

Synthesis and Characterization of Maleic Acid Polymer for Use as Scale Deposits Inhibitors

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ABSTRACT: The problem of scale formation in oil field production facilities is encountered as a result of mixing of injection water (Lias) rich in sulfate with formation water (Ordovicien) rich in barium.¹ A large number of methods have been developed for the prevention of these deposits. In this work, poly(maleic acid) was studied to ascertain its suitability as an inhibitor of barium sulfate scale deposits. It was synthesized by a free radical solution polymerization. Two different initiators were used namely a potassium persulfate and a redox system composed of potassium persulfate/sodium-hypophosphite monohydrate. Their concentrations were varied to obtain low-molecular weight polymers. Physical and chemical properties of the polymers obtained were measured by infrared and UV/

VIS spectrometry, solubility test, viscosimetry, refractometry, and liquid chromatography. The effectiveness of poly(maleic acid) formulations as scale inhibitor was studied by turbidimetric tests. The most effective inhibitor formulation was found to be that based on poly(maleic acid) prepared via a redox initiating system. This polymer, used at a concentration of 3 ppm, presented the highest effectiveness namely 96% and 88% at room and oil well temperature, respectively, when compared with two commercial inhibitors. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3095–3102, 2010

Key words: polymer synthesis; barium salt; maleic acid; scale inhibition; industrial application

INTRODUCTION

Water injection used for oil displacement and/or pressure maintenance during the course of oil production may lead to the formation of mineral scales such as sulfates, carbonates, and phosphates of calcium, magnesium, and barium. Moreover, the use of continual injection “wash-water,” to dilute the produced formation brine and prevent halite precipitation, will also cause a sulfate scaling problem in the production equipment.

Scale begins to form when the state of any natural fluid is perturbed such that the solubility limit for one or more components is exceeded. Solubility concentrations are exceeded for various reasons, such as partial evaporation of the water phase, a change in pH, pressure, or temperature, or the introduction of additional ions which form insoluble compounds with the ions already present in the solution.² These products precipitate on the surfaces of equipment forming scales or deposits which can be very hard to remove and ultimately can clog pipes.

The problem of barium sulfate scale deposits encountered in the Tin Fouyé-Tabankort (TFT) an

Algerian oilfields region arises from the mixture of two different incompatible waters during secondary oil recovery namely the injection water (Lias) which is rich in sulfates and the oil well water (Ordovicien) which contains barium; this results in the formation and precipitation of barium sulfate.

The most effective method to prevent scale deposition is the use of scale inhibitors such as phosphorous containing compounds (inorganic polyphosphates and organo-phosphorous compounds, most notably phosphonates) and low-molecular weight polycarboxylates.³

It is supposed that the antiscalant agent is adsorbed on the growth sites of the scalent crystal altering its growth pattern so that the crystals are formed more slowly and are highly distorted. The adsorbed antiscalant reinforces the repulsion between the particles; thus, it disperses solids and prevents precipitated crystals from agglomerating and depositing on surfaces.^{4,5}

Recently, the polymerization of maleic acid that was considered for a long time as impossible started to draw much attention and its application as a scale inhibitor is considered to be very promising.

In this work, we have considered the polymerization of maleic acid by different initiator systems to obtain a low-molecular weight polymer whose effectiveness as a Barium sulfate scale deposits inhibitor was evaluated by turbidity test in one of the

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TABLE I
Synthesis Recipes

Polymer formulations		Concentrations (mole/1 mole of maleic acid monomer)		
		K ₂ S ₂ O ₈	Na ₂ H ₂ PO ₂ ·H ₂ O	HSCH ₂ COOH
Series 1	PMA.1	0.021	–	–
	PMA.2	0.042	–	–
	PMA.3	0.064	–	–
	PMA.4	0.085	–	–
Series 2	PMA.5	0.012	0.021	–
	PMA.6	0.025	0.043	–
	PMA.7	0.038	0.065	–
	PMA.8	0.051	0.087	–
Series 3	PMA.9	0.012	0.021	0.062
	PMA.10	0.012	0.021	0.125
	PMA.11	0.012	0.021	0.188

toughest Algerian oil field environment namely that of the TFT oil producing region.

EXPERIMENTAL WORK

Materials

Maleic acid (MA) and Thioglycolic acid (TGA) supplied by Merck.

Potassium peroxydisulfate and Sodium hypophosphite monohydrate were from Riedel.

Commercial scale inhibitors AD18 and AD20 were supplied by CECA S.A France.

Polyethylene glycol from Fluka.

All chemicals are reagent grade and were used as received.

Polymerization setup and procedure

Poly(maleic acid) was synthesized by a free radical solution polymerization process. Before polymerization, 70% of the carboxylic acid charge of the maleic acid monomer was neutralized by Sodium hydroxide. The polymerization was carried out in aqueous media following three different procedures namely by using an oxidizing agent in the first one, with a redox system in the second, with a redox system and a transfer agent in the third, and finally last one giving us three series of polymers.

The polymer formulations recipes are presented in Table I.

The polymerization setup is composed of a 500 mL four-necked reactor, a magnetic stirrer, a condenser, N₂ inlet and outlet, a thermometer, and a heating oil bath.

In the first procedure, the preneutralized maleic acid monomer (MA) and bi-distilled water were introduced first into the reactor; the system was purged throughout the reaction with nitrogen. The reaction was carried out at constant temperature (90°C ± 0.5°C) under slow agitation. When the poly-

merization temperature was reached, the potassium persulfate initiator (K₂S₂O₈) was added batch wise, and the reaction was left for a period of 75 min⁶ under slow agitation.

In the second procedure, a reducing agent namely sodium hypophosphite monohydrate (NaH₂PO₂·H₂O) was added at the beginning of the polymerization reaction with the maleic acid monomer and water before the introduction of potassium persulfate. In the third and last procedure, the transfer agent, thioglycolic acid (HSCH₂COOH), was also added at the beginning of the reaction before the incorporation of potassium persulfate. The concentration of each of these materials was varied, whereas the monomer concentration was kept constant (25%).

The polymer formed was recovered by precipitating twice in excess of methanol and drying in an oven under vacuum at 50°C, until constant weight is obtained.

Polymer characterization

Solubility test

About 50 mg of polymer sample are placed into small test tubes and quantities of various solvents are added. The mixtures are stored at room temperature for several hours with occasional shaking.⁷ The test tubes were checked periodically to detect any solubility of the polymer.

FTIR spectroscopy

A Nicolet Magna 560 apparatus was used to obtain Infra Red spectrum. The polymer sample pellets were obtained by mixing with KBr. The spectrum is obtained after only one scan.

Viscometry

The viscosity measurements were performed according to ISO/R1628, 1970 (E) at a constant temperature

(25°C ± 1°C) with a single bulb Ubbelohde viscometer. The polymer was dissolved at five different concentrations in a 1M NaCl solution. The intrinsic viscosity was determined according to the Huggins equation.

Potentiometry

pH measurements were made using a D 1820 Weilheim pH DIGI 550 pH-mV meter which was calibrated before use with two pH solutions (pH 4 and pH 7). The polymer samples were dissolved in bi-distilled water at 1% concentration. All the measurements were made at about 25°C.

UV/VIS spectroscopy

Determination was carried out with a Perkin-Elmer instrument (Lambda 25) UV/VIS spectrometer. Polymer samples dissolved in bi-distilled water were scanned from 200 to 700 nm. The same procedure was followed for the maleic acid monomer, and all the additives incorporated during the polymerization process (the initiator and the transfer agent).

The results obtained were used in HPLC for polymer molecular weight determination test.

Refractive index determination (RI)

Polymer solutions with concentrations ranging from 0.1 wt % to 1 wt % were obtained by dissolving the polymers in bi-distilled water. The RI's of the different solutions were measured according to ASTM D1045-58. The obtained RI's are extrapolated to 100% concentration to yield the RI of the polymer.⁸

The value obtained was used in high-performance liquid chromatography (HPLC) for molecular weight determination.

Molecular weight analysis

The determination of the polymer molecular weights was carried out using a Waters 996 HPLC instrument equipped with a pump and a degasser. Detection was performed by a UV-absorption detector and a differential refractometer. The columns set were calibrated with polyethylene glycol with different molecular weights (6000–4000–2000–1000–600–400).

A solution of 1% sodium lauryl sulfate known as the mobile phase or the eluent was passed through the columns. The test was carried out at room temperature and at a constant flow rate (1 mL/min). The injected solution was passed through three aqueous columns.

The weight average molecular weights (M_w) of the polymer samples were calculated from the polyethylene glycol calibration curve.

Scale inhibition test

The effectiveness of the synthesized polymer as a BaSO₄ scale inhibitor with respect to the TFT region was evaluated by a turbidity test.

Turbidity is the measure of relative sample clarity. It is defined as an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. The intensity of the light scattered is measured by a photo-detector and displayed on a digital readout.

The turbidity test is performed according to the ISO 7027–1999 using a Hach model 2100N laboratory turbidimeter.

Turbidimeters also called nephelometers normally report the turbidity in terms of NTU (Nephelometric Turbidity Units).

A previous study¹ has shown that maximum precipitation of (Ba, Ca, Sr)-SO₄ is obtained at a mixture of 40% of Lias and 60% of Ordovicien waters. It was also observed that BaSO₄ is the most predominant deposit compared with CaSO₄ and SrSO₄ since it constitutes about 87.5% of the total deposit formed.

The injection (Lias) and the underground (Ordovicien) waters were reconstituted on the basis of the results obtained from the analysis of these two waters obtained from TFT 207 and TFT 97 wells, respectively.¹

The polymer solution concentration was varied from 10 to 2000 ppm. First, the test was performed at room temperature (18°C ± 2°C) to select the optimum concentration where the highest effectiveness is obtained. After that the most efficient formulations with their optimum concentrations were selected and tested for their effectiveness at high temperature (90°C ± 2°C) which is the underground oil well temperature.

Two commercial scale inhibitors (AD18 and AD20) were also tested under the same conditions to compare their effectiveness with the synthesized polymer formulations.

After appropriate calibration, the scale inhibition test is carried out by first diluting the polymer sample at 10% (w/v) with bi-distilled water. The solution obtained is then mixed with Lias water at different concentrations (10, 30, 50, 100, 200, 500, 1000, 2000 ppm) to form the injection water polymer solutions which are slowly added to the formation "Ordovicien" water. The mixture of injection and formation water is then stirred slowly (300 rpm) for a period of 1 h.

At the end of the test, the turbidity value is directly read on the turbidimeter.

The effectiveness of the polymer as scale inhibitor is calculated as follows:

$$\% \text{ Effectiveness} = \frac{[(Tu)_0 - (Tu)]}{(Tu)_0} \times 100 \quad (1)$$

where $(Tu)_0$ is the turbidity of the sample without inhibitor and (Tu) is the turbidity of the sample in the presence of the inhibitor both expressed in (NTU).

RESULTS AND DISCUSSION

Synthesis

Literature is scarce on maleic acid homo-polymerization; it deals mainly with its copolymerization. This may be due to the difficulty in polymerizing this monomer particularly in an aqueous medium. This was experimentally verified at the beginning of this study since the synthesis of maleic acid polymer in aqueous medium was not very successful due to the low rate of conversion obtained (less than 20%). The variation of monomer, solvent, and initiator concentrations did not resolve the problem.

To overcome this problem the maleic acid monomer was neutralized⁹ which permitted to obtain high conversions. Conversions were determined on a weight to weight basis. The conversions varied from 92 to 99% for series 1, from 87 to 98% for series 2, and finally from 87 to 99% for series 3.

Polymer characterization

Polymer solubility

Poly(maleic acid) is found to be soluble in water and in ethylene glycol and slightly soluble in di-ethylene glycol but it is not soluble in most of the other commonly used solvents such as acetone, methanol, ethanol, toluene, tetrahydrofuran, benzylalcohol, isooctane, *n*-heptane, dekalin, xylene, propyl-acetate, vinyl-acetate, cyclohexanone, dioxane, diethylether, petroleum ether, benzaldehyde, aniline, *m*-cresol, anisol, nitrobenzene, 1,2 ethane dichloride, 1-butane chloride, and carbon tetrachloride.

FTIR spectroscopy

The IR spectrum of PMA is similar to the IR spectrum reported in the literature.⁶ The main characteristic peaks are the broad absorption band which is due to the OH bond present in the COOH group. This is clearly observed in the range of 3610 cm^{-1} to 3000 cm^{-1} . The C=O bond of carboxylic acid was observed in the range 1870 cm^{-1} to 1650 cm^{-1} especially at 1675 cm^{-1} . Two bands arising from CO

TABLE II
Intrinsic Viscosities of Series 1, 2, and 3

Polymer formulations		$[\eta]$ (dL/g)
Series 1	PMA.1	0.026
	PMA.2	0.023
	PMA.3	0.017
Series 2	PMA.4	0.013
	PMA.5	0.019
	PMA.6	0.013
	PMA.7	0.012
Series 3	PMA.8	0.008
	PMA.9	0.011
	PMA.10	0.010
	PMA.11	0.009

stretching and OH bending appear in the spectrum. These are 1320 cm^{-1} to 1210 cm^{-1} and 1400 cm^{-1} to 1350 cm^{-1} , respectively. Both of these bands involve some interaction between CO stretching and in-plane COH bending.¹⁰

Viscometry

The intrinsic viscosities of series 1. The intrinsic viscosity $[\eta]$ measured in a specific solvent is related to the viscosity average molecular weight M_v by the Mark-Houwink equation:

$$[\eta] = K M_v^a \quad (2)$$

Since the Mark-Houwink constants of poly(maleic acid) are not available, it can be taken into account from the earlier relation that the intrinsic viscosity being linearly proportional to the molecular weight gives a good indication on the latter.

The intrinsic viscosities of polymers of series 1, 2, and 3 are shown in Table II.

We can see that the intrinsic viscosity $[\eta]$ of the polymers obtained by varying the initiator potassium persulfate ($K_2S_2O_8$) concentration decreases as the initiator concentration increases. This can be explained by the fact that increasing the concentration of the initiator will generate a high concentration of free radicals that react with the monomer rather than the developed microradicals; therefore, lower chain length polymer are produced with low-molecular weights and hence low viscosities are obtained.

The intrinsic viscosities of series 2. We can see from the intrinsic viscosities of series 2 corresponding to PM5, PM6, PM7, and PM8 that by increasing both the oxidizing and reducing agents concentrations at a constant ratio leads to the same observation as earlier, i.e., the intrinsic viscosity decreases as the rate of the initiating system increases.

The presence of the reducing agent ($NaH_2PO_2 \cdot H_2O$) accelerates the thermal decomposition of

TABLE III
Refractive Indices of PM1, PM5, PM9, and Maleic Acid Monomer

Polymer formulations	Refractive indices
PM1	1.4777
PM5	1.5273
PM9	1.4587
Maleic acid	1.4900

the initiator $K_2S_2O_8$ and hence more free radicals are produced¹¹ which leads to rapid monomer consumption, resulting in the formation of shorter chains and low-molecular weight polymers, so low viscosities are obtained.

The intrinsic viscosities of series 3. In series 3, transfer agent is added at different concentrations with a constant concentration of the initiating redox system (5%) since at this concentration the intrinsic viscosity is lower than that obtained with 5% of $K_2S_2O_8$.

As shown in Table II the intrinsic viscosity of the polymer decreases as the transfer agent concentration is increased up to 5% when compared with the intrinsic viscosity of PM5 where no transfer agent is added. This is due to the fact that the presence of the transfer agent stops rapidly the propagating macroradicals leading to shorter polymeric chains hence lower intrinsic viscosities.

Increasing the transfer agent concentration further than 5% does not have a great influence on the intrinsic viscosity.

UV/VIS spectroscopy

The spectrum of the synthesized poly(maleic acid) shows a wide absorption band in the region between 200 and 240 nm. The absorption is at a maximum at 210.39 nm which corresponds to the CO absorbance. It was reported¹² that the maximum absorbance is observed at 215 nm.

For the raw materials used in the polymerization process, it was found that their maximum absorption is at 209.96, 195.04, 191.12, and 234.02 for maleic acid; potassium persulfate; sodium hypophosphite; and thioglycolic acid, respectively.

Refractive index determination

The different refractive indices are obtained by a direct extrapolation of the data to 100% concentration. The results obtained for PM1, PM5, PM9, and the maleic acid monomer are presented in Table III.

Molecular weight analyses

Using the polyethylene glycol calibration curve, the molecular weights of the different formulations of

series 1, series 2, and series 3 are calculated by hand directly from the chromatograms obtained. The measured values are relative values equivalent to the molecular weights of the standard used. So, they may be described as "polyethylene glycol equivalent molecular weights."

Polymer molecular weights of series 1. As shown in Table IV, the molecular weights of the polymer samples of series 1 decreased as the initiator $K_2S_2O_8$ concentration increases.

It is observed that the optimum initiator concentration is reached at 10% where a further increase in the initiator concentration has no influence on the polymer molecular weight.

Polymer molecular weights of series 2. The different results show that varying the concentration of $K_2S_2O_8/Na_2H_2PO_2 \cdot H_2O$ resulted in a decrease of molecular weight. The presence of sodium hypophosphite monohydrate accelerated the decomposition of $K_2S_2O_8$. The presence of more free radicals leads to short chain formation and so, the polymer molecular weight is reduced.

The optimum initiation system concentration is obtained at 10% due to the fact that not a high variation in the polymer molecular weight is observed with the increase in the $K_2S_2O_8/Na_2H_2PO_2 \cdot H_2O$ concentration.

The molecular weight obtained by using 5% of the redox initiation system ($K_2S_2O_8/Na_2H_2PO_2 \cdot H_2O$) is lower than when using 5% of $K_2S_2O_8$ only. This may be explained by the fact that the reducing agent acted in the same time as a transfer agent in the polymerization reaction.

Polymer molecular weights of series 3. It is known that the incorporation of a transfer agent in the polymerization reaction results in a decrease in the molecular weight of the produced polymer. The results show that not a great variation was observed when using the different transfer agent concentrations. This may be due to the fact that the transfer agent

TABLE IV
Polymer Molecular Weights (M_w) of Formulations of Series 1, 2, and 3

Polymer formulations	Molecular weight M_w	
Series 1	PMA.1	5751
	PMA.2	4438
	PMA.3	4392
	PMA.4	4380
Series 2	PMA.5	4400
	PMA.6	4380
	PMA.7	4370
	PMA.8	4318
Series 3	PMA.9	4360
	PMA.10	4340
	PMA.11	4319

TABLE V
Comparison of the Efficiencies of Series 1 Formulations at Different Polymer Solution Concentrations

Concentrations (ppm)	Polymers efficiencies (%)			
	PM1	PM2	PM3	PM4
10	16.82	45.48	38.62	40.49
30	48.28	75.54	84.48	92.24
50	67.28	81.52	86.97	90.00
100	83.95	86.10	93.30	83.83
200	86.29	90.65	90.90	83.67
500	82.21	83.76	77.50	56.07
1000	72.55	67.07	52.64	33.95
2000	61.68	27.72	27.10	25.20

cannot have a great influence in the range of this low-molecular weight polymer (4400).

Scale inhibition tests

The effectiveness of the different polymer formulations as BaSO₄ scale inhibitors were obtained both at room and underground oil well temperatures.

As only 10% of the mother polymer solution prepared was used, the effective final concentrations of active polymers are 1, 3, 5, 10, 20, 50, 100, and 200 ppm, respectively.

Effectiveness of the polymer samples at room temperature

The inhibition effectiveness of series 1. The results of this test show that the effectiveness of the polymer as a scale inhibitor increases by increasing the concentration of the polymer until an optimum dosage is obtained where the effectiveness reaches a maximum value, after that it starts to decrease until no more effectiveness is observed.

As shown in Table V, the higher effectiveness (92.24%) is obtained at 30 ppm polymer solution of PM4, whereas PM3 presented its best effectiveness (93.30%) at 100 ppm. Both PM1 and PM2 attained their maximum efficiencies which are 86.29% and 90.65%, respectively, at a concentration of 200 ppm.

Decreasing the molecular weight result in better inhibition effectiveness, since the maximum effectiveness rates were obtained for PM3 and PM4 compared with PM1 and PM2.

At a dosage of 30 ppm, the effectiveness level of the different polymer formulations increased by decreasing the molecular weight. PM4 is the most efficient BaSO₄ scale inhibitor of series 1 compared with PM1, PM2, and PM3 with a level of 92.24%.

The inhibition effectiveness of series 2. The inhibitor effectiveness increases by increasing the polymer solution dosage. After maximum effectiveness is

TABLE VI
Comparison of the Efficiencies of Series 2 Formulations at Different Polymer Solution Concentrations

Concentrations (ppm)	Polymers efficiencies (%)			
	PM5	PM6	PM7	PM8
10	42.67	38.62	25.54	56.07
30	48.90	61.68	78.59	95.48
50	51.71	85.98	89.50	92.24
100	59.87	92.46	96.38	84.17
200	89.93	88.90	93.05	75.07
500	86.41	87.16	90.65	59.50
1000	81.91	75.42	86.44	58.56
2000	58.87	64.17	65.10	21.81

obtained, increasing the dosage will decrease the polymer effectiveness.

As illustrated in Table VI, the decrease in molecular weight results in the increase in the polymer inhibition effectiveness at lower polymer concentrations. For PM5, the higher inhibition effectiveness is found to be 89.93% at 200 ppm, whereas for PM6 and PM7, the higher efficiencies were 92.46% and 96.38% at 100 ppm. The best results of series 2 were obtained with PM8 where the inhibitor effectiveness reached 95.48% at only 30 ppm.

The inhibition effectiveness of series 3. The inhibition effectiveness test using PM9, PM10, and PM11 polymer solutions showed the same results as the above concerning the increase in the inhibitor effectiveness with dosage until an optimum level, then it starts to decrease for PM9, PM10, and PM11. This means that dosing is a very important operating parameter since under-dosing leads to scale formation, whereas over-dosing enhances sludge formation.¹³

We can see that the highest inhibition effectiveness is obtained using PM9 with an effectiveness of 92.24% at a concentration of 500 ppm compared with PM10 which presented only 63.86% effectiveness at the same concentration. However, PM11 was not very efficient since its highest effectiveness reached was 61.65% only at a concentration of 200 ppm as shown in Table VII. This is quite surprising

TABLE VII
Comparison of the Efficiencies of Series 3 Formulations at Different Polymer Solution Concentrations

Concentrations (ppm)	Polymers efficiencies (%)		
	PM9	PM10	PM11
10	30.84	14.33	18.38
30	53.58	35.51	42.99
50	57.32	48.50	49.22
100	54.51	56.12	57.72
200	61.05	61.21	61.65
500	92.24	63.86	22.74
1000	75.66	40.49	20.56
2000	66.66	39.47	14.95

TABLE VIII
The Best Polymers Inhibition Efficiencies at Different Concentrations

Formulations	Efficiencies (%) polymer concentrations (ppm)				
	30	50	100	200	500
PM1	–	–	–	86.29	–
PM2	–	–	–	90.65	–
PM3	–	–	93.30	–	–
PM4	92.24	–	–	–	–
PM5	–	–	–	89.93	–
PM6	–	–	92.46	–	–
PM7	–	–	96.38	–	–
PM8	95.48	–	–	–	–
PM9	–	–	–	–	92.24
PM10	–	–	–	–	63.86
PM11	–	–	–	–	61.65

since it has a low-molecular weight similar to PM8 which is the best inhibitor. Therefore, we must consider another factor which can be the polymer configuration which might play a vital role in the inhibition of deposits.

General conclusions. The different formulations presented different inhibition effectiveness rates as illustrated in Table VIII.

We can see that the molecular weight range of the synthesized polymers (5751–4318) is efficient for the inhibition of barium sulfate scale formation with different efficiencies. The best one was PM8 of series 2 with an average molecular weight of 4318. It was also observed that decreasing the molecular weight will increase the inhibition effectiveness of the polymer.

The best inhibition effectiveness rates were obtained with polymers of series 2 especially with PM6, PM7, and PM8. The polymers PM3 and PM4 of series 1 were also very effective, whereas that of series 3 were not very efficient since their best results were found to be 61.65% at 200 ppm. These polymers were thus selected to be tested at high temperature (90°C).

This test which compares the inhibition effectiveness of the different polymers of the three series at room temperature showed that the best results are obtained with PM8 with a maximum effectiveness of 95.48% at a dosage of 30 ppm. It has to be mentioned that this dosage represents that of the polymer solution (10% w/w) which corresponds in fact to 3 ppm of the active polymer dosage.

Effectiveness of AD18 and AD20. The results of scale inhibition of two commercial products (AD18 and AD20) are shown in Table IX.

We can see that these two scale inhibitors present almost the same rate of effectiveness with 92.12% and 92.22% for AD18 and AD20, respectively, at an

TABLE IX
The Efficiencies of AD18 and AD20 at Different Concentrations

Concentrations (ppm)	Efficiencies of commercial polymers (%)	
	AD18	AD20
10	92.12	92.22
30	76.74	89.77
50	33.03	46.78

optimum concentration of 10 ppm. Increasing the dosage up to 30 ppm and 50 ppm resulted in a decrease in the effectiveness of both AD18 and AD20.

Effectiveness of the polymer samples at high temperature

PM3 and PM4 of series 1 and PM6, PM7, and PM8 of series 2 being the most effective polymers were tested under high temperature, i.e., 90°C.

The results presented in Table X show that the inhibition effectiveness decreases as the temperature increases.

PM8 shows the highest inhibition effectiveness, i.e., 87.77% at 30 ppm. The two other formulations PM4 and PM7 have 86.07% and 84.24% efficiencies at 50 ppm and 100 ppm, respectively.

Effectiveness of AD18 and AD20 at high temperature. The results of the two commercial products when tested at high temperature were also lower than that obtained at room temperature as mentioned earlier for the polymers samples. It was also observed as shown in Table XI that the commercial product AD20 presented high-inhibition effectiveness 88.54% at 10 ppm but AD 18 presented a decreased effectiveness with a maximum of 54.56% at the same concentration.

Comparison of the inhibition efficiencies of PM8 and poly(acrylic acid)

The comparison of the inhibition effectiveness of PM8 and the synthesized poly(acrylic acid) (PAA) reported in Ref. 14 shows that poly(maleic acid) presents the best results both at room temperature

TABLE X
The Influence of High Temperature (90°C) on Polymer Inhibition Efficiencies

Concentrations (ppm)	Polymers efficiencies (%) at 90°C				
	PM3	PM4	PM6	PM7	PM8
30	–	71.85	–	–	87.77
50	–	86.07	–	–	79.30
100	75.65	–	76.46	84.24	65.92
200	51.60	–	78.91	72.83	–

TABLE XI
The Influence of High Temperature on AD18 and AD20 Inhibition Efficiencies

Concentrations (ppm)	Polymers efficiencies (%) at 90°C	
	AD18	AD20
10	54.56	88.54
30	27.40	76.39
50	21.97	–

and at high temperature compared with poly(acrylic acid). At room temperature; the PAA having a molecular weight of 820 presents the best effectiveness (98.70%) at 20 ppm, whereas PM8 shows an effectiveness of 95.48% at only 3 ppm. At higher temperature, PM8 presents good inhibition effectiveness at 90°C with 87.77% effectiveness at 3 ppm when compared with poly(acrylic acid) whose effectiveness decreases sharply especially over 50°C where it attains only 4.65%.

General conclusions of the scale inhibition test. The scale inhibition test performed at room temperature and at the underground TFT field temperature (90°C) revealed that PM8 is the best barium sulfate scale inhibitor compared with the other polymer formulations. It is better than the two commercial products (AD18 and AD 20) and it is more efficient than poly(acrylic acid) especially at high temperature. All the results are summarized in Table XII.

CONCLUSIONS

From this study, it can be concluded that

- If previously neutralized, then the poly(maleic acid) can be easily synthesized by a free radical solution polymerization in an aqueous medium and relatively low-molecular weight polymers can be obtained by using a redox system as initiator instead of oxidant initiators only.
- In our case, the optimum concentration of potassium persulfate ($K_2S_2O_8$) was found to be 10%.

TABLE XII
Summary of Efficiencies Results

	Concentration (ppm)	Efficiencies (%) at 25°C	Efficiencies (%) at 90°C
PM 8	3	95.48	87.77
AD 18	10	92.12	55.56
AD 20	10	91.22	88.54
PAA	20	98.70	4.65 (at 50°C)

- For the redox initiation system, the lowest molecular weight was obtained at a concentration of 20%.
- The use of a transfer agent has not influenced greatly the polymer molecular weight.
- The scale inhibition test as applied to a very hard water revealed that poly(maleic acid) is an excellent scale inhibitor of barium sulfate at room temperature and at 90°C (the TFT underground oil well temperature).
- The best results are obtained with PM8 having a polymer molecular weight of 4318 both at room temperature and high temperature with an effectiveness of 95% and 88%, respectively, with an optimum dosage of 3 ppm.
- PM8 is more effective scale inhibitor than the two commercial scale inhibitors AD18 and AD20 both at room and high temperatures.
- The effectiveness of PM8 is better both at room and high temperatures when compared with the results obtained using poly(acrylic acid).

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