

## EFFECT OF POLYMETHACRYLATE AND BIOSURFACTANT MIXTURE AS POUR POINT DEPRESSANTS FOR WAXY CRUDE OIL

T.T. Khidr, and H.S. El-Sheshtawy\*

*Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt*

Received February 22, 2019; Accepted May 13, 2019

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### Abstract

This paper describes the synthesis copolymers by having as an initial step the synthesis of the alkyl methacrylate monomers by transesterification of methyl methacrylate (MMA) with NAFOL20+A and NAFOL 1822B blend alcohols. The copolymerization of these monomers with MMA was then performed, with molar ratios of 50:50 for alkyl methacrylate: methyl methacrylate. All products were characterized by FTIR and gel permeation chromatography (GPC). Also, the rhamnolipids biosurfactant was synthesized by *Pseudomonas aeruginosa* ATCC-10145. The prepared copolymers were evaluated individually and mixed with the biosurfactant as pour point depressants improvers for waxy crude oil. It was found that; 1000 ppm PC22MMA copolymer with 250 ppm biosurfactant was exhibited the maximum pour point ( $\Delta p_p = 30^\circ\text{C}$ ). From the results indicated that, the performance of the polymeric flow improver dissolved in chloroform was better than the effect of pure copolymer. Also, the results indicate that the higher molecular weight copolymer PC22MMA has better efficiency on pour point of waxy crude oil. In general, the biosurfactant enhanced the depression of the polymer additive and prevent them to grow up, consequently the pour point depress.

**Keywords:** Copolymer; Biosurfactant; Pour point; Solvent; Waxy crude oil.

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## 1. Introduction

Crude oil consists of n-paraffin waxes that tend to be separated from oil when the temperature of crude oil falls below the wax appearance temperature. With decreasing temperature, the waxes generally crystallize as an interlocking network of fine sheets; thereby entrapping the remaining liquid fuel in cage-like structures [1]. Several methods Khidr and Omar [2] have been available to improve the low-temperature properties of crude oil. Pretreatment with pour point depressants (PPD) is an attractive solution for transportation of waxy crude oils via pipelines. The bio-chemical treatments such as, polymeric compounds with biosurfactants referred to as "wax-crystal modifier", is being widely used to improve flow properties and/or combat wax deposition for waxy crude oils. Biosurfactants are surface active compounds produced by different living microorganisms. These compounds are mostly on microbial cell surfaces or excreted extracellular hydrophobic and hydrophilic moieties that confer the ability to accumulate between fluid phases, thus reducing surface and interfacial tension at the surface and interface respectively [3]. They possess the characteristic property of reducing the surface and interfacial tension using the same mechanisms as chemicals surfactants [4]. Biosurfactants are fundamentally classified according to their chemical structure and microbial origin. The major classes of biosurfactants are glycolipids, phospholipids, polymeric biosurfactants and lipopeptides (surfactin). The best known glycolipids are rhamnolipids, sophorolipids and trehalolipids [5].

The wax crystal modifiers are materials that have similar chemical structure to the wax that is precipitating. The model wax crystal modifiers are polymeric compounds constituted by one or more hydrocarbon chain(s) (wax-like) and polar portion. This kind of compounds can co-precipitate or co-crystallize with wax by taking the position of wax molecules on the crystal lattice through the hydrocarbon chains. Meanwhile, it also places a steric hindrance on the crystal

which can be interfere the growth and aggregation of wax crystals, and frequently reduce the pour point of crude oils [6]. Recently avoiding and/or solving the wax deposition problems is therefore an economically beneficial target which can be highly achieved by introducing a polymeric chemical additive in the ppm level to the crude oil in order to reduce its pour point temperature [7]. Although, crude oil treatment with chemical additives is not the only known solution for inhibition of wax deposition, it can be also preferred solution over other options like pigging, heating, and biological treatments. Pour point depressants (PPD) and flow improvers are polymeric additives that used to decrease the pour point and enhance the flow characteristics of crude oil, respectively. In doing that PPD's and flow improvers should possess oil-loving long chains in addition to polar groups such as ester, amine, and hydroxyl groups [8].

In this work synthesis, characterization and evaluation of the performance of various methyl methacrylate-blended alkyl methacrylate copolymers individually or in mixtures with biosurfactant as flow improvers as pour point depressant additives for crude oil and the present study is to produce of biosurfactant by *Pseudomonas aeruginosa* ATCC-10145.

## 2. Experimental

### 2.1. Materials

The following chemicals were used, methacrylic acid, methyl methacrylate, p-toluene sulphonic acid, toluene were attained as analytical reagents from Aldrich chemical. Two linear long chain alcohol blend (NAFOL 20+A) and (NAFOL 1822 B) were supplied from CONDE chemical company with the typical analysis listed in Table 1.

Table 1 Typical analysis of linear long-chain alcohol blends (NAFOL)

Properties	NAFOL 20+A	NAFOL 1822 B
Composition , wt %		
C16-OH	0.9	0.2
C18-OH	24.3	15.0
C20-OH	24.4	14.8
C22-OH	38.2	69.8
C24-OH	9.9	0.2
C26-OH	2.3	-
Average carbon number Cav, (calculated)	20	22
Density g/cm <sup>3</sup> at 70 °C	0.803	0.802
Solidification point, °C	56-60	63-65
Ester No. mg KOH/g	9.9	0.16
Acid No. mg KOH/g	0.05	0.01
Water, wt%	0.06	0.04
Flash point, °C	208	204
Iodine No. mgL/100 mg	8.2	0.23

Egyptian waxy crude oil sample was collected from Qarun Petroleum Company. Their physicochemical properties are listed in Table 2.

Table 2. Physicochemical properties of the investigated crude oil

Test	Method	Result
Density@15°C Kg/L	ASTM D1298	0.8652
Pour point °C	ASTM D97	21
Flash point °C (PMC)	ASTM D93	200
Kinematic viscosity, cSt at 40°C	ASTM D445	243.59
at 100°C		18.94
Wax content, wt%	UOP 46/64	11.01
n-paraffins, wt%	ASTM D2887	62.27
Iso- paraffin, wt%	ASTM D2887	4.12
Total paraffins content, wt%	Urea adduct	66.39
Average carbon number (n)	calculated	28.56

## 2.2. Synthesis of the alkyl methacrylate

### 2.2.1. Esterification of methacrylate monomers

NAFOL 1822B methacrylate ester monomer was prepared by the reaction of 62.4 g (0.2 mol) of NAFOL 1822B alcohol blend and 25.8 g (0.3 mol) of methacrylic acid in a round bottom flask equipped with a Dean and Stark trap to remove the water of reaction azeotropically as it is formed. The reaction was carried out by 100 ml of toluene as a solvent, at reflux temperature, P-toluenesulphonic acid (0.5 g) was used as a catalyst and hydroquinone (0.6 g) as a polymerization inhibitor. Esterification reactions were repeated at the same preceding conditions for preparing NAFOL 20+A methacrylate. The two prepared monomers were then purified by distilling off the solvent at the end of esterification at reduced pressure, then the reaction mixture was extracted with n-hexane, washed with distilled water to remove the catalyst and any unreacted acid until the washings become neutral, then separation of organic layer. Eventually, the crude esters were recrystallized twice from acetone (3.0 mL/g) at 0°C. The prepared monomers showed white waxy like appearance.

### 2.2.2. Synthesis of alkyl methacrylate copolymer

In a two-necked round-bottomed flask, methyl methacrylate and NAFOL1822B/20+A methacrylate were added in the molar ratio of 50:50. Polymerization was performed in a toluene solution, using benzoyl peroxide (1 mol %) as the initiator. The reaction was performed at 80°C for 10 h, under nitrogen atmosphere and magnetic stirring. Afterwards, the toluene was evaporated under low pressure. The poly (NAFOL1822B methacrylate-co-methyl methacrylate) (P22MMA) / poly (20+A) methacrylate-co-methyl methacrylate) (P20MMA) were then purified in chloroform/methanol, and vacuum dried at 75°C, until constant weigh.

## 2.3. Characterization of additives

Spectra of the synthesized esters and different copolymer were measured by using FTIR. Spectrometer Model Type Mattson–Infinity Series Bench top 961. The mean molecular weight (Mn) of the polymers was determined by (GPC) Waters model 510 using polystyrene standard, ultra-styragel column, and tetrahydrofuran as an eluent.

## 2.4. Bacterial strains

*Pseudomonas aeruginosa* ATCC-10145 was purchased from the microbial resources center (MIRCEN), Faculty of Agriculture, Ain Shams University, Cairo, Egypt.

## 2.5. Media preparation and production of biosurfactant

The bacterial strains were streaked on a nutrient agar slant and incubated for 24 h at 30°C. Two loops of culture were inoculated in 25 mL of nutrient broth in a 50 ml Erlenmeyer flask and incubated in a rotary shaker 150 rpm at 30°C for 8–12 h until cell numbers reach 108 CFU/mL, an aliquot of 2 mL of inoculum was transferred to 100 ml of Bushnell Huss Mineral Salt medium (BHMS) in a 250 ml Erlenmeyer flask and the cultures were incubated on a temperature controlled shaker incubator at 150 rpm and 30°C for 96 h, the medium contained (g/L): dipotassium phosphate 1.0, magnesium sulfate 0.2, calcium chloride 0.02, potassium dihydrogen phosphate 1.0, ammonium nitrate 1.0, ferric chloride 0.05. The carbon source as glucose was added to make the final concentration 1% (w/v).

## 2.6. Recovery of biosurfactant

The crude rhamnolipids biosurfactant produced by *Pseudomonas aeruginosa* was recovered from the culture supernatant after the removal of cells by centrifugation at 10.000·g for 20 min. Rhamnolipids were then precipitated by acidification of the supernatant to pH 2.0 and allowing the precipitate to form at 4°C overnight. The precipitate thus obtained was pelleted at 10.000·g for 15 min, the precipitate was dissolved in 0.05 M sodium bicarbonate (pH 8.6), reacidified, and recentrifugation at 12.000·g for 20 min, following centrifugation, the precipitate

was extracted with chloroform/methanol (2/1) three times. The organic solvent was evaporated using a rotary evaporator and a yellowish oily residue was obtained [9].

## 2.7. Testing for surface activity

### 2.7.1. Measuring surface tension

An efficient biosurfactant with high efficiency must be able to reduce surface tension to less than 40 mN/m. To measure the surface tension, 50 mL of culture liquid containing biosurfactants was isolated and transferred to a sterile falcon. In this study, a tensiometer device ((Krüss-tensiometer K6, GmbH Hamburg, German) was used. It should be noted that, since surface tension is a function of ambient temperature, to obtain a more accurate result, influx surface tension of all the samples was measured at the same temperature of 24°C by the tensiometer device. For each sample, surface tension was measured for three times [10].

### 2.7.2. Emulsification activity ( $E_{24}$ )

A volume of 3 mL of kerosene was vortexed with 3 mL of supernatant for 2 min and allowed to settle for 24 h, and then the emulsification index ( $E_{24}$ ) was estimated as follows:

$$(E_{24}) = h_{\text{emulsion}}/h_{\text{total}} \times 100\%,$$

where  $h_{\text{emulsion}}$  is the height of emulsion layer and  $h_{\text{total}}$  is the height of total liquid column.

### 2.7.3. Critical micelle concentration (CMC)

The determination of CMC was performed by several dilutions of free-cell fermented medium containing rhamnolipid. Superficial tension was measured using SIGMA 70 digital tensiometer (KSV Instruments LTD, Helsinki, Finland) at room temperature (ASTM D71).

### 2.7.4. Antimicrobial tests

The rhamnolipid compound was tested for antibacterial activity against Gram positive bacteria such as (*Bacillus pumilus* and *Micrococcus luteus*) and Gram negative such as (*Sarcina lutea*) and the antifungal activity was screened against *Penicillium chrysogenum*, yeast against *Candida albicans* by agar diffusion technique. This technique was tested in [11].

### 2.7.5. Evaluation pour point depressant for additive with crude oil

The prepared compounds were evaluated as pour point depressants using crude oil through the pour point tests according to the ASTM-97-93 respectively. The effect of additive concentration was investigated by using different concentration ranging from (500-2500) ppm.

## 3. Results and discussion

### 3.1. Synthesis of the additives

A representative IR pattern of NAFOL 1822B methacrylate monomer is shown the C-H stretching vibration of -CH<sub>3</sub>- and -CH<sub>2</sub>- groups absorbed strongly at 2917-2850 cm<sup>-1</sup>. The ester C=O appeared as a strong absorption at 1720cm<sup>-1</sup> and the presence of the ester functionality was further supported by the appearance of a C-O stretching vibration at 1180cm<sup>-1</sup>. Appeared at 1637cm<sup>-1</sup> the characteristic C=C stretching whereas the C-H in plane deformation. Vibrations of methacrylate ester monomers appeared as doublets at 1322 and 1297cm<sup>-1</sup>. A strong absorption of the bending vibration of C-(CH<sub>2</sub>) N-C of the long alkyl chain of the ester appeared at 719cm<sup>-1</sup>. The poly (NAFOL1822B methacrylate-co-methyl methacrylate) (P22MMA)/poly (20+A) methacrylate-co-methyl methacrylate) (P20MMA), all of them present bands in the region corresponding to stretching vibration band of C-H (2850 and 2920 cm<sup>-1</sup>) that are much more intense than for the methyl methacrylate, accompanied by stretching vibration band for C=O (1720 cm<sup>-1</sup>), C=C (1640 cm<sup>-1</sup>) and multiple bands of C-C(C=O)-O, characteristic of a ,b-unsaturated esters (1320, 1295 and 1160 cm<sup>-1</sup>). These bands, related with the absence of the stretching vibration band for the O-H bond of fatty alcohol in the

3200–3300  $\text{cm}^{-1}$ , not only indicated the formation of methacrylic monomers but also confirmed the purity of the products.

### 3.2. Effect of molecular weight of additive on pour point of waxy crude oil

From the results demonstrated influence of the copolymer additive on the pour points. It can be observed that high average molecular weight wax inhibitor of P22MMA additive (15.896) shows better efficiency for reduction of pour point of waxy crude oil. The crystal growth rate of the lower molecular weight of P20MMA additive (10.891) wax inhibitor is much slower than that of the higher molecular weight wax inhibitor. As the crystal growth rate of higher molecular weight flow improver is faster, it cannot co-crystallize with reduced size of wax crystals. This is the reason why higher molecular weight wax inhibitor shows better efficiency for waxy oil.

### 3.3. Effect of concentration of additive on pour point of waxy crude oil

The results are shown in Figure 1 the polymeric additives PC20MMA and PC22MMA were investigated as PPDs on crude oil. From the Figure 1 it can be noticed that with increasing the concentration of the additives an increase in the pour point depression was achieved. This means that at this concentration ranges the additives may co-crystallize with the paraffin wax and modify their crystal structure. At higher concentrations of additives, the side way growth becomes more difficult for the wax crystals [12].

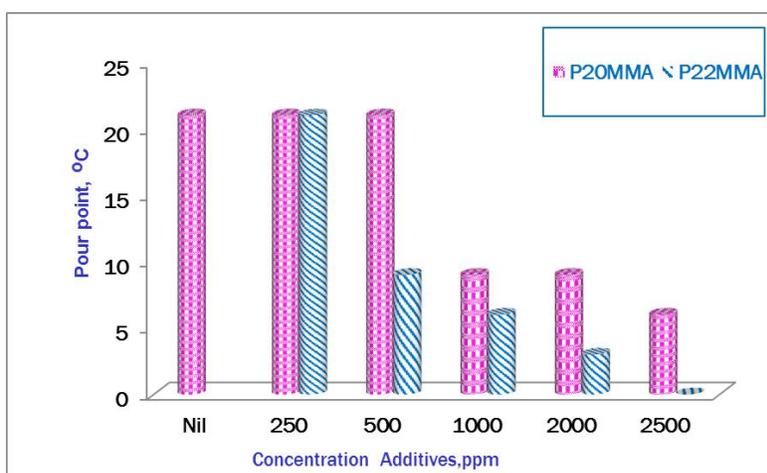


Fig. 1. Relation between additive concentration and pour point for crude oil

### 3.4. Results of studying surface activity

Biosurfactant production was studied using *Pseudomonas aeruginosa* with Bushnell Huss Mineral Salt medium (BHMS). In the present the yield of the biosurfactant was (1 g/L), Moussa *et al.* [13] was represented that the most favorable carbon sources for rhamnolipid (RL) biosurfactant production were glucose and glycerol (both at 40g/L), giving a RL yield of 0.3 and 0.25g/L, respectively. Also, Ndlovu *et al.* [14] was investigated that maximum rhamnolipid production was observed in the MSM supplemented with glucose (307mg L<sup>-1</sup>).

Surface activity of the obtained biosurfactant, Table 3 proved that the rhamnolipids biosurfactant could reduce the surface tension to 31 mN/m, which was acceptable in terms of its purity.

Table 3 Evaluation of some surface properties of the biosurfactant produced by *Pseudomonas aeruginosa*

Surface tension (mN/m)	CMC (mg/L)	Emulsification activity (%)
31	50	70

It was stated by Mulligan [15] that a good surfactant can lower the surface tension of water from 72 to 35 mN/m. Moreover, the production of biosurfactants by *Pseudomonas aeruginosa* AK6U lowered the surface tension to 30 mN/m [16]. Figure 2 displays the results of surface tension related to different concentrations of rhamnolipids present in free-cell medium. A lower CMC of the surfactant means that the concentration required for this surfactant to form micelles is also lower. Therefore, the surfactant can change the surface properties and exhibit functions such as emulsification, solubilization and foaming even at a relatively low concentration.

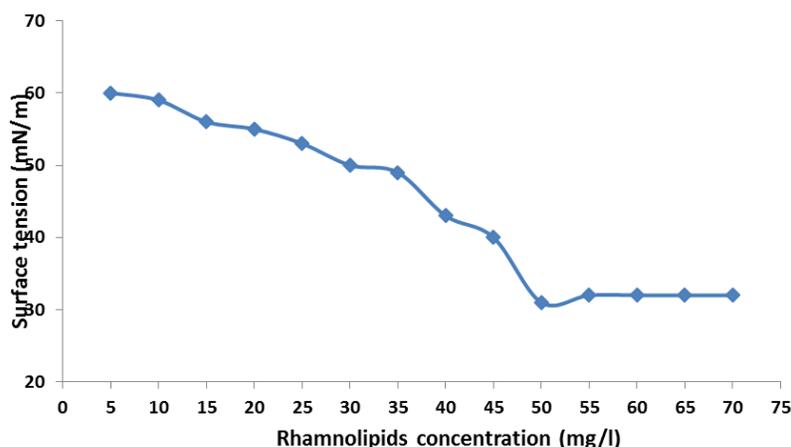


Fig. 2. Determination of critical micelle concentration of rhamnolipids biosurfactant

In the present study the surface tension decreased from 60 to 31 mN/m with small increases in the rhamnolipids concentrations up to 50 mg/L. Further the addition of rhamnolipids concentration had no effect until 70 mg/L. Nitschke and Pastore [17] reported that the CMC of biosurfactant obtained from *Bacillus subtilis* was 33 mg/L. The CMC of rhamnolipid fermentation liquor was 386 mg/L was investigated by Daoshan *et al.* [18]. Determination of emulsification power of rhamnolipids depends on the carbon source used to produce rhamnolipids [19]. In the present study the glucose was examined for their effectiveness of biosurfactant production. The *P. aeruginosa* was able to obtain 60 % emulsification activity using kerosene as hydrocarbon source. Rahman *et al.* [20] was illustrated that emulsification activity of the rhamnolipid biosurfactant produced by *P. aeruginosa* DS10-129 was higher than 70% using all the hydrocarbons tested, including xylene, benzene, hexane, crude oil, kerosene, gasoline and diesel.

### 3.5. Effect of solvent on pour point of waxy oil

Chloroform is good solvent for methacrylates. Effect of crude oil dilution with different solvent concentration was shown in Table 4. As shown influence of wax inhibitor/pour point depressant and solvent concentration was compared.

Upon addition of 10% solvent, pour point of waxy oil reduced from 21 to less than  $-3^{\circ}\text{C}$ . The reduction of pour point by addition of solvent is due to the dissolution of asphaltenes. Of course, the effect of dilution may also play a major role in reducing the pour point. Probably the pour point reduction is achieved due to the effect of dilution. This study showed that treatment of crude oil with P20MMA, P22MMA with biosurfactant and P22MMA with biosurfactant additives alone are lower sufficient. In fact the crude oil will give lower viscosity after dissolution of crude oil by solvent and subsequent treatment with additives.

Table 4. Effect of solvent with additives on the pour point of crude oil

Symbol	Concentration of solvent (chloroform)	Concentration of different additive (wt%)	Pour point reduction, °C							
			Nafol 20+A		Nafol 1822B		Nafol 20+A+bio-surfactant		Nafol 1822B+bio-surfactant	
			PP	Δ PP	PP	Δ PP	PP	Δ PP	PP	Δ PP
A1	0	0	21	0	21	0	21	0	21	0
A2	0	1	21	0	18	3	18	3	15	6
A3	2	1	18	3	15	6	18	3	12	9
A4	5	1	12	9	9	12	15	6	6	18
A5	8	1	6	15	3	18	12	9	0	21
A6	10	1	6	15	0	21	9	12	-3	24

PP = pour point, °C, Δ PP = change of pour point depression, °C

### 3.6. Effect of blended biosurfactant with polymeric additive on pour point of crude oil

The polymeric additive PC20MMA/ PC22MMA were blended with biosurfactant at different ratios and the results were listed in Table 5 and Figure 3.

Table 5 Effect of the blends ratios of PC20MMA and PC22MMA with biosurfactant on the pour point of crude oil

Blend number	PPD (ppm)	Biosurfactant (ppm)	PP (°C)	Δ PP (°C)
B1	2000 PC20MMA	-	6	15
B2	1000 PC20MMA	1000	3	18
B3	1000 PC20MMA	500	3	18
B4	1000 PC20MMA	250	-3	24
B5	500 PC20MMA	1000	12	9
B6	2000 PC22MMA	-	0	21
B7	1000 PC22MMA	1000	-3	24
B8	1000 PC22MMA	500	-6	27
B9	1000 PC22MMA	250	-9	30
B10	500 PC20MMA	1000	9	12

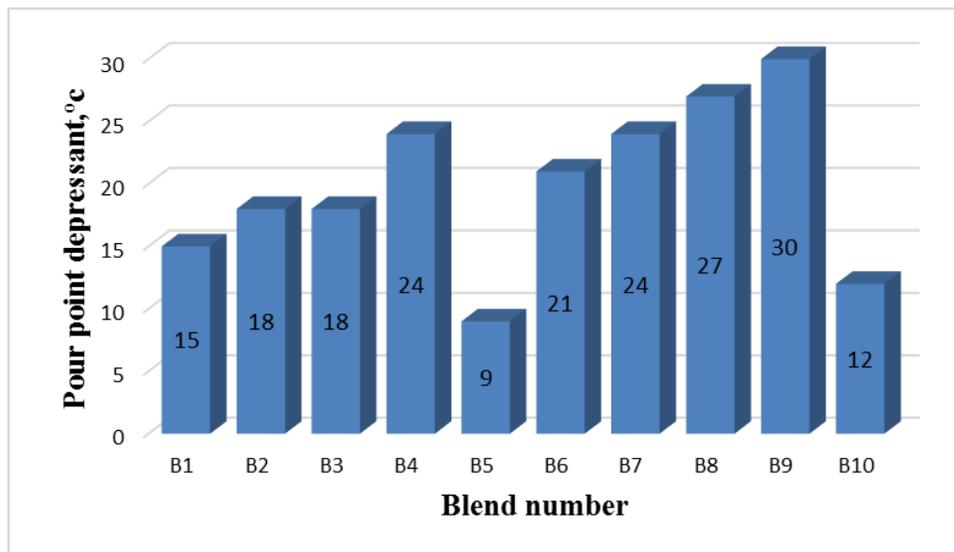


Fig.3. Effect of the blend ratios of PC20MMA and PC22MMA with biosurfactant on pour point depressant of crude oil

By inspecting the presented data in Table 5 it was found that B2 and B3 achieved  $\Delta pp=18^{\circ}C$  and C4 exhibit  $\Delta pp=24^{\circ}C$  while B7 and B8 exhibited  $\Delta pp=24^{\circ}C$  and  $27^{\circ}C$  respectively. The maximum depression in pour point was obtained by B9  $\Delta pp=30^{\circ}C$ , as shown in Figure 3. This

observation means that the positive synergistic effect of the blend depends on the number of alkyl groups in the surfactant molecule and its concentration in the blend. So that the best results as pour point depressant for crude oil achieved with 1000 ppm PC22MMA + 250 ppm biosurfactant. In general, the biosurfactant enhanced the depression of the polymer additive and prevent them to grow up, consequently the pour point depress.

#### 4. Conclusion

Synthesis of the poly (NAFOL1822B methacrylate-co-methyl methacrylate) (P22MMA)/poly (20+A) methacrylate-co-methyl methacrylate) (P20MMA) by polymerization between NAFOL 1822B methacrylate/NAFOL20+A methacrylate with methyl methacrylate, all the products were characterized by Fourier transform infrared spectrometer FTIR and gel permeation chromatography analysis GPC.

The efficiency of the prepared compounds as pour point depressants increases by increasing the concentration and by increasing the molecular weight of the prepared additives. When the additive dissolved in chloroform was better effect as pour point depressant for crude oil than the effect of pure one. Higher molecular weight additive PC22MMA showed better efficiency as a flow improver than additive PC20MMA. When the polymeric additive blended with biosurfactant has better effect than that of polymeric additive alone as pour point depressant for crude oil.

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To whom correspondence should be addressed: Dr. H. S. El-Sheshtawy, Egyptian Petroleum Research Institute (EPRI), 1 Ahmed El-Zomor Street, El-Zohour Region, Nasr city, 11727 Cairo, Egypt, e-mail [hudaelsheshtawy@yahoo.com](mailto:hudaelsheshtawy@yahoo.com)