Hyperbranched Polyglycerols, Obtained from Environmentally Benign Monomer, as Reactive Clays Inhibitors for Water-Based Drilling Fluids

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ABSTRACT: To prevent the degradation of the borehole and also the disintegration and dispersion of drilled cuttings, different shale stabilizing additives are used in water-based drilling fluids (WBFs). Glycols, poly(ethylene glycol), glycerols, and polyglycerol derivatives, also called polyols, have been used to inhibit shales containing reactive clays in WBF. These additives are normally used in conjunction with KCl to reduce clay swelling and dispersion of drilled cuttings. Highly branched polymers have become an important field in current polymer science. Such materials typically exhibit compact, globular structures in combination with an exceptionally high number of sites with functional groups. They have unique properties that differ significantly from their linear counterparts, and the hyperbranched polyglycerol (hPG) is an important hyperbranched polymer that can be produced from an environmentally benign monomer, the glycerol carbonate. In this article, the clay inhibitive properties of hPG were evaluated by different test methods including bentonite inhibition test, cuttings recovery, and X-ray diffraction measurements. The results show that the hPG has a great potential to be used as an environmental friendly inhibitor additive in WBFs. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40384.

INTRODUCTION

One of the important functions of the drilling fluid is to prevent the degradation of wellbore walls and the disintegration or dispersion of drilled cuttings into the fluid.[1,2] In the drilling operations, reactive shales are responsible for 90% of wellbore stability problems.[3,4] To prevent borehole instability, different shale inhibitors are used in water-based drilling fluids (WBFs).[5,6] Glycols, poly(ethylene glycol) (PEG), glycerols, and polyglycerol derivatives, also called polyols, have been used as additives in WBFs and are normally employed in conjunction with KCl to reduce clay swelling and dispersion of drilled cuttings.[7] Another common drilling fluid inhibitor is the poly (diallyldimethylammonium chloride) (PDADMAC). Due to its cationic structure, it is very effective to avoid clay swelling, but unfortunately it is also very toxic.

Dendrimers show very interesting properties in the solid state and also in solution because of their high branching, globular shape, lack of entanglements, and large number of modifiable surface functional groups, as well as internal cavities.[8] In contrast to dendrimers,[9] which are generally tediously prepared and present limited structure growth, many hyperbranched polymers can be synthesized in one step from ABn-type ($n \geq 2$) monomers and can be produced in large quantities, being thus cost-effective.[10,11] Highly branched polymers have become an important field in current polymer science. A main emphasis in this area has been placed on polymers with tree like or "cascade type" branching, with a branch-on-branch topology. Such materials typically exhibit compact, globular structures in combination with an exceptionally high number of sites with functional groups. They have unique properties that differ significantly from their linear counterparts, because the conformation of such polymers is restricted by their molecular architecture, and in contrast to linear polymer chains, entanglements are negligible.[12,13]

Hyperbranched polyglycerols (hPGs) is one of the important hyperbranched polymers, which can be synthesized in one-pot with commercially available glycidol.[14] The general structure of hPG is displayed in Scheme 1.
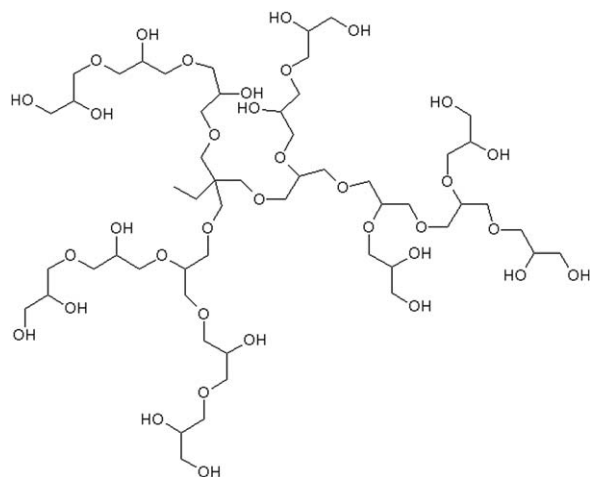
Scheme 1. Schematic drawing of hyperbranched poly(glycerol) initiated by 1,1,1-tris(hydroxymethyl)propane (TMP). Garamus et al.[13]

Rokicki et al.[15] produced a hPG from glycerol carbonate by anionic polymerization, using the partially deprotonated 1,1,1-tris(hydroxymethyl)propane as a central core and a polymerization initiator (Scheme 2). The glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is a monomer obtained from renewable starting materials: glycerol and dimethyl carbonate (DMC). Apart from that, the hPG obtained is even less cytotoxic than the structurally similar, well-established PEG.[16–19]

To evaluate the inhibitive properties of a drilling fluid, the oil industry uses the cuttings rolling test, which evaluates the effect of drilling fluid on the shale cuttings size after a period of contact. This test provides a quantitative estimation of the resistance to hydration and to mechanical dispersion of shale cuttings after contact with the drilling fluid.[20] In this article, the clay inhibitive properties of the hPG were compared with that of two conventional inhibitors, potassium chloride and PDADMAC. They were evaluated by different test methods including bentonite inhibition test, cuttings recovery, and X-ray diffrac-

tion (XRD) measurements. For this purpose, bentonite clay was used without any further treatment to simulate borehole conditions.

EXPERIMENTAL

Materials
PEG400—PEG—400 Da, and low-molecular-weight PDADMAC were supplied by Sigma Aldrich. hPG polymers with different molar masses (500, 1000, 2000, and 6000 Da) were used in this study. The 2000 and 6000 Da polymers (called PG2000 and PG 6000, respectively) were supplied by Johannes Gutenberg-Universität Mainz, and the 500 and 1000 Da polymers (called 500P and 1000P, respectively) were synthesized according to procedure described by Rokicki et al.[15]

### Characterization of Synthesized Products
The synthesized products were characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), and real-time attenuated total reflectance (ATR)-FTIR. ^{1}H NMR and ^{13}C NMR spectra were recorded in d6-DMSO with a Brucker Advance DPX-200 spectrometer, operating at 300 and 75.4 MHz, respectively. Measurements of the molecular weight were performed with a GPC Waters apparatus using water as an eluent at 25°C and PEG for calibration. FTIR measurements were carried out using a Nicolet 740FTIR spectrometer, which ranged from 4000 to 400 cm^{-1}. Real-time ATR-FTIR measurements were performed with a Mettler ToledoReactIR45 Infrared Spectrometer equipped with a EASYMAX 102 reactor.

Clays Characterization
Shale samples and the bentonite used in the tests were gently supplied by Bentonorte Company (Paraíba, Brazil) and were characterized by XRD and fluorescence.

Methods
Bentonite Inhibition Test. The bentonite inhibition test is used routinely as a screening method to determine the ability of
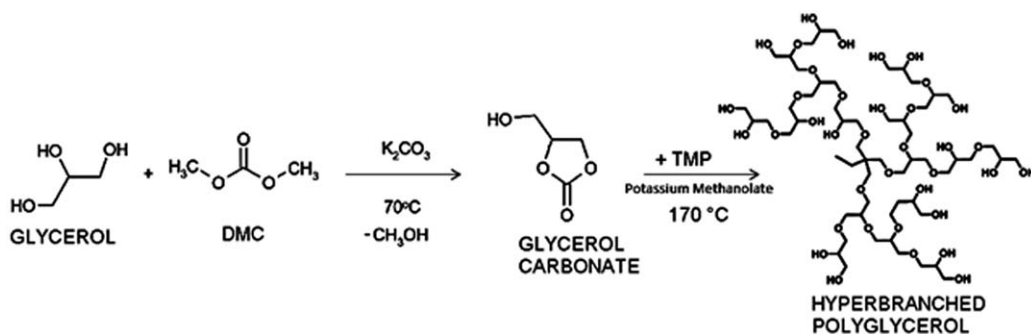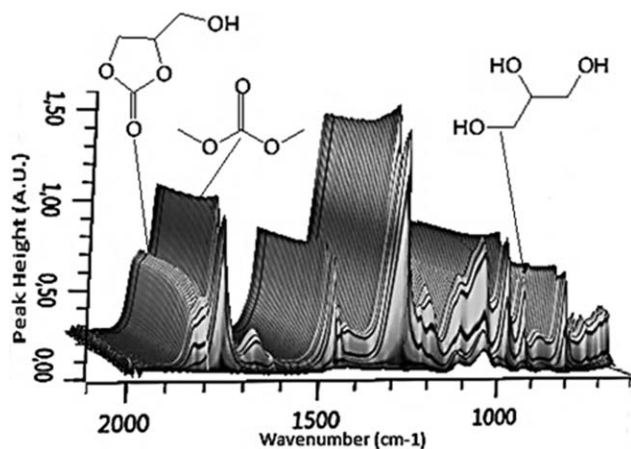

Scheme 2. Synthesis of hyperbranched polyglycerol, from glycerol and dimethyl carbonate. Rokicki et al.[15]

Table I. X-ray Diffraction—Clay Composition

Sample	Smectite (%)	Ilite (%)	Kaolin (%)	Clorite (%)	Quartz (%)	Hematite (%)	Feldspate (%)
Shale C	68.37	7.66	19.77	—	4.2	—	—
Shale R	80.96	—	5.44	—	0.5	13.1	—
Bentonite	81.73	2.16	8.61	—	7.5	—	—

Table II. X-ray Florescence—Clay Composition

Element	Bentonite (%)	Shale C (%)	Shale R (%)
Si	35.2	46.5	45.6
Al	18.3	28.2	13.1
Fe	34.6	16.5	37.5
Mg	1.3	2.7	1.4
Ca	2.7	0.8	0.4
K	3.2	2.6	0.2

Table III. GPC Characterization of Hyperbranched Polyglycerol

Sample	Mn (Da)	Mw (Da)	Polydispersity index (PDI) (Mw/Mn)
500P	506	636	1.25
1000P	616	904	1.46
PG2000	2052	3520	1.71
PG6000	5307	8995	1.69

Figure 1. Transesterification reaction progress monitored by real-time FTIR of the reaction mixture and observing the changes of the signal derived from the cyclic carbonate carbonyl group (1792 cm^{-1}).

additives to prevent bentonite from swelling and to maintain a low rheological profile.[21] During the test, different concentrations of bentonite in 350 mL of deionized water were prepared and stirred for 20 min. They were sealed and kept static for 24 h. After that, the suspensions were again stirred for 20 min, and their rheology was measured.

Rheological Properties. A Fann viscometer model 35A was used to obtain the rheological behavior of samples and to calculate plastic viscosity and yield point according to API recommended practice of standard procedure for field testing of WBFs.[22]

Cuttings Rolling Tests. This test estimates the degree to which a drilling fluid formulation can cause shale to swell and disintegrate

when immersed in a fluid. The cuttings rolling tests were performed following the shale particle disintegration test protocol, according to API recommended practice of standard procedure for laboratory testing of drilling fluids, which is slightly modified using a highly reactive shale (Shale R).[23] Resuming, 2.5 g of sized clay (Shale R) was put in a roller oven cell and kept rolling for 15 min at 60°C with 15 mL of the fluid to be tested. After rolling, the dispersed and intact material collected on 0.12 and 4.76 mm sieves, respectively, were dried and weighted. The percent recovery of clay was calculated on a dry mass basis as follows:

$$\%R = W/W_o \times 100$$

where, W and W_o are the weight after and before rolling, respectively. All polymers were tested with no purification steps at a concentration range of 2% to 20% (wt.) and combined with 3% KCl (wt.). The results were compared to the ones from control fluids that consisted of distilled water potassium chloride solution and PDADMAC solution.

Drilling Fluids Formulation Tests. The drilling fluids formulation tests were performed according to American Petroleum Institute (API) recommended practice of standard procedure for laboratory testing of drilling fluids.[23] In this case, the cuttings rolling tests were done using the shale C.

Clay/Polymer Adsorptions by X-ray Diffraction Analysis. XRD analysis was performed using Miniflex II, Cu Source, 30 Kv, 15 mA, 2°−72°, 2°/min. The clay/polymer adsorptions were carried out adding 1 g of bentonite to a polymer solution. After agitation in a shaker for 2 h, the samples were centrifuged, and the clay was dried at 70°C, under vacuum (−420 mmHg) for 24 h. The XRD analysis was performed, and the samples were kept inside a desiccator with constant relative humidity (48%) for 24h. After this procedure, the XRD analysis was performed again.
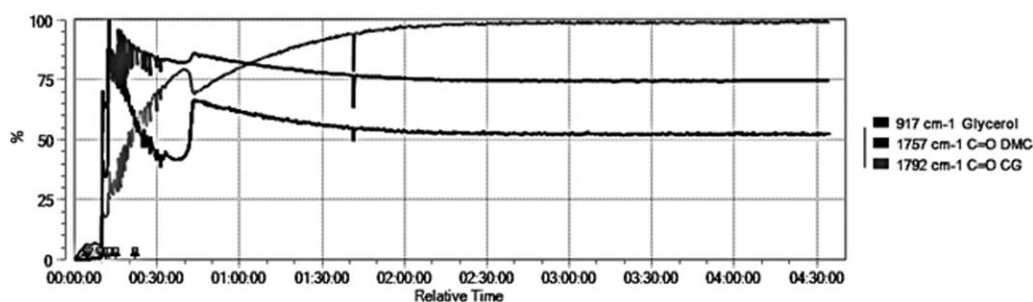
Figure 2. Real-time ATR-FTIR—changes of signals derived from the cyclic carbonate carbonyl group (1792 cm^{-1}), DMC carbonyl group(1757 cm^{-1}), and (C-O) glycerol (917 cm^{-1}) during reaction time.
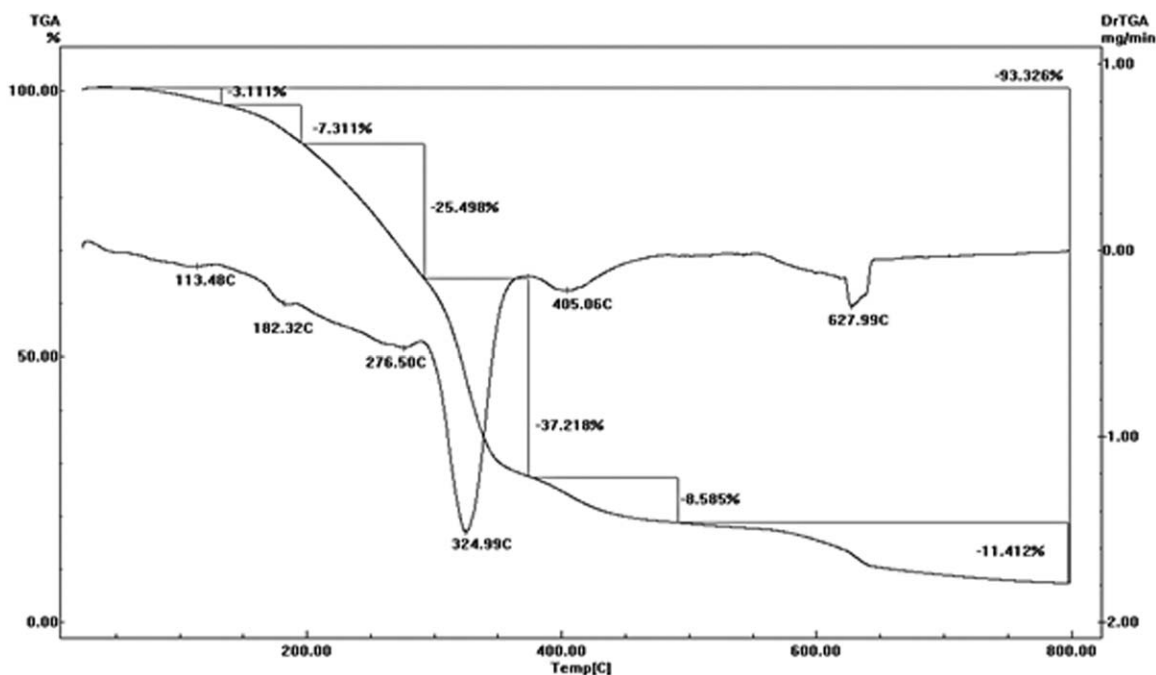
Figure 3. TGA characterization—thermal stability of hyperbranched polyglycerol (1000P).

RESULTS AND DISCUSSION

Clays Properties

Tables I and II show X-ray characterization results for the clays used in this study, which reveals the use of high content of smectite.
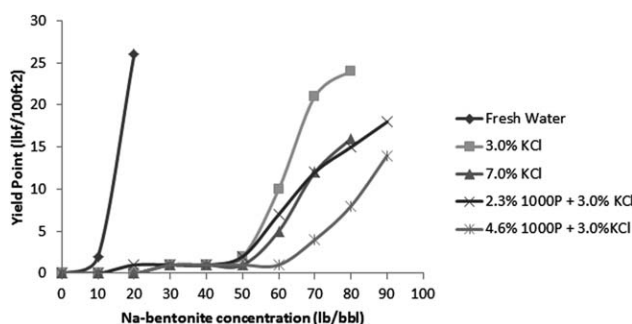

Figure 4. Bentonite inhibition test—dependence of inhibitors solutions yield point with bentonite concentration.
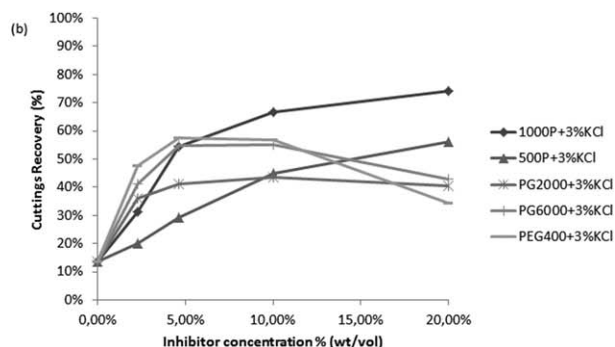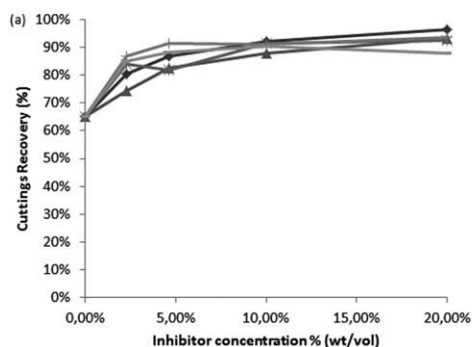
Synthesized Materials

Glycerol carbonate was synthesized and characterized according to the procedures described by Rokicki et al.[15] The reaction progress was monitored by real-time ATR-FTIR (Figures 1 and 2). Figures 1 and 2 show the appearance of C=O stretching band derived from the cyclic carbonate carbonyl group (1792 cm^{-1}). The band derived from DMC carbonyl group (1757 cm^{-1}) could be found until the end of the reaction, because this reactant was used in excess (3 : 1 for DMC : Glycerol). The real-time ATR-FTIR graph (Figure 2) clearly shows that the transesterification reaction was practically completed after 3 h. The ^{1}H NMR, ^{13}C NMR, and FTIR data from synthesized materials match the characteristics given in Ref. 15.

GPC and TGA

Table III shows the GPC Mn, Mw, and PDI results for the synthesized and commercial hPGs. The results from the thermogravimetric analysis (Figure 3) show that the synthesized hPG 1000P is thermally stable, with its main degradation occurring between 200 and 400°C.
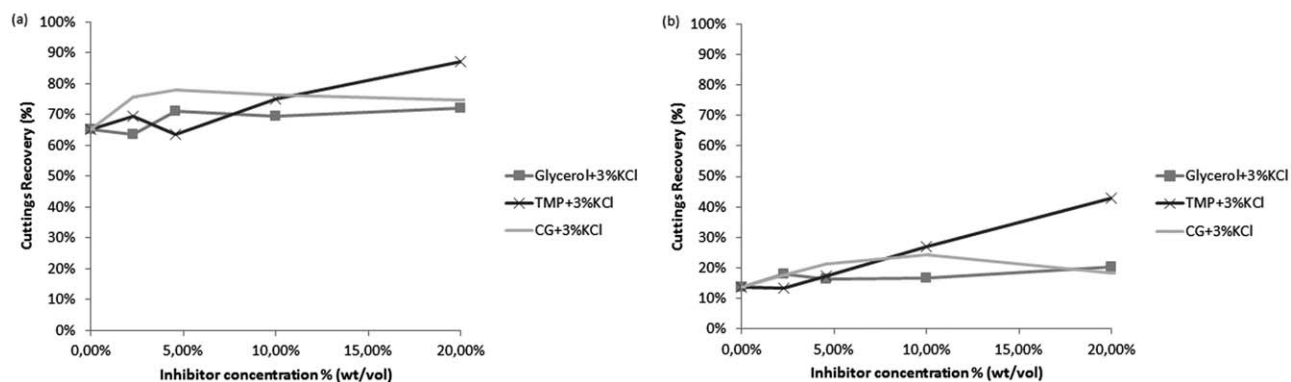

Figure 5. Cuttings recovery results obtained with different inhibitors: (a) dispersed material and (b) intact material.

Figure 6. Cuttings recovery results obtained with different reactants as inhibitors: (a) dispersed material and (b) intact material.
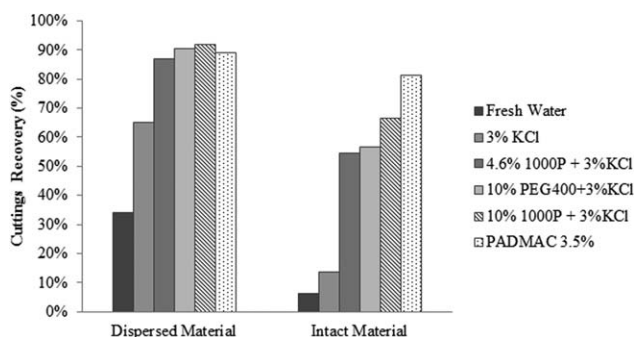

Figure 7. Cuttings recovery results for inhibitors 1000P, KCL, PEG400, and PDADMAC (LMW).

Bentonite Inhibition Test

The bentonite inhibition test determines the ability of an additive to prevent bentonite from swelling and, consequently, to maintain a low rheological profile. The results show that the hPG obtained (1000P) exhibits superior performance, when compared to KCl solutions, in inhibiting the hydration and swelling of bentonite. The yield points of dispersions with different concentrations of inhibitors were measured, and the results are shown in Figure 4. The yield point value for the dispersion with no inhibitor increases sharply after the first additions of bentonite, whereas for dispersions with inhibitors, the

yield values change (sharply) only at higher clay concentrations. The results show that the hPG exhibits a better performance when compared to KCl in inhibiting the hydration and swelling of bentonite. The 4.6% (wt.) of 1000P with 3% (wt.) KCl solution demonstrates a superior inhibiting performance.

Cuttings Rolling Tests

The cuttings recovery tests (Figures 5–8) estimate the degree to which a drilling fluid formulation can cause shale to swell and disintegrate when immersed in a fluid. These tests were used to compare the inhibition properties of hPGs with different molar masses and also used to compare with the performance of the commercial inhibitors PEG400—PEG—400 Da and PDADMAC. Figure 5 shows the cuttings recovery results for dispersed material (a) and intact material (b) obtained with different inhibitors. All hyperbranched polymers were able to enhance the cuttings recovery, compared to that obtained with KCl solution. As expected, the cuttings recovery increases with the solution concentration. However, PEG400, PG2000, and PG6000 exhibit a different behavior, whereas at 20% concentration, the recovery decreases. Probably, these polymers, at very high concentrations, suffer an aggregation process, which causes a decrease in efficiency. The cuttings recovery results of intact material [Figure 5(b)] reveals that the 1000P with 3% of KCl solution reaches better results than PEG—400 Da, 500P, PG2000, and PG6000.
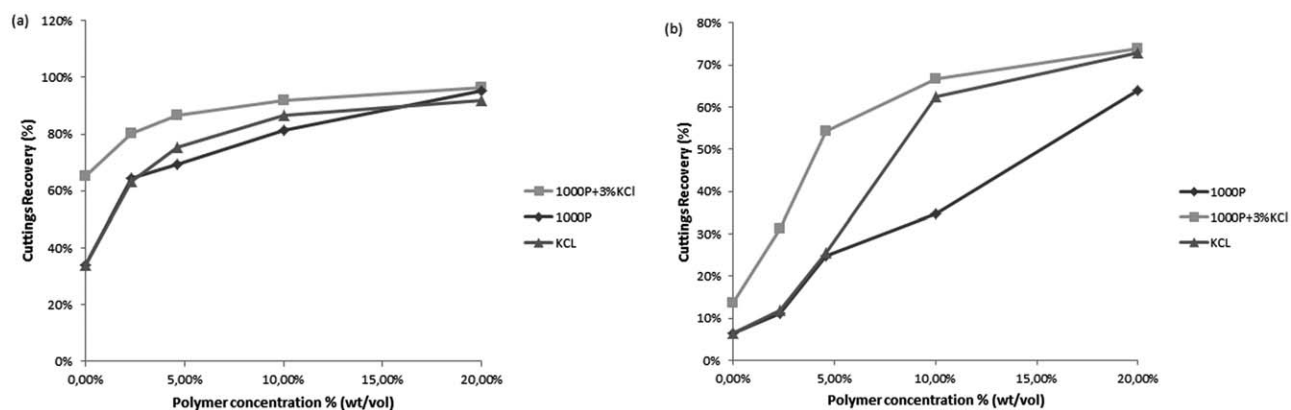

Figure 8. Cuttings recovery results obtained with inhibitors KCl, 1000P, and 1000P + 3% KCl: (a) dispersed material and (b) intact material.
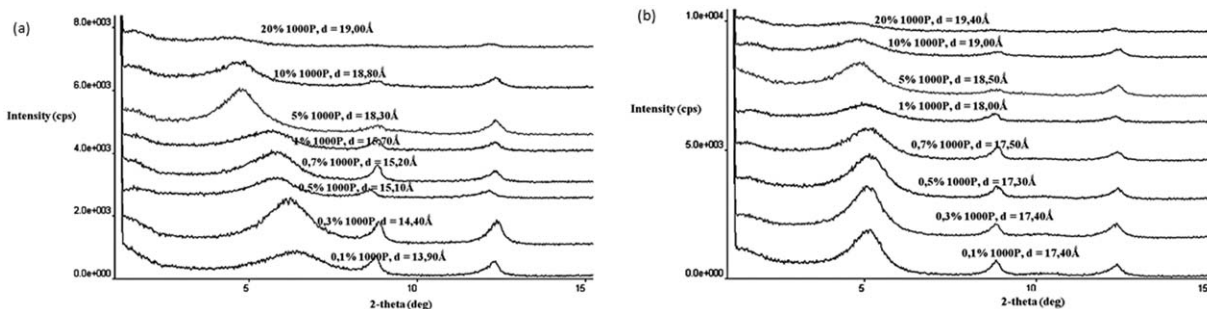
Figure 9. X-ray diffraction—adsorption polymer/bentonite tests obtained with different concentrations of 1000P. (a) Dried samples and (b) humid samples.

All the reactants and raw materials used to synthesize hPG were also tested to verify their effect on the inhibition process (Figure 6). The results show that the reactants have practically no effect as inhibitors.

The graphs shown in Figure 7 allow a comparison of the results from four commercial inhibitors: 1000P, KCl, PEG400, and PDADMAC low molecular weight (LMW). The graphs show good and similar results for dispersed material among the nonionic polymers, 1000P and PEG400, at 10% concentration, and the cationic polymer, PDADMAC, at 3.5% concentration. The

last one shows a better performance at lower concentration due its cationic structure. For intact material, the graph shows better performance of 1000P as compared to the one for PEG400.

The graphs from Figure 8 show the results of tests with KCl, 1000P, and 1000P plus 3 % KCl solutions for dispersed material (a) and intact material (b), and the solution of 1000P plus 3% (wt.) KCl solution demonstrates superior inhibiting performance than KCl and 1000P inhibitors alone, suggesting that the improvement in the inhibition comes from a synergy of potassium ion with hPG in solution. Another point is that KCl reaches good results at very high concentrations, but the use of these concentrations would be impracticable due to environmental restrictions.

X-ray Diffraction Analysis

The clay interlayer spacings (d) obtained using Bragg's equations were measured by XRD with dried and also humid samples (after 24 h on desiccator with 48% of relative humidity) and are displayed in Figure 9(a,b), respectively. Normally, the interlayer spacing of clay, in solution, will increase dramatically due to the water molecules penetration. Figure 9 reveals that at higher concentration of 1000P, the interlayer spacing remains almost constant after the clay was dried and also after placed in a controlled humidity environment. This behavior of the interlayer spacing indicates that the clay hydration can be effectively prevented by the presence of hPGs.

Drilling Fluid Formulation

To evaluate the inhibiting properties of hPG as a drilling fluid additive, four common formulations of WBFs were tested. Table IV shows the formulations and results from API drilling fluids tests[22] and percent of cuttings recovery. All formulations presented evidence of good inhibition behavior and adequate drilling fluids properties; indeed, the formulation of fluid #1 shows excellent results with 98% of cuttings recovery.

Table IV. Drilling Fluids Formulations and API Tests

Conc. (lb/bbl)	Fluid 1	Fluid 2	Fluid 3	Fluid 4
Water	350	350	350	350
CMC (type II)	2.0	2.0	2.0	2.0
Xantam gum	1.0	1.0	1.0	1.0
CMC (HV)	1.0	1.0	0	0
Modified starch	0	0	8.0	8.0
NaOH	0.25	0.25	0.25	0.25
KCl	15.0	15.0	15.0	15.0
Inhibitor (1000P)	8.0	0	8.0	0
CaCO$_3$	30.0	30.0	30.0	30.0
Barite	30.0	30.0	30.0	30.0
API results after rolling, 16 h, 60°C				
600 rpm	92	85	67	62
300 rpm	70	64	42	44
200 rpm	58	54	33	34
100 rpm	42	39	21	22
6 rpm	13	12	4	6
3 rpm	10	10	3	4
Gi	11	10	5	6
Gf	15	14	6	6
pH	8.5	8.5	9	9
Filtrate API (mL)	12.0	13.1	3.3	3.6
Weight (ppg)	9.4	9.4	9.4	9.4
% Cuttings recovery results				
#30 (0.12 mm)	98.04%	93.58%	80.50%	63.86%
#8 (4.76 mm)	88.78%	76.94%	66.20%	37.66%

CONCLUSIONS

The 500 and 1000 Da molar mass polymers were synthesized successfully following synthetic route as described previously by Rokicki et al. and used with no purification steps. The clay inhibitive properties of the hPGs obtained from an environmentally benign monomer were compared to the ones from conventional inhibitors such as potassium chloride, PDADMAC, and PEG, being evaluated by different test methods. The results of

the inhibition experiments suggest that hPGs are thermally stable and able to inhibit, in conjunction with KCl, the dispersion and disintegration of clay cuttings. The hPG shows great potential to be used as an environmental friendly inhibitor additive in WBFs, being less cytotoxic than PEG and cationic polymers.

ACKNOWLEDGMENTS

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