

## Chapter-IV

*Acrylate terpolymer based polymeric  
additives as a pour point depressant  
and viscosity modifier for lube oil*

### **1.4.1 Introduction**

The materials that are largely used to reduce friction and wear between interacting surfaces and to assist the relative motion of solid bodies are called lubricants. Important advancements in lubricant industry have consequently led to tremendous revolution in the field of engines, high speed machinery and manufacturing industries. These developments have also created enormous potential for modern engines and equipments that are operating under more harsh and challenging environments. But, to achieve such a high level of performance, lubricating oils are always formulated with diverse class of additives.<sup>1</sup> These oils are thus a combination of a base oil and various additives. Removal of heat, reducing the thermal or oxidative degradation of oils, suspension and removal of wear particles, minimizing rust and corrosion are some of the key roles that can be played by an additive.<sup>2</sup>

Also, low viscosity of oil creates a potential problem as it causes a drop in the oil's lubricating ability at high temperature. Better oils by maintaining an ample viscosity at high temperature allows smooth interaction of interacting surfaces. Viscosity modifiers or viscosity index improvers (VII) are polymers that are usually added to the base oils to serve this particular purpose.<sup>3</sup> They allow the lubricants to meet certain high-temperature viscosity targets while preserving acceptable low-temperature fluidity. The polymer chains of VII adopt a coiled aggregation at low temperature in order to minimize their effect on viscosity. This means that they have a small hydrodynamic volume and a minimum association with the bulk oil and the effect is a very little viscosity increase. But, when the temperature is increased, the situation is reversed and the chains have a tendency to straighten out with increased polymer chain entanglements causing an increase in the oil's viscosity.<sup>4</sup> In other words, the polymers

become more soluble at higher temperatures and, consequently cause an increase in viscosity. Viscosity Index or VI is an arbitrary parameter that indicates this effect of change of temperature on the kinematic viscosity of oil.<sup>5</sup> Oils with higher VI ratings are more useful, as they are more stable under changing temperature conditions and suggest a narrower change in viscosity over a standard temperature range of operation.

Again, in low temperature, where the solubility of dissolved waxy hydrocarbons of mineral oils is sufficiently low, they tend to separate from the oil forming a rigid network of crystals.<sup>6</sup> While doing so, they capture the remaining oil in cage-like structures and stop the oil from flowing or pouring. This lowest temperature at which the oil will still pour or flow is defined as the pour point of the oil. In order to improve the pour point, wax crystal modifiers alternatively known as pour point depressants (PPD) are mixed to the oil.<sup>7</sup> Generally the pour point improves with the increasing PPD concentration in the base stock. However, there also exist an optimum concentration for almost every PPD where after the pour point deteriorates with the increasing PPD concentration. Various theories have been put forward by different groups of researchers about the mechanism of action of PPDs among which nucleation, adsorption, co-crystallization and improved wax solubility are widely accepted.<sup>8,9</sup> The deterioration in the pour point depression property of the additives with the increasing PPD fraction is sometimes because of the strong linkage of the PPD molecules with the waxy hydrocarbons present in the oil. Due to such a strong association, the PPD molecules become more bulky and less soluble ultimately making it less effective.<sup>10</sup>

Acrylates and methacrylates are some of the well documented viscosity modifier and pour point depressant from years.<sup>11</sup> A lot of work has been carried out considering the polymerisation of two acrylate or methacrylate monomers but reports regarding terpolymerization are very few. The introduction of a third monomer into the polymer

moiety can sometime initiate new properties and features to the polymer and offer additional parameters to control the copolymer properties. With this view in mind, the present work comprises the synthesis of acrylate based terpolymers using octyl, decyl and dodecyl alcohol. The prepared terpolymers were evaluated for their performance as PPD and VII under identical condition.

### **1.4.2 Experimental Section**

#### **1.4.2.1 Materials**

1-Octanol (GC 98%) and 1-decanol (GC 98%) were purchased from Loba Chemie Pvt., Ltd. 1-Dodecanol (GC 98%) and acrylic acid (GC 99%, stabilized with 0.02 % hydroquinone mono methylether) were obtained from Sisco Research Laboratories Pvt., Ltd. Toluene was refluxed for 2 h in presence of sodium and purified by distillation to be used as a solvent. H<sub>2</sub>SO<sub>4</sub> and hydroquinone were obtained from Merck Specialities Pvt., Ltd. AIBN was purchased from Spectrochem Pvt., Ltd., and methanol (GC 98%) was obtained from Thomas Baker (Chemicals) Pvt., Ltd. The two base oils (BO1 and BO2) were collected from Indian Oil Corporation Limited, India (Table 1.4.1).

#### **1.4.2.2 Esterification**

The ester, dodecyl acrylate (DDA) was synthesised by reacting 1.1 mol of acrylic acid with 1 mol of dodecyl alcohol. The reaction was performed in a three necked reaction kettle in the presence of 0.25 % hydroquinone (with respect to the reactants) as inhibitor for the polymerization of acrylic acid, conc. H<sub>2</sub>SO<sub>4</sub> as catalyst and under a slow stream of deoxygenated nitrogen. The alcohol and the acid were mixed with an

equal weight of toluene (as a solvent), the mixture was steadily heated and the temperature was increased up to 403 K with the help of a thermostat. Assessment of the completeness of the reaction was done by monitoring the quantity of water collected in the Dean-Stark apparatus connected with the reaction kettle. The other two esters, decyl acrylate (DA) and octyl acrylate (OA) were also prepared using acrylic acid, decyl alcohol and octyl alcohol respectively following the same procedure.

#### ***1.4.2.3 Purification of the prepared esters***

The prepared esters were purified by adding 1 g of charcoal to it and refluxing it for 3 hour. The charcoal was then filtered off and the filtrate was rinsed in a separating funnel with 0.5N NaOH solution. The process was repeated several times to make sure the total elimination of any unreacted acids. The ester was then rinsed a number of times with distilled water to eliminate any NaOH (if left in small amount) until it became neutral to pH paper. The ester was finally left over night on anhydrous CaCl<sub>2</sub> for drying. The CaCl<sub>2</sub> was removed by filtration and the toluene was recovered by distillation under reduced pressure. The ester left was ready to be used in the polymerization process.<sup>12</sup>

#### ***1.4.2.4 Synthesis of the terpolymers***

The terpolymerization reaction was performed in a four necked round bottom flask fitted with a heating jacket system, a thermometer, a reflux condenser, and equipped with a magnetic stirrer. The flask was also connected with an inlet for the introduction of nitrogen gas. The prepared esters, OA, DA and DDA were placed in the flask in a 1:1:1 (w/w) ratio and toluene was added to it (as a solvent). The initiator

AIBN (0.4% of the monomers) was then added to the reaction mixture and it was heated and kept for 6 h at 353 K to prepare the terpolymer. After the stipulated time, the reaction mixture was allowed to cool to room temperature. Finally, to stop the polymerization reaction and precipitate the polymer, the mixture was transferred into cooled methanol with continuous stirring. Further, for purification of the polymer, it was precipitated by methanol from its hexane solutions repetitively and then dried under vacuum at 313 K. Similar polymerizations using different ratios of OA, DA and DDA (2:1:1, 1:2:1, and 1:1:2 respectively) were also carried out and the polymers were purified under the same conditions (Table 1.4.2).

### **1.4.3 Measurements**

#### **1.4.3.1 Spectroscopic measurements**

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

#### **1.4.3.2 Determination of molecular weight of the prepared terpolymers**

The molecular weights of the prepared terpolymers were determined by using gel permeation chromatography (GPC) system (Waters Corporation; USA) equipped with a 2414 refractive index detector (polystyrene calibration), Waters 515 HPLC pump in HPLC grade THF (0.4% w/v) as an eluent at 40°C.

### **1.4.3.3 Evaluation of the prepared polymers as PPDs in base oils**

The prepared polymers were tested for their pour point (PP) depression ability according to the ASTM D97-09 method on a Cloud and Pour Point Tester (WIL-471, India) in two base oils (BO1 and BO2). The effect of polymer concentration on the PP was investigated by using different percentages of the polymer.

### **1.4.3.4 Evaluation of the prepared polymers as VIIs in base oils**

The alteration of kinematic viscosity (KV) of oil with the variation of temperature is denoted by an arbitrary dimensionless number called VI. The VI was evaluated according to the ASTM D2270 method for the two base oils blended with different percentages of the additive at 40°C and 100°C.<sup>13</sup> The effectiveness of an additive as VII is assessed by the increase in the VI value of the base oils after addition of the additive. The KV was determined by the equation,

$$KV = (Kt - L/t) \rho \quad \text{Eq. (2)}$$

where K and L are viscometric constants;  $t$  is the time of flow of the lube oil blended with different mass fraction of the additive to pass through the two calibrated marks in the Ubbelohde viscometer and  $\rho$  is density of the additive doped lube oil.<sup>14</sup>

The densities of the additive doped oils were determined with the help of a DMA 4500 M vibrating-tube density meter (Anton paar, Austria) and the time of flow of the oils were recorded with a digital stopwatch. All the measurements per batch were made in duplicate. The VI value was determined from the following standard empirical equation,

$$VI = 3.63(60 - 10^n) \quad \text{Eq. (3)}$$

where  $n$  is a constant depending upon the temperature range chosen for the oil. The value of  $n$  was calculated by the equation,

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad \text{Eq. (4)}$$

where  $v_1$  and  $v_2$  are the kinematic viscosities of the oil blended with the additive at lower and higher temperature respectively. The value of  $k$  is independent of the nature of the oil and is a function of temperature alone. The value of  $k$  was found to be 2.715 for the given temperature range.<sup>15</sup>

#### **1.4.4 Results and discussion**

##### **1.4.4.1 Spectroscopic analysis**

The FT-IR spectra of the polymer P-1 (Fig. 1.4.1) showed signal for the stretching vibration of ester carbonyl (C=O) at  $1735.8 \text{ cm}^{-1}$  while the broad signals in the regions of  $1465.8 \text{ cm}^{-1}$  and at  $1164.9 \text{ cm}^{-1}$  were due to the stretching vibrations of ester C–O–C group. The signals observed in the regions of  $1072.3 \text{ cm}^{-1}$  and  $717.5 \text{ cm}^{-1}$  were for the C–H bending vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups while the peaks observed in the regions of  $2923.9 \text{ cm}^{-1}$  and  $2854.5 \text{ cm}^{-1}$  were for the stretching vibrations of paraffinic C–H bonds.

In the  $^1\text{H-NMR}$  spectra (Fig. 1.4.2), the polymer P-1 displayed the presence of the proton of  $-\text{COOCH}_2$  group by appearing as a broad peak centred at 4.01 ppm. Signals also appeared in the range of 0.861 to 0.903 ppm and 1.268 to 1.602 ppm for all the methyl and methylene protons respectively.

The proton decoupled  $^{13}\text{C-NMR}$  spectra (Fig. 1.4.3) displayed peak at 174.6 ppm for the carbonyl carbons of the ester groups. The absence of unsaturation in the polymer was indicated by the nonappearance of any olefinic peaks in the spectra. All the

other synthesised polymers (P-2, P-3 and P-4) showed similar peaks in their FT-IR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectrum indicating that the prepared polymers are in good agreement with the expected structures.

#### ***1.4.4.2 Performance of the prepared polymers as PPD***

Evaluation of the synthesised polymers for their PPD performances showed good results (Figs. 1.4.4 and 1.4.5) in the base oils under investigation. The results pointed out that the prepared polymer P-4 is more efficient as PPD than the other polymer samples in both the base oils. Also, it is clearly noticeable that the effectiveness of all the polymers as PPD increased with its decreasing concentration in the base oils. This outcome can be explained by the fact that the solvation power of any solvent decreases with decreasing temperature. So, when the temperature is lowered during pour point analysis, but the concentration as well as the molecular weight of the polymer is increased in the oil, there occurs a substantial reduction in the solvation power and the polymers become less soluble in the oil. This reduction in the solvation capability reduces the PP efficiency of the polymers in the oil.<sup>16</sup>

#### ***1.4.4.3 Performance of the prepared polymers as VII***

Assessment of the results (Table 1.4.3), as obtained, showed that the VI values increased with the increase in polymer percentage irrespective of the base oil and the polymer used. A critical analysis of the VI values also showed that polymer P-4 has the most superior performance as VII followed by polymer P-3, P-1 and P-2. The results suggested that the performance of the prepared polymers as VII is directly proportional

to the alkyl chain length of the acrylate used. Also, the increase in the alkyl chain length has a direct effect on increasing the molecular mass of the polymers (Table 1.4.2). Thus, the increased effective radius of polymer micelle with the increased molecular weight of the polymer can be the cause of this direct relationship of VI with the chain length of the acrylate.<sup>17</sup> Besides, the increase in the VI values with increasing polymer percentage in the base oil can be the result of increased hydrodynamic volume of the polymer. Hydrodynamic volume is the volume of the polymer and the associated oil. At higher temperature there occurs an increase in the power of solvation of the oil and, therefore, an expansion of polymer molecules and increase in the size of the micelle takes place.<sup>18</sup> Thus, higher the percentage of polymer in the oil, higher is the volume of the micelle and subsequently higher will be its association with the oil leading to higher VI.<sup>3</sup>

#### **1.4.5 Conclusions**

The systematic analysis of the synthesised polymers revealed that all the polymers performed as efficient PPDs and VIIs. The VI values, as obtained, increased with an enhancement in polymer percentage in the oil and terpolymer P-4 with the highest ratio of DDA acted as a superior VI improver compared to the other polymers. Also, it was established that the terpolymer P-4 is more efficient as PPD for the given lube oils under consideration. Thus, a significant modification of base oil properties has been achieved by addition of these polymers to the given lube oils.

#### **1.4.6 References**

References are given in BIBLIOGRAPHY section under Chapter-IV of Part-I (Page No. 201-203).

#### 1.4.7 Tables and figures

**Table 1.4.1: Physical properties of base oils**

<b>Properties</b>	<b>Method</b>	<b>B01</b>	<b>B02</b>
Viscosity at 40 °C (cSt)	ASTM D445	7.132	23.387
Viscosity at 100 °C (cSt)	ASTM D445	1.849	3.911
Density (g.cm <sup>-3</sup> ) at 40 °C	ASTM D4052	0.83645	0.85492
Viscosity index	ASTM D2270	80	85
Pour point, °C	ASTM D97	-3	-6

**Table 1.4.2: Terpolymer designation and molecular weight**

<b>Terpolymer designation</b>	<b>Monomer feed ratio (w/w)</b>			<b>Molecular weight</b>	
	<b>Octyl acrylate</b>	<b>Decyl acrylate</b>	<b>Dodecyl acrylate</b>	<b>M<sub>n</sub></b>	<b>M<sub>w</sub></b>
P-1	1	1	1	17633	22395
P-2	2	1	1	16200	19926
P-3	1	2	1	18734	27351
P-4	1	1	2	20986	28752

Table 1.4.3: Viscosity index (VI) values of polymers (P-1 to P-4) doped in base oils

Polymer	Base oil	Concentration of polymer doped base oils (w/w)					
		VI					
		0%	1%	2%	3%	4%	5%
P-1	BO1	80	86.21	93.31	98.69	106.2	113.6
	BO2	85	90.25	97.37	102.9	109.2	118.3
P-2	BO1	80	85.73	91.19	97.55	104.6	110.1
	BO2	85	89.3	94.21	99.41	106.3	113.4
P-3	BO1	80	86.49	94.62	101.5	109.7	116.4
	BO2	85	90.12	98.04	106.3	114.3	122.6
P-4	BO1	80	90.56	97.14	105.5	112.6	121.8
	BO2	85	94.64	102.9	108.2	118.8	127.1

Figure 1.4.1: IR spectra of polymer P-1

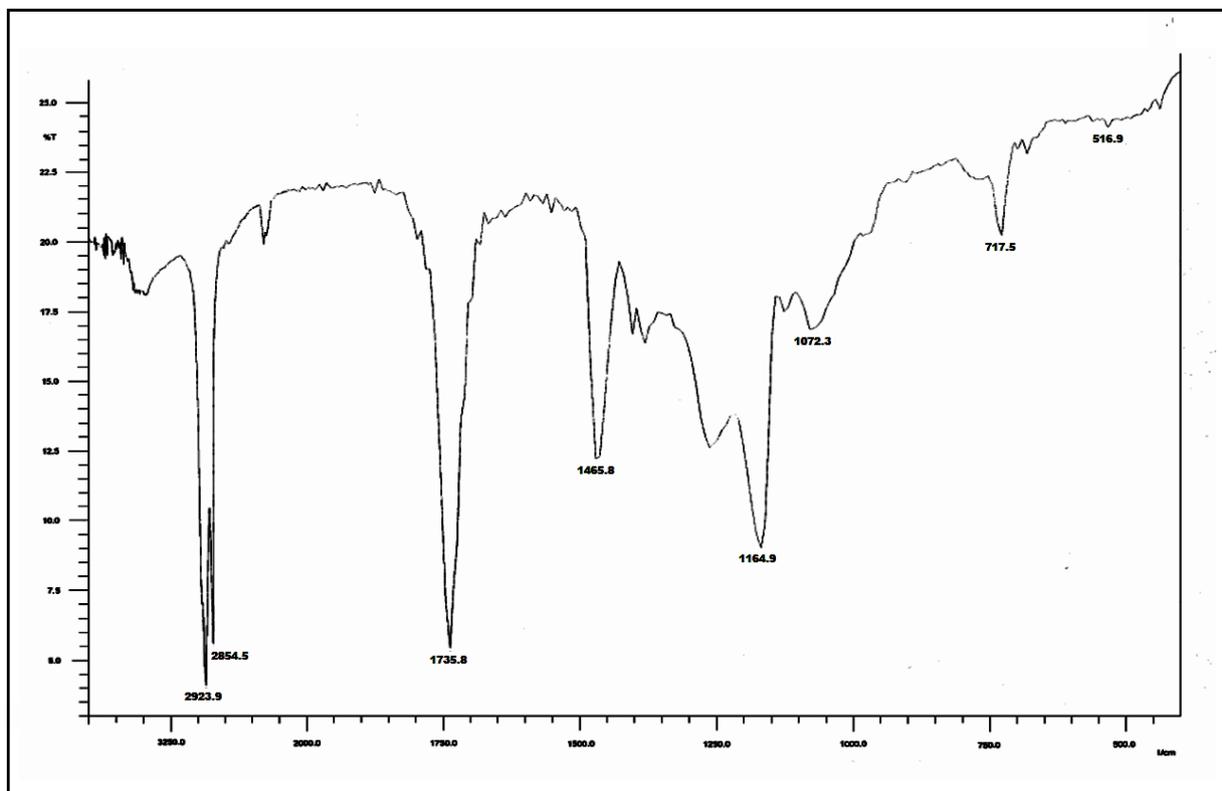


Figure 1.4.2:  $^1\text{H}$ -NMR spectra of polymer P-1

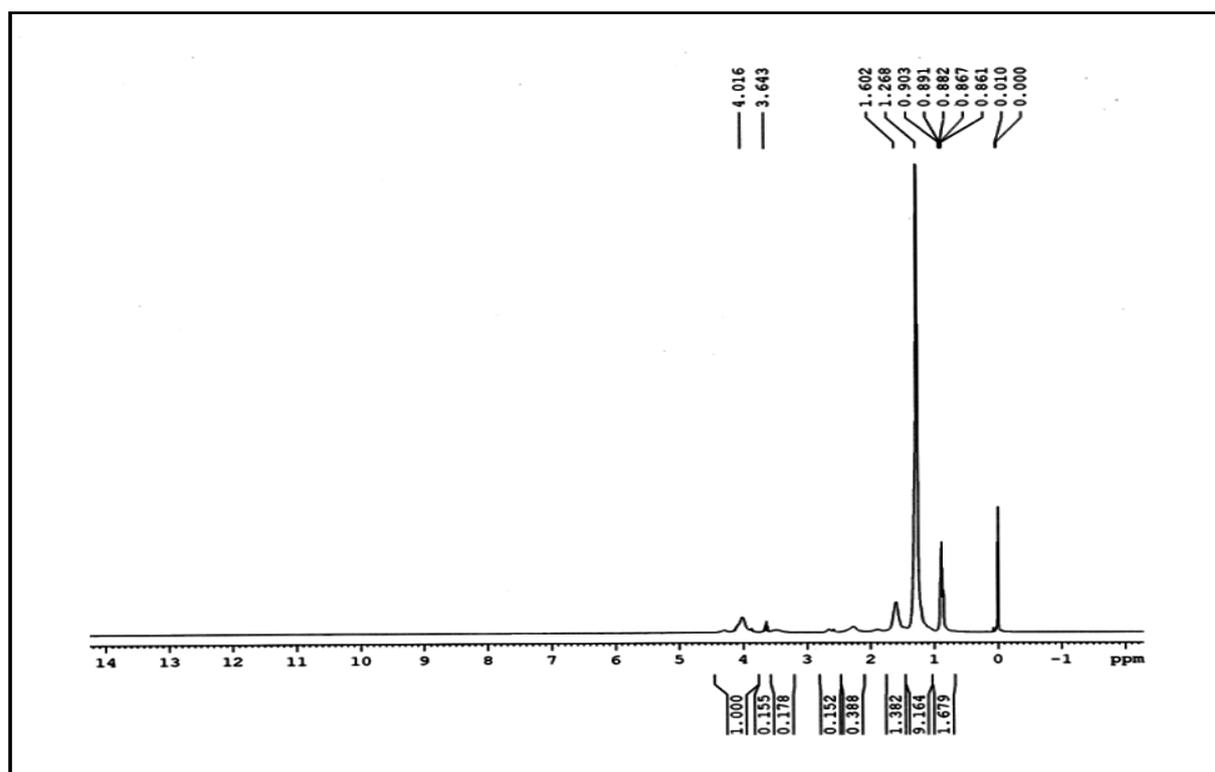


Figure 1.4.3:  $^{13}\text{C}$ -NMR spectra of polymer P-1

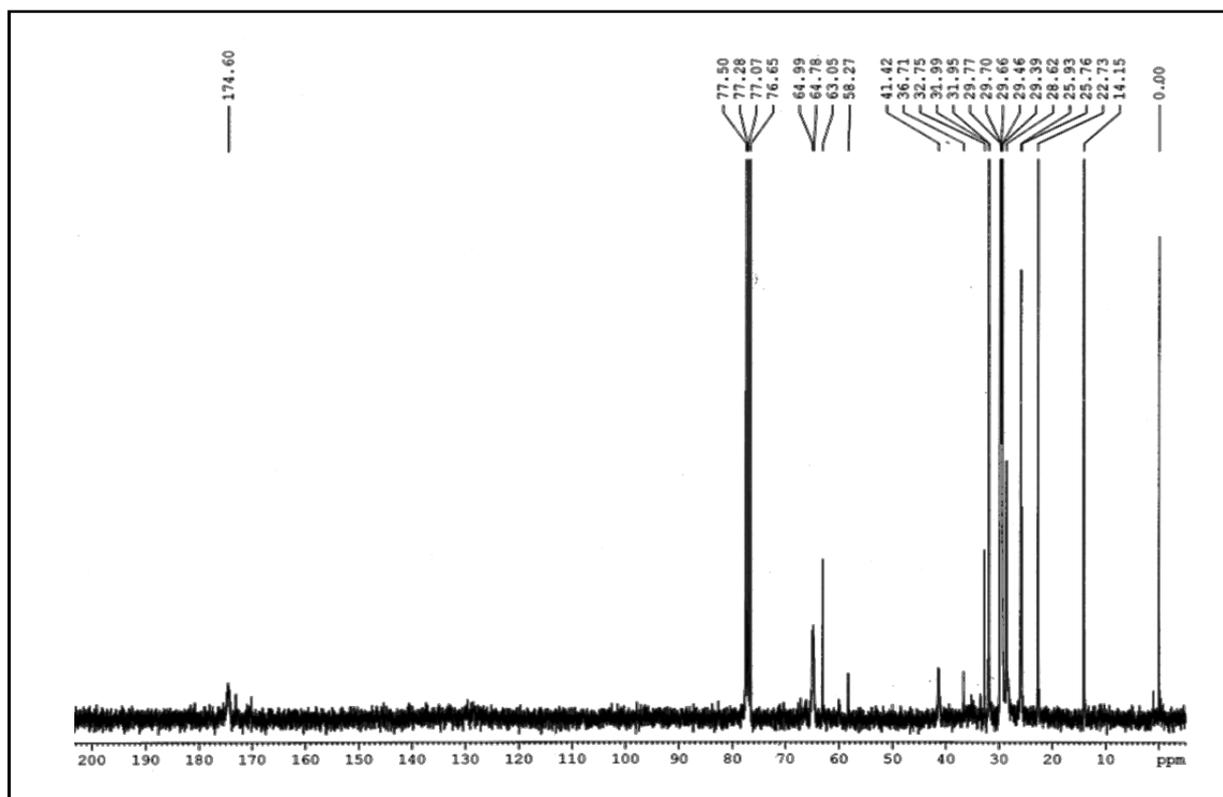


Figure 1.4.4: Comparison of pour point values of the polymers in BO1

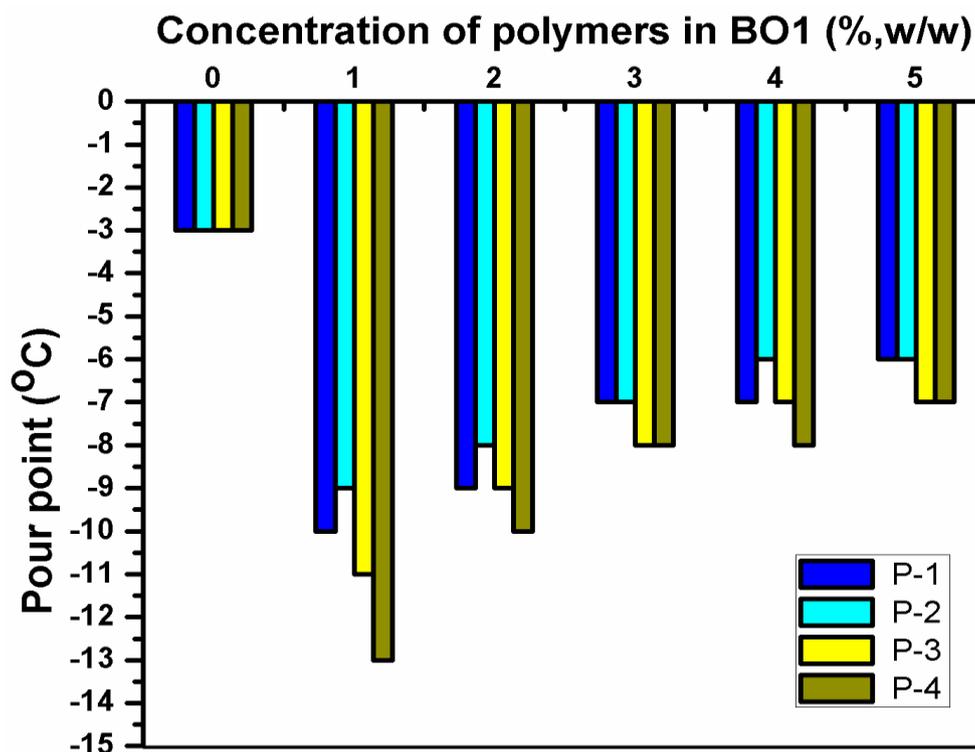


Figure 1.4.5: Comparison of pour point values of the polymers in BO2

