5	–	14544	33121	2.28
$P_3$	1.0	–	14100	32699	2.32

<b>P<sub>4</sub></b>	1.5	–	13812	30611	2.22
<b>P<sub>5</sub></b>	2.0	–	13514	30219	2.24
<b>P<sub>6</sub></b>	–	0.1	13000	28900	2.22
<b>P<sub>7</sub></b>	–	0.5	13109	30100	2.30
<b>P<sub>8</sub></b>	–	1.0	13777	30127	2.29
<b>P<sub>9</sub></b>	–	1.5	13549	29903	2.21
<b>P<sub>10</sub></b>	–	2.0	13400	30000	2.24
<b>P<sub>11</sub></b>	0.1	–	12511	28400	2.27
<b>P<sub>12</sub></b>	0.5	–	12914	28854	2.23
<b>P<sub>13</sub></b>	1.0	–	12814	28103	2.19
<b>P<sub>14</sub></b>	1.5	–	12611	28004	2.22
<b>P<sub>15</sub></b>	2.0	–	12031	27899	2.32
<b>P<sub>16</sub></b>	–	0.1	12006	29910	2.49
<b>P<sub>17</sub></b>	–	0.5	12870	30059	2.34
<b>P<sub>18</sub></b>	–	1.0	13048	30101	2.31
<b>P<sub>19</sub></b>	–	1.5	13005	30000	2.31
<b>P<sub>20</sub></b>	–	2.0	12954	29801	2.30

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P<sub>1</sub> to P<sub>10</sub> and P<sub>11</sub> to P<sub>20</sub> represent homopolymer of isodecyl acrylate and copolymers of isodecyl acrylate with styrene respectively

### II.B.5.b. Spectroscopic analysis

The IR spectrum of all the prepared homopolymers and copolymers showed clear peak ranging from  $1730\text{ cm}^{-1} - 1737\text{ cm}^{-1}$  corresponding to ester carbonyl. For example, the IR spectrum of one of the homopolymers ( $P_1$ ) and one of the copolymers ( $P_{11}$ ) have been shown below (**Figure II.B.1** & **Figure II.B.2**). In case of the homopolymer peak at  $1734\text{ cm}^{-1}$  corresponded to ester carbonyl group whereas in case of the copolymer, ester carbonyl stretching frequency appeared around  $1733\text{ cm}^{-1}$ . Here, peaks around  $2990\text{ cm}^{-1}$  corresponded to aromatic C=C of styrene present in the copolymers. No peak is obtained above  $3000\text{ cm}^{-1}$  which indicates absence of C=C unsaturation and supports complete polymerisation in all the cases.

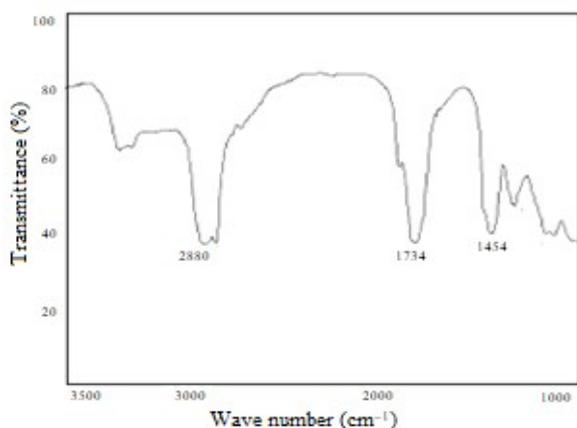


Figure II.B.1: FT-IR spectrum of  $P_1$

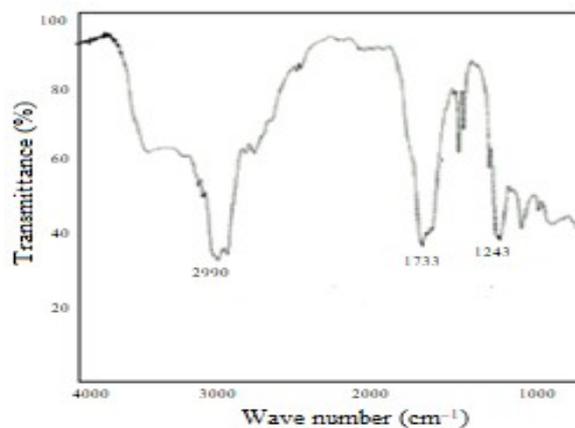
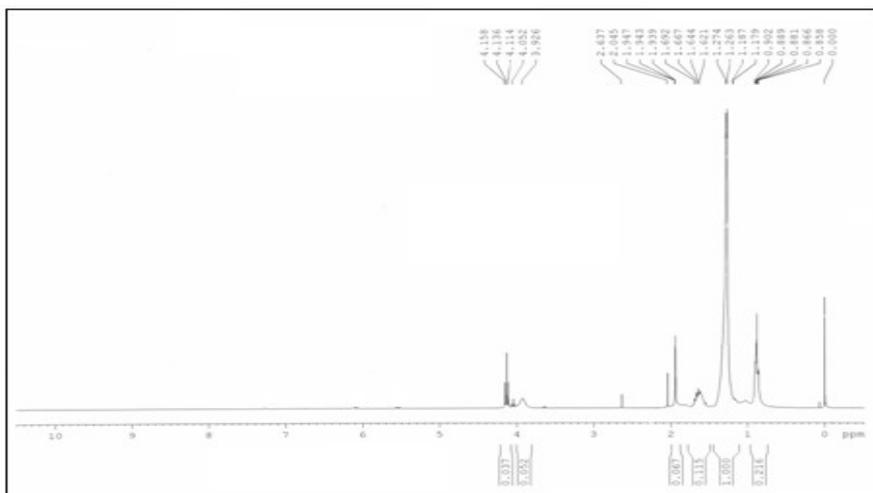
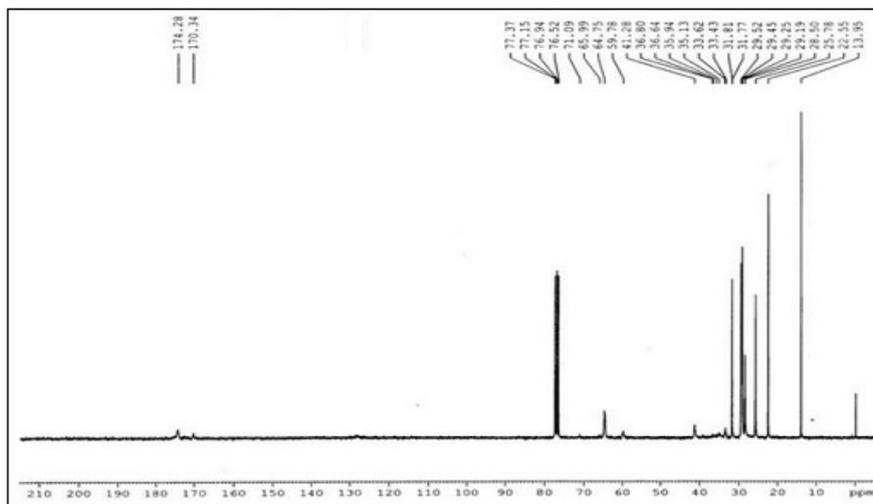


Figure II.B.2: FT-IR spectrum of  $P_{11}$

The results obtained in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy of the homopolymer  $P_1$  are given in **Figure II.B.3** and **Figure II.B.4** respectively. In  $^1\text{H}$  NMR spectrum, peaks appeared at 3.92–4.15 ppm due to presence of  $-\text{OCH}_2-$  protons and other protons appeared at 0.92–1.69 ppm. In the  $^{13}\text{C}$  NMR spectra ester carbonyl carbon produced peak around at 174.3 ppm and  $-\text{OCH}_2-$  carbons appeared in the range from 59.8–65.9. The  $-\text{CH}_2-$  carbons attached to the ester group appeared around 40 ppm and the rest  $\text{sp}^3$  carbons appeared below upto 13.9 ppm.



**Figure II.B.3:**  $^1\text{H}$  NMR spectrum of  $\text{P}_1$



**Figure II.B.4:**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_1$

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy of the copolymers gave almost similar result. For example,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for  $\text{P}_{11}$  is given here (**Figure II.B.5 & Figure II.B.6**). In  $^1\text{H}$  NMR, aromatic protons for styrene group produced peaks at 7.01–7.33 ppm, protons for  $-\text{OCH}_2-$  groups of the ester produced peaks in the range from 3.93–4.35 ppm,  $-\text{CH}_2-$  protons attached with the carbonyl carbon accounted for the peaks in the region from 2.42–2.94 ppm and rest protons produced lower peaks at 0.93–1.29 ppm. In  $^{13}\text{C}$  NMR spectrum, the peaks at 170.5–175.2 ppm indicated the presence of ester carbonyl carbon. Peak in the range from

121.7–133.3 ppm accounted for the presence of aromatic moiety styrene. Peaks in the range 62.7–66.2 ppm appeared for  $-OCH_2-$  carbons. Other carbons attached with ester group produced peaks in the range 28.5–32.5 ppm. The rests accounted for other methyl and methylene carbons in the range 14.1–26.2 ppm.

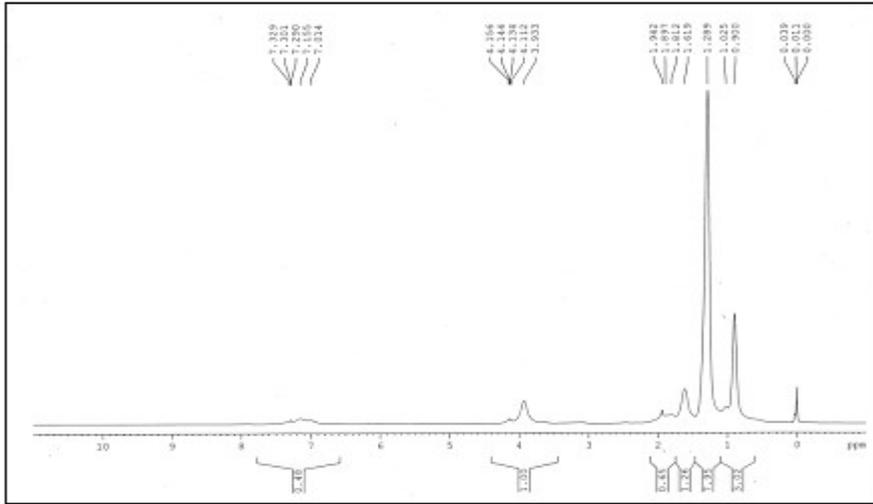


Figure II.B.5:  $^1H$ -NMR spectrum of  $P_{11}$

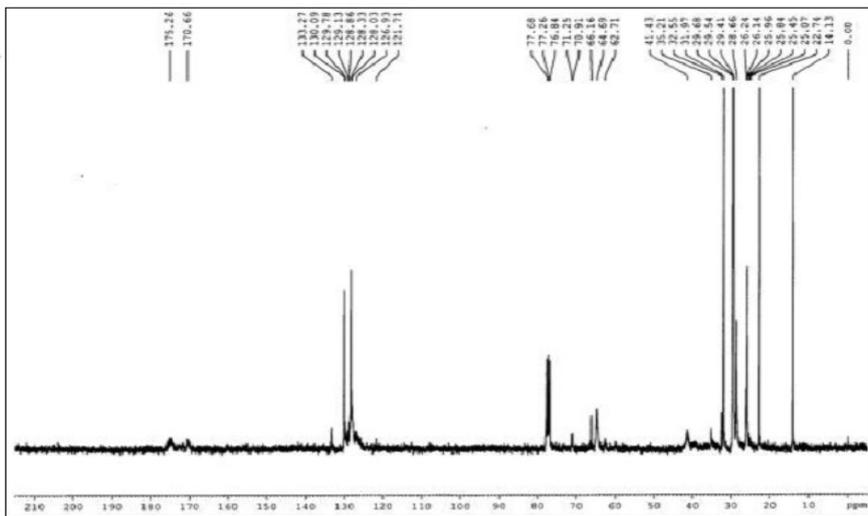


Figure II.B.6:  $^{13}C$ -NMR spectrum of  $P_{11}$

### II.B.5.c. Performance evaluation as pour point depressant

When the temperature decreases and reaches towards pour point wax crystals come out of the base oil and gradually gets bigger in shape and finally form a 3–D network of wax crystal which entraps the liquid and at some point immobilises the oil. Pour point depressants do not in any way affect the temperature at which the wax crystals grow or the amount of wax precipitates out, rather they modify the growing pattern of the waxes [31]. With decreasing temperature PPDs also come out of the solution as crystals along with the wax crystals and form a PPD backbone on the wax crystals. Due to this PPD backbone there plays a steric hindrance which keeps the wax crystals far apart and prevents the formation of 3–D network of wax crystal. Thus PPDs improve the flow property of base oil. Generally polymers with long alkyl chain, high molecular weight are good enough in this field [32].

**Table II.B.2: Pour point (PP) data (°C) with respect to the different concentrations (% w/w) of the additives in BO**

Conc <sup>n</sup>	PP data in BO1					PP data in BO2				
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%
<b>P<sub>1</sub></b>	-8.9	-9.1	-9.4	-9.4	-9.2	-11.7	-11.9	-12.3	-12.6	-12.6
<b>P<sub>2</sub></b>	-9.0	-9.2	-9.5	-9.7	-10.0	-12.2	-12.4	-12.7	-12.9	-12.8
<b>P<sub>3</sub></b>	-8.8	-9.0	-9.3	-9.5	-9.7	-12.0	-12.3	-12.8	-12.7	-12.7
<b>P<sub>4</sub></b>	-8.9	-9.3	-9.6	-9.6	-9.4	-12.2	-12.4	-12.7	-12.6	-12.3
<b>P<sub>5</sub></b>	-8.7	-9.1	-9.3	-9.7	-9.6	-11.9	-12.5	-12.6	-12.5	-12.2
<b>P<sub>6</sub></b>	-8.4	-8.7	-9.0	-9.2	-9.4	-11.4	-11.7	-11.9	-11.9	-11.8
<b>P<sub>7</sub></b>	-8.4	-8.8	-9.1	-9.4	-9.4	-11.0	-11.2	-11.5	-11.8	-11.8
<b>P<sub>8</sub></b>	-8.6	-8.9	-9.2	-9.5	-9.6	-11.3	-11.6	-11.8	-12.0	-12.0
<b>P<sub>9</sub></b>	-8.5	-8.8	-9.0	-9.3	-9.4	-11.2	-11.4	-11.5	-11.7	-11.5

<b>P<sub>10</sub></b>	-8.6	-8.9	-9.1	-9.5	-9.4	-11.1	-11.3	-11.6	-11.8	-11.8
<b>P<sub>11</sub></b>	-10.7	-10.9	-11.2	-11.4	-11.3	-13.2	-13.6	-13.9	-14.1	-14.2
<b>P<sub>12</sub></b>	-10.9	-11.0	-11.3	-11.5	-11.5	-13.4	-13.9	-14.0	-13.8	-13.8
<b>P<sub>13</sub></b>	-10.9	-11.1	-11.4	-11.4	-11.2	-13.0	-13.3	-13.6	-14.0	-14.1
<b>P<sub>14</sub></b>	-10.8	-11.0	-11.2	-11.2	-10.9	-13.3	-13.5	-13.7	-14.0	-14.0
<b>P<sub>15</sub></b>	-10.7	-10.9	-11.1	-11.3	-11.4	-13.1	-13.5	-13.8	-14.2	-14.0
<b>P<sub>16</sub></b>	-11.0	-11.3	-11.5	-11.8	-11.8	-14.3	-14.7	-15.1	-15.0	-14.9
<b>P<sub>17</sub></b>	-11.1	-11.4	-11.6	-11.7	-11.6	-14.2	-14.8	-15.0	-14.8	-14.6
<b>P<sub>18</sub></b>	-11.1	-11.4	-11.6	-11.9	-11.9	-14.5	-14.9	-15.5	-15.9	-15.8
<b>P<sub>19</sub></b>	-10.9	-11.3	-11.6	-11.6	-11.5	-14.1	-14.6	-15.2	-15.0	-15.0
<b>P<sub>20</sub></b>	-11.0	-11.2	-11.5	-11.7	-11.7	-14.2	-14.6	-14.9	-15.2	-15.2

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Conc<sup>n</sup> represents concentrations (% w/w) of the additives in base oil (BO)

Analysing the pour point data given in **Table II.B.2**, it may be said that all the prepared polymers acted as good flow improvers. But the copolymers are proved to be better PPDs than the homopolymers. Styrene incorporation in additive is well known to form an effective pour point depressant. This is also supported by our results. Among all P<sub>18</sub> copolymer prepared using 1.0% AIBN, showed highest pour point depression in both the base oils (BO1 and BO2). Homopolymers may be because of their higher molecular weight are less soluble in the base oil and hence are lesser effective as pour point depressant than the copolymers.

#### **II.B.5.d. Performance evaluation as viscosity index improver**

Solubility of the polymer, its molecular weight and composition play important role on its performance as viscosity index improver [33]. It is said that polymers exist as random coils in base oil solutions. As the temperature increases 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 decrease in viscosity with increase in temperature [34].

**Table II.B.3: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO1**

Conc <sup>n</sup>	1%		2%		3%		4%		5%	
	KV <sub>1</sub>	KV <sub>2</sub>								
<b>P<sub>1</sub></b>	6.713	2.101	6.736	2.130	6.749	2.172	6.763	2.201	6.785	2.243
<b>P<sub>2</sub></b>	6.721	2.123	6.747	2.140	6.768	2.193	6.787	2.241	6.821	2.315
<b>P<sub>3</sub></b>	6.718	2.113	6.741	2.140	6.762	2.184	6.779	2.220	6.803	2.261
<b>P<sub>4</sub></b>	6.712	2.103	6.734	2.121	6.739	2.164	6.755	2.181	6.771	2.210
<b>P<sub>5</sub></b>	6.710	2.091	6.728	2.101	6.735	2.142	6.751	2.172	6.761	2.190
<b>P<sub>6</sub></b>	6.704	2.041	6.711	2.062	6.723	2.091	6.738	2.102	6.747	2.131
<b>P<sub>7</sub></b>	6.709	2.071	6.723	2.090	6.731	2.112	6.744	2.131	6.753	2.151
<b>P<sub>8</sub></b>	6.710	2.081	6.725	2.102	6.736	2.142	6.749	2.163	6.762	2.181
<b>P<sub>9</sub></b>	6.704	2.061	6.710	2.071	6.722	2.101	6.739	2.123	6.743	2.140
<b>P<sub>10</sub></b>	6.705	2.061	6.712	2.083	6.724	2.112	6.743	2.148	6.747	2.165
<b>P<sub>11</sub></b>	6.703	2.042	6.708	2.066	6.719	2.089	6.734	2.101	6.739	2.125
<b>P<sub>12</sub></b>	6.702	2.041	6.706	2.059	6.716	2.081	6.729	2.101	6.738	2.125
<b>P<sub>13</sub></b>	6.703	2.033	6.707	2.051	6.718	2.083	6.734	2.103	6.740	2.121
<b>P<sub>14</sub></b>	6.701	2.035	6.704	2.051	6.713	2.071	6.726	2.092	6.734	2.125

<b>P<sub>15</sub></b>	6.701	2.031	6.705	2.052	6.713	2.078	6.727	2.101	6.735	2.123
<b>P<sub>16</sub></b>	6.704	2.052	6.711	2.072	6.723	2.101	6.739	2.121	6.743	2.152
<b>P<sub>17</sub></b>	6.708	2.072	6.721	2.092	6.729	2.110	6.741	2.140	6.750	2.171
<b>P<sub>18</sub></b>	6.709	2.073	6.723	2.091	6.730	2.121	6.743	2.143	6.754	2.182
<b>P<sub>19</sub></b>	6.705	2.063	6.711	2.085	6.724	2.113	6.742	2.149	6.748	2.162
<b>P<sub>20</sub></b>	6.704	2.051	6.712	2.060	6.722	2.091	6.740	2.113	6.745	2.135

Conc<sup>n</sup> represents concentration in % w/w; KV<sub>1</sub> & KV<sub>2</sub> represent kinematic viscosity at 40°C & 100°C respectively

**Table II.B.4: Kinematic viscosities (KV) with respect to the different concentrations of the additives in BO2**

<b>Conc<sup>n</sup></b>	<b>1%</b>		<b>2%</b>		<b>3%</b>		<b>4%</b>		<b>5%</b>	
	<b>KV<sub>1</sub></b>	<b>KV<sub>2</sub></b>								
<b>P<sub>1</sub></b>	24.371	4.810	24.423	4.961	24.503	5.152	24.569	5.340	24.643	5.505
<b>P<sub>2</sub></b>	24.382	4.861	24.457	5.082	24.541	5.292	24.622	5.484	24.711	5.720
<b>P<sub>3</sub></b>	24.376	4.821	24.432	4.990	24.519	5.191	24.593	5.390	24.667	5.561
<b>P<sub>4</sub></b>	24.363	4.770	24.408	4.873	24.479	5.025	24.523	5.142	24.618	5.270
<b>P<sub>5</sub></b>	24.352	4.730	24.393	4.821	24.447	4.933	24.502	5.051	24.586	5.182
<b>P<sub>6</sub></b>	24.337	4.651	24.360	4.723	24.418	4.810	24.464	4.912	24.558	5.029
<b>P<sub>7</sub></b>	24.350	4.722	24.371	4.802	24.438	4.900	24.482	5.019	24.571	5.161
<b>P<sub>8</sub></b>	24.353	4.735	24.388	4.818	24.441	4.950	24.497	5.061	24.573	5.211
<b>P<sub>9</sub></b>	24.339	4.702	24.365	4.763	24.423	4.851	24.469	4.965	24.561	5.089

<b>P<sub>10</sub></b>	24.342	4.723	24.373	4.789	24.432	4.891	24.478	5.025	24.567	5.137
<b>P<sub>11</sub></b>	24.332	4.629	24.355	4.691	24.413	4.789	24.460	4.878	24.554	5.009
<b>P<sub>12</sub></b>	24.335	4.642	24.359	4.709	24.415	4.802	24.462	4.889	24.556	5.023
<b>P<sub>13</sub></b>	24.330	4.621	24.353	4.678	24.410	4.769	24.458	4.869	24.551	4.989
<b>P<sub>14</sub></b>	24.328	4.601	24.350	4.667	24.408	4.759	24.456	4.859	24.550	4.981
<b>P<sub>15</sub></b>	24.327	4.591	24.347	4.649	24.407	4.752	24.453	4.838	24.548	4.969
<b>P<sub>16</sub></b>	24.341	4.732	24.368	4.789	24.425	4.901	24.472	5.001	24.575	5.109
<b>P<sub>17</sub></b>	24.353	4.731	24.391	4.820	24.438	4.981	24.492	5.108	24.563	5.283
<b>P<sub>18</sub></b>	24.353	4.738	24.375	4.818	24.440	4.943	24.491	5.058	24.575	5.252
<b>P<sub>19</sub></b>	24.340	4.701	24.374	4.802	24.435	4.918	24.479	5.029	24.569	5.148
<b>P<sub>20</sub></b>	24.338	4.678	24.362	4.729	24.420	4.838	24.465	4.931	24.560	5.039

Conc<sup>n</sup> represents concentration in % w/w; KV<sub>1</sub> & KV<sub>2</sub> represent kinematic viscosity at 40°C & 100°C respectively

**Table II.B.5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO**

<b>Conc<sup>n</sup></b>	<b>VI data in BO1</b>					<b>VI data in BO2</b>				
	<b>1%</b>	<b>2%</b>	<b>3%</b>	<b>4%</b>	<b>5%</b>	<b>1%</b>	<b>2%</b>	<b>3%</b>	<b>4%</b>	<b>5%</b>
<b>P<sub>1</sub></b>	107	115	128	137	149	118	130	144	158	169
<b>P<sub>2</sub></b>	113	119	133	151	170	122	139	154	168	184
<b>P<sub>3</sub></b>	109	117	131	143	155	119	132	147	161	173
<b>P<sub>4</sub></b>	105	112	126	132	141	115	123	134	143	152

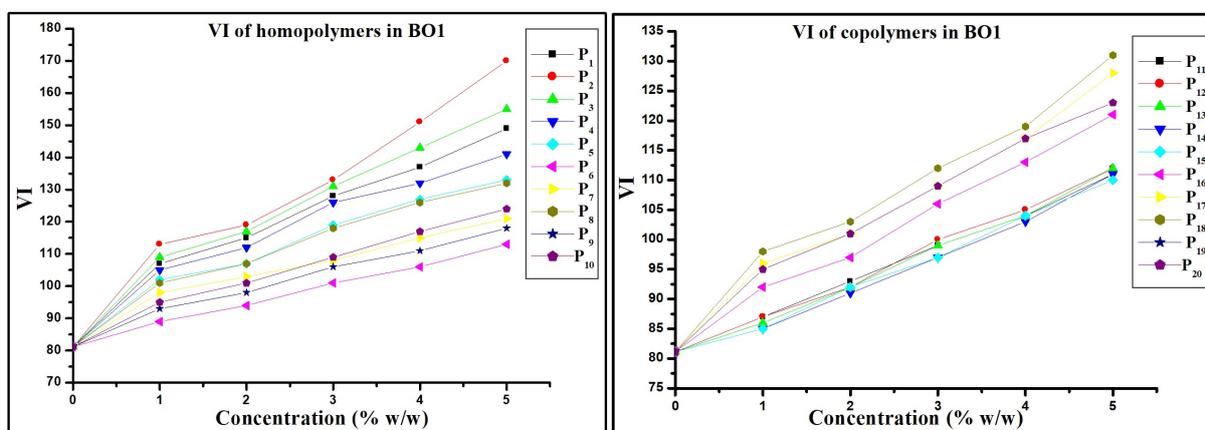
<b>P<sub>5</sub></b>	102	107	119	127	133	112	119	127	136	145
<b>P<sub>6</sub></b>	89	94	101	106	113	106	111	118	125	134
<b>P<sub>7</sub></b>	98	103	108	115	121	111	117	125	133	144
<b>P<sub>8</sub></b>	101	107	118	126	132	112	118	129	137	148
<b>P<sub>9</sub></b>	93	98	106	111	118	110	114	121	129	138
<b>P<sub>10</sub></b>	95	101	109	117	124	111	116	124	134	142
<b>P<sub>11</sub></b>	87	93	99	104	111	104	109	116	123	132
<b>P<sub>12</sub></b>	87	92	100	105	112	105	110	117	124	133
<b>P<sub>13</sub></b>	86	92	99	104	112	103	108	115	122	131
<b>P<sub>14</sub></b>	85	91	97	103	111	102	107	114	121	130
<b>P<sub>15</sub></b>	85	92	97	104	110	101	106	113	120	129
<b>P<sub>16</sub></b>	92	97	106	113	121	112	117	125	132	140
<b>P<sub>17</sub></b>	96	101	109	117	128	112	119	131	140	153
<b>P<sub>18</sub></b>	98	103	112	119	131	113	119	128	137	151
<b>P<sub>19</sub></b>	95	101	109	117	123	110	117	126	135	143
<b>P<sub>20</sub></b>	90	94	102	107	114	108	112	120	127	135

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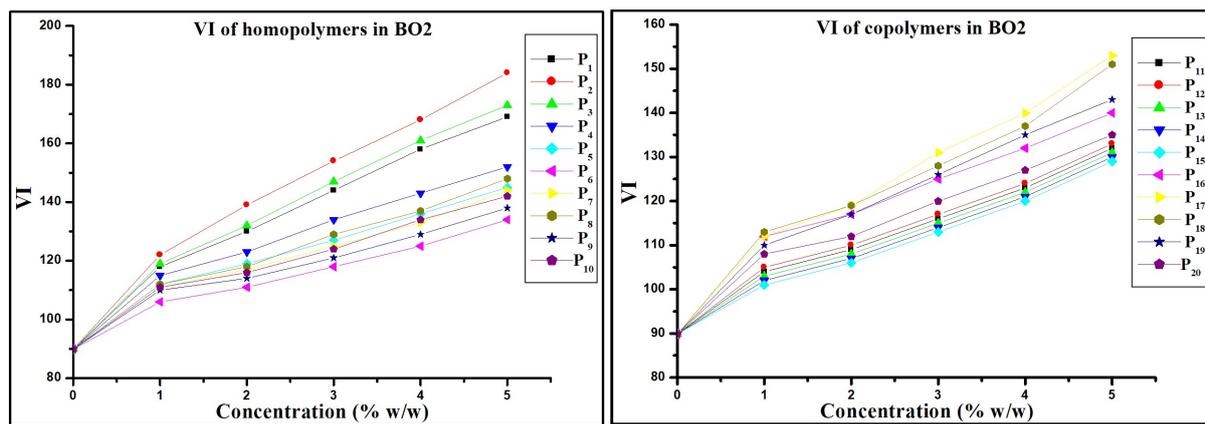
Conc<sup>n</sup> represents concentration in % w/w

It is seen from the **Table II.B.3** and **II.B.4** that the homopolymers exhibited better kinematic viscosity at all concentrations compared to the copolymers. Higher molecular weight of the homopolymers may be the reason behind it since higher the molecular weight of the polymer higher is the volume it exposed in the solution and hence higher viscosity is observed.

Comparing all the data from **Table II.B.5** and the figures, P<sub>2</sub> homopolymer has been proved to be the best viscosity index improver among all the prepared polymers. The homopolymers are also associated with higher viscosity index values again due to their higher molecular weight [35]. The comparison among the homopolymers is well understood from the **Figure II.B.7**. Among the homopolymers, P<sub>2</sub> i.e. the homopolymer of isodecylacrylate having highest molecular weight prepared using 0.5% BZP showed highest kinematic viscosity values at all concentrations in both the base oils.



**Figure II.B.7: Variation of viscosity index with respect to the different concentrations of the additives in BO1**



**Figure II.B.8: Variation of viscosity index with respect to the different concentrations of the additives in BO2**

Graphical representation of VI data of the copolymers (**Figure II.B.8**) shows clear comparison between their viscometric properties. Among the copolymers, P<sub>18</sub> i.e. the copolymer of isodecyl acrylate and styrene prepared using 1% AIBN, exhibited better result as viscosity index improver than all the copolymers. Overall it may be said that homopolymers prepared using BZP initiator are proved to be better viscosity index improver. With increasing concentration of the polymer in the base oil, total volume of the polymer micelle increases and hence the viscosity index data also increases with increasing concentration of the polymer in base oil [36].

### II.B.5.e. Shear stability index analysis

PSSI and PVL data (**Table II.B.6, II.B.7 and II.B.8**) provide a clear picture about acceptability of polymer as a shear stable additive.

**Table II.B.6: Kinematic viscosity after shear at 100°C (<sup>s</sup>KV<sub>2</sub>) and PVL data with respect to the different concentrations of the additives in BO1**

Conc <sup>n</sup>	1%		2%		3%		4%		5%	
	<sup>s</sup> KV <sub>2</sub>	PVL								
<b>P<sub>1</sub></b>	2.071	1.43	2.081	2.35	2.101	3.22	2.112	4.09	2.131	4.91
<b>P<sub>2</sub></b>	2.093	1.42	2.101	1.87	2.135	2.74	2.157	3.57	2.012	4.76
<b>P<sub>3</sub></b>	2.085	1.42	2.088	2.34	2.112	3.21	2.132	4.05	2.159	4.87
<b>P<sub>4</sub></b>	2.077	1.43	2.079	1.89	2.103	2.78	2.113	3.21	2.131	3.62
<b>P<sub>5</sub></b>	2.062	1.44	2.057	1.90	2.069	3.27	2.076	4.15	2.089	4.57
<b>P<sub>6</sub></b>	2.055	1.20	2.059	1.90	2.068	3.27	2.079	3.70	2.078	4.59
<b>P<sub>7</sub></b>	2.051	0.97	2.058	1.44	2.071	1.89	2.080	2.35	2.087	2.79
<b>P<sub>8</sub></b>	2.029	0.54	2.035	1.21	2.046	2.11	2.045	2.62	2.051	3.71
<b>P<sub>9</sub></b>	2.041	0.92	2.044	1.26	2.056	2.09	2.062	2.74	2.068	3.36

<b>P<sub>10</sub></b>	2.043	0.82	2.052	1.35	2.067	2.04	2.081	2.76	2.091	3.19
<b>P<sub>11</sub></b>	2.031	0.46	2.039	1.02	2.046	1.63	2.053	2.24	2.061	2.78
<b>P<sub>12</sub></b>	2.029	0.54	2.031	0.93	2.041	1.87	2.044	2.67	2.049	3.35
<b>P<sub>13</sub></b>	1.981	2.41	2.034	0.78	2.045	1.68	2.051	2.33	2.057	2.97
<b>P<sub>14</sub></b>	1.983	2.32	2.035	0.73	2.041	1.40	2.046	2.11	2.056	3.02
<b>P<sub>15</sub></b>	1.986	2.14	2.036	0.68	2.047	1.11	2.061	1.86	2.066	2.54
<b>P<sub>16</sub></b>	2.036	0.86	2.046	1.16	2.058	2.00	2.067	2.50	2.076	3.44
<b>P<sub>17</sub></b>	2.048	1.06	2.058	1.53	2.068	1.99	2.083	2.66	2.097	3.36
<b>P<sub>18</sub></b>	2.049	1.01	2.058	1.53	2.072	2.26	2.079	2.85	2.097	3.81
<b>P<sub>19</sub></b>	2.039	1.02	2.047	1.59	2.057	2.51	2.067	3.41	2.074	3.98
<b>P<sub>20</sub></b>	2.036	0.68	2.037	1.12	2.049	1.96	2.056	2.56	2.063	3.14

Conc<sup>n</sup> represents concentration in % w/w

**Table II.B.7: Kinematic viscosity after shear at 100°C (<sup>s</sup>KV<sub>2</sub>) and PVL data with respect to the different concentrations of the additives in BO2**

Conc <sup>n</sup>	1%		2%		3%		4%		5%	
	<sup>s</sup> KV <sub>2</sub>	PVL								
<b>P<sub>1</sub></b>	4.749	1.25	4.868	1.81	5.019	2.52	5.159	3.37	5.249	4.54
<b>P<sub>2</sub></b>	4.810	1.03	4.990	1.77	5.172	2.27	5.320	2.92	5.510	3.67
<b>P<sub>3</sub></b>	4.756	1.24	4.901	1.80	5.038	2.89	5.178	3.89	5.278	5.04
<b>P<sub>4</sub></b>	4.701	1.47	4.762	2.26	4.851	3.39	4.891	4.86	4.960	5.88

<b>P<sub>5</sub></b>	4.652	1.68	4.708	2.28	4.760	3.45	4.843	5.15	4.844	6.56
<b>P<sub>6</sub></b>	4.531	2.58	4.551	3.60	4.569	4.99	4.590	6.52	4.619	8.15
<b>P<sub>7</sub></b>	4.612	1.91	4.668	2.70	4.712	3.88	4.758	4.99	4.833	6.39
<b>P<sub>8</sub></b>	4.639	1.90	4.681	2.70	4.748	4.04	4.790	5.34	4.828	7.29
<b>P<sub>9</sub></b>	4.578	2.55	4.602	3.36	4.629	4.54	4.651	6.25	4.690	7.68
<b>P<sub>10</sub></b>	4.609	2.33	4.629	3.14	4.673	4.49	4.722	5.98	4.762	7.21
<b>P<sub>11</sub></b>	4.512	2.59	4.523	3.62	4.541	5.22	4.549	6.76	4.575	8.78
<b>P<sub>12</sub></b>	4.519	2.59	4.531	3.82	4.649	5.21	4.570	6.54	4.590	8.56
<b>P<sub>13</sub></b>	4.513	2.39	4.562	2.56	4.520	5.24	4.533	6.98	4.543	9.01
<b>P<sub>14</sub></b>	4.502	2.17	4.511	3.43	4.522	5.04	4.532	6.79	4.542	8.83
<b>P<sub>15</sub></b>	4.489	2.18	4.487	3.44	4.501	5.26	4.501	7.02	4.509	9.26
<b>P<sub>16</sub></b>	4.609	2.54	4.642	3.13	4.689	4.29	4.708	5.80	4.753	7.05
<b>P<sub>17</sub></b>	4.628	2.11	4.678	2.90	4.768	4.22	4.807	5.69	4.900	7.19
<b>P<sub>18</sub></b>	4.650	1.89	4.689	2.69	4.748	3.85	4.812	4.94	4.911	6.48
<b>P<sub>19</sub></b>	4.601	2.13	4.655	3.13	4.709	4.27	4.754	5.57	4.802	6.79
<b>P<sub>20</sub></b>	4.549	2.78	4.561	3.59	4.591	5.17	4.609	6.49	4.644	7.94

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Conc<sup>n</sup> represents concentration in % w/w

**Table II.B.8: PSSI data with respect to the different concentrations of the additives in BO**

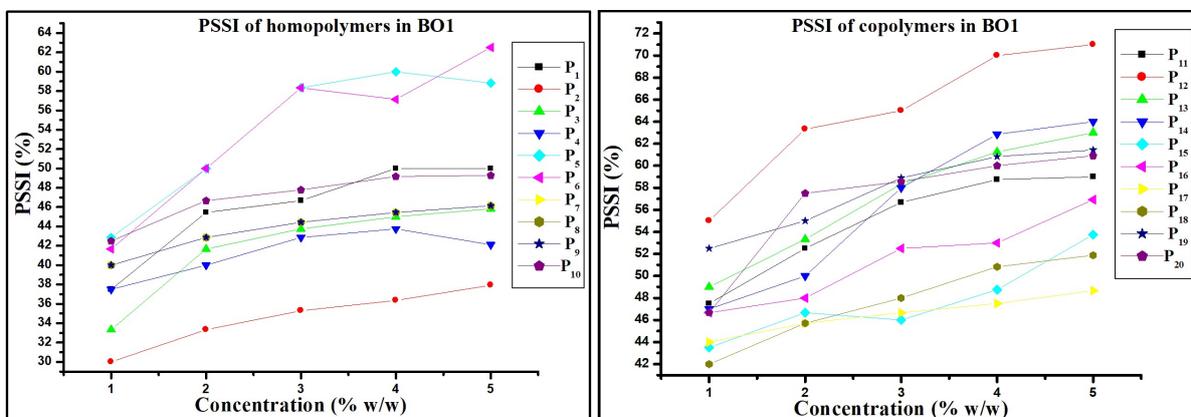
<b>Conc<sup>n</sup></b>	<b>PSSI (%) data in BO1</b>					<b>PSSI (%) data in BO2</b>				
	<b>1%</b>	<b>2%</b>	<b>3%</b>	<b>4%</b>	<b>5%</b>	<b>1%</b>	<b>2%</b>	<b>3%</b>	<b>4%</b>	<b>5%</b>

<b>P<sub>1</sub></b>	37.50	45.45	46.67	50.00	50.00	17.65	18.37	19.12	20.69	24.27
<b>P<sub>2</sub></b>	30.00	33.33	35.29	36.36	37.93	12.82	13.43	14.63	15.84	16.80
<b>P<sub>3</sub></b>	33.33	41.67	43.75	45.00	45.83	17.14	17.31	20.83	22.83	25.69
<b>P<sub>4</sub></b>	37.50	40.00	42.86	43.75	42.11	23.33	27.50	30.91	37.31	38.75
<b>P<sub>5</sub></b>	42.86	50.00	58.33	60.00	58.82	26.67	31.43	36.96	44.83	47.89
<b>P<sub>6</sub></b>	41.67	50.00	58.33	57.14	62.50	66.67	68.00	70.59	72.73	73.21
<b>P<sub>7</sub></b>	40.00	42.86	44.44	45.45	46.15	36.00	39.39	44.19	46.29	47.83
<b>P<sub>8</sub></b>	55.00	62.50	62.86	68.75	71.82	34.62	38.23	41.67	45.76	51.35
<b>P<sub>9</sub></b>	47.50	52.00	55.00	58.00	60.00	52.17	55.17	57.89	63.26	63.93
<b>P<sub>10</sub></b>	42.50	46.67	47.78	49.17	49.28	44.00	48.39	52.38	54.55	56.06
<b>P<sub>11</sub></b>	47.50	52.50	56.67	58.75	59.00	75.00	77.27	78.13	80.49	81.48
<b>P<sub>12</sub></b>	55.00	63.33	65.00	70.00	71.00	70.59	75.00	75.76	76.19	78.18
<b>P<sub>13</sub></b>	49.00	53.33	58.33	61.25	63.00	73.33	80.00	83.33	85.00	86.54
<b>P<sub>14</sub></b>	47.00	50.00	58.00	62.86	64.00	76.92	80.00	82.76	84.62	86.27
<b>P<sub>15</sub></b>	43.50	46.67	46.00	48.75	53.75	83.33	88.89	89.28	91.89	92.00
<b>P<sub>16</sub></b>	46.67	48.00	52.50	53.00	56.92	46.15	46.88	48.83	54.72	56.25
<b>P<sub>17</sub></b>	44.00	45.71	46.67	47.50	48.67	38.46	40.00	41.18	46.03	46.91
<b>P<sub>18</sub></b>	42.00	45.71	48.00	50.83	51.88	33.33	37.14	40.43	42.37	43.59
<b>P<sub>19</sub></b>	52.50	55.00	58.89	60.83	61.43	43.48	45.45	46.67	50.00	51.47
<b>P<sub>20</sub></b>	46.67	57.50	58.57	60.00	60.91	61.90	65.38	67.57	69.57	70.17

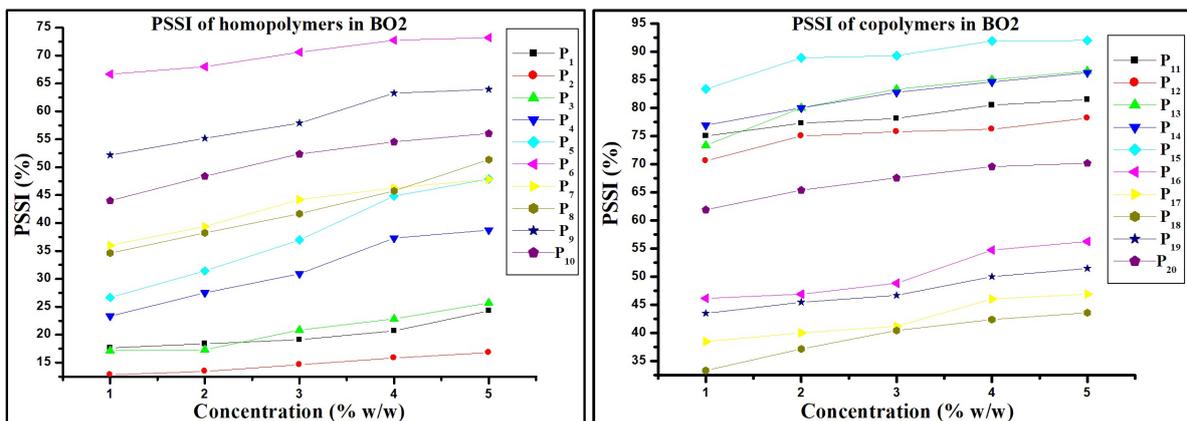
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Conc<sup>n</sup> represents concentration in % w/w

Modern additives are required to facilitate the engine oil getting strong enough against severe mechanical shear. Basically under extreme pressure, additive in lube oil solution undergoes molecular degradation and loses its viscosity improvement property. Hence to be recommended as a good additive for multi-grade engine oil, it must be less prone towards molecular degradation against mechanical stress. Analysing all the data obtained from **Table II.B.6, II.B.7 and II.B.8** it may be concluded that P<sub>2</sub> homopolymer exhibited higher stability against mechanical shear at all concentrations in both the base oil. It implies that viscosity loss after shear in case of P<sub>2</sub> is least among all the prepared polymers.



**Figure II.B.9: Variation of PSSI with respect to the different concentrations of the additives in BO1**



**Figure II.B.10: Variation of PSSI with respect to the different concentrations of the additives in BO2**

It is also seen that the homopolymers prepared using BZP initiator are comparatively better shear stable. Styrene inclusion in additive generally makes it more susceptible towards molecular degradation under shear. As a result, our prepared copolymers are associated with higher PSSI values. Among the copolymers, P<sub>18</sub> i.e. the copolymer prepared using 1% AIBN is more shear stable. Again higher the concentration of the additive in the lube oil solution higher is PVL and PSSI values. This observation is more evident from the graphical representations (**Figure II.B.9 & Figure II.B.10**).

### **II.B.6. Conclusion**

This comparative study reveals that percentage of the initiator either BZP or AIBN used during the polymerisation process does play an important role in determining the properties from molecular weight to viscometric properties of the additives in lube oil. Data obtained from GPC summarises that homopolymers of isodecyl acrylate prepared using BZP are associated with higher molecular weight than those prepared using AIBN whereas reverse observation was obtained in case of copolymers with styrene. The homopolymer prepared using 0.5% BZP showed highest molecular weight among all the prepared polymers. This homopolymer is also proved to be better viscosity modifier and better extreme pressure additive. But the copolymers are better pour point depressants than the homopolymers. Among all the polymers the copolymer prepared using 1% AIBN showed highest pour point depression. Thus the above study may help us to choose proper dosage of initiator while polymerisation to prepare a polymeric additive as per our required property.

### **II.B.7: REFERENCES**

References for chapter II.B are given in bibliography section (page 127–130).