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Al-Azhar Bulletin of Science: Section A

SYNTHESIS, CHARACTERIZATION, AND EVALUATION OF ALLYL POLYMERIC ADDITIVES AS POUR POINT DEPRESSANT

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ABSTRACT

Pour point depressants (PPDs) are commonly used as chemical wax inhibitors and rheological property improvers in the oil and gas industry in order to improve the flow ability of crude oil. In this study, polymeric additives based on stearyl acrylate (StA)-acrylic acid (AA)-allyl oleate (AO) were prepared via the free radical polymerization method. The obtained polymers were characterized by FTIR, ^{1}H-NMR, GPC, *TGA, and DTA. The results* indicated the successful formation of the copolymers. The prepared polymers were investigated as PPDs and rheology modifiers for the Egyptian waxy North Qattara crude oils, and the results indicated that *the pour point depression had a direct relationship with the concentrations of the prepared additives.* The StA/AA additive (polymer I) achieved the greatest pour point reduction at 1500 ppm dose from 18 °C to 0 °C. In addition, the prepared polymeric additives reduced the yield stress and viscosity of the tested crude oil as compared to untreated crude oil. It can be concluded that the prepared copolymers could be used as effective pour point depressants.

Keywords*:* Pour point depressants; Stearyl acrylate; Allyl oleate; Acrylic acid; Wax crude oil.

1. INTRODUCTION

Waxy crude oil is famous for having major challenges during transportation and storage, especially in cold regions. This is caused by the presence of large volumes of paraffin wax in the crude oil, which obstructs crude oil flow due to wax precipitation. The wax precipitation occurs when the temperature of the crude oil in the pipeline lower than the wax appearance temperature (WAT) [1, 2]. Physical and chemical approaches can be used to improve the transit of waxy crude oil via pipelines [3, 4]. One method is to heat the pipeline; however, because of the high electricity consumption, this can be a costly process. Emulsification and the addition of pour point depressants (PPDs) are two chemical processes that can be used in the transportation of waxy crude oil [5, 6]. There are different kinds of polymers that are used as PPDs to disrupt the formation of the paraffin crystallites. Many theories explained the interactive mechanism of action of PPDs, amongst co-crystallization, adsorption, nucleation, or improved solubility of paraffinic wax are widely accepted [7, 8].

PPDs or flow improvers are used to alleviate processing problems of the crude oil especially during transportation which consume excessive energy. They are added to waxy crude oils to improve their rheology, ensuring efficiency and safety during pipeline transmission [9, 10].

The polymeric additive that contains long alkyl chains are the main additives used to improve the flow ability of high-wax-content crude oils at low temperatures. Many scientists worked on the development of polymeric additives to prevent wax deposition or to lower the pour point of crude oil. Ahmed *et al.* [11] developed polymeric additives from octadecyl methacrylate and methyl methacrylate with different molar ratios and characterized them by FTIR, ^{1}H-NMR and GPC. The findings demonstrated the additives' effectiveness as viscosity index improvers and pour point depressants and the additive of 70% octadecyl methacrylate units reduced the pour point by a 15 °C. It was noticed that the efficacy of the produced additive as a viscosity index improver improves as the concentration of additives increases. Khidr *et al.* [12] prepared four copolymers by copolymerization of octadecyl acrylate with maleic anhydride and reacted the resultant copolymer with octadecyl alcohol, hexadecyl amine, benzyl alcohol, and aniline. They characterized the polymers by FTIR, ^{1}H-NMR and GPC and assessed them in absence and presence of oil soluble surfactants as pour point depressants for waxy crude oil.

Patel *et al.* [13] used the free radical solution polymerization to create three comb-shaped copolymers of n-alkyl oleate and maleic anhydride, which were then reacted with hexadecyl amine to obtain poly (n-alkyl oleate-co-hexyl oleate-co-hexadecyl maleimide). They characterized the copolymers using FTIR and GPC and evaluated them for their pour point depression properties and rheology modifiers with and without additives using the Fan Viscometer. They came to the conclusion that the prepared polymers reduce the pour point effectively and act as viscosity index improvers.

In this study, we aim to design pour point depressants from allyl oleate (AO) and stearyl acrylate (SA) as long chain-based monomers, and acrylic acid (AA) as a polar monomer by free radical polymerization in the presence of benzoyl peroxide as an initiator. The combination of both characters in one pour point depressant is necessary for providing the interaction with paraffin crystal and inhibiting the crystals growth, respectively. Evaluation of the terpolymers as pour point depressants was recorded.

2. EXPERIMENTAL WORK

2.1. Materials used in the study

Acrylic acid, a chemically pure grade inhibited with 180–220 ppm methyl ethyl hydroquinone (MEHQ), was obtained from EIF chem. (ATO) company, France. Benzoyl peroxide (BPO) was supplied by Merck. Stearyl alcohol, allyl alcohol, oleic acid, and para toluene sulfonic acid (PTSA) were obtained from Sigma-Aldrich Company, Ltd., USA. Xylene and toluene were supplied by Adweic Chem. Company, Egypt. The Egyptian waxy North Qattara crude oils were used for evaluating the performance of the synthesized polymeric additives. Table 1 shows the analysis *of the* North Qattara *crude oil.* Other reagents were analytical grade and were not purified further.

Table 1. Analysis of the *North Qattara* crude oil

Test	**Method**	**Result**
Specific Gravity @ 60/60 °F	ASTM D-1298	0.858
API Gravity @ 60 °F	ASTM D-1298	33.5
BS&W %vol.	ASTM D-4007	0.3
Water Content %vol.	IP 74/70	0.3
Pour Point °C	ASTM D-97	18
Viscosity Kinematics@40°C cSt.	ASTM D-445	9.8
Wax content (wt. %)	UOP 46/64	25
Asphaltene Content % wt.	IP 143/57	2.5
Resin content wt. %	ASTM 5062-09	9

2.2. Synthesis of stearyl acrylate monomer (StA)

As described in previous work [14], the stearyl acrylate was prepared with a slight modification: In a two-necked round flask equipped with a thermometer and a reflux condenser, 0.1 mole of stearyl alcohol and 0.1 mole of acrylic acid were reacted in toluene (100 ml) at 150 °C. To act as a catalyst, 0.1 g of PTSA was added to the mixture. The liberated water from the esterification reaction was collected by using a dean and stark separator.

The reaction was continued for 6 h until the liberation of the theoretical amount of water. Purification methods were performed several times by washing the product with sodium carbonate solution on cold ice, and then filtering it with filter paper. The esterification was performed in the presence of hydroquinone (0.1 g H.Q) as an inhibitor to avoid partial polymerization of AA. The esterification reaction was shown in scheme 1a.

2.3. Synthesis of allyl oleate monomer (AO)

The allyl oleate ester is prepared by reacting 0.02 mole of oleic acid and 0.02 mole of allyl alcohol following the same conditions as in StA synthesis. Scheme 1b represents the synthesis reaction. Herein, the product appears as a white precipitate that undergoes purification several times by washing with sodium carbonate solution to achieve a highly purified product with a yield of 80%.

2.4. Copolymerization of AA and StA (Polymer I)

By free radical polymerization [15-17], the stearyl acrylate ester (0.01 mole) and acrylic acid (0.01 mole) were copolymerized by placing them into reaction reactor with 6 mL xylene as solvent. Approximately, 0.097 gm (2×10^{-4} mole) of BPO as an initiator was added to the mixture. The reaction mixture was heated at 150 °C in an oil bath for 6 hours under stirring. The resulting polymer was precipitated in methanol. The purification was done by washing several times with warmed methanol. The polymer formed was filtered, dried, and weighted.

2.5. Terpolymerization of StA, AA, AO

As described above, the allyl oleate ester, stearyl acrylate ester, and acrylic acid were placed in a reaction reactor with 6 mL of xylene as the solvent. The feed composition was as shown in Table 2. The precipitation and purification were similar to those of Polymer I.

2.6. Characterization

The Thermo Fisher Nicolet IS10, USA spectrophotometer, was used to record the Fourier transform infrared (FT-IR) spectra in the range of 4000-400 cm^{-1} with a 4.0 cm^{-1} resolution. Samples were mixed with KBr matrix pellets. Mercury-300BB NMR 300, Shimadzu Qp-2010 plus, was utilized to record the ^{1}H-NMR spectroscopy in $CDCl_3$ as solvent. TGA-50 Shimadzu (DTG-60H detector) was used to investigate the thermal profile of polymers under nitrogen in the temperature range of 0–600 °C (10 °C/min) using a platinum pan as a reference material. The molecular weights (number average and weight average) of the polymers were determined by gel permeation chromatography (GPC) device (Waters e2695 HPLC separation module with 2414 RI detector) using THF as a solvent and a styrogel column at ambient temperature.

2.7. Evaluation tests

2.7.1. Pour point

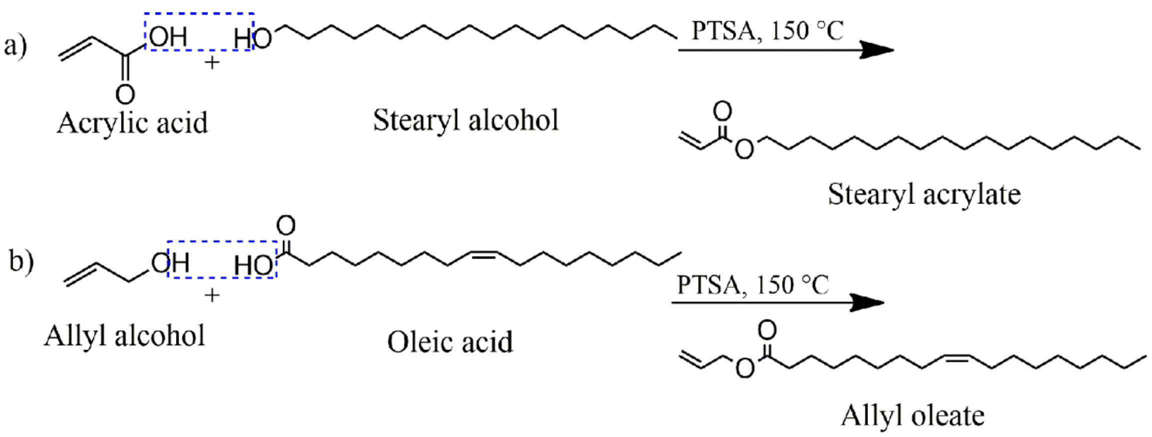
At varied concentrations of the prepared polymers (500 to 1500 ppm), the pour point of a waxy crude oil was evaluated using the Koehler pour point and a cloud point refrigerator in accordance with the ASTM D-97 standard test technique.

2.7.2. Rheological Measurements

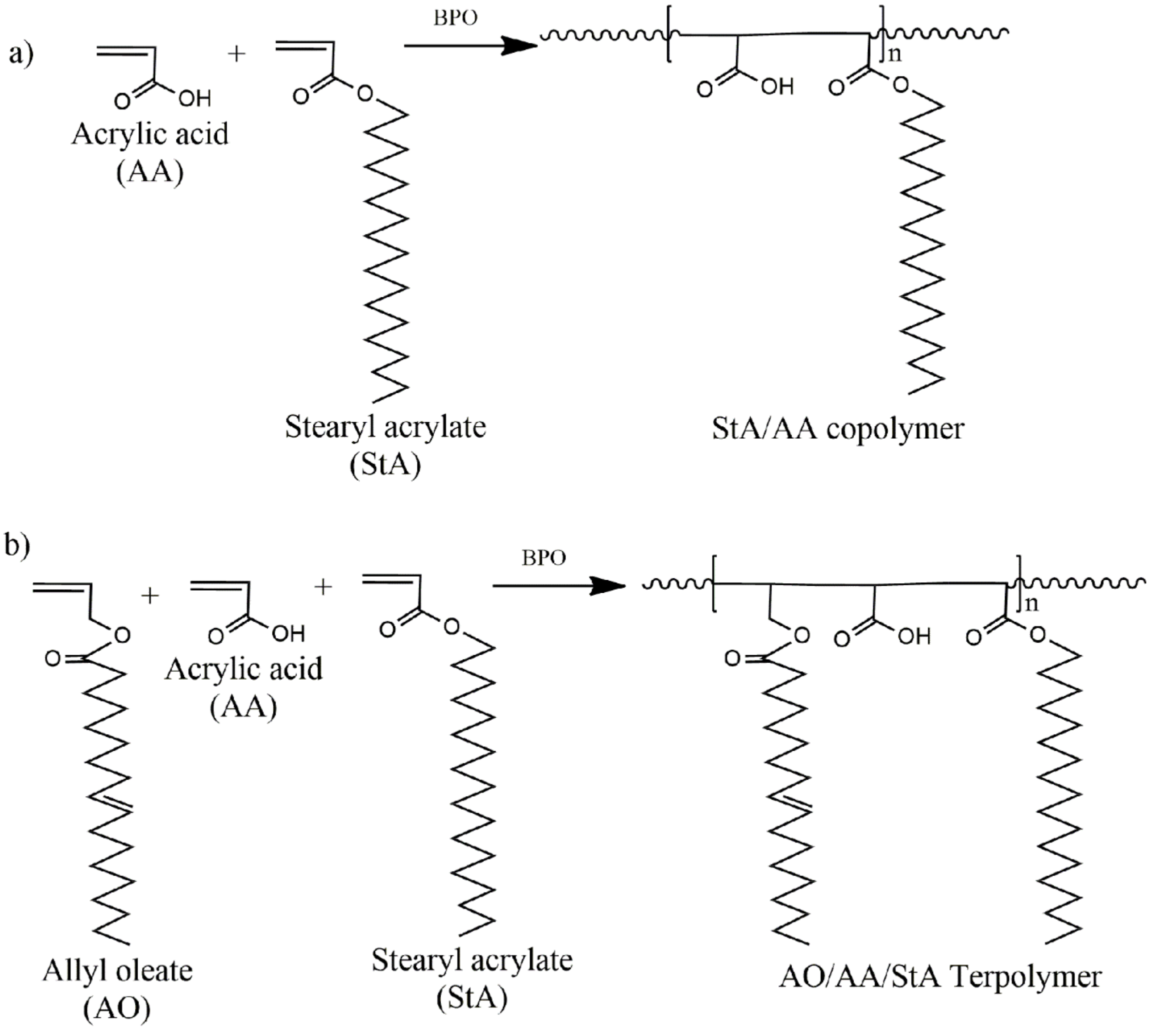
Through rheological studies at varied concentrations ranging from 500 ppm to 1500 ppm, the produced polymers were assessed to improve the flow characteristics of the tested crude oils. At temperatures of 15^{o}C, 18^{o}C, and 21^{o}C, measurements of the shear rate-apparent viscosity and shear rate-shear stress relations were obtained.

Table 2. Feed composition data and reaction conditions for synthesis of the polymeric additives

Polymer code	Monomers molar ratio StA:AA:AO	Weights of monomers (g)			BPO (g)	Time (h)	Temperature (°C)	Yield (%)
		StA	AA	AO				
I	1.0:1.0: 0.0	3.245	0.72	0.0	0.097	6	150	88 %
II	1.0:0.8:0.2	3.245	0.57	0.644	0.097	6	150	70%
III	1.0:0.5.0.5	3.245	0.36	1.61	0.097	6	150	66%



Scheme 1: Synthesis reaction of a) stearyl acrylate and b) allyl oleate



Scheme 2: Synthesis reaction of a) StA/AA copolymer and b) AO/AA/StA terpolymer

3. RESULTS AND DISCUSSIONS

In this work, polymeric additives from acrylic acid, stearyl acrylate, and allyl oleate were prepared by free radical polymerization in the presence of BPO as an initiator. When the polymerization medium is heated, the BPO dissociates into radical species that work to initiate the polymerization reaction, resulting in the formation of the polymeric additives, as shown in scheme 2.

3.1. Characterization of prepared polymeric additives

3.1.1. FTIR

The infrared spectra of the purified polymeric additives prepared in this study are presented in Fig. 1. For the three copolymers (I, II, and III), the peaks at 2919.7 and 2851.24 cm^{-1} could be due to aliphatic (-CH-) groups. The peak at about 1736.58 cm^{-1} due to the carbonyl stretching of the ester group. The broad peak (3200–3650 cm^{-1}) is attributed to the intermolecular hydrogen bonding established between the hydroxyl groups of the acrylic acid units. The appearance of this broad peak in addition to the ester group peak indicates the polymerization reaction. The peak at 1163 cm^{-1} is assigned to the stretching vibration of C-O groups. The peaks at about 1627 cm^{-1} due to C=C stretch of allyl oleate in polymer II and polymer III.

3.1.2. ^{1}HNMR

The StA/AA copolymer and the AO/AA/StA terpolymer structures were confirmed by ^{1}HNMR spectroscopy using $CDCl_3$ as the solvent and TMS as an internal reference. The spectra are illustrated in Fig. 2**.** Fig. 2a demonstrated peaks at chemical shift 0.9 ppm indicate primary alkyl group ($–CH_3$), peaks at chemical shift 1.2 to 1.6 ppm indicate methylene groups of the side chains, peaks at chemical shift 2.3 to 2.6 ppm due to α-hydrogen attached to carbonyl group, peaks at chemical shift 3.4 to 3.7 ppm indicate CH_2 adjacent to O atom. The peak at 7.2 ppm is due to the solvent used (chloroform). The appearance of vinyl protons at 5.4 ppm in Fig. 2b indicates incorporation of allyl oleate into the terpolymer backbone.

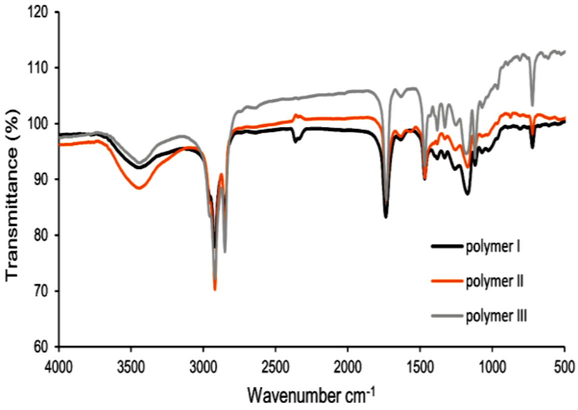


Fig. (1). FTIR of the prepared polymeric additives.

3.1.3. Thermal analysis of the polymers

Thermal analysis of polymer I, II, and III was done by TGA, DTG, and DTA as shown in Figure 3. The TGA data of the three polymers are presented in Table 3. As observed, the weight loss of the three samples increased as the temperature was increased. Based on the weight loss% at 300°C, the polymer III has higher thermal stability than the other two samples. This may be attributed to that increasing the allyl oleate monomer in the terpolymer composition creates side crystallinity, which binds the chains close together physically. Accordingly, this increases the energy required to push the chains apart from each other, which in turn increases the thermal stability [18, 19]. This observation was supported by the higher DTG peak of the polymer III below 350 °C as shown in Table 3 and Fig. 3b. The thermal behavior of the three samples at temperatures higher than 350 °C is approximately similar due to the successive breakage of the main hydrocarbon chain. From Fig. 3c, it is observed that the three polymers show endothermic peaks below 150 °C due to desorption of the bound solvents used in the polymerization reaction, as well as those used in the purification step. The exothermic peaks that appeared after a temperature of 377 °C for the three samples are indicative of the heat evolved during the decomposition of the polymer chains.

3.1.4. Molecular Weight

GPC is an important tool to determine the average molecular weights of polymeric additives. Table 4 displays the molecular weight data in terms of number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI), obtained by the GPC technique using THF as an eluent. The results indicated that the molecular weight of the polymeric additive significantly decreased with increasing the allyl oleate content. However, the broadening of molecular weight distribution increased with decreasing allyl oleate content.

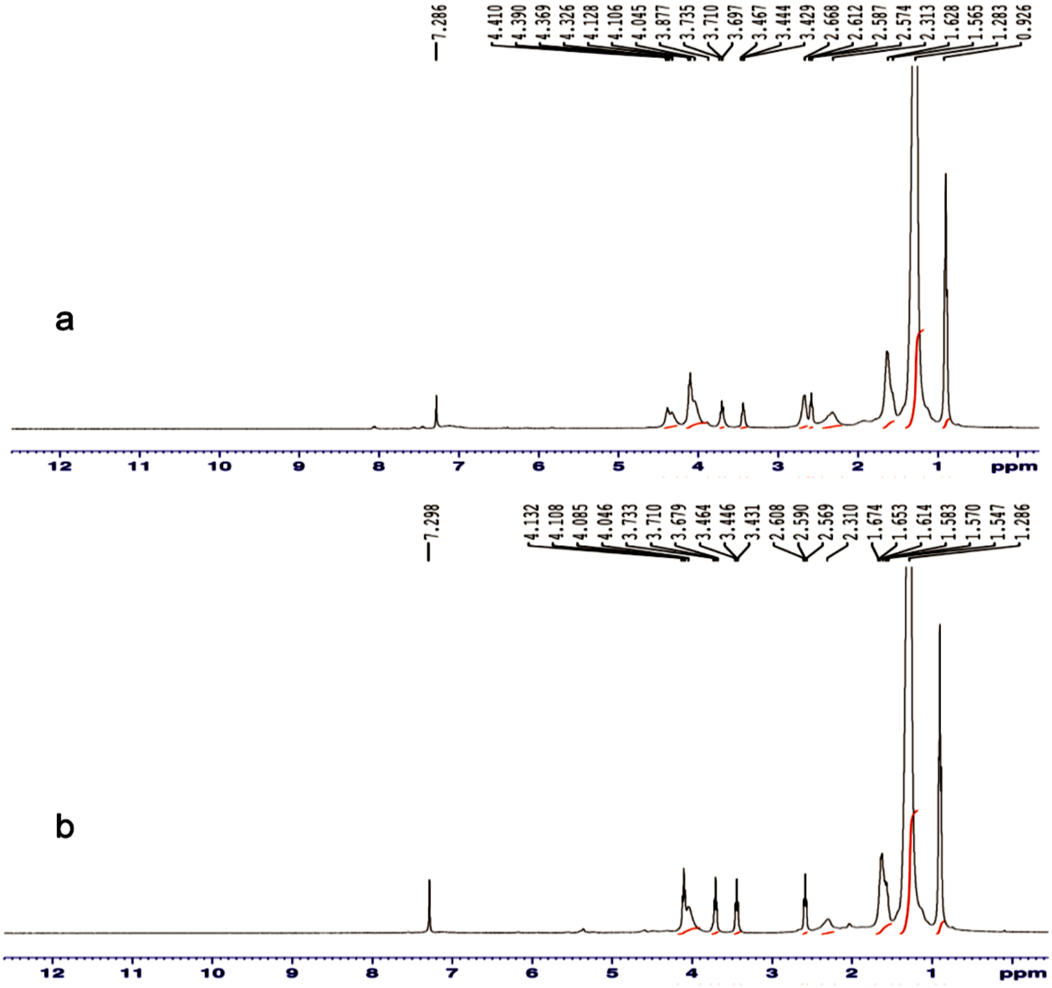


Fig. (2). ^{1}HNMR of the prepared polymeric additives, (a) Polymer I and (b) Polymer III.

Table 3: TGA and DTG data of the three polymers

Sample	Weight loss (%) at temperature (°C)					DTG peaks <350 (°C)
	200	300	400	500	600	
Polymer I	3.29	44.4	93.35	97.9	98.9	272.7, 320.4
Polymer II	13.86	29.77	88.41	95	95.9	105, 336.7
Polymer III	3.82	16.63	91.48	97.03	98.62	342.7

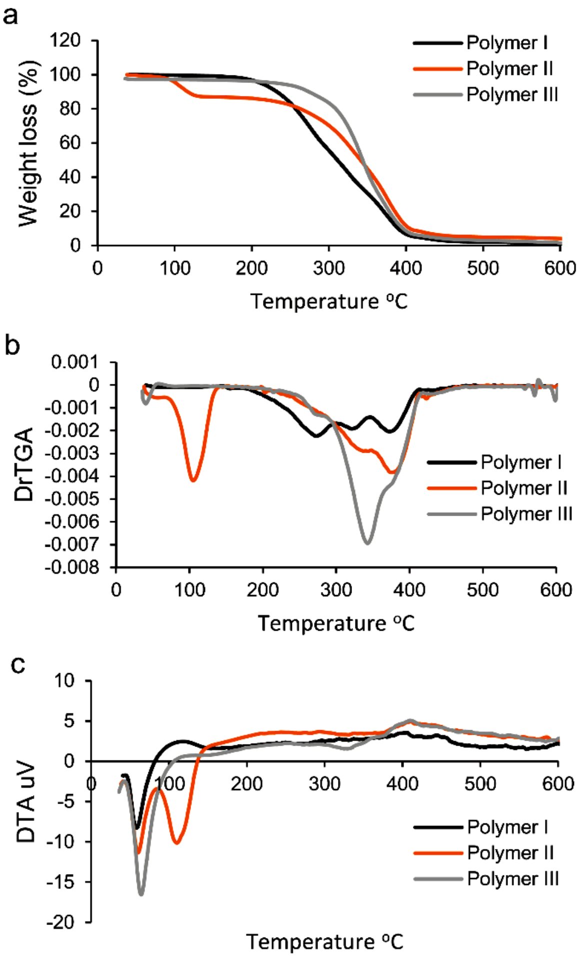


Fig. (3). a) TGA, (b) DTG, and (c) DTA data of the prepared polymeric additives

Table 4: The average molecular weight of the prepared polymeric additives

Polymer Type	Molecular weight (g/mol)		PDI
	M_n	M_w	
Polymer I	2006	23740	11.835
Polymer II	1608	9219	5.732
Polymer III	1342	4232	3.153

3.2. Evaluation of the prepared polymers as a flow improver

3.2.1. Pour point

The pour points of crude oil after treatment with the prepared polymeric additives polymer I, polymer II, and polymer III were determined at three concentrations: 500, 1000, and 1500 ppm. The data of pour points were presented in Table 5.

Table 5: Effect of the prepared polymeric additives on the pour point of crude oil.

Polymeric Additive	Dose (ppm)				Injection Temp °C
	0 (Blank)	500	1000	1500	
Polymer I	18	6	3	0	45
Polymer II		12	12	6	
Polymer III		12	12	9	

The data in Table 5 shows that the prepared additives were effective in reducing the pour point of North Qattara crude oil. The efficiency of the polymeric additive to reduce the pour point is assigned to its ability to crystallize with the paraffin wax through its long alkyl chain and modify their crystal structures. This prevents the paraffin chains from interlocking and facilitates their dispersion into the oil phase, which overcomes the flow problems. It is recognized that co-crystallizing or adhering wax lamella with polymer chains of additive leads to a structural transition for the paraffinic wax from platelet like to a spherulitic crystal structure that is significantly correlated with lowering the pour point[6, 20]. As shown from Table 5, the pour point depression was directly proportional to the concentrations of the prepared additives. The maximum pour point depression was attained at a concentration of 1500 ppm for the three polymers. The additive polymer I reduced the pour point temperature from 18 to 0 °C (Δpp = 18 °C) at a dose of 1500 ppm and from 18 to 6 at a dose of 500 ppm. Polymer II and Polymer III have reduced the pour point by 6 °C at a concentration of 1000 ppm, and at 1500 ppm the pour point decreased to 6 by polymer II and to 9 by polymer III. The lower efficiency of Polymer II and Polymer III as compared with polymer I could be attributed to the lower average molecular weight distribution. The reduction in pour point becomes more noticeable as the additive's molecular weight increases; additionally, the molecular weight should have a broad distribution to cover the n-paraffin distribution [11, 21, 22] [23, 24]. On the other hand, Polymer II and Polymer III contain more long chains in the polymeric backbone, which makes them less soluble and cannot properly crystallize along the wax particles to modify the crystal structure, therefore, having a small effect on pour point depression [20]. These results indicated that the prepared additives were effective in reducing the pour point of the tested crude oil, and Polymer I was the most effective additive.

3.2.2. Viscosity measurements

In this study, the viscosity measurements for the untreated and treated crude oils were determined at different temperatures of 15, 18, and 21 °C, keeping the concentration of the polymeric additive constant at 1500 ppm. Figures 4, 5, 6, and 7 represent the change in shear stress (Figures a) and viscosity (Figures b) as a function of the shear rate. Table 6 shows the rheological parameters for the untreated and treated crude oils with 1500 ppm of each polymeric additive. The yield value is an essential rheological parameter, that offers beneficial information about the flow of crude oils below their pour point [6]. Table 6 shows that the tested crude oil has a high yield value at a temperature lower than its pour point. Also, Figure 4a reveals that the rheological behavior of untreated crude oil is non-Newtonian yield-pseudoplastic and that viscosity was significantly decreased by cooling at a shear rate lower than 20 S^{-1}. As a result of the high wax concentration, gelled crude forms at low temperatures due to the crystallization of the wax, affecting the crude oil viscosity. From Figures 5-7, it is obvious that the prepared polymeric additives decrease the yield stress as well as the viscosity of the tested crude oil as compared with untreated crude oil. Also, the shear stress and the viscosity of the treated crude oils decrease as the temperature is increased from 15°C to 21°C (a temperature that is higher than the PP of *North Qattara crude oil).* At 21°C the yield stress decreases notably near to zero. The reason behind this effect is that the polymer–oil interaction at low temperatures is minimal due to the limited dispersion in the oil phase. As the temperature increases, the interaction of the polymeric additive with the crude oil increases as well as the effective hydrodynamic volume of the polymer, thereby increasing the effective volume fraction of the viscosity modifier. This, in turn, leads to a decrease in crude oil viscosity. on the other hand, the increase in temperature results in a weakening of the network strength between paraffin particles due to thermal motion and hence viscosity decreases.

Table 6: Rheological parameters for the treated and untreated crude oils at various temperatures.

Chemical name	Temp. (°C)	Bingham Yield value (D/cm2)
Untreated (blank)	15	43.55
	18	8.36
	21	2.77
Polymer I	15	0.22
	18	0.15
	21	0.13
Polymer II	15	2.28
	18	1.06
	21	0.18
Polymer III	15	0.11
	18	0.06
	21	0.23

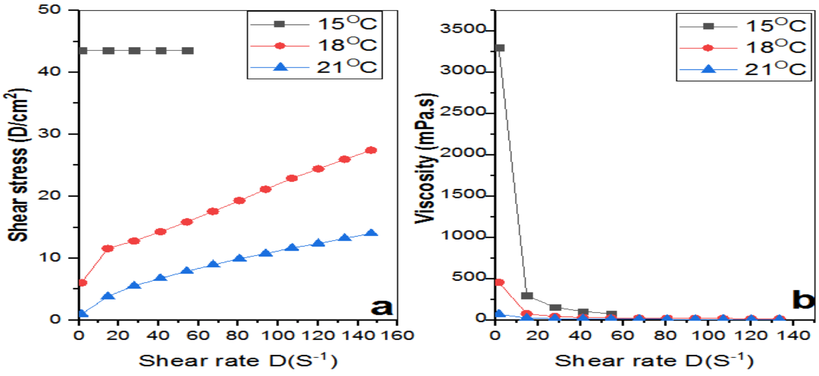


Fig. (4). (a) shear rate versus shear stress and (b) shear rate versus viscosity for untreated crude oil at 15°C, 18°C, 21°C.

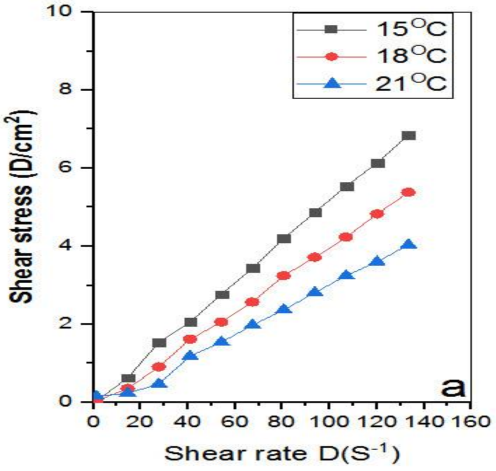


Fig. (5). (a) shear rate versus shear stress and (b) shear rate versus viscosity for crude oil treated with 1500 ppm concentration of polymer I at 15, 18, 21°C.

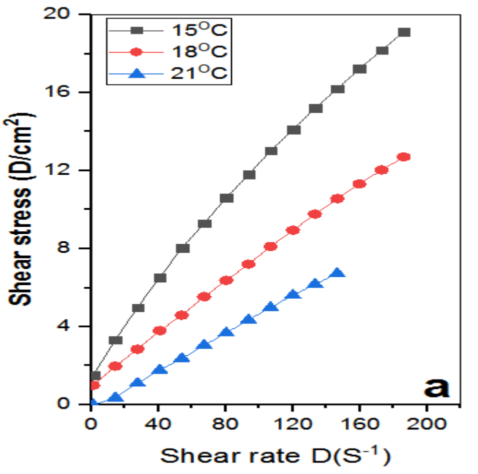


Fig. (6). (a) shear rate versus shear stress and (b) shear rate versus viscosity for crude oil treated with 1500 ppm concentration of polymer II at 15, 18, 21°C.

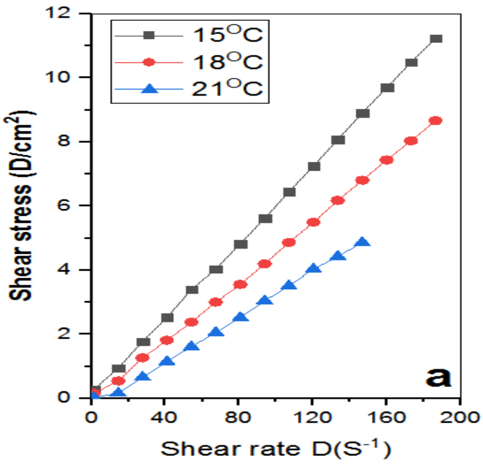


Fig. (7). (a) shear rate versus shear stress and (b) shear rate versus viscosity for crude oil treated with 1500 ppm concentration of polymer III at 15, 18, 21°C.

CONCLUSIONS

Polymeric additives for pour point depression were prepared in this study from acrylic acid, stearyl alcohol, and allyl oleate by free radical-induced polymerization in *xylene as the solvent*, using benzoyl peroxide as an initiator. The synthesized polymeric additives were investigated as pour point depressants (PPDs) for *North Qattara* crude oil. The findings indicated that the produced additives were effective in lowering the pour point of the tested crude oil, with AA/StA copolymer (Polymer I) being the most effective at a concentration of 1500 ppm. In comparison to untreated crude oil, the produced polymeric additives reduce yield stress and viscosity of the tested crude oil to minimum values.

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Conflict of interest

The authors declare no conflicts of interest in this work

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تحضير، توصيف وتقييم إضافات بوليمريه أليل كمخفضات نقطة الانسكاب

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الملخص

تُستخدم محسنات سريان زيت البترول (PPDs) بشكل شائع كمثبطات شمع كيميائية ومحسنات خصائص ريولوجية في صناعة النفط والغاز من أجل تحسين قدرة تدفق النفط الخام. في هذه الدراسة ، تم تحضير إضافات بوليمرية تعتمد على أكريلات الستيريل (StA) ، حمض أكريليك (AA) وأليل أوليات (AO) عبر طريقة بلمرة الجذور الحرة. تم تأكيد تحضير الاضافات البترولية التي تم الحصول عليها بـ FTIR ، 1 H-NMR ، GPC ، TGA و DTA وأشارت النتائج إلى التكوين الناجح للبوليمرات المشتركة. تم فحص الاضافات البترولية الناتجة على أنها محسنات سريان زيت البترول PPDsومعدلات ريولوجيا ، وأظهرت النتائج أن انخفاض نقطة السريان له علاقة مباشرة بتركيزات الاضافات المحضرة. حققت المادة المحضرة من (I) AA/StA أكبر انخفاض في نقطة السريان عند جرعة 1500 جزء في المليون من 18 درجة مئوية إلى 0 درجة مئوية. بالإضافة إلى ذلك ، تقلل الاضافات البوليمرية المحضرة من إجهاد الخضوع ولزوجة الزيت الخام المختبَر مقارنةً بالنفط الخام غير المعالج. يمكن أن نستنتج أن البوليمرات المحضرة يمكن أن تستخدم كمحسنات فعالة لسريان زيت البترول المختبر.