

## **CHAPTER III**

### **Additives for crude oil**

## **CHAPTER III.A**

### **Development of methacrylate based polymeric additives for crude oil**

#### **III.A.1. INTRODUCTION**

Crude oil is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins [1]. When the temperature decreases paraffin precipitates out from the crude oil and forms wax crystals. With additional wax precipitation, the crystals grow into plates and finally, if the temperature is decreased far enough, the plates will grow together to form a three-dimensional network which traps the oil molecules and deteriorate the flow properties of the oil i.e. immobilizes the oil [2]. The lowest temperature at which the flow property of fluid is ceased, called the pour point. Other constituents of crude oil such as asphaltenes also play important role while ascertaining the behaviour of crude oil. These large heterogeneous molecules with condensed aromatic nuclei may associate to form colloidal sized particles that strongly influence the viscosity of the oil medium and affect the crystallization of the wax [3–6]. Hence waxy crude oil causes many problems during storage and transportation mainly because of this crystallization and deposition of paraffin wax crystals in the flow line causing a number of handling problems as well in regions where the service temperatures are or become seasonally very low [7].

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. When wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures with each other that inhibited the flow property. Some commercially available properly designed polymeric flow improvers are poly (ethylene-co-vinyl acetate) (EVA) [8], poly (ethylene-butene) [9], polymethacrylates [10, 11], and modified maleic anhydride copolymers [12, 13]. Basically these polymeric wax inhibitors consist of a non polar long hydrocarbon chain of 14 to 25 carbon atoms in addition with a polar segment typically

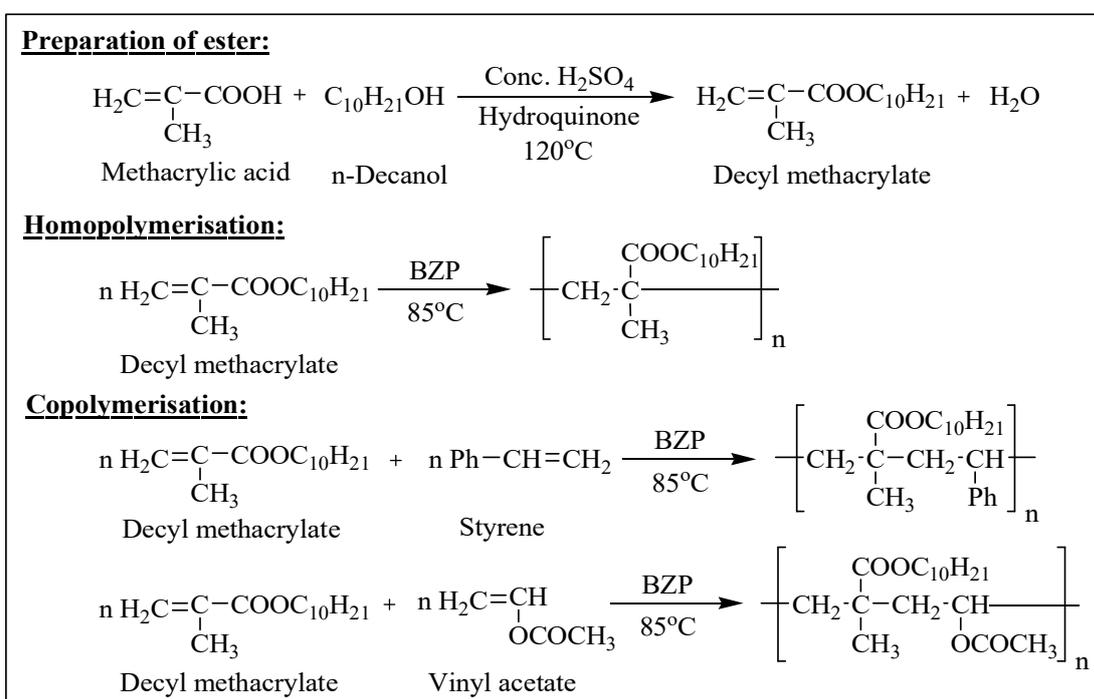
acrylates or acetates. The hydrocarbon part is responsible for the interaction between the additive and paraffin of the oil while the polar part limits the degree of co-crystallization and thus inhibits the aggregation stage.

### **III.A.2. BACKGROUND AND OBJECTIVE**

Recently Chen et al. investigated the interaction of crude oil waxes with polyacrylate pour point depressants (PPDs) bearing different structures and reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax-crystal precipitation and improve crude oil low-temperature fluidity [14]. Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups [15]. 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 for crude oil [16, 17]. For example, polybehenyl acrylate with a lower MW exhibited better efficacy as a flow improver for asphaltene-rich crude oil [18] and acrylate/methacrylate polymer additives with a lower range of MWs achieved the optimum effectiveness for waxy crude oils [19]. According to Kuzmic et al., polymeric additives of alkyl acrylate with styrene, acrylic acid, and 1-vinyl-2-pyrrolidone with MWs below 20000 were not efficient for crude oils from Croatian oil fields [20] while in another study by Taraneh et al., it was reported that ethylene vinyl acetate copolymer with a higher MW was the better additive for crude oils with low asphaltene contents [21]. T. J. Behbahani had investigated the influence of different concentrations of polymeric flow improver such as dodecylpolymethacrylate and tetradodecylpolymethacrylate on pour point of waxy oils and found that the higher molecular weight flow improver (tetradodecylpolymethacrylate) had better efficiency on pour point of waxy oils [22]. Moreover the performance of a flow improver is also related to the wax and asphaltene composition in the crude oil [15–17, 20]. Hence it can be summarized that the performance of a polymeric flow improver is dependent upon both the structure of the flow improver and the oil composition [23].

Vinyl acetate copolymer, acrylate copolymer and their derivatives [24, 25] are broadly applicable to improve the flow ability of very waxy crude oil, diesel fuel and other base oils at

low temperature. Vinyl acetate copolymers satisfy most of the properties which a good additive must possess. On the other hand methacrylate polymers, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today due to the molecular structure of the polymers and the tremendous flexibility in chemical structure. In the present context, we have prepared homopolymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions and evaluated them as flow improver for crude oil collected from Oil India Ltd, Duliajan, Assam (India).



**Scheme III.A: Preparation of decyl methacrylate; its homopolymerisation and copolymerization with styrene and vinyl acetate separately**

### III.A.3. EXPERIMENTAL SECTION

#### III.A.3.a. Materials

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), Styrene (99%, Sigma–Aldrich), Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Decyl alcohol (DA, 98%, SRL Pvt. 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 recrystallization before use. Conc. H<sub>2</sub>SO<sub>4</sub> (98%, Merck Specialties Pvt. Ltd.) was used as received. Crude oil was collected from Oil India Ltd, Duliajan, Assam (India). Before experiment the crude oil was tested for pour point and was found 24°C. The properties of the crude oil are listed in **Table III.A.1**.

**Table III.A.1: Specification of the crude oil**

<b>Source</b>	Duliajan, Assam
<b>Pour point</b>	24°C
<b>Density</b>	900 Kg/m <sup>3</sup>
<b>Plastic viscosity</b>	5.2 mPa.S at 27°C
<b>Yield value</b>	10 dy/cm <sup>2</sup> at 30°C
<b>Wax content</b>	>10%

### **III.A.3.b. Preparation of ester and its purification**

The ester (decyl methacrylate, DMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of decyl alcohol in the presence of concentrated sulfuric 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 [26].

### **III.A.3.c. Preparation of polymers**

The polymers (homo and copolymers) were prepared by free radical polymerization (**Scheme III.A.**) at different percentage composition of monomers (**III.A.2**) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in Chapter II.A [26].

### **III.A.4. MEASUREMENTS**

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

The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) in the same manner as mentioned in Chapter IIA.

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

FT-IR and NMR data were obtained following the same procedure as mentioned in Chapter IIA.

#### **III.A.4.c. Performance evaluation as pour point depressants in crude 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).

### **III.A.5. RESULTS AND DISCUSSION**

#### **III.A.5.a. Molecular Weight Analysis**

The experimental values of  $M_n$ ,  $M_w$  and PDI (polydispersity index) of the prepared polymers are tabulated in **Table III.A.2**. Molecular weight is one of the most important factors to determine the flow improvement property of a polymer. From this table, it can be stated that on increasing the percentage of styrene or vinyl acetate both the number average molecular weight and weight average molecular weight gradually increases. But the copolymers of vinyl acetate are less poly-dispersed than those of styrene based copolymers.

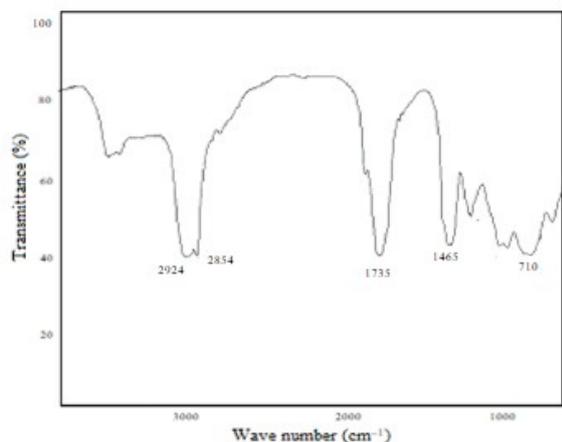
**Table III.A.2: Percentage composition,  $M_n$ ,  $M_w$  and PDI values of polymers (P<sub>1</sub> to P<sub>9</sub>)**

Polymer code	% of DMA	% of Sty.	% of VA	$M_n$	$M_w$	PDI
P <sub>1</sub>	100.0	–	–	20482	49682	2.42
P <sub>2</sub>	97.5	2.5	–	21592	58982	2.73
P <sub>3</sub>	95.0	5.0	–	27457	77688	2.83
P <sub>4</sub>	92.5	7.5	–	28946	81556	2.82
P <sub>5</sub>	90.0	10.0	–	30345	93842	3.09
P <sub>6</sub>	97.5	–	2.5	21575	33018	1.53
P <sub>7</sub>	95.0	–	5.0	24013	35842	1.49
P <sub>8</sub>	92.5	–	7.5	56866	66210	1.16
P <sub>9</sub>	90.0	–	10.0	61990	81219	1.31

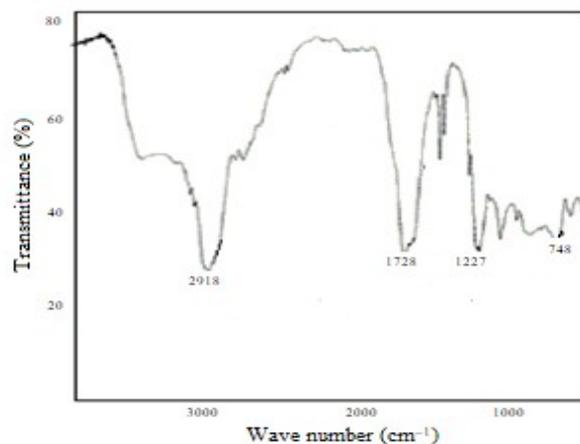
DMA = Decyl methacrylate, Sty. = Styrene, VA = Vinyl acetate,  $M_n$  = Number average molecular weight,  $M_w$  = Weight average molecular weight, PDI = Polydispersity index

### III.A.5.b. Spectroscopic analysis

The homopolymer of decyl methacrylate, P<sub>1</sub> shows IR absorption band at 1735 cm<sup>-1</sup> (**Figure III.A.1**) corresponding to the ester carbonyl group. Due to the presence of –CH<sub>2</sub>CH<sub>3</sub> group the peak at 2854 cm<sup>-1</sup> and 2924 cm<sup>-1</sup> appeared and for the CO stretching vibration the peak at 1465 cm<sup>-1</sup> appeared. The IR spectra of copolymers of decyl methacrylate with styrene (P<sub>2</sub> to P<sub>5</sub>) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1735 cm<sup>-1</sup> shifted to 1728 cm<sup>-1</sup> in the copolymer. For example, IR spectrum of P<sub>3</sub> has been shown in **Figure III.A.2**.

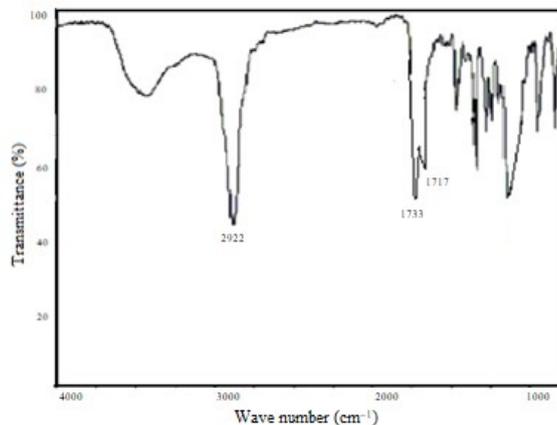


**Figure III.A.1: FT-IR spectrum of P<sub>1</sub>**



**Figure III.A.2: FT-IR spectrum of P<sub>3</sub>**

For the copolymers of decyl methacrylate and vinyl acetate (P<sub>6</sub> to P<sub>9</sub>) the IR spectra are similar and showed the following results: Peaks at 1733 cm<sup>-1</sup> and 1717 cm<sup>-1</sup> indicate the presence of ester carbonyl groups and the peak at 2922 cm<sup>-1</sup> is for the -CH<sub>2</sub>CH<sub>3</sub> group. IR spectrum of P<sub>7</sub> is given for instance (**Figure III.A.3**).



**Figure III.A.3: FT-IR spectrum of P<sub>7</sub>**

In the <sup>1</sup>H NMR spectrum of the homopolymer, P<sub>1</sub> (**Figure III.A.4**), the methyl and methylene protons appeared in the range of 0.89 to 1.93 ppm for all alkyl groups and a broad peak at 3.93 ppm for the protons of -OCH<sub>2</sub>- group. Absence of any peak in the range of 5–6 ppm corresponds to sp<sup>2</sup> carbon confirms the polymerisation. In <sup>13</sup>C NMR spectrum of the homopolymer (**Figure III.A.5**), the peaks at 177.5 ppm indicated the presence of ester carbon.

The peaks at 65.0 ppm and 64.9 ppm confirmed the presence of  $\text{-OCH}_2\text{-}$  carbon and peaks in the range of 14.2–45.1 ppm accounted for all  $\text{sp}^3$  carbon atoms of alkyl groups. Absence of  $\text{sp}^2$  carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120–150 ppm.

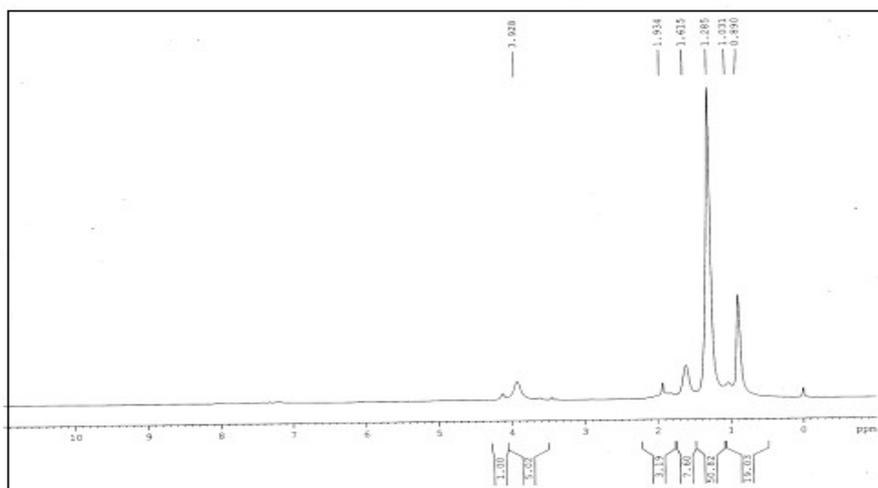


Figure III.A.4:  $^1\text{H}$  NMR spectrum of  $\text{P}_1$

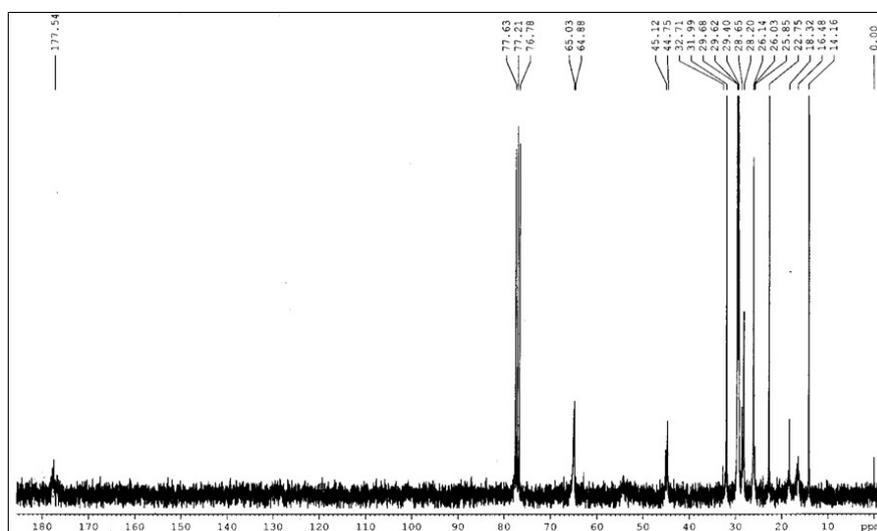
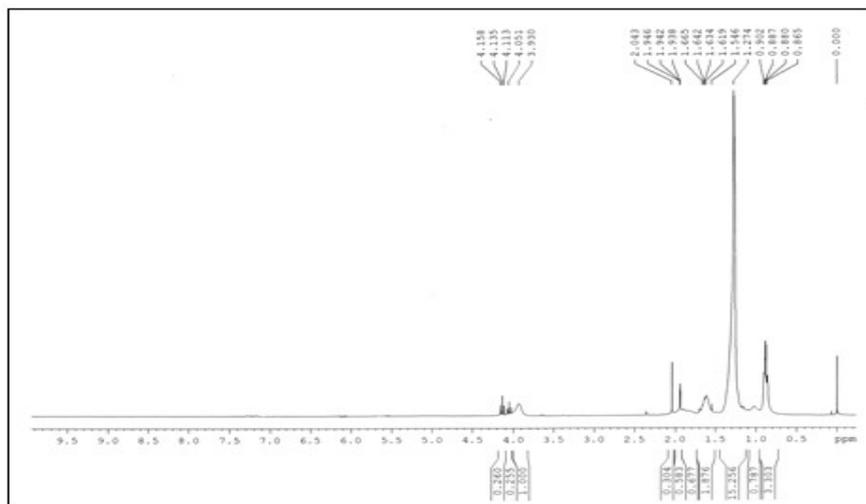


Figure III.A.5:  $^{13}\text{C}$  NMR spectrum of  $\text{P}_1$

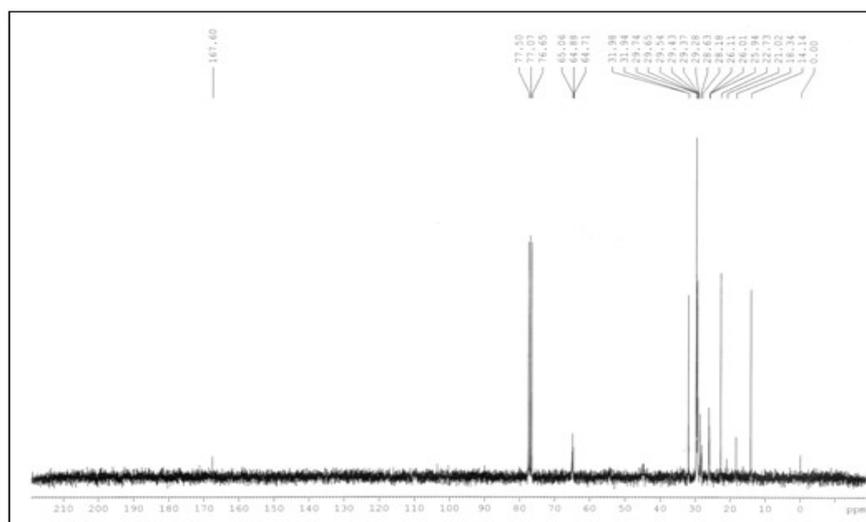
In the  $^1\text{H}$  NMR spectrum of the copolymers of styrene, a broad peak at 7.01–7.33 ppm appeared for the protons of phenyl group. As for example  $^1\text{H}$  NMR spectrum of  $\text{P}_3$  is given in



In the  $^1\text{H}$  NMR spectrum of  $\text{P}_7$ , one of the copolymers of vinyl acetate (**Figure III.A.8**), a broad peak at 3.93–4.16 ppm indicated the protons of  $-\text{OCH}_2-$  groups. The hydrogen atoms attached to  $\text{sp}^3$  carbons appeared in the range of 0.86 ppm to 2.64 ppm. Absence of any peak in the range of 5–6 ppm confirmed the polymerisation successfully.



**Figure III.A.8:**  $^1\text{H}$  NMR spectrum of  $\text{P}_7$



**Figure III.A.9:**  $^{13}\text{C}$  NMR spectrum of  $\text{P}_7$

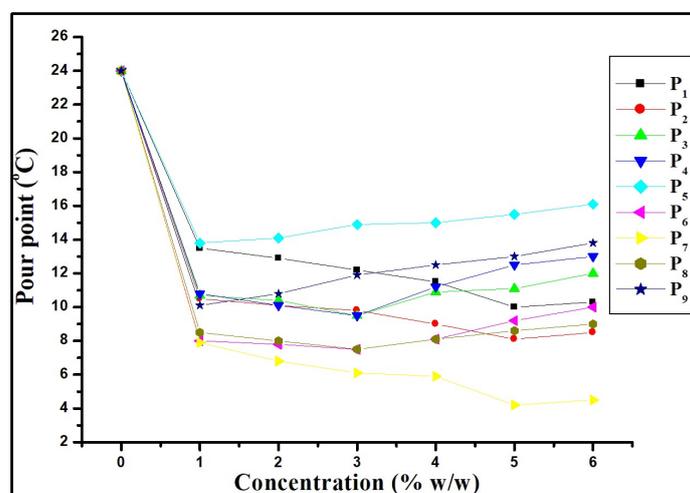
In  $^{13}\text{C}$  NMR spectrum of this copolymer (**Figure III.A.9**), the peaks at  $\delta$  176.7–176.8 ppm were due to the presence of ester carbonyl group. The peaks at 64.7–65.4 ppm corresponded to the  $-\text{COCH}_3$  methyl carbon and  $-\text{OCH}_2-$  carbons, peaks ranging from 14.1–45.1 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 polymerization.

### III.A.5.c. Analysis of pour point values

The experimental values of pour point are given in **Table III.A.3**. The values suggest that all the prepared polymers ( $\text{P}_1$  to  $\text{P}_9$ ) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for Duliajan crude oil.

**Table III.A.3. Pour point data with respect to the different concentrations of the additives in crude oil**

Polymer code	Pour point ( $^{\circ}\text{C}$ ) of additives doped crude oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
<b>P<sub>1</sub></b>	24	13.5	12.9	12.2	11.5	10	10.3
<b>P<sub>2</sub></b>	24	10.5	10.1	9.8	9.0	8.1	8.5
<b>P<sub>3</sub></b>	24	10.7	10.4	9.5	10.9	11.1	12.0
<b>P<sub>4</sub></b>	24	10.8	10.1	9.5	11.2	12.5	13.0
<b>P<sub>5</sub></b>	24	13.8	14.1	14.9	15.0	15.5	16.1
<b>P<sub>6</sub></b>	24	8.0	7.8	7.5	8.1	9.2	10.0
<b>P<sub>7</sub></b>	24	7.9	6.8	6.1	5.9	4.2	4.5
<b>P<sub>8</sub></b>	24	8.5	8.0	7.5	8.1	8.6	9.0
<b>P<sub>9</sub></b>	24	10.1	10.8	11.9	12.5	13.0	13.8



**Figure III.A.10: Variation of pour point with respect to the different concentrations of the additives in crude oil**

The obtained result is better represented in the above **Figure III.A.10**, where a sharp decrease in pour point of the crude oil is observed in presence of the additives. The copolymers (P<sub>2</sub> to P<sub>9</sub>) are better than the homopolymer (P<sub>1</sub>) as FI. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of decylmethacrylate and styrene (P<sub>2</sub> to P<sub>5</sub>), P<sub>2</sub> copolymer with the lowest percentage of styrene (2.5%) acts as the better FI than the others and using 5% (w/w) solution of this polymer we get the lowest pour point of 8.1°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that P<sub>3</sub> to P<sub>5</sub> copolymers with higher percentage of styrene gradually showed higher pour point and at 6% (w/w) solution P<sub>5</sub> copolymer with highest percentage of styrene (10%, w/w) shows highest pour point of 16.1°C. The vinyl acetate copolymers (P<sub>6</sub> to P<sub>9</sub>) showed better results than the copolymers of styrene. These polymers are better FI and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals that happened in case of styrene copolymers. The P<sub>7</sub> copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4.2°C. Polymers with higher molecular weights especially P<sub>5</sub> and P<sub>9</sub> showed comparatively poor results. It may be because of their low solubility in the crude oil.

### **III.A.6. CONCLUSION**

From the above study it is found that homopolymer of decyl methacrylate and its copolymer with styrene and vinyl acetate are effective as flow improver for the crude oil. The vinyl acetate based copolymers are better flow improver than styrene based copolymers. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight of polymer has a significant role in relation to the performance of the polymers as flow improvers for crude oil.

### **III.A.7. REFERENCES**

References for chapter III.A are given in bibliography section (page 131–133).

## **CHAPTER III.B**

### **Polymer blend: A new approach towards flow improvement of crude oil**

#### **III.B.1. INTRODUCTION**

Constant industrialization and considerable increase in energy consumption have increased the demand for oil which is supposed to be the main energy source all over the World [1, 2]. To meet the global requirement heavy and even extra heavy crude oil are getting enough attention due to limited and declining source of light or medium crude reserves. But storage and transportation of crude oil through pipelines is one of the challenging issues especially at cold areas or where the temperature becomes seasonally very low. The composition of crude oil, its density, viscosity and ambient temperature conditions are key factors behind such problem.

Crude oil, basically a form of unprocessed oil, is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins [3] and other heavy metal may be present in it depending on the geological background [4]. As the temperature decreases, paraffins in the crude crystallize out forming a three dimensional matrix of wax crystals which begin to trap the molecules of liquid hydrocarbon until the oil ceases to flow [5–8]. Thus Paraffin deposition diminishes oil production and its removal from the pipeline is also a high cost issue. Pour point depressants (PPDs) or flow improvers (FIs) are substances which modify the growing pattern of the wax crystals and limit their aggregation and thus enhance the flow even at low temperature. An efficient PPD should be a linear polymer or copolymer having pendant hydrocarbon groups in the polymeric backbone [9]. Several polymers have been evaluated as wax crystal modifiers and among them poly(ethylene-co-vinyl-acetate) copolymers are vastly used since they possess good efficiency as crude oil flow modifiers and wax deposition inhibitor [10, 11]. Hemant P. Soni synthesized copolymers of maleic anhydride and esters of n-alkyl alcohols with oleic acid and methacrylic acid and evaluated them as efficient pour point depressants and flow improvers for crude oil from Gandhar oil field, Gujarat, India [5]. Another study was conducted on Algerian crude oil by D. Djemiat et al where the

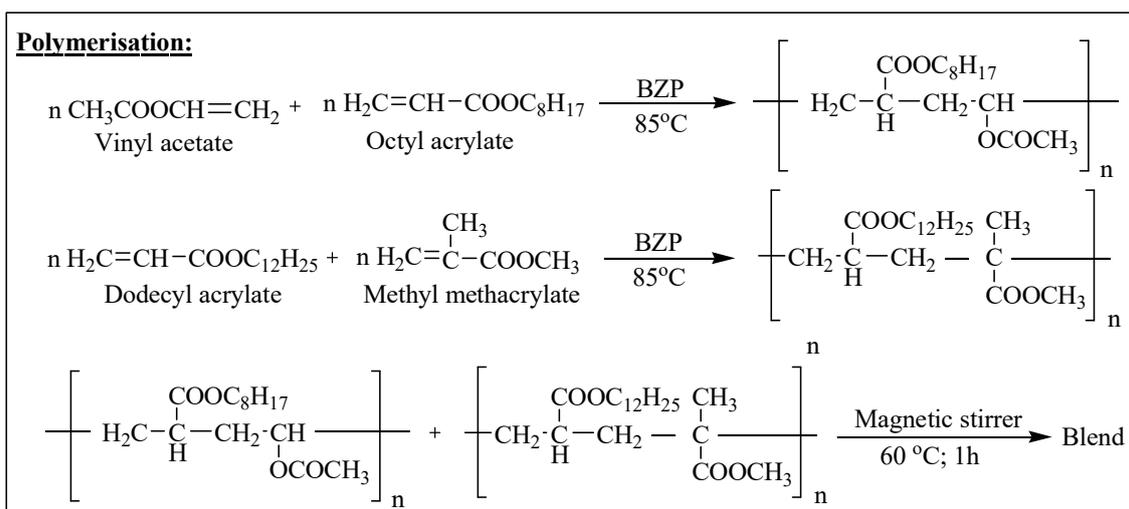
addition of the copolymer, poly(ethylene-co-vinyl-acetate) containing 12% of vinyl acetate, improved the rheological parameters and hence the flow property of crude oil [12].

While considering the flow property of crude oil viscosity is another important parameter which is strongly influenced by the presence of asphaltenes, very large heterogeneous molecules with condensed aromatic nuclei containing heteroatoms such as nitrogen, sulfur and oxygen, and metals such as vanadium, iron, and nickel [13–15]. Presence of strong bonds like C=S drastically increases the viscosity of the crude [16, 17]. Asphaltenes themselves also may associate to form colloidal sized particles leading to large aggregates and thus increase the viscosity of heavy crude [18–20]. Thus during storage or transportation of crude oil, these asphaltenes and paraffins precipitate out forming multiphase flow leading to large pressure drops, increased pumping costs, blocked pipelines and hence huge production loss ranging up to millions of dollars every year [21].

### **III.B.2. BACKGROUND AND OBJECTIVES**

Various preventive methods such as mechanical methods, thermal treatment and chemical methods are commonly employed to overcome the troubles associated with crude oil extraction, storage and transportation. The oldest and the most popular one is dilution of crude with light hydrocarbons, organic solvents like methyl tert-butyl ether, tert-amyl methyl ether, etc, alcohols like pentanol, hexanol, etc, gasoline and middle distillates like kerosene [22]. These diluents reduce the viscosity of crude oil thereby facilitating its transportation through pipelines. But this process requires another well maintained pipeline for carrying the solvent which is itself a cost increasing factor, again identifying proper diluent to oil ratio for different crude oil depending upon its composition and finally recovery of the oil from diluent are not less than an ordeal [23]. Several studies have utilised chemicals such as surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer in crude oil application [24]. Castro et al. reported that the viscosity of Mexican crude oil was reduced using the terpolymer consisting of high percentage of styrene and low percentage of n-butylacrylate and vinyl acetate [7]. Joonaki et al. developed an ionic additive named IRAN91 which reduced viscosity up to 64% of heavy oil collected from Marun oil field, Bangestan

reservoir [25]. Several studies have reported some well designed nanoparticles as efficient viscosity reducers of heavy crude oil [26, 27]. Olusegun Peter Akinyemi et al. successfully investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil [28]. An environmentally friendly and cost effective additive for light and heavy crude oils of Oman was reported by Salam K. Al-Dawery and Saleh K. Al-Shereiqi [29]. They used waste bio materials such as fiber of palm tree, date palm kernel and walnut shell materials as viscosity reducing agents on light and heavy crude oils of Oman. In another study by Manojkumar Gudala it was found that addition of 2000 ppm potato starch to the 85% Heavy crude oil and 15% water mixture at 40°C decreased viscosity of the crude by 80.24% which is an excellent and very inspiring result [30].



**Scheme III.B: Polymerisation of vinyl acetate with octyl acrylate and dodecyl acrylate with methyl methacrylate; blending of prepared polymers**

Today polymer blending has attracted much attention as an easy and economic method for developing new polymeric materials with huge and versatile applications in commercial sector. In our previous work we investigated the properties of polymeric blend in comparison of its parent copolymers and established that the polymeric blend possessed much better mechanical and thermal stability when treated in lubricating oil as additive [31]. Now since for crude oil extraction and transportation we require mechanically and thermally stable additives so that they

do not undergo easy degradation under severe mechanical stress, we tried to evaluate the polymer blend as flow improver for crude oil. We prepared the blend following the above **Scheme III.B.**

### **III.B.3. EXPERIMENTAL SECTION**

#### **III.B.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. The crude oil was collected from IOCL, Assam having pour point of 27°C and densities of 0.851 and 0.808 g/cc at 40°C and 100°C respectively.

#### **III.B.3.b. Preparation and purification of esters**

The esters dodecyl acrylate (DDA) and octyl acrylate (OA) were prepared and purified as per the procedure mentioned earlier in Chapter II.A.

#### **III.B.3.c. Preparation of copolymers and blend**

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>, were prepared by free radical polymerization in presence of BZP as initiator (0.5% w/w, with respect to the total monomer) following the same procedure as reported in Chapter II.A [32]. The process of blending is mentioned in Chapter II.A [31].

### **III.B.4. MEASUREMENTS**

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

The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) were measured by GPC method (Water 2414, polystyrene calibration) following the same procedure as mentioned in Chapter II.A. The values are given in **Table III.B.1**.

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

FT-IR and NMR data were obtained following the same procedure as mentioned in Chapter IIA.

#### **III.B.4.c. Performance evaluation as pour point depressants in crude 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 copolymers and their blend. 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 III.B.1**.

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

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the crude oil containing the copolymers and the blend was determined at 40°C and 100°C. Different concentrations of the polymers in the crude (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive-doped crude oil. All of the experimental data, given in **Table III.B.2** were noted by taking an average of three experimental results under identical conditions in each case.

#### **III.B.4.e. Shear stability measurement**

Shear stability of a polymer is a measurement of its mechanical stability against shearing condition. It is measured following the equations provide in **Chapter I** under section **I.A.1.b**. The PVL and PSSI values are measured here preparing 1%-6% solutions (% w/w) of the prepared copolymers and their blend in the crude oil as per ASTM D-3945 method and are given in **Table III.B.3**.

## **III.B.5. RESULTS AND DISCUSSION**

### **III.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 ( $P_1$ ,  $P_2$ ) and their blend are given in Table 1. Analysing 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.

### **III.B.5.b. Spectroscopic analysis**

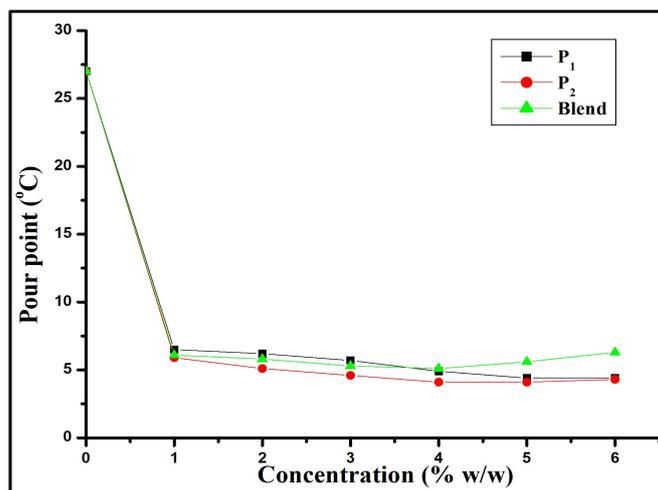
Spectral data along with analysis for the prepared polymers are given previously in **Chapter II.A.**

### **III.B.5.c. Performance evaluation as pour point depressant**

The pour point data given in **Table III.B.1** clearly prove that both the prepared copolymers ( $P_1$  and  $P_2$ ) and their blend are good pour point depressants for the crude oil. Among them all,  $P_2$  copolymer i.e. copolymer of dodecyl acrylate and methyl methacrylate gave the best result as ppd. Longer alkyl chain of this copolymer might play better role in the co-crystallisation process in crude oil [34]. At 4% concentration (% w/w) in the crude oil this copolymer exhibited highest depression in pour point from 27°C (untreated crude) to 4.1°C. At higher concentrations the polymers, especially the blend which is of higher molecular weight became less effective due to lower solubility. It implies that solubility is a major factor while considering flow improvement of crude oil. Graphical representation (**Figure III.B.1**) clearly indicates that a distinct decrease in pour point is obtained when the prepared additives were added to the crude oil.

**Table III.B.1: Molecular weight and Pour point data (°C)**

		P <sub>1</sub>	P <sub>2</sub>	Blend
<b>Molecular weight and polydispersity index data</b>	<b>M<sub>n</sub></b>	25339	13644	34110
	<b>M<sub>w</sub></b>	53374	31166	58693
	<b>PDI</b>	2.11	2.28	1.72
<b>Pour point data (°C) with respect to the different concentrations (% w/w) of the additives in crude oil</b>	<b>0</b>	27	27	27
	<b>1</b>	6.5	5.9	6.1
	<b>2</b>	6.2	5.1	5.8
	<b>3</b>	5.7	4.6	5.3
	<b>4</b>	4.9	4.1	5.1
	<b>5</b>	4.4	4.1	5.6
	<b>6</b>	4.4	4.3	6.3



**Figure III.B.1: Variation of pour point at different concentrations of the additives**

### III.B.5.d. Performance evaluation as viscosity index improver

Viscosity is another important parameter when dealing with crude oil. It may be mentioned here that the measured kinematic viscosities at 40°C and 100°C of the untreated crude oil are 11.243 and 2.926 cSt respectively. While analysing the data obtained from viscometric measurements (Table III.B.2 and Figure III.B.2), it is evident that the prepared copolymers and their blend are effective viscosity reducers for the crude oil under consideration. Interestingly, here the polymeric blend showed highest reduction in kinematic viscosity of the crude oil. At 3% concentration in crude oil this polymer blend showed highest reduction in kinematic viscosity which is over 50%. Its comparatively higher molecular weight might be the reason behind this better efficiency.

**Table III.B.2: Viscosity Index (VI) data with respect to the different concentrations of the additives in crude oil**

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	5.953	2.217	233	7.358	2.327	142	5.877	2.213	242
2	5.861	2.230	239	7.147	2.317	153	5.728	2.193	254
3	5.673	2.193	262	6.735	2.237	158	5.496	2.165	277
4	5.513	2.176	280	6.724	2.231	157	5.473	2.157	276
5	5.507	2.171	278	6.722	2.229	157	5.465	2.153	276
6	5.504	2.167	276	6.717	2.227	156	5.462	2.151	275

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.

It is noted that at 40°C, the effect of the additives in reduction of kinematic viscosity is prominent, but at 100°C the effect is very little since at this higher temperature the viscosity the untreated crude oil itself is highly diminished. At higher concentrations the efficiency of the

polymers was reduced due to lower solubility which fact again cites the importance of solubility factor for effectiveness of additives in crude oil.

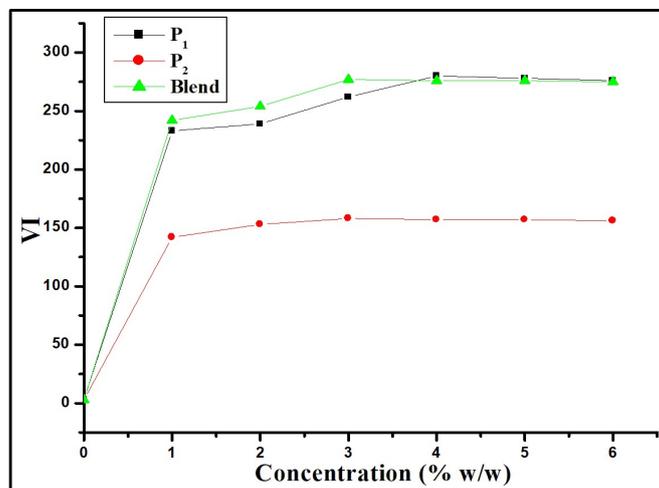


Figure III.B.2: Variation of viscosity index at different concentrations of the additives

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

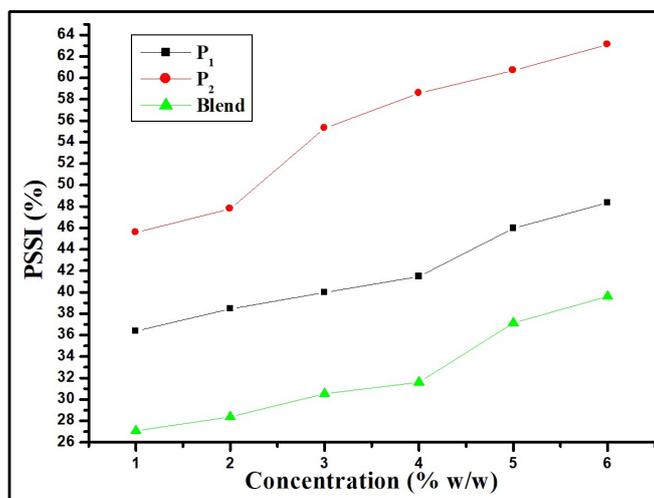
Analysing the PVL and PSSI data given in **Table III.B.3**, we found that polymeric blend showed lowest PVL and PSSI values at all concentrations simply indicating highest stability against mechanical shear. This result really inspired us the most towards improvement of flow properties of crude oil. In crude oil extraction or transportation, stability factor of the additive must be taken into account against severe shear experienced during the turbulent flow of crude oil. Hence crude oil additives must be stable enough and must not lose their activity undergoing easy degradation.

So our prepared polymer blend may be a good candidate to be nominated as an efficient flow improver for the crude oil under consideration. The graphical representation (**Figure III.B.3**) better shows the comparison. It is evident from here that the polymer blend is better shear stable than the copolymers. Variation of shear stability with concentration is also clearly marked from the graphical representation.

**Table III.B.3: PVL & PSSI data with respect to the different concentrations of the additives in crude 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
1	2.475	2.600	2.406	11.64	11.73	8.72	36.39	45.58	27.07
2	2.481	2.608	2.401	12.62	12.56	9.48	38.45	47.78	28.38
3	2.486	2.618	2.394	13.36	17.03	10.58	39.97	55.29	30.53
4	2.487	2.638	2.412	14.29	18.24	11.82	41.47	58.56	31.60
5	2.518	2.652	2.440	15.98	18.98	13.33	45.96	60.69	37.13
6	2.534	2.668	2.458	16.94	19.80	14.27	48.35	63.09	39.61

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



**Figure III.B.3: Variation of PSSI at different concentrations of the additives**

Copolymer of dodecyl acrylate and methyl methacrylate (P<sub>2</sub>) exhibited highest PSSI value which indicates that this copolymer is more prone to mechanical degradation under shear than others. With increasing concentration of the polymers in the crude oil, PVL values as well as PSSI values increase.

### **III.B.6. CONCLUSION**

The above study may be summarised as follows. Both the copolymers and their blend can act as efficient flow improvers for crude oil collected from Assam. Methacrylate-based copolymer was proved to be the better one as pour point depressant due to its longer alkyl chain. But in case of viscosity reduction vinyl acetate-based copolymer and the blend exhibited better performance. Most importantly the polymer blend in crude oil showed highest stability against mechanical shear. But further study is needed to ensure its efficiency in other crude oils also. However, since polymer blending is a cheaper and less time consuming process compared to preparation and characterization of new polymeric material, the above study may open a new horizon of flow improver for crude oil where polymer blend may occupy the prominent position as an efficient and stable flow improver.

### **III.B.7: REFERENCES**

References for chapter III.B are given in bibliography section (page 134–136).