



Novel Homo-and Co-polymers Based on 7-Methacryloyloxy-4-methylcoumarin: Synthesis, Antimicrobial Activity, Pour-Point Depressants and Their Effects on the Rheology of the Waxy Crude Oil



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Abstract

This study aimed to synthesize new polymeric additives including homo- and co-polymers based on 4-methyl-2-oxo-2H-chromen-7-yl methacrylate monomer and evaluating their activity as potential antimicrobials and as pour-point depressants for modification of waxy crude oil rheology. The resultant compounds were characterized by their IR, ¹H NMR and ¹³C NMR spectral data. The formation of the new polymers, namely, poly(7-methacryloyloxy-4-methylcoumarin) [poly(MAOMC)] homo-polymer, poly(7-methacryloyloxy-4-methylcoumarin-co-vinylacetate) [poly(MAOMC)-co-(VA)] and poly(7-methacryloyloxy-4-methylcoumarin-co-octadecyl 4-(methacryloyloxy)benzoate) [poly(MAOMC)-co-(OMAOB)] co-polymers was based on free radical polymerization. The polymerization reaction was carried at 70±2°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator and dimethylformamide (DMF)/toluene as a solvent in the case of homo-polymer [poly(MAOMC)] and co-polymer [poly(MAOMC)-co-(VA)], while polymerization proceeds at the same temperature by using benzoyl peroxide as an initiator and toluene as a solvent in the case of co-polymer [poly(MAOMC)-co-(OMAOB)]

The activities of the resultant compounds as potential antibacterial agents were evaluated against the two Gram-positive (*Bacillus cereus* and *Staphylococcus aureus*), the four Gram-negative (*Escherichia coli*, *Neisseria gonorrhoeae*, *Pseudomonas aeruginosa*, and *Salmonella typhimrium*) bacterial strains, and as antifungal agents against two fungal species (*Aspergillus flavus* and *Candida albicans*). The results showed that MAOMC monomer and poly(MAOMC)-co-(OMAOB) copolymer indicated moderate potent activity towards the bacterial and fungal strains used. At the other extreme, the influence of coumarin and octadecyl benzoate based compounds on the pour-point depression and on the rheological properties of crude oil with low asphaltene content was studied. The results indicated that all three polymers exhibited very good efficiency as additives to improve the flow-ability of the tested crude oil. Moreover, the poly(MAOMC)-co-(OMAOB) co-polymer was found to exhibit the highest performance to reduce and depress the pour-point of the tested crude oil and decrease the viscosity to a large extent due to the presence of two aromatic units with the long aliphatic carbon chain in its structure.

Keywords: Coumarin; pour-point depressants; rheology; poly(7-methacryloyloxy-4-methylcoumarin); poly(7-methacryloyloxy-4-methylcoumarin-co-vinylacetate); poly(7-methacryloyloxy-4-methylcoumarin-co-octadecyl 4-(methacryloyloxy)benzoate)

Introduction

Coumarin or benzopyran-2-one derivatives have great significant attention in many applications over the years, especially in industrial and medicinal applications. The latter applications include their utility as antimicrobial [1,2], antioxidant [3,4], antiviral [5], anticancer [6,7], anti-inflammatory [8-10] and anticoagulant agents [11]. Industrial applications involving fluorescent brighteners [12, 13] and laser dyes [14-16] as well as a huge number of applications [17] were also reported. Also, coumarin polymers have many applications in

electro-optical, liquid crystalline, and energy transferring materials [18-20].

Our present study proved the suitability of the new compounds as promising additives for modifying the rheology of waxy crude oil. Paraffins in crude oil and their items especially gas oil, diesel fuel, warming oil, middle distillates, and residual fuel oil have a significant challenges during production, storage, transportation [21-23], refining and utilization at low temperatures, prompting increment of pour-point, cloud point, viscosity, and wax

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affidavit because of thermal changes forced on delivered liquid. Cold flow added substances particular, flow improvers or pour-point depressants for example, the monoester of methacrylate anhydride/(meth)acrylate ester [24-26], depressants, for example, alkyl sulphonates, inhibitors or wax precious stone modifiers, for example, copolymer ethylene/vinyl acetate derivatives copolymers [27-29]. Most stream-adding substances were ashless polymeric mixes with varying alkyl chain length that coordinate with the normal chain length of wax established in the crude oil and their products [30, 31]. Moreover, and due to the importance to know the performance of the prepared additives, rheological measurements of the treated crude oil were studied [32-35]. On the other hand, antimicrobials evaluation of the resultant homopolymer and co-polymers based on coumarin monomer was measured.

Experimental

Materials

IR spectra (KBr discs) were recorded on an FTIR plus 460 IR spectrophotometer (Shimadzu, Japan). NMR spectra were measured on a BRUKER spectrometer operating at 400 MHz and 100 MHz for ^1H and ^{13}C nuclei, respectively, in $\text{DMSO}-d_6$ with $\text{Si}(\text{CH}_3)_4$ as an internal standard at Faculty of Pharmacy, Ain Shams University, Egypt. Shifts were given in ppm and the abbreviations were as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). The reagents and solvents were purchased from commercially available grade purity.

All the chemicals that were used through the present investigation were supplied from international companies and were analytical grade. Asphaltene was extracted from crude oil, supplied from the General Petroleum Company (GPC), Egyptian waxy crude oils were submitted from Khaldia Petroleum Company fields at Egyptian Western Desert. The *n*-paraffin distribution of the isolated waxes was determined by gas chromatography analysis according to ASTM D-2887. The physicochemical characteristics of the tested crude oil were listed in Table 1.

Methods

Synthesis of 7-Hydroxy-4-methylcoumarin

It was prepared according to the method reported in the literature [36].

Table 1 Physical Characteristics of the Tested Crude Oil

| Properties | Method | Results |
|--------------------------------------|----------------|---------|
| Specific Gravity @ 60/60 (°F) | ASTM D-1298 | 0.8293 |
| API Gravity @ 60 (°F) | ASTM D-1298 | 39.2 |
| Basic sediment & water (BS&W) % vol. | ASTM D-4007 | 0.7 |
| Water Content % vol. | IP 74/70 | 0.7 |
| Pour Point (°C) | ASTM D-5853 | 27 |
| Viscosity Kinematics@40 (°C) cSt. | ASTM D-445 | 6.39 |
| Wax content (wt. %) | UOP 46/64 | 8.78 |
| Conradson Carbon residue (% wt.) | IP 13/94 | 1.32 |
| Average Carbon Number (n) | IP372/85 (GLC) | 17.9 |
| Ash content (% wt.) | IP 4/94 | 0.0059 |
| Sediment by extraction (% wt.) | IP 24/55 | 0.016 |
| Sulfur Content (% wt.) | ASTM D-4294 | 0.4 |
| Resin content | ASTM D-5062 | 3.97 |
| Asphaltene Content (% wt.) | IP 143/57 | 0.63 |
| IBP (°C) | 57 | |
| Recovery @ 100 °C ml | | 5 |
| Recovery @ 125 °C ml | | 12 |
| Recovery @ 150 °C ml | IP 24/25 | 17 |
| Recovery @ 175 °C ml | | 22 |
| Recovery @ 200 °C ml | | 27 |
| Recovery @ 225 °C ml | | 31 |
| Recovery @ 250 °C ml | | 37 |
| Recovery @ 275 °C ml | | 41 |
| Recovery @ 300 °C ml | | 46 |

Synthesis of 7-Methacryloyloxy-4-methylcoumarin (MAOMC) Monomer

MAOMC was synthesized according to the procedure reported in the literature [37] as follows:

A solution of 7-hydroxy-4-methyl coumarin (0.01 mole), absolute alcohol (55 ml) and NaOH (0.01 mole) was heated for 30 minutes with stirring at 60°C, cooled to room temperature, and then to 0-5°C in an ice bath. In a separating funnel, freshly prepared methacryloyl chloride (0.01 moles) was added dropwise (0-5°C) with stirring. After the addition, the reaction mixture was stirred for 90 minutes and then poured into ice water mixture until a white colored powder (solid) product separated out. The solid product was filtered, washed with water then recrystallized from ethanol.

IR (KBr, ν cm^{-1}): 3122 (CH aromatic ring), 2991 (CH_3 , CH_2), 1744 (C=O ester), 1704 (C=O coumarin)

ring), 1613 (C=C), 1276, 1149 (asymmetric and symmetric C-O-C), 893 (CH bending mode of vinyl group), 748 (rocking mode of vinyl group).

$^1\text{H NMR}$ (DMSO- d_6) δ (ppm): 1.90 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 6.13, 6.79 (d, 2H, H₂C=), 6.71 (s, 1H, coumarin-H), 7.00-7.61 (m, 3H, C₆H₃).

MS m/z (%): 244.41 [M^+] (40.14), 211.75 (100.00).

Synthesis of Poly [7-methacryloyloxy-4-methylcoumarin (MAOMC)-co-vinyl acetate (VA)]

An equimolar amount of MAOMC and vinyl acetate in toluene and dimethylformamide, azobisisobutyronitrile (ABIN) was added. The reaction mixture was heated at $70\pm 2^\circ\text{C}$ with stirring. After the specific time, the reaction mixture was cooled to room temperature and the resulting polymer solution was slowly poured in an excess of methanol. The resultant solid co-polymer which resulted via free radical polymerization was purified by re-precipitation with methanol.

IR (KBr, ν cm^{-1}): 3065 (CH aromatic ring), 2923, 2852 (CH₃, CH₂), 1784 (C=O ester), 1731 (broad C=O coumarin ring), 1618, 1512 (C=C), 1271, 1179 (asymmetric and symmetric C-O-C).

$^1\text{H NMR}$ (DMSO- d_6) δ (ppm): 1.23 (s, 3H, CH₃), 1.46 (s, 3H, CH₃), 1.56, 1.73 (m, 4H, 2CH₂), 1.89 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 6.80 (s, 1H, Coumarin-H), 7.10-7.95 (m, 3H, C₆H₃).

Homo-polymer of 7-Methacryloyloxy-4-methylcoumarin [Poly (MAOMC)]

To a solution of an equimolar amount of MAOMC in toluene and dimethylformamide, azobisisobutyronitrile (ABIN) was added. The reaction mixture was heated at $70\pm 2^\circ\text{C}$ with stirring. After the specific time, the reaction mixture was cooled to room temperature and the resulting polymer solution was slowly poured in an excess of methanol. The resultant solid homo-polymer which resulted via free radical polymerization was purified by re-precipitation with methanol.

IR (KBr, ν cm^{-1}): 3067 (CH aromatic ring), 2923, 2852 (CH₃, CH₂), 1770 (C=O ester), 1695 (broad C=O coumarin ring), 1609, 1512 (C=C), 1279, 1164 (asymmetric and symmetric C-O-C).

$^1\text{H NMR}$ (DMSO- d_6) δ (ppm): 1.22 (s, 3H, CH₃), 1.53 (s, 2H, CH₂), 2.49 (s, 3H, CH₃), 6.82 (s, 1H, coumarin-H), 7.32-8.01 (m, 3H, C₆H₃).

Synthesis of Octadecyl 4-hydroxybenzoate

To a solution of an equimolar amount of para hydroxyl benzoic acid and decanol in xylene (10 mL), sulfuric acid or *p*-toluene sulfonic acid were added. The ingredients were charged in a three-necked flat bottom flask fitted with a Dean-Stark trap. Hydroquinone was added as a polymerization inhibitor. The flask was then placed in an oil bath set at 50°C for 30 min., stirring rate 500 rpm for 3.5 hrs and the reaction was carried out at the reflux temperature until the theoretical amount of water was collected. The esters were recovered by immersing the flask in an ice bath. The product formed was collected by filtration and purified by re-crystallization from methanol.

IR (KBr, ν cm^{-1}): 3398 (OH), 2916, 2849 (CH₃, CH₂), 1714 (C=O ester), 1606, 1512 (C=C), 1280, 1165 (asymmetric and symmetric C-O-C).

$^1\text{H NMR}$ (DMSO- d_6) δ (ppm): 0.85 (t, 3H, CH₃), 1.26, 1.29, 1.31, 1.40, 1.80 (m, 32H, 16CH₂), 4.21-4.27 (q, 2H, CH₂), 6.84-6.86, 7.80-7.82 (m, 4H, C₆H₄), 10.30 (s, 1H, OH).

MS m/z (%): 392.52 [$M^+ + 2$] (19.97), 391.55 [$M^+ + 1$] (100.00), 390.61 [M^+] (86.93), 389.97 [$M^+ - 1$] (29.79), 388.94 [$M^+ - 2$] (1.10).

Synthesis of Octadecyl 4-(methacryloyloxy)benzoate Monomer

To a solution of octadecyl 4-hydroxybenzoate (0.01 mole), freshly prepared methacryloyl chloride (0.01 mole) was added dropwise ($0-5^\circ\text{C}$) with stirring. After the addition, the reaction mixture was stirred for 90 minutes and then poured into ice water mixture until a white colored powder (solid) product separated out. The solid product was filtered, washed with water then re-crystallized from methanol.

IR (KBr, ν cm^{-1}): 2954, 2920, 2850 (CH₃, CH₂), 1721 (C=O ester), 1638, 1511 (C=C), 1230, 1175 (asymmetric and symmetric C-O-C).

$^1\text{H NMR}$ (DMSO- d_6) δ (ppm): 0.85 (t, 3H, CH₃), 1.16, 1.24, 1.59, 1.88 (m, 30H, 15CH₂), 2.41 (s, 3H, CH₃), 4.08 (q, 2H, CH₂), 4.58 (m, 2H, COO-CH₂), 5.66, 6.01 (m, 2H, H₂C=), 7.12-7.77 (m, 4H, C₆H₄).

MS m/z (%): 458.99 [$M^+ + 1$] (17.11), 458.34 [M^+] (26.72), 172.60 (100.00).

Synthesis of Poly [7-methacryloyloxy-4-methylcoumarin (MAOMC)-co-octadecyl 4-(methacryloyloxy)-benzoate (OMAOB)]

An equimolar amount of MAOMC and OMAOB in toluene, benzoyl peroxide was added. The reaction mixture was heated at $70 \pm 2^\circ\text{C}$ with stirring. After the specific time, the reaction mixture was cooled to room temperature and the resulting polymer solution was slowly poured in an excess of methanol. The resultant solid co-polymer which resulted via free radical polymerization was purified by re-precipitation with methanol.

IR (KBr, ν cm^{-1}): 3226 (CH aromatic ring), 2957, 2925, 2840, 2855 (CH_3 , CH_2), 1717 (C=O ester), 1675 (broad C=O coumarin ring), 1607, 1512 (C=C), 1275, 1168 (asymmetric and symmetric C-O-C).

^1H NMR ($\text{DMSO-}d_6$) δ (ppm): 0.85 (t, 3H, CH_3), 1.02 (2s, 6H, 2CH_3), 1.17, 1.25 (m, 28H, 14CH_2), 1.56, 1.62 (m, 4H, 2CH_2), 1.87 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 4.02 (q, 2H, CH_2), 4.10 (m, 2H, COO-CH_2), 6.69 (s, 1H, coumarin-H), 6.80-7.81 (m, 7H, C_6H_3 , C_6H_4).

^{13}C NMR ($\text{DMSO-}d_6$) δ (ppm): 14.4, 18.0, 18.6 (CH_3), 22.5, 29.4 (CH_2), 31.7 (CH_2 in repeated unit chain), 42.2 (C in repeated unit chain), 55.4 (CH_2), 89.1, 115.5, 127.9, 154.3 (Aromatic carbon), 164.0, 164.5, 172.4 (C=O).

Antimicrobial Activity Evaluation

The antimicrobial activities of the prepared tested compounds were studied on Mueller-Hinton agar plates by the disc diffusion technique against gram-positive (*Bacillus cereus* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli*, *Neisseria gonorrhoeae*, *Pseudomonas aeruginosa*, and *Salmonella typhimrium*) bacterial strain Table 2 [38]. Also, two fungal species were used in the evaluation, namely *Aspergillus flavus* and *Candida albicans*. Ampicillin (AM 20 μg) was used as a standard antibacterial agent obtained from Bioanalyse® Ltd. UK also Amphotericin B was used as a reference Antifungal agent. Sterile Whatman filter paper discs (6 mm) were individually impregnated with 10 μl of solvent (distilled water, chloroform, DMSO) containing 20 μg concentration of each sample at a pH value of 6. All the discs were dried aseptically and placed on the surface of Mueller-Hinton agar

plates seeded with 1.8×10^8 cfu/ml (0.5 OD^{600}) of the test bacteria. Following 24 h incubation at 37°C , plates were examined for the presence of inhibition zones. The inhibition zones surrounding the disks were measured (mm) considering only halos larger than 6 mm. [39] Inhibition zones obtained are the mean of three replicates for each experiment.

Measurement of the Prepared Compounds as Flow Improvers

The Pour-Point Depression Determination

This methodology which was used for the determination of oil pour-points was based on an adaptation of the ASTM D-5853. Solutions of the synthesized compounds in toluene at different concentrations (100, 200, 500 and 1000 ppm) were prepared. Oil samples were placed in a glass jar with a thermometer in the top as manifested in. The tested crude oils were heated up to 60°C for 2 hrs and the additives were added. The investigated samples were shaken for 3 minutes and the temperature was kept constant for 5 minutes and then transferred to the test jars. The jars were transferred to a water bath at 48°C . The samples were inspected at temperature intervals of 3°C and as long as the oil was fluid, it was returned to the cooling baths. If the sample was not solidified, it was cooled progressively in coolants held cooled down to 27°C then to 0, -9, -18 and -37°C until its solidification. The pour-point is set at 3°C above the temperature at which the oil becomes solid. The results were presented as a pour-point reduction in relation to the pour-point of the pure gas oil. The pour-points of samples in the absence and presence of polymeric additives were determined and the results were presented in Table 3.

Rheological Measurements

All rheological measurements were measured using Brookfield viscometer on equipped with a thermostatted cooling system for temperature control. The preconditioned samples before and after additive beneficiation were heated to 60°C for 30 min and then loaded on the rheometer to start the tests. The rheological behavior of the untreated and treated crude oils by using the latter additive compounds have been determined at the most efficient concentration (1000 ppm) through a viscometer. The measurements were carried at constant temperature below and above the pour-point of the crude oil [at 0, 3, 9, 12, 21 and 24°C and blank at 27 and 30°C] so, the shear stress versus shear rate and viscosity versus shear rate curves were drawn at the latter selected temperatures.

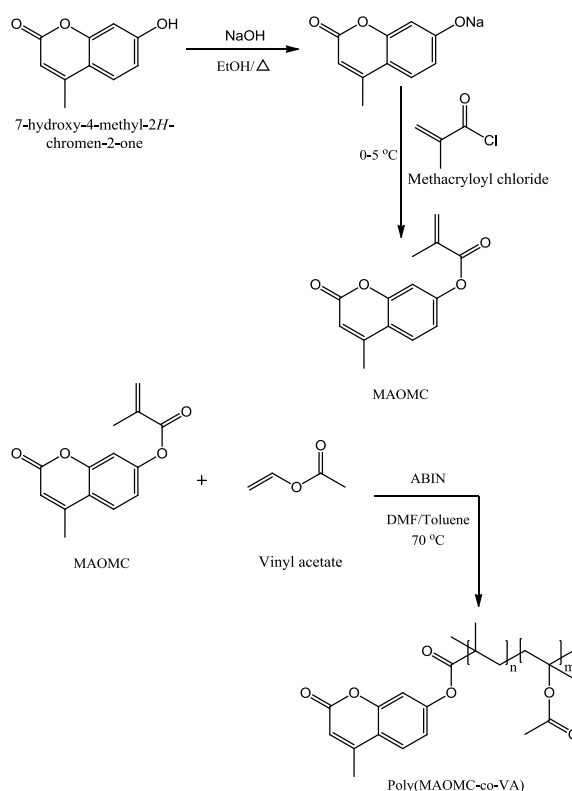
Results and Discussion

Chemistry

In this study, we focused on the synthesis of new co-polymers based on coumarin moiety as new additives (pour-point depressants), and as antimicrobial agents. The starting compound 7-methacryloyloxy-4-methylcoumarin (MAOMC) monomer was prepared according to the previous method indicated in the literature. IR spectrum of the latter monomer showed the presence of the vinyl group at ν 2991 cm^{-1} , CH bending mode of the vinyl group at ν 893 cm^{-1} , and rocking mode at ν 748 cm^{-1} . The appearance of the ester groups at ν 1744 cm^{-1} and at ν 1704 cm^{-1} elucidated the proposed structure. Also, two bands at ν 1276 cm^{-1} and ν 1149 cm^{-1} were assigned to ν c-o-c symmetric and asymmetric stretching vibration of the ester group. Moreover, the ^1H NMR of the latter monomer indicated the presence of two methyl groups at δ = 1.90 and 2.36 ppm in coumarin moiety and methacrylate unit, respectively. The two non-equivalent methylene protons appeared at δ = 6.13 and 6.79 ppm. Also, Mass spectrum of (MAOMC) monomer exhibited a molecular ion m/z 244.41 corresponding to molecular formula $\text{C}_{14}\text{H}_{12}\text{O}_4$ which confirmed the proposed structure.

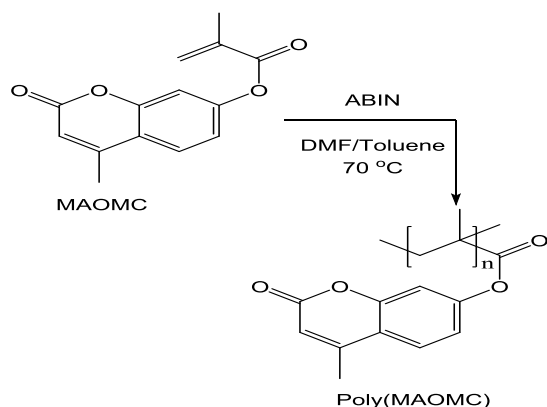
The reactivity of the 7-methacryloyloxy-4-methylcoumarin (MAOMC) monomer to form different co-polymers was studied. Thus, the free radical polymerization reaction of MAOMC monomer and vinyl acetate in azobisisobutyronitrile (ABIN) and toluene/dimethylformamide was illustrated (Scheme 1). The structure of the resultant copolymer poly [7-methacryloyloxy-4-methylcoumarin (MAOMC)-co-vinyl acetate (VA)] was elucidated by spectral data. The IR spectrum assigned two bands at ν 2923 and 2852 cm^{-1} due to the presence of methyl and methylene groups.

The appearance of the two bands at ν 1784 and 1731 cm^{-1} attributed to the ester groups which confirmed the resultant copolymer. In addition, the ^1H NMR of the latter co-polymer indicated the presence of two signals at δ = 1.56 and δ = 1.73 ppm due to the methylene groups in the repeated unit chain of the resultant copolymer which elucidated its structure. Moreover, the signals at δ = 1.89 and 2.26 ppm attributed to the two methyl groups in vinyl and coumarin moieties, respectively. The signals at δ = 6.80 ppm and at δ range 7.10-7.95 ppm confirmed the coumarin ring.



Scheme 1 Synthesis of (MAOMC) monomer and Poly (MAOMC-co-VA)

Scheme 2, described the formation of the homopolymer of 7-methacryloyloxy-4-methylcoumarin [poly (MAOMC)] through the free radical polymerization reaction in toluene/dimethylformamide and azobisisobutyronitrile (ABIN). The structure of the poly (MAOMC) was confirmed by its spectral data. In the IR spectrum, the presence of the two bands at ν 1770 and at ν 1695 cm^{-1} was attributed to the ester groups which elucidated the proposed structure. Also, the appearance of the asymmetric band at 1279 cm^{-1} and symmetric band at ν 1164 cm^{-1} for the (C-O-C), the group confirmed the resultant structure. In the ^1H NMR spectrum, the appearance of the CH_2 at δ = 1.53 ppm confirmed the formation of the homo-polymer of MAOMC.



Scheme 2 Synthesis of Poly (MAOMC)

Moreover, the reactivity of MAOMC monomer to form a different co-polymer [poly (MAOMC-co-AAOB)] was studied (Scheme 3). In the first, we focused to synthesize the octadecyl 4-hydroxybenzoate which prepared by the reaction of para hydroxyl benzoic acid and decanol in xylene and sulfuric acid or *p*-toluene sulfonic acid. The IR spectrum of the prepared ester was confirmed its structure, where the presence of the sharp band at $\nu=3398\text{ cm}^{-1}$ was due to the hydroxyl group. Also, the two bands at $\nu=2916$ and 2849 elucidated the appearance of the CH_3 and CH_2 groups. The band at $\nu=1714\text{ cm}^{-1}$ and the two bands at 1280 and 1165 cm^{-1} assigned the presence of the ester group. The presence of the ester group, triplet at $\delta=0.83$ ppm and quartet at δ in range $4.21\text{--}4.27$ ppm in the ^1H NMR spectrum of the latter compound elucidate its structure. Moreover, the appearance of the signals in the range at δ $1.26\text{--}1.80$ ppm showed the presence of the methylene group in the long aliphatic chain. Signals at δ $6.84\text{--}7.82$ ppm and at 10.30 ppm were assigned the presence of the phenyl moiety and the OH group, respectively. In the mass spectrum of octadecyl 4-hydroxybenzoate the existing $[\text{M}^+]$ ion ($m/z=390.61$) confirmed the molecular weight of this compound. The presence of another peaks at m/z 392.52 , 391.55 (base peak), 389.97 and 388.94 represents the ions $[\text{M}^{+2}]$, $[\text{M}^{+1}]$, $[\text{M}^{-1}]$ and $[\text{M}^{+2}]$, respectively which also, elucidate the structure.

The octadecyl 4-(methacryloyloxy)benzoate (OMAOB) monomer was prepared by the reaction of (OMAOB) with methacryloyl chloride. The resultant IR spectrum explained its structure due to the appearance of many characteristic bands. These bands such as CH aromatic band at $\nu=3100\text{ cm}^{-1}$, three bands at $\nu=2954$, 2920 and 2850 cm^{-1} due to the presence of CH_3 and CH_2 groups, bands at $\nu=1721$, 1695 cm^{-1} attributed to the ester group and two bands at $\nu=1230$, 1175 cm^{-1} assigned to asymmetric

and symmetric C-O-C, respectively. In addition, the ^1H NMR of the latter monomer elucidated its structure due to the presence of many significant signals at a certain range. Thus, the terminal methyl group in the long-chain appeared triplet at $\delta=0.83$ ppm, many signals at $\delta=1.16$, 1.24 , 1.59 , and 1.88 ppm were attributed to methylene groups in the long chain and the other methyl group appeared at a high value ($\delta=2.41$ ppm) due to the presence of the ($\text{CH}_2=\text{C}-$) group beside it. Also, the presence of the two bands at $\delta=5.66$ and 6.01 ppm assigned the proposed structure of the monomer. The mass spectrum of the latter monomer was confirmed its structure by appearance of the molecular ion peak $[\text{M}^+]$ at $m/z=458.34$ which corresponding to its molecular weight. Also, the presence of other peaks at $m/z=458.99$ and 172.60 were corresponding to $[\text{M}^{+1}]$ ion peak and the base peak, respectively.

The 7-methacryloyloxy-4-methylcoumarin (MAOMC) monomer reacted with octadecyl 4-(methacryloyloxy)benzoate (OMAOB) monomer in toluene and benzoyl peroxide by the free radical polymerization reaction. The resultant copolymer [(MAOMC)-co-(OMAOB)] was confirmed by its spectral data which all elucidated the proposed structure. The bands which appeared at ν 2957 , 2925 , 2840 and 2855 cm^{-1} confirmed the presence of the CH_3 and CH_2 groups in the aliphatic long chain. The band at 1717 cm^{-1} assigned the presence of the ester group. ^1H NMR of the co-polymer assigned many signals which also confirmed the co-polymer structure. The signals at $\delta=1.17$ and 1.25 ppm showed the presence of the methylene groups in the aliphatic long chain and the other signals at $\delta=1.56$ and 1.62 ppm were attributed to the methylene groups in the repeated unit of the co-polymer chain. Moreover, the signals in the range of δ $6.80\text{--}7.81$ ppm indicated the two phenyl groups for the coumarin and benzoate moieties. ^{13}C NMR also elucidated the co-polymer structure where the signals at $\delta=14.4$, 18.0 , and 18.6 ppm indicated the presence of the CH_3 group and the signals at $\delta=31.7$ and 42.2 ppm for the CH_2 and carbon atom in the repeated unit chain of the co-polymer. Other signals at $\delta=89.1$, 115.5 , 127.9 , and 154.3 ppm attributed to the aromatic carbon where the signals at $\delta=164.0$, 164.5 , and 172.4 ppm due to the carbonyl groups.

Antimicrobial Evaluation

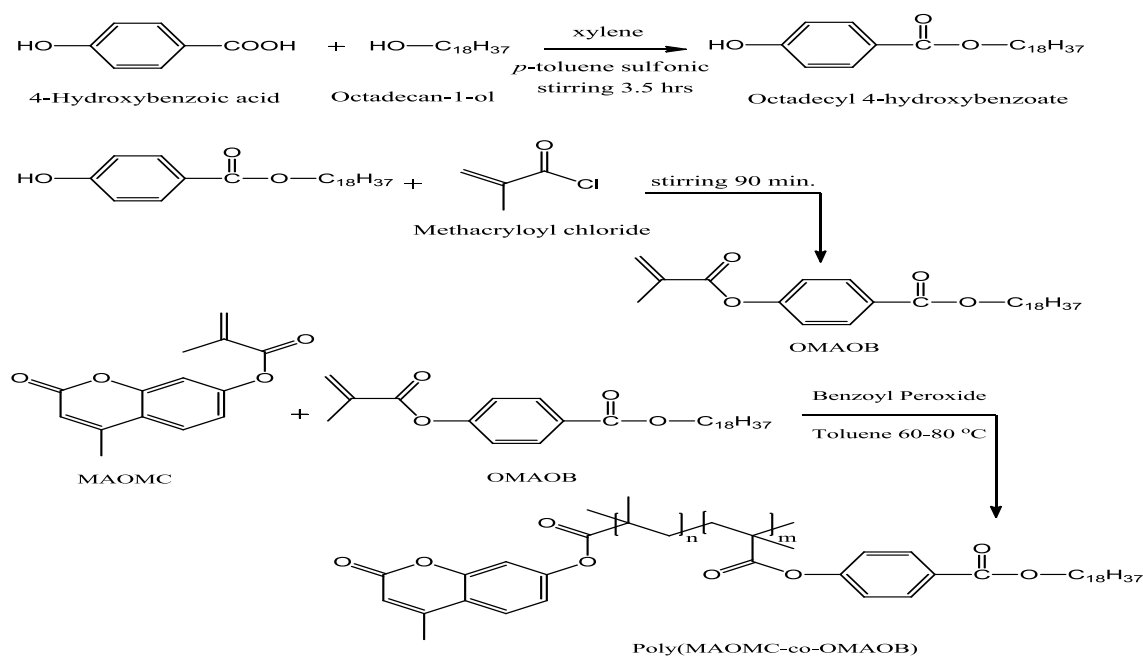
The antimicrobial activity evaluation was measured for all the new resultant co-polymers, monomers, homo-polymer, 7-hydroxy-4-methyl-2H-chromen-2-one, and for octadecyl 4-hydroxybenzoate. Two bacterial strains Gram-

positive (2 species) and Gram-negative (4 species) were used. On the other hand, two fungal strains (2 species) were used in the evaluation (Table 2). The results showed that two compounds namely, poly(MAOMC) and poly(MAOMC-co-VA) indicated no activity towards all the bacterial and fungal strains used. Moreover, all the tested compounds showed no activity against the two fungal strains used (*Aspergillus flavus* and *Candida albicans*), except the copolymer Poly(MAOMC-co-OMAOb) showed moderate activity towards *Candida albicans* strain. Also, the OMAOb Monomer appeared some activity towards only two Gram-negative bacterial species *Pseudomonas aeruginosa* and *Salmonella typhimrium*. On the other hand, the other four compounds namely, 7-hydroxy-4-methyl-2H-chromen-2-one, MAOMC monomer, octadecyl 4-hydroxybenzoate, and poly(MAOMC-co-OMAOb) assigned moderated activity towards all the Gram-positive and Gram-negative bacterial strains used.

From the above results, we can conclude that the resultant poly(MAOMC-co-OMAOb) copolymer was the most potent compound for all the species of bacterial and fungal used. These encourage us to prepare another series from this copolymer and compared its activity. Figure 1 illustrated the antibacterial activity of the most potent compounds against the standard reference ampicillin.

Evaluation of the Synthesized Compounds as Flow Improver

By analyzing using gas chromatography, the paraffin contents of the tested crude oil were measured to determine the average molecular-weight distribution of wax. Figure 2 showed the carbon number distribution of n-paraffin of the tested crude oil, which were 17.9.



Scheme 3 Synthesis of Octadecyl-4-hydroxybenzoate, OMAOB monomer and poly(MAOMC-co-OMAOb)

Table 2 Antimicrobial Activity of the Coumarin and Octadecyl Benzoate Based Compounds Against Bacterial and Fungi species

| Compd. Name | Inhibition zone diameter (mm/mg sample) | | | | | | | |
|-------------------------------------|---|------------------------------|-------------------------|--------------------------------|-------------------------------|------------------------------|---------------------------|-------------------------|
| | Bacterial Species | | | | | | Fungal Species | |
| | Gram-Positive Bacterial Strain | | | Gram-Negative Bacterial Strain | | | <i>Aspergillus flavus</i> | <i>Candida albicans</i> |
| | <i>Bacillus cereus</i> | <i>Staphylococcus aureus</i> | <i>Escherichia coli</i> | <i>Neisseria gonorrhoeae</i> | <i>Pseudomonas aeruginosa</i> | <i>Salmonella typhimrium</i> | | |
| 7-Hydroxy-4-methyl-2H-chromen-2-one | 13 | 14 | 11 | 12 | 12 | 13 | 0.0 | 0.0 |
| MAOMC Monomer | 10 | 14 | 13 | 13 | 15 | 16 | 0.0 | 0.0 |
| Poly(MAOMC) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Poly(MAOMC-co-VA) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Octadecyl 4-hydroxybenzoate | 11 | 12 | 10 | 10 | 12 | 11 | 0.0 | 0.0 |
| OMAOB Monomer | 0.0 | 0.0 | 0.0 | 0.0 | 9 | 9 | 0.0 | 0.0 |
| Poly(MAOMC-co-OMAOB) | 10 | 10 | 11 | 11 | 11 | 11 | 0.0 | 10 |
| Ampicillin | 26 | 21 | 25 | 28 | 26 | 26 | ----- | ----- |
| Amphotericin B | ----- | ----- | ----- | ----- | ----- | ----- | 17 | 21 |

Solvent used: DMSO solutions

- Zone of inhibition is expressed in the form of Mean \pm Standard deviation (mm).
- Well diameter (6mm). -100 μ l was tested

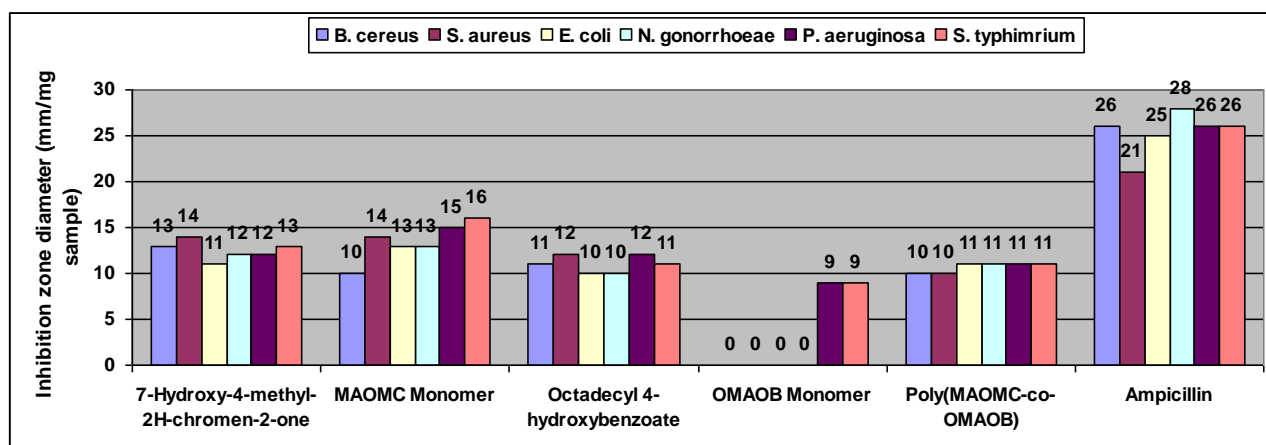
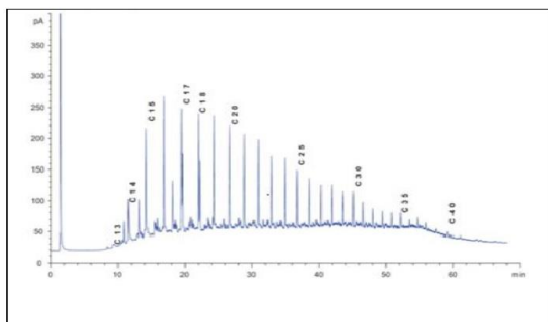


Fig. 1 The antibacterial activity of the most active compounds against the standard ampicillin**Fig. 2** Carbon number distribution of *n*-paraffin in the tested crude oil

The Influence of Coumarin and Octadecyl Benzoate Based Compounds on the Pour-Point

The influence of the monomers, copolymers, homo-polymer, 7-hydroxy-4-methyl-2*H*-chromen-2-one, and octadecyl 4-hydroxybenzoate on the pour-points of crude oil were studied. The oil field of the Egyptian Western Desert was tested. Table 3 and Figure 3 summarized the results for all the tested compounds. The pour-points were measured at a different concentration from 100, 200, 500 to 1000 ppm for all the tested compounds and for the blank crude oil. As the standard reference, the tested blank crude oil has a pour-point at 27 °C. The results found that all the tested polymeric compounds reduced the pour-points of the crude oil, by increasing the concentrations and all the resultants data were promising values. The pour-points depression for 7-hydroxy-4-methyl-2*H*-chromen-2-one, octadecyl 4-hydroxybenzoate and MAOMC monomer indicated moderate values, while OMAOB Monomer showed potent pour-point depression from 12 °C at concentration 200 ppm (depressed by 15 °C), 9 °C at concentration 500 ppm (depressed by 18 °C) and 3 °C at concentration 1000 ppm (depressed by 24 °C). The two co-polymers compounds and the homo-polymer namely, poly(MAOMC), poly(MAOMC-co-VA), and poly(MAOMC-co-OMAOB), illustrated high efficiency in reducing the pour-points than the other tested compounds. The poly(MAOMC) homo-polymer can reduce the pour-points from 15 °C at concentration 100 ppm (depressed by 12 °C) to 9 °C at concentration 500 and 1000 ppm (depressed by 18 °C). Moreover, the co-polymer poly(MAOMC-co-

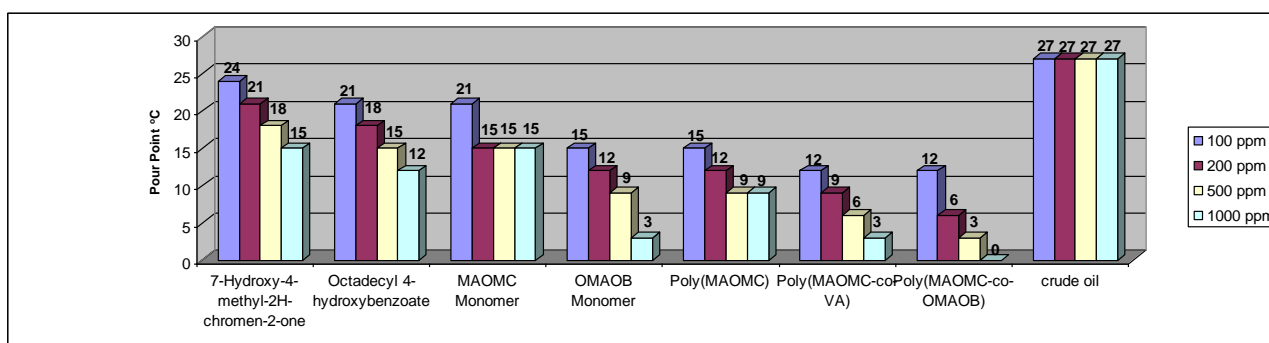
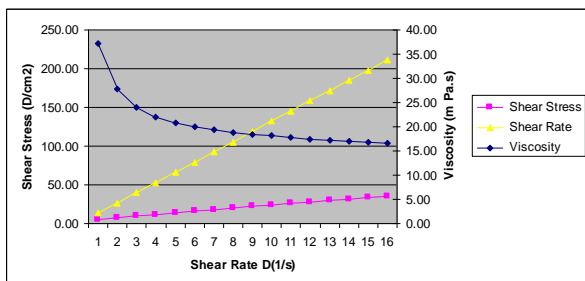
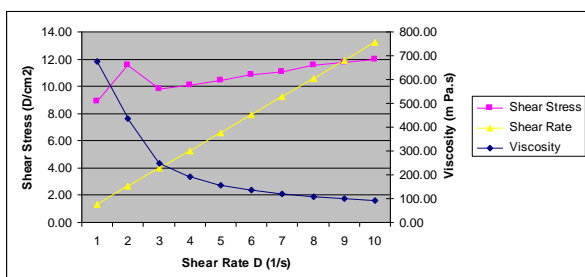
VA) represented a good additive, where it reduced the pour-point from 12 °C at concentration 100 (depressed by 15 °C), 9 °C at concentration 200 ppm (depressed by 18 °C), 6 °C at concentration 500 ppm (depressed by 21 °C), and 3 °C at concentration 1000 ppm (depressed by 24 °C). The second co-polymer poly(MAOMC-co-OMAOB) was the most efficient and showed excellent results in reducing the pour-point of the crude oil. The latter co-polymer reduced the pour-point from 12 °C at a concentration 100 (depressed by 15 °C), 6 °C at concentration 200 ppm (depressed by 21 °C), 3 °C at concentration 500 ppm (depressed by 24 °C) and 0 °C at concentration 1000 ppm (depressed by 27 °C). These data indicated that this co-polymer can be used as a very good additive with high efficiency to reduce the pour-point of the tested crude oil. This an excellent efficiency of the latter co-polymer, attributed to the containing the aromatic units with long aliphatic carbon chain in its structures.

The Rheological Properties

To enhance the flow-ability of the waxy crude oil at low temperatures, the pretreatment with the coumarin and octadecyl benzoate based compounds as polymeric additives was an effective method. The performance of the latter additives depends on the rheological properties of the treated crude oil. [40] The following Figures (4 and 5), explained the rheograms of the neat or untreated crude oil taken at temperatures above and at its pour-point (27 and 30 °C). It can be noted that the untreated oil at 30 °C (above the pour-point) follows the Newtonian behavior. The latter behavior obtained when the shear stress increased by increasing the share rate and by reducing the yield stress. However, at the pour-point of the crude oil 27 °C, it showed the non-Newtonian yield pseudo-plastic rheological behavior with yield stress required for initiating flow. So, the shear-diminishing behavior of crude oil was obtained.

Table 3 The Effect of the Coumarin and Octadecyl Benzoate Based Compounds on the Pour-Points of Crude Oil

| Concentration in ppm | Pour-Points of the Tested Compounds (°C) | | | | | | | crude oil |
|-------------------------|---|---------------------------------|------------------|------------------|-------------|-----------------------|--------------------------|--------------|
| | 7-Hydroxy-4- methyl-2H- chromen-2-one | Octadecyl 4- hydroxybenzoate | MAOMC Monomer | OMAOB Monomer | Poly(MAOMC) | Poly(MAOMC- co-VA) | Poly(MAOMC- co-OMAOB) | |
| 100 | 24 | 21 | 21 | 15 | 15 | 12 | 12 | 27 |
| 200 | 21 | 18 | 15 | 12 | 12 | 9 | 6 | 27 |
| 500 | 18 | 15 | 15 | 9 | 9 | 6 | 3 | 27 |
| 1000 | 15 | 12 | 15 | 3 | 9 | 3 | 0 | 27 |

**Fig. 3** The influence of the tested compounds on the pour-points depression at different concentrations.**Fig. 4** The rheogram of untreated crude oil at 30 °C (above its pour-point)**Fig. 5** The rheogram of untreated crude oil at 27 °C (at its pour-point)

The following curves illustrated the relation between the shear stress versus share rate and viscosity versus share rate of the treated crude oil with the prepared additives at concentration 1000 ppm of poly(MAOMC) homo-polymer, poly(MAOMC-co-VA) co-polymer and poly(MAOMC-co-OMAOB) co-polymer taken at the different temperatures which higher than its pour points for each one of them. The temperature was an important factor that affect strongly in the viscosity of waxy crude oil. By increasing the temperature of treated cured oil, the decreasing will be notated in the corresponding

viscosity. The latter notated was illustrated through the following curves Figures 6 and 7 for [poly(MAOMC)], 8 and 9 for [poly(MAOMC-co-VA)], 10 and 11 for [poly(MAOMC-co-OMAOB)].

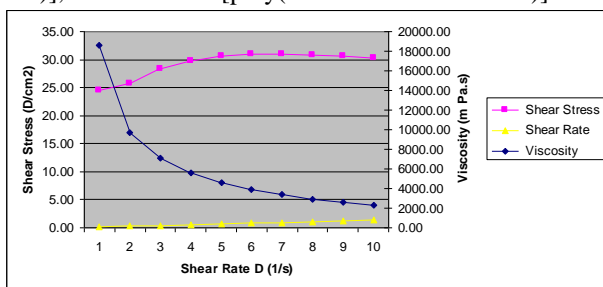


Fig. 6 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC) at 21 °C

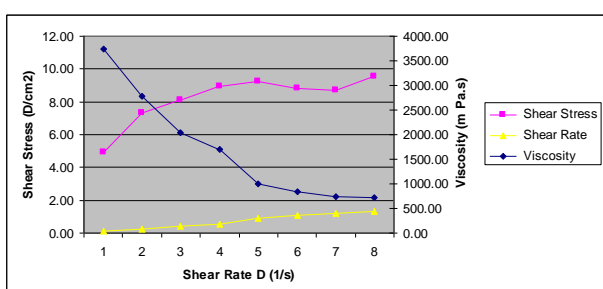


Fig. 7 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC) at 24 °C

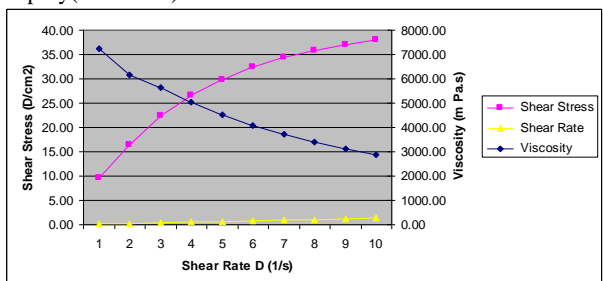


Fig. 8 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC-co-VA) at 9 °C

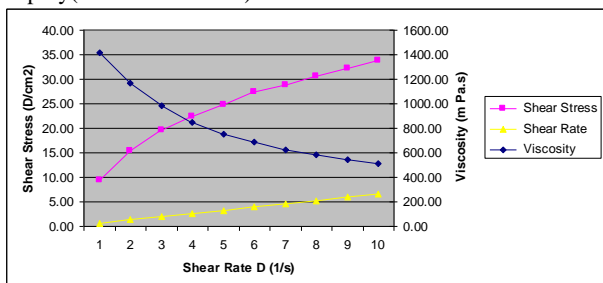


Fig. 9 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC-co-VA) at 12 °C

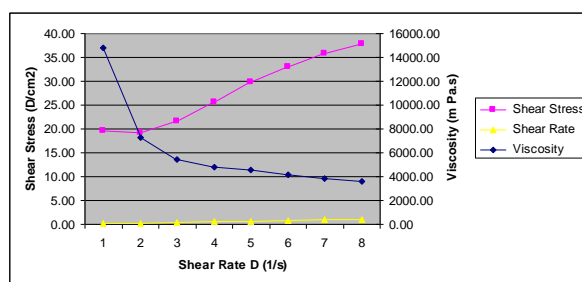


Fig. 10 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC-co-OMAOB) at 0 °C

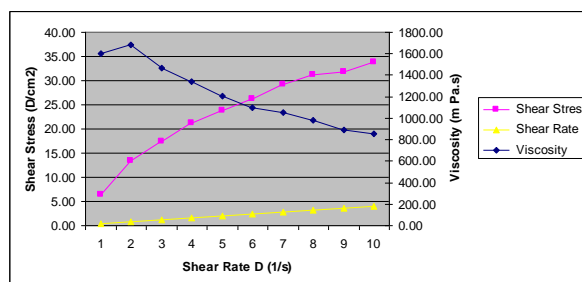


Fig. 11 Relation between the shear rate, shear stress and viscosity of crude oil treated with 1000 ppm concentration of poly(MAOMC-co-OMAOB) at 3 °C

On the other hand, the structures of all the resultants homo- and co-polymers effect on its performance. The good relationship between pour-points and the rheological measurements were attributed to the additive structures. The presence of the aromatic rings in all the prepared additives explained the higher pour-points depression, also the long carbon chain which presents in the poly(MAOMC-co-OMAOB) co-polymer, responsible for the promising result as pour-point depressant.

Conclusion

Poly(MAOMC) homo-polymer and co-polymers of MAOMC with vinyl acetate and of MAOMC with octadecyl 4-(methacryloyloxy)benzoate were synthesized by free radical polymerization. The structures of the obtained compounds were elucidated by IR, ^1H NMR and ^{13}C NMR spectral data. On the other hand, the antimicrobials evaluation was tested against two Gram-positive (*Bacillus cereus* and *Staphylococcus aureus*), four Gram-negative (*Escherichia coli*, *Neisseria gonorrhoeae*, *Pseudomonas aeruginosa*, and *Salmonella typhimrium*) bacterial strains and two fungal species (*Aspergillus flavus* and *Candida albicans*). The results indicated that moderate activity towards the bacterial species used for MAOMC monomer, and for OMAOB monomer only for two Gram-negative *Pseudomonas aeruginosa*, and *Salmonella typhimrium* species. The resultant poly(MAOMC-co-OMAOB) co-polymer showed that potent activity for inhibition of the growth of the bacterial and fungal strains used expect for the *Aspergillus flavus* strain. On the other hand, the synthesized polymers were evaluated as pour-

point depressants and their effects on the rheology of the crude oil were studied. The pour-point and rheology properties results explained that all the synthesized homopolymer and the two co-polymers exhibited very good efficiency at the different concentrations used. The poly(MAOMC)-co-(OMAOb) co-polymer showed high efficiency as pour-point depressant and can be used as a very good additive to improve the flow-ability of the tested low asphaltene content waxy crude oil, also decreased the yield stress and viscosity. This effective influence of the latter co-polymer attributed to the two aromatic ring units present in its structure. The promising results for the pour-points depression for all the resultant poly(MAOMC), poly(MAOMC-co-VA) and poly(MAOMC-co-OMAOb)] compounds will encourage us to prepare many different series and study the effects of its chemical structure as a pour-point improver of the waxy crude oil.

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Compliance with Ethical Standards

Conflict of Interest: The authors confirm that there is no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

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البوليمر المتماثل والكوبوليمرات المبنية على 7-ميثاكريلولوكسي-4-ميثيل كومارين:

تشديد، النشاط المضاد للميكروبات، خافضات نقطة الانسكاب وتأثيرها على ريولوجيا النفط الخام الشمعي

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هدفت الدراسة إلى تشديد إضافات بوليمرية جديدة من البوليمر المتماثل والكوبوليمرات المبنية على مونومر ميثاكريلات 4-ميثيل-2-اوكسو-H2-كرومين-7-ايل ميثاكريلات وتقييم نشاطها كمضادات ميكروبية محتملة وكخافضات لنقطة الإنسكاب لتعديل ريولوجيا النفط الخام الشمعي . تم التحقق من خصائص المركبات الناتجة بواسطة البيانات الطيفية IR و ^1H NMR و ^{13}C NMR. تم تشكيل البوليمرات الجديدة وهى البوليمر المتماثل بولى (7-ميثاكريلولوكسي-4-ميثيل كومارين) [بولى (MAOMC)] و بولى (7-ميثاكريلولوكسي-4-ميثيل كومارين - كو - أسيتات الفينيل) [بولى (MAOMC)-co-(VA)] كبوليمر و بولى (7-ميثاكريلولوكسي-4-ميثيل كومارين - كو - أوكتا دبسيل 4- (ميثاكريلولوكسي) بنزوات [بولى (MAOMC)-co-(OMAOb)] كبوليمر اعتمادا على بلمرة الشقوق الحرة. تم تكوين البوليمر المتماثل [بولى (MAOMC)] والكوبوليمر بولى (MAOMC)-co-(VA) عن طريق بلمرة الشقوق الحرة عند 70 ± 2 درجة مئوية باستخدام 2،2-أزو ثنائى أيزو بيوترونيتريل (AIBN) كمركب بدء التفاعل وباستخدام مذيبات مثل ثنائى ميثيل فورماميد وطولوين، بينما تم تحضير الكوبوليمر الأخر [بولى (MAOMC)-co-(OMAOb)] عند نفس درجة الحرارة باستخدام البنزويل بيروكسيد كبادئ للتفاعل والطولوين كمذيب.

تم تقييم أنشطة المركبات الناتجة كعوامل محتملة مضادة للميكروبات ضد السلالات البكتيرية ، اثنتين موجبة الجرام (*Bacillus cereus* و *Staphylococcus aureus*) ، وأربع سلالات سالبة الجرام (*Escherichia coli* ، *Neisseria gonorrhoeae* ، *Pseudomonas aeruginosa* ، و *Salmonella typhimrium*) ، و كعوامل مضادة للفطريات ضد نوعين من السلالات

الفطرية (*Candida albicans* و *Aspergillus flavus*). أظهرت نتائج المونومر (MAOMC) والكوبوليمر [بولي (MAOMC)-co-(OMAOB)] وجود نشاط قوي معتدل تجاه السلالات البكتيرية والفطرية المستخدمة. في الطرف الآخر، تمت دراسة تأثير مركبات الكومارين وأوكتايسيل بنزوات في انخفاض نقطة الإنسكاب وعلى الخصائص الانسيابية للنفط الخام ذات المحتوى الأسفلتي المنخفض. حيث أشارت النتائج أن البوليمرات الثلاثة أظهرت كفاءة جيدة جدا كإضافات لتحسين قدرة تدفق النفط الخام المختبر. علاوة على ذلك، وجد أن الكوبوليمر [بولي (MAOMC)-co-(OMAOB)] يظهر أعلى أداء لتقليل وخفض نقطة إنسكاب النفط الخام المختبر وتقليل اللزوجة إلى حد كبير بسبب وجود وحدتين من حلقات البنزين مع سلسلة الكربون الأليفاتية الطويلة.