

Synthesis, Characterization, and Working Mechanism of a Synthetic High Temperature (200°C) Fluid Loss Polymer for Oil Well Cementing Containing Allyloxy-2-hydroxy Propane Sulfonic (AHPS) Acid Monomer

Constantin Tiemeyer, Johann Plank

Chair for Construction Chemicals, Institute for Inorganic Chemistry, Technische Universität München, Garching, Germany
Correspondence to: J. Plank (E-mail: johann.plank@bauchemie.ch.tum.de)

ABSTRACT: A polymer comprising of 2-acrylamido-2-methyl propane sulfonic acid, *N*, *N*-dimethyl acrylamide, allyloxy-2-hydroxy propane sulfonic acid (AHPS), acrylic acid, and *N*, *N*-methylene bisacrylamide was synthesized by aqueous free radical copolymerization and tested as high temperature performing fluid loss additive (FLA) in oil well cement. Successful incorporation of AHPS was confirmed and characteristic properties of the copolymer were determined using size exclusion chromatography. The FLA showed excellent water retention in cement at 200°C/70 bar. At this temperature, polymer structure changed from branched to linear and hydrodynamic size decreased by ~50%, thus indicating potential fragmentation, while performance remained unaffected by these alterations. The FLA copolymer does not viscosify cement slurries which is advantageous in high temperature well cementing. The working mechanism of the AHPS-based copolymer was found to rely on reduction of filtercake permeability which is caused by a voluminous coprecipitate of the FLA with tartaric acid retarder, mediated by Ca²⁺ ions. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: AHPS monomer; AMPS[®]; fluid loss additive; high-temperature polymer; oil well cement; copolymers; oil and gas; radical polymerization

Received 21 May 2012; accepted 20 June 2012; published online

DOI: 10.1002/app.38262

INTRODUCTION

The cementing of oil and gas wells is one of the most important and challenging operations performed in the construction of a well bore. There difficulties may arise from extraordinarily high pressures and temperatures which may range up to 2000 bar and 260°C, respectively, and high salinity occurring in reservoir fluids at great depths. These conditions make it difficult to control the properties of the cement slurry.^{1,2} To ensure a cement seal which is impermeable to fluids and gases, chemical additives are included into the slurry formulation.³

One important group of additives are fluid loss additives (FLAs). These admixtures prevent uncontrolled loss of water from the cement slurry by lowering the leak off rate of water into the surrounding through formation of a tight filtercake. According to the work published by “Desbrieres,” anionic or nonionic FLAs reduce filtercake permeability of cement slurries.^{4,5} Three plausible mechanisms are discussed for this effect: (1) adsorption of large macromolecules on cement whereby the effective pore diameter is decreased; (2) hydrated and swollen polymer particles (e.g., microgels) or polymer films plug and constrict the pores in a filtercake; and (3) the FLA modifies the filtercake structure.

Currently, a huge variety of different fluid loss polymers are used by the oil industry. An example for a nonionic FLA is unmodified or crosslinked polyvinyl alcohol, which works by formation of a polymer film within the cement filtercake.^{6,7} Also, cellulose ethers such as hydroxyethyl cellulose (HEC) and carboxymethyl HEC (CMHEC) have been successfully used in oil well cementing.^{8–10} The working mechanism of HEC was found to rely on a dual effect, namely intramolecular water sorption and formation of hydrocolloidal associated polymer networks.¹¹ In contrast, the working mechanism of CMHEC is dosage-dependent. At low dosages, adsorption presents the predominant mode of action, whereas above a certain threshold concentration (the “overlapping” concentration), associated polymer networks form and enact fluid loss control.¹² Finally, cationic polyethyleneimine was also found to reduce cement fluid loss when an anionic dispersant is present as it allows formation of insoluble polyelectrolyte complexes.^{13,14}

Still, the largest group of cement FLAs are co- or terpolymers derived from acrylamide and/or 2-acrylamido-2-methyl propane sulfonic acid (AMPS[®]).^{15–17} To meet the industry’s demand for salt tolerant, nonretarding FLAs which also perform well at

Table I. Phase Composition (Q-XRD, Rietveld), Specific Density, Specific Surface Area (Blaine), and d_{50} Value of API Class G Oil Well Cement Sample

C_3S (wt %)	C_2S (wt %)	C_3A_c (wt %)	C_4AF (wt %)	Free CaO (wt %)	$CaSO_4 \cdot 2H_2O$ (wt %)	$CaSO_4 \cdot 0.5H_2O$ (wt %)	$CaSO_4$ (wt %)	Specific density (kg/L)	Specific surface area (cm ² /g)	d_{50} value (μ m)
59.6	22.8	1.2	13.0	< 0.3	2.7 ^a	0.0 ^a	0.7	3.18	3058	11

^aMeasured by thermogravimetry. C_3S : tricalcium silicate ($Ca_3(SiO_4)O$); C_2S : dicalcium silicate (Ca_2SiO_4); C_3A_c : cubic modification of tricalcium aluminate ($Ca_3Al_6O_{13}$); C_4AF : tetra calcium aluminate ferrite ($Ca_4Al_2Fe_2O_{10}$).

elevated temperatures, high molecular weight copolymers containing AMPS[®] and *N,N*-dimethyl acrylamide (NNDMA) have been developed.¹⁸ These copolymers exhibit considerably improved temperature stability (up to $\sim 150^\circ C$) and are stable against hydrolysis under the strongly alkaline pH conditions of aqueous cement dispersions as well as against salt contents up to 18% by weight of cement (bwoc) of NaCl. Recent work has shown that the water retention effect of AMPS[®]-NNDMA copolymers relies on adsorption onto the cement surface.¹⁹ A problem of those copolymers is their enormous viscosifying effect on the cement slurry. However, deep high temperature wells require high slurry densities (low water to cement ratios) to ensure enough hydrostatic overburden pressure against the reservoir. In these cement slurries, viscosifying additives are very undesirable because they require additional dosages of dispersant to decrease slurry rheology. This effect creates a complicated admixture system and also increases cost. Hence, there is a demand for an FLA which performs well under high temperature conditions and does not viscosify the cement slurry. Recently, a graft copolymer composed of humic acid, AMPS[®], NNDMA, and acrylic acid (AA) exhibiting only a minor viscosifying effect and high effectiveness at $150^\circ C$ has been presented.²⁰

Recently, 2-allyloxy-2-hydroxy propane sulfonic acid (AHPS) monomer became industrially available. The aim of this work was to study its suitability as a new building block in high temperature stable water-soluble copolymers useful for high temperature/high pressure (HT/HP) cementing systems. For this purpose, a forpolymer was synthesized from AHPS, AMPS[®], NNDMA and AA and *N,N*-methylene bisacrylamide (NNMBA) crosslinking agent, and characterized and tested with respect to its effectiveness as cement fluid loss at $200^\circ C$. Moreover, the polymer was designed such as to disperse cement and thus reduce slurry rheology which is preferable on high temperature wells. Temperature stability was probed by exposing the forpolymer dissolved in cement pore solution to $200^\circ C$ over a period of 8 h and subsequent molecular characterization and cement fluid loss measurements. Additionally, the working mechanism of the copolymer was identified by determination of filtercake permeability, of retained amount on cement and by coprecipitation experiments. From this data, a mode of action is proposed.

EXPERIMENTAL

Materials

Oil Well Cement. An American Petroleum Institute (API) Class G oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) corresponding to API Specification 10A was used.²¹ Its clinker composition was determined by quantitative

powder X-ray diffraction technique using "Rietveld" refinement. The results are displayed in Table I. The amounts of gypsum ($CaSO_4 \cdot 2H_2O$) and of hemihydrate ($CaSO_4 \cdot 0.5H_2O$) present in the cement sample were measured by thermogravimetry. Free lime (CaO) was quantified using the extraction method established by Franke.²² According to the method developed by "Blaine," the specific surface area of the cement sample was found to be 3058 cm²/g while its specific density was 3.18 kg/L, as measured by Helium pycnometry. Particle size distribution of the cement sample was determined using a laser-based particle size analyzer which yielded a d_{50} value of 11 μ m (see Table I).

Silica Flour. A commercial sample (SSA-1 from Halliburton, Celle, Germany) containing (wt %) quartz 97.60, CaO 0.57, MgO 0.18, Al₂O₃ 0.17, TiO₂ 0.06 (determined by X-ray fluorescence analysis), and 1.40 loss of ignition was used. Its specific surface area (Blaine method) was 1857 cm²/g. Its average particle size (d_{50} value) was 32.7 μ m. Specific density of the silica flour was found at 2.65 kg/L.

Synthesis of the AHPS-based FLA. The polymer containing AMPS[®], NNDMA, AHPS, and AA was synthesized by aqueous free radical copolymerization. A very minor amount of NNMBBA was incorporated as crosslinker. The feeding molar ratios between AMPS[®] : NNDMA : AHPS : AA : NNMBBA were 1 : 0.63 : 0.5 : 0.3 : 0.004. Laboratory grade AMPS[®] (Type 2402, Lubrizol, Wickliffe, OH; AMPS[®] is a registered trademark of the Lubrizol company), NNDMA (Sigma-Aldrich Chemical, Munich, Germany), AHPS (BIMAX, Glen Rock, PA), AA (Merck KgaA, Darmstadt, Germany), and NNMBBA (Sigma-Aldrich Chemical) were used as received. In a typical preparation, 91.2 g (0.44 mol) of AMPS[®], 27.48 g (0.28 mol) of NNDMA, and 0.28 g ($1.8 \cdot 10^{-3}$ mol) of solid NNMBBA were dissolved in 66 mL of a degassed 23.3 wt % aqueous NaOH. This monomer solution has to be kept at pH > 7 and at a temperature < $28^\circ C$ to avoid homopolymerization. Separately, 111.6 g (0.22 mol) of a 38.8 wt % aqueous AHPS solution were degassed with N₂ in a five-necked, 2-L round-bottom flask and heated up to $60^\circ C$. To initiate polymerization, 0.68 g of a 9 wt % aqueous sodium persulfate solution were fed into the AHPS solution. Subsequently, using a peristaltic pump, the mixture of AMPS[®], NNDMA, and NNMBBA was added at a constant speed to the AHPS solution over a total period of 130 min. Simultaneously, 4.16 g of the Na₂S₂O₈ initiator solution were added as well. The mixture was kept at $60^\circ C$ under stirring for additional 30 min. Then, the reaction flask was heated to $80^\circ C$ and 6.89 g of initiator solution were added within 30 min to achieve maximum conversion of the monomers. Finally, within 15 min, 9.36 g (0.13 mol) of AA and 20.6 mL of Na₂S₂O₈ solution were added separately to

the reaction mixture and kept stirring for another 30 min. The reaction was quenched by addition of 16.7 g of a 10 wt % aqueous sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$) solution and 800 mL deionized (DI) water. The resulting slightly viscous, yellowish copolymer solution possesses a solid content of 15 wt % and exhibits a pH value of ~ 5 .

Retarder. A commercial sample (HR-25[®], tartaric acid) from Halliburton GmbH, Celle, Germany was used for high temperature retardation of cement.

Instruments and Procedures

Cement and Silica Flour Characterization. Phase composition of the cement sample was obtained by X-ray powder diffraction using a Bruker axS D8 Advance instrument from Bruker, Karlsruhe, Germany with Bragg–Brentano geometry. Topas 3.0 software was used to quantify the amounts of individual phases present in the sample by following Rietveld's method of refinement.²³ The instrument was equipped with a scintillation detector using Cu K_α ($\lambda = 1.5406 \text{ \AA}$) radiation with a scanning range between 5° and $80^\circ 2\theta$. Specific density of the cement sample was measured on an Ultracycrometer[®] 1000 (Quantachrome Instruments, Boynton Beach, FL). The specific surface area of the sample was determined using a Blaine instrument (Toni Technik, Berlin, Germany). The average particle size (d_{50} value) was obtained from a laser-based particle size analyzer (1064 instrument from Cilas, Marseille, France).

Oxide composition of SSA-1 silica flour was determined using an X-ray fluorescence spectrometer (Axios from PANalytical, Almelo, The Netherlands). Specific density, specific surface area, and average particle size (d_{50} value) of the silica sample were measured using the same instrumentation as described above for cement.

Polymer Characterization. Solid contents of the aqueous polymer solutions were determined using an infrared drying balance (MA35 from Sartorius AG, Göttingen, Germany). Drying conditions were 10 min at 110°C . The values presented are the averages obtained from three separate measurements.

Before analysis, the copolymer solution was dialyzed for 1 day with a Spectra/Por[®] dialysis membrane (MWCO 15,000) from Spectrum Laboratories, Rancho Dominguez, CA to remove any unreacted monomers and salts. The purified aqueous polymer solution was freeze dried using an ALPHA 1-4 LD plus apparatus from Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz, Germany.

Size exclusion chromatography (Waters Alliance 2695 from Waters, Eschborn, Germany) equipped with a refractive index detector 2414 (Waters, Eschborn, Germany) and an 18° angle dynamic light scattering detector (Dawn EOS from Wyatt Technologies, Santa Barbara, CA) was used. The synthesized FLA was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Molecular weights (M_w and M_n) and polymer radii ($R_{h(z)}$ and $R_{g(z)}$) were determined using 0.2 M aqueous NaNO_3 solution (adjusted to pH 9.0 with NaOH) as eluent at a flow rate of 1.0 mL/min. Because of different molecular characteristics, the aged FLA and the FLA without crosslinker were sep-

rated on another gel permeation chromatography (GPC) instrument. For them, an Ultrahydrogel[™] precolumn and three Ultrahydrogel[™] columns (120, 250, and 500; Waters, Eschborn, Germany) with a 0.1 M aqueous NaNO_3 solution (adjusted to pH 12.0 with NaOH) as an eluent at a flow rate of also 1.0 mL/min were used. The value of dn/dc used to calculate M_w and M_n for all polymers was 0.156 mL/g (value for polyacrylamide).²⁴

Furthermore, a ^1H NMR spectrum of the purified dry FLA was recorded on a JOEL JMX-GX-270 spectrometer (JOEL GmbH, Eching bei München, Germany). The spectrum was referenced internally to deuterium oxide (Merck KGaA, Darmstadt, Germany) which was used as solvent.

An IR spectrum of the purified dry copolymer was measured on a total reflectance Fourier transform spectrometer (ATR-FTIR) (Vertex 70 from Bruker Optics, Karlsruhe, Germany). It was acquired in transmittance mode on a Diamond ATR crystal cell (MPV; Pro from Harrich Scientific Products, Pleasantville, NY) by accumulation of 128 scans at a resolution of 4 cm^{-1} and a spectral range of $4000\text{--}350 \text{ cm}^{-1}$.

Elemental analysis (C, N, S, H, Na) of the purified dry FLA were carried out on a Perkin Elmer 2400 analyzer (Perkin Elmer, Waltham, MA).

Specific anionic charge amounts of the polymers were determined in cement pore solution or aqueous 0.1 M NaOH (pH = 13, with and without 0.6 g/L Ca^{2+}) using a PCD 03 pH apparatus (BTG Müttek GmbH, Herrsching, Germany). Charge titration was carried out according to a literature description using a 0.001 N solution of laboratory grade poly(diallyl dimethyl ammonium chloride) from BTG Müttek GmbH, Herrsching, Germany as cationic polyelectrolyte.²⁵ The values presented in this study are the average obtained from three independent measurements. The deviation for this method was found to be $\pm 5^\circ\text{C/g}$.

Additionally, thermal aging of the FLA in an OFITE roller oven (OFI Testing Equipment, Houston, TX) was conducted. There, 350 mL of polymer dissolved in cement pore solution (concentration: 8 wt %) were poured into a 500-mL Teflon liner which was placed into a stainless steel grade ageing cell and closed. A pressure of 35 bar was applied to the cell which was rotated at 25 rpm in the roller oven. The oven was then heated up to a temperature of 200°C and left rotating for 8 h. After this time, the cell was removed from the oven and cooled with water to room temperature.

Cement Slurry Preparation. Cement slurries were prepared in accordance to the procedures described in "Recommended Practice for Testing Well Cements," API Recommended Practice 10B, issued by the API.²⁶ At first, the cement was dry blended with silica flour at a weight ratio of 65 : 35 to avert cement compressive strength retrogression occurring at temperatures above 115°C . The slurries were then mixed at a water-to-cement (w/c) ratio of 0.50 (considering the amount of silica, this value corresponds to a w/solid ratio of 0.325) using a blade-type laboratory blender obtained from Waring Products (Torrington, CT). Admixture dosages are generally stated in % bwoc. Before cement/silica addition, the synthesized FLA was dissolved in the mixing DI water. In

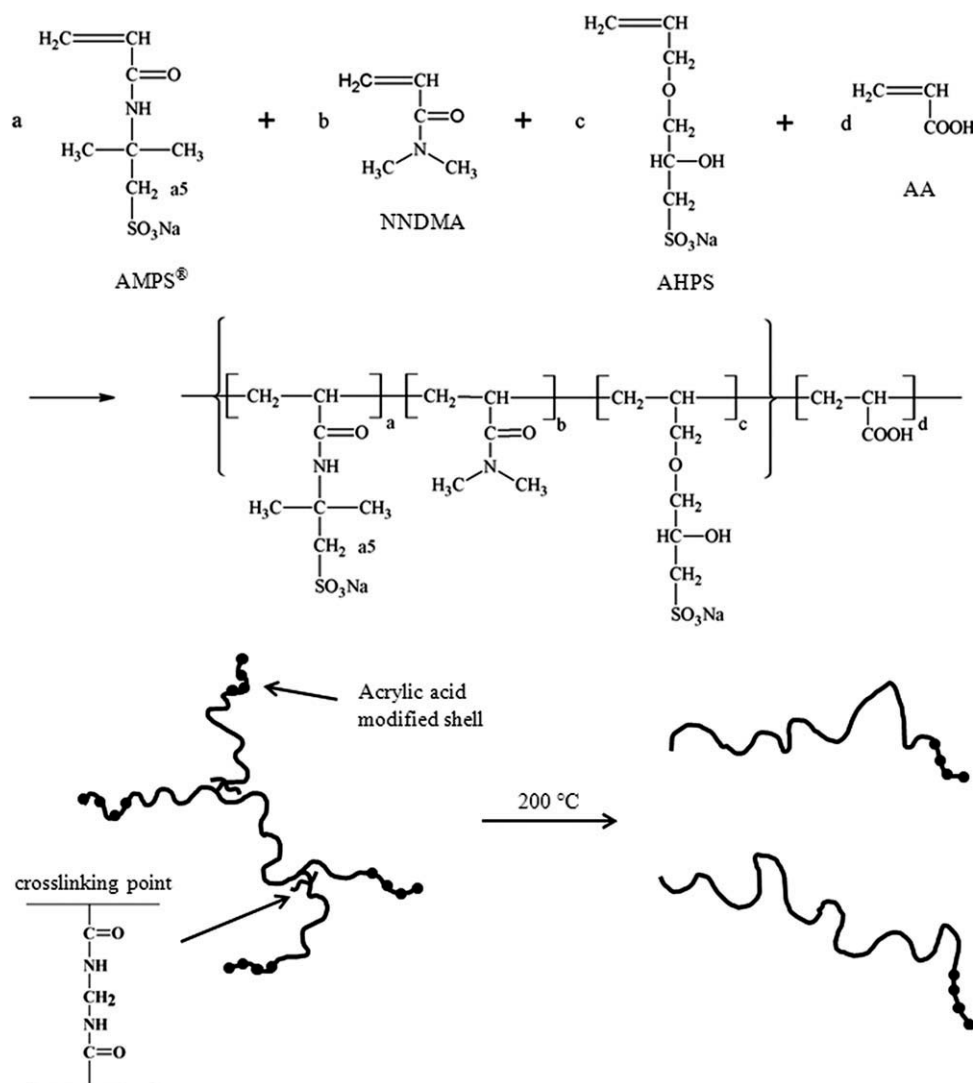


Figure 1. Reaction scheme, proposed structure, and decomposition pattern for the AHPS copolymer.

contrast to this, powdered HR-25[®] retarder was always dry blended with cement/silica. Then, within 15 s, the binder mixture was added to the mixing water placed in the cup of a Waring blender, and mixed for 35 s at 12,000 rpm. Pore solution of the neat cement slurry (no polymer present) was prepared by vacuum filtration (12 mbar) of the cement slurry using a diaphragm vacuum pump (Vacuubrand GmbH, Wertheim, Germany).

Rheology. For rheological characterization of cement slurries, a Couette-type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston, TX) equipped with R1 rotor sleeve (rotor radius: 18.4 mm), B1 bob (radius: 17.3 mm, height: 38.0 mm), and F1 torsion spring was used. The values of the viscometer reading were recorded for six rotational speeds (3, 6, 100, 200, 300, and 600 rpm). The value of shear stress, τ (Pa) was calculated by including the torsion spring factor (N , cm/degree), the shear stress constant for the effective bob surface (cm⁻³), and the shear rate constant (s⁻¹/rpm).²⁶

API Stirred Fluid Loss. Stirred fluid loss was measured at 200 °C using a high temperature, high pressure (HTHP) stirred

fluid loss cell (model 7120 from Chandler Engineering, Tulsa, OK). Design of this HTHP filter cell and its operation are described in detail in a norm issued by the API.²⁶ After pouring the slurry into the HTHP cell, a pressure of 35 bar N₂ is applied and the cell is heated up to 200 °C within 1 h under constant stirring (150 rpm). Note: these conditions are extreme and for safety reasons, extreme caution must be exercised when operating this pressure equipment. When this temperature is reached, stirring is halted and filtration is carried out through a 22.6 cm² (3.5 in²) mesh metal sieve placed at the bottom of the cell which is exposed to a differential pressure of 70 bar N₂. The filtrate volume collected after 30 min was doubled as required by API RP 10B and designated as API fluid loss of the corresponding slurry.²⁶ The values reported for the respective API fluid loss test represent the average obtained from three individual measurements. Maximum deviation of the fluid loss value was ± 10 mL/30 min.

Retained Amounts. Amounts of polymers retained on cement were determined from the filtrate collected by vacuum filtration.

Table II. Molar Masses (M_w , M_n), Polydispersity Index (PDI), Hydrodynamic Radius ($R_{h(z)}$), Radius of Gyration ($R_{g(z)}$), and Anionic Charge Amount in Cement Pore Solution of the AHPS-Based Fluid Loss Additive Prepared With and Without *N, N*-Methylene Bisacrylamide and of the FLA After 8 h Exposure to 200°C

AHPS colymer	M_w (Da)	M_n (Da)	PDI (M_w/M_n)	$R_{g(z)}$ (nm)	$R_{h(z)}$ (nm)	Anionic charge amount in CPS ^a (C/g)
As synthesized	400,000	140,000	2.9	30.9	27.7	-486
Synthesized without <i>N, N</i> -methylene bisacrylamide	210,000	63,000	3.4	29.1	16.4	-516
After exposure to 200°C/8 h	234,500	63,000	3.7	32.2	17.5	-446

^aCPS: cement pore solution.

A High total organic carbon (TOC) II apparatus (Elementar, Hanau, Germany) equipped with a CO₂ and NO_x detector was used to quantify polymer concentrations. Before conducting the TOC analysis, the alkaline cement filtrate containing the unadsorbed polymer was adjusted to pH 7.0 by adding 0.01 M H₃PO₄. From the difference in polymer concentrations contained in the initial solution (no cement present) and after contact with cement, the amount of polymer retained was calculated.

Precipitation by Calcium. Solutions of additives (FLA, tartaric acid) (50 mL of 1 wt %) in 0.1 M aqueous NaOH (pH = 13) were combined with 0.66 g of solid CaCl₂ × 2 H₂O (corresponding to 1.8 g/L Ca²⁺). The resulting mixture was stirred for 10 min and centrifuged at 8500 rpm for 10 min with a Biofuge Primo R (Heraeus, Newport Pagnell, England). The supernatant was analyzed for its polymer content using the TOC method as described before.

RESULTS AND DISCUSSION

Composition and Properties of the AHPS Copolymer

The synthesis process used here was designed so as to produce a very slightly crosslinked AHPS/AMPS[®]/NNDMA terpolymer as a core which possesses an AA-modified shell as a result of delayed AA addition. The rationale behind this specific molecular design was as follows: AMPS[®] monomer was intended for water solubility yet high calcium stability of the polymer; NNDMA was incorporated to obtain a relatively stiff linear polymer chain which is beneficial for fluid loss control; AHPS monomer was included for high temperature stability while the function of AA was to provide cement dispersion as a result of high anionic charge which can provide electrostatic repulsion between cement particles (note that in previous experiments, it was found that random incorporation of AA into the terpolymer was less effective for cement dispersion than incorporation into the outer sphere of the macromolecule, as was chosen here); and NNMBMA crosslinker was used to boost the molecular weight of the polymer which was assumed to improve fluid loss performance. A reaction scheme and a proposed structure for the resulting core-shell polymer are presented in Figure 1.

At first, molecular properties of the synthesized and purified polymer were established by size exclusion chromatography. The GPC spectrum of the purified copolymer shows a uniform copolymer possessing a relatively narrow molecular weight distribution. The molecular parameters are exhibited in Table II. For the FLA, molar masses of 4.0×10^5 g/mol (M_w) and

1.4×10^5 g/mol (M_n), respectively, were found. The relatively high molecular masses and the broad polydispersity index (PDI) of 2.9 are typical for a radical polymerization. Additionally from the GPC data, the solution structure of the solved polymer can be derived after calculation of the Burchard parameter (ratio of R_g/R_h).²⁷ For the FLA, a value of ~1.1 was obtained, representing the structure of a branched molecule (see Figure 1).

To assess the impact of crosslinking, a copolymer was prepared without the crosslinker NNMBMA and characterized by size exclusion chromatography (SEC) (see Table II). The molecule thus obtained exhibited significantly decreased molar masses [2.1×10^5 g/mol (M_w) and 6.3×10^4 g/mol (M_n), respectively], compared to the crosslinked FLA. Also, the hydrodynamic radius decreased from 27.7 nm for the crosslinked polymer to 16.4 nm without NNMBMA. This result indicates a significant change in polymer conformation. The Burchard parameter of the noncrosslinked copolymer was ~1.8, indicating the solution structure of a linear macromolecule. According to these results, branching was indeed accomplished in the initial reaction by NNMBMA (see Figure 1).

Next, successful incorporation of AHPS and actual molar composition of the copolymer were determined. It is well established that radical copolymerization of allyl alcohol and its ether derivatives with other monomers is very difficult because they form resonance-stabilized radicals, which exhibit a strong tendency for recombination.²⁸ Thus, it was necessary to prove successful incorporation of AHPS monomer into the polymer. For this purpose, a ¹H NMR spectrum of purified copolymer was recorded in D₂O (Figure 2). The broad peak between 1.0 and 1.8 ppm can be assigned to methylene protons present in the backbone of the polymer and to methyl protons of AMPS[®] monomer. The CH protons located along the backbone appear as several small overlapping peaks between 2.9 and 2.7 ppm. The methyl protons of NNDMA as well as the methylene protons of AMPS[®] and AHPS are indicated by the broad peak between 2.9 and 3.5 ppm. Although quantitative interpretation of the spectrum was impossible due to massive overlapping of peaks, presence of AHPS was clearly evidenced by the peak at $\delta = 4.18$ ppm, which indicates the methyl group next to the sulfonate group present in AHPS. Incorporation of AHPS monomer into the polymer also was verified by powder FTIR spectroscopy (Figure 3). First, the broad band around 3320 cm⁻¹ originated from the valence vibration of the N—H bond of the amido fragment present in AMPS[®]. At 2910 cm⁻¹, C—H stretch vibrations of methyl and methylene groups appear. The

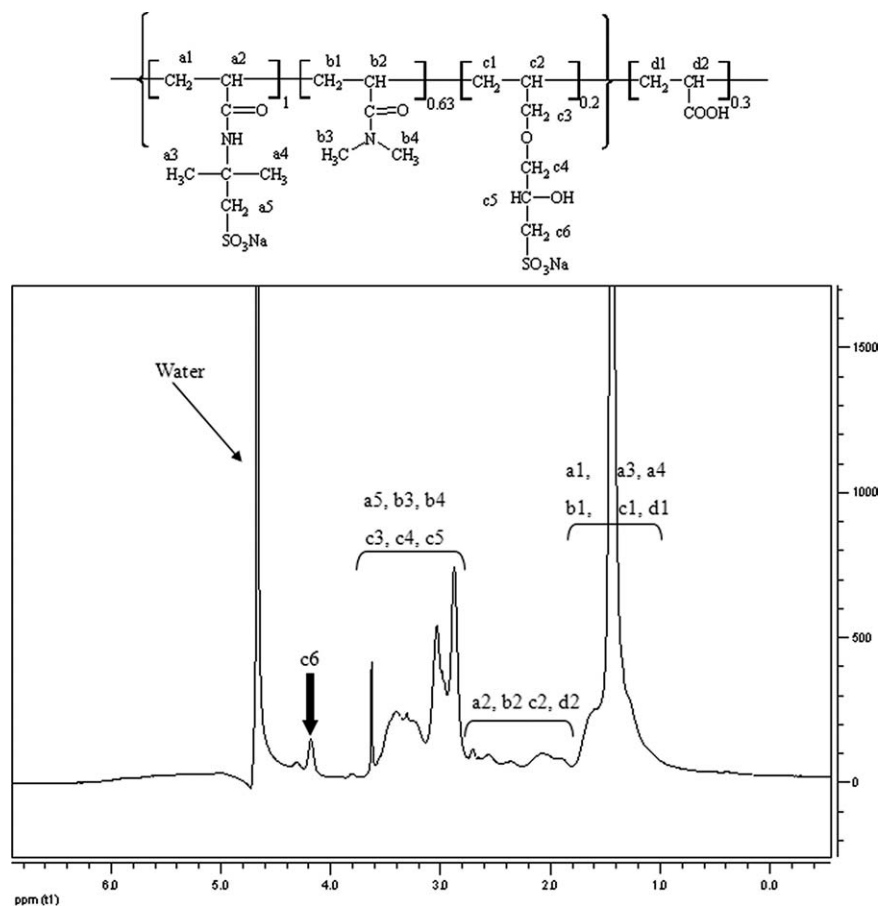


Figure 2. ^1H NMR spectrum of dialyzed AHPS-based FLA, measured in D_2O .

stretch vibrations of the carbonyl moiety of AMPS[®] and NNDMA and the deformation vibration of the secondary amine in AMPS[®] occur between 1700 and 1530 cm^{-1} . The absorption bands around 1400 cm^{-1} can be attributed to deformation vibrations of methyl groups and to valence vibrations of free carboxylate groups present in the AA. The intensive absorptions at 1170 cm^{-1} and 1150 cm^{-1} are characteristic for valence vibrations of secondary amines. Finally, the absorption bands of sulfonate groups present in AMPS[®] and AHPS were present at 1030 and 620 cm^{-1} . At 1100 cm^{-1} , a typical band for an ether group (C—O—C stretch vibration) was observed which is specific for AHPS, thus confirming successful incorporation of this less reactive monomer into the polymer. Finally, molar composition of the FLA was calculated from elemental analysis data of the purified polymer (see Table III). Because of the small amount of *N,N*-bismethylene acrylamide crosslinker used in the synthesis, this monomer was disregarded in the calculation. On the basis of this data, a molar composition of AMPS[®] : NNDMA : AHPS : AA = $1 : 0.63 : 0.2 : 0.3$ was found for the polymer. This result suggests that compared to the feeding molar ratios (AMPS[®] : NNDMA : AHPS : AA = $1 : 0.63 : 0.5 : 0.3$), only 40% of the AHPS monomer added were incorporated into the polymer, as a result of its low reactivity.

In cement pore solution, an anionic charge amount of -486 C/g was found for the purified FLA. This value confirms the high

anionic character of the copolymer which stems from the presence of sulfonate and carboxylate functionalities. These groups possess a high potential for chelation of divalent cations. In cement pore solution, calcium ions which are produced from the dissolution of the clinker phases are most prominent. Thus, the calcium-binding capacity of the AHPS-based FLA was determined in NaOH (pH = 13) in presence and absence of 0.6 g/L Ca^{2+} ions. It was found that presence of calcium ions slightly reduces the anionic charge amount from -509 C/g (without

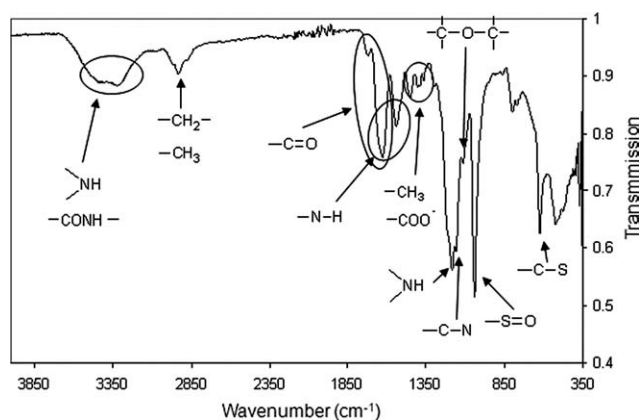


Figure 3. Powder FT-IR spectrum of dialyzed AHPS-based FLA.

Table III. Found and Calculated Elemental Compositions (wt %) for the AHPS-Based Fluid Loss Additive

Contents	C	N	S	H	Na	O
Found	36.88	5.74	9.59	6.64	6.90	34.24
Calculated ^a	36.77	6.22	10.45	5.66	9.39	31.51

^aCalculated for idealized copolymer composition (molar ratio) of AMPS[®]: NNDMA: AHPS: AA = 1: 0.63: 0.2: 0.3.

Ca²⁺) to -439 C/g. This reduction is likely owed to the chelation of calcium ions by the carboxylate groups present in the FLA.

Fluid Loss Performance

Dynamic filtration properties of cement/silica flour slurries containing increased dosages (0.2–1.4% bwoc) of the AHPS-based FLA and a fixed dosage of 2% bwoc of tartaric acid retarder were obtained at 200°C. This high dosage of retarder is essential to prevent premature setting of the cement at this temperature. Measurements of the slurry without FLA were not possible because of excessively high viscosity. The results for the slurries incorporating the FLA are shown in Table IV. There API fluid loss decreased exponentially with increasing polymer dosage. The copolymer reached maximum effectiveness at a dosage of 1.0% bwoc where an API fluid loss of 66 mL was achieved. The minimum concentration of FLA needed to achieve an API fluid loss of less than 100 mL (which is commonly applied in the field) lies at 0.8% bwoc. This value presents a relatively low dosage, considering the extremely harsh conditions of 200°C. Thus, it is demonstrated that the synthesized fluid loss polymer presents a suitable admixture for high temperature wells.

Effect on Rheology

The effect of the copolymer on cement slurry rheology was tested at 95°C by adding different dosages to cement slurries. The data obtained are presented in Table V. At an addition of only 0.2% bwoc of the FLA, a decrease in cement slurry rheology was observed. Further increased dosages resulted in even lower rheology. At ≥0.6% bwoc of FLA, the viscosity values measured at high shear rate increased slightly, whereas the low shear rate values decreased further. Apparently, this FLA

Table IV. Dynamic Filtrate Viscosity, Filter Cake Permeability and API Fluid Loss of Cement/Silica Slurries Containing Different Dosages of AHPS-Based Fluid Loss Polymer and 2% bwoc of Retarder, Measured at 200°C

FLA dosage (% bwoc)	Dynamic filtrate viscosity @ 95°C (mPa·s)	Filtercake permeability (μD)	API fluid loss (mL)
0.2	0.31	4414	3216 ^a
0.4	0.32	55	344 ^a
0.6	0.33	23	225 ^a
0.8	0.34	15	92
1.0	0.33	8	66
1.2	0.34	3	46
1.4	0.34	3	44

^aCalculated values (total dehydration in less than 30 min).

possesses strong dispersing ability for cement as a result of incorporation of AA into the outer sphere of the macromolecule. The negatively charged AA interacts with positively charged sites existing on the surface of the cement particle, leading to an electrostatic repulsion between them. Through this mechanism, particle agglomeration is hindered and the cement slurry is dispersed. This property renders the copolymer suitable for high density cement slurries characterized by low w/c ratios which are prevalent in high temperature wells.

Table VI shows the rheological properties of cement/microsilica slurries at a fixed dosage of 2% bwoc of tartaric acid retarder and at increasing dosages of the AHPS-based fluid loss polymer, measured at 95°C. Here, the dispersive character of the FLA is observed up to a dosage of 0.4% bwoc. Further addition of the copolymer leads to a very minor increase in slurry viscosity. This effect seems to stem from a specific interaction between the FLA and this retarder which was evidenced in subsequent experiments. The results allow to conclude that in combination with this retarder, the synthesized FLA does not increase cement slurry rheology. Such property presents a huge advantage over common high temperature synthetic FLAs which typically exhibit a strong viscosifying effect.¹⁸

The combination of good fluid loss performance at 200°C and the dispersive character makes the novel forpolymer superior over other commonly used high temperature FLAs. At lower temperatures (<150°C), cellulose ether-based FLAs dominate the market due to their favorable cost effectiveness and their high environmental compatibility. However, these polymers also retard cement. To overcome these deficiencies, synthetic sulfonated copolymers based on AMPS[®] monomer were developed. Currently, one of the most commonly used FLAs is a copolymer comprised of AMPS[®] and NNDMA. However, this copolymer shows good fluid loss performances only up to 150°C which is insufficient for high temperature wells. Additionally, its strong viscosifying effect on cement slurries renders it unfavorable for high temperature cementing. Recently, a novel graft copolymer composed of humic acid, AMPS[®], NNDMA, and AA was introduced which provides excellent fluid loss performance at 150+°C.²⁰ Still, this polymer exhibits a slight viscosifying effect.

Temperature Stability of AHPS Copolymer

To study the effect of high temperature on the AHPS-based FLA, the polymer was dissolved in cement pore solution (concentration: 8 wt %) and exposed to 200°C for 8 h in a roller oven. After aging, the color of the polymer solution had changed from yellowish to slightly brown. This observation instigates that the FLA became partially oxidized and perhaps fragmented. This assumption was confirmed by SEC data for the aged polymer (see Table II). There as a result of thermal

Table V. Shear Rate-Dependant Rheology (Viscosity) of Cement/Silica Slurries Containing Different Dosages of AHPS-Based Fluid Loss Additive, Measured at 95°C

FLA dosage (% bwoc)	Viscosity (mPa), measured at different shear rates (s^{-1}) of					
	1022	511	340	170	10.2	5.1
0	n.m. ^a	317	402	583	2508	4695
0.2	298	209	257	387	1387	2027
0.4	101	116	128	160	960	1601
0.6	113	128	121	122	267	427
0.8	132	137	130	128	213	320
1.0	151	161	160	163	266	320

^an.m. = not measurable (too thick to test).

exposure, the molecular weights of the aged FLA were reduced by ~45% from 400,000 to 234,500 Da, compared to those for the unaged copolymer. Obviously, as a result of high temperature, the forpolymer undergoes fragmentation into smaller polymer chains possessing different lengths, as is indicated by the increased PDI (from 2.9 for the unaged polymer to 3.7 after aging). Also, the steric size ($R_{h(z)}$) of the polymer decreased from 27.7 (no thermal treatment) to 17.5 nm for the aged FLA. Calculation of the Burchard parameter produced a value of ~1.6 which is characteristic for a linear molecule. Obviously, owed to the extreme temperature conditions, the FLA breaks down into main and side chain fragments, and branching by NNMBA no longer occurs.

To study the influence of thermal aging on the fluid loss performance of the copolymer, stirred fluid loss tests were conducted at 200°C. The result is shown in Table VII. At a dosage of 1.2% bwoc, the cement slurry containing unaged FLA exhibits an API filtrate value of 46 mL, whereas the thermally treated polymer produces a filtrate of 52 mL. This result demonstrates that fluid loss performance of the AHPS-modified polymer is not much affected by the extreme temperature, although a significant change in polymer conformation occurs. This finding is surprising, because in an earlier study, it has been shown for a CaAMPS[®]-NNDMA copolymer that a conformational change (coiling) instigated by elevated sulfate concentrations present in cement pore solution led to a significant decrease in polymer

performance.²⁹ Obviously, the AHPS-modified polymer is more robust with respect to its performance.

Working Mechanism of the Polymer

To understand the working mechanism of the forpolymer, the correlation between API fluid loss, dynamic filtrate viscosity, and filtercake permeability was studied. The data presented in Table IV were obtained at 200°C in the presence of various dosages of the AHPS-based FLA and of 2% bwoc of retarder. First, its effect on filtrate viscosity was studied. If filtrate viscosity increases, then the rate of water loss from the cement filtercake would slow down and API fluid loss would decrease. Here, it is shown that the FLA does not impact the filtrate viscosity which remained relatively constant at a low value of ~0.33 mPa×s. Hence, filtrate viscosity has no influence on fluid loss performance. However, a clear correlation between API fluid loss and filtercake permeability was observed: At rising polymer dosage, API fluid loss decreased from 3216 (FLA dosage 0.2% bwoc) to 42 mL (FLA dosage 1.4% bwoc). At the same time, filtercake permeability was reduced from 4414 to 3 μD. This result clearly demonstrates that the AHPS-based FLA is working by reduction of cement filtercake permeability. The FLA reduces the pore space and thus hinders the passage of water through the filtercake pores. This effect can be explained by several mechanisms which are discussed in the following section.

Table VI. Shear Rate-Dependant Rheology (Viscosity) of Cement/Silica Slurries Containing 2% bwoc of HR-25[®] Retarder and Increasing Dosages of the AHPS-Based Fluid Loss Additive, Measured at 95°C

FLA dosage (% bwoc)	Viscosity (mPa), measured at different shear rates (s^{-1}) of					
	1022	511	340	170	10.2	5.1
0	n.m. ^a	240	230	295	1654	2881
0.2	n.m. ^a	209	198	221	640	854
0.4	n.m. ^a	154	147	147	374	427
0.6	n.m. ^a	209	180	179	373	429
0.8	n.m. ^a	255	260	279	374	427
1.0	n.m. ^a	273	280	282	375	427
1.2	n.m. ^a	n.m. ^a	378	362	429	534

^an.m. = not measurable (too thick to test).

Table VII. Shear Rate-Dependant Rheology, Measured at 95°C and API Fluid Loss Values (Measured at 200°C) of Cement/Silica Slurries Containing 1.2% bwoc AHPS-Based FLA Before and After Thermal Exposure

Polymer	Viscosity (mPa) at different shear rates (s ⁻¹) of						API fluid loss @ 200°C ^b (mL)
	1022	511	340	170	10.2	5.1	
As prepared	n.m. ^a	n.m. ^a	378	361	427	533	46
Thermally treated	n.m. ^a	252	269	301	373	427	52

^an.m. = not measurable (too thick to test), ^bSlurry contained 2% bwoc of HR-25[®] retarder.

The AHPS-based FLA possesses a relatively high anionic charge which leads to the assumption that it may interact with positively charged sites on the surface of cement. To investigate, retained amounts of the FLA and of the retarder were determined by TOC measurements of filtrates obtained from the stirred HTHP filtration tests. The results are displayed in Figure 4. Generally, the retained amount of the retarder is constant at ~19.5 mg/g as a result of nearly complete precipitation in the form of calcium tartrate. Whereas, the retained amount of AHPS-based FLA increases linearly from 2.0 mg/g cement at a dosage of 0.2% bwoc to 13.6 mg/g cement at 1.4% bwoc dosage. If polymer adsorption on cement was the sole working mechanism, then the retained amounts should be represented by a “Langmuir” type adsorption isotherm. This means that the retained amounts should first increase linearly until a saturation point is achieved. However, this behavior was not observed for the FLA used here. Consequently, this copolymer does not work by adsorption on cement at high temperatures. To investigate further, precipitation of the AHPS copolymer and the tartaric acid retarder by calcium was studied.

Table VII shows that after addition of 1.8 g/L Ca²⁺, the solved amount of the retarder is reduced from 10 to 3.7 g/L. This reduction of 63% can be explained by precipitation of calcium

tartrate (indeed a white precipitate was observed). On the other hand, the solved amount of individual AHPS copolymer is not much affected by calcium ions. The small decrease of 5% is within the margin of error of the method. Surprisingly, combination of the AHPS-based FLA with tartaric acid retarder showed ample quantity of white precipitate in the presence of calcium. The solved amount of retarder was found at 5.3 g/L which is slightly higher than in absence of FLA (3.7 g/L). This observation can be explained by the calcium-binding capability of the AA-building block present in the shell of the forpolymer. It chelates free dissolved calcium ions which after complexation no longer are accessible for the retarder. Hence, smaller amounts of retarder will precipitate. Opposite to this trend, the solved amount of the FLA decreased from 9.5 g/L (no retarder present) to 7.5 g/L in presence of retarder. This result signifies that the AHPS-based FLA interacts with the retarder by coprecipitation with calcium ions. This phenomenon explains the increasing retained amounts of FLA as shown in Figure 4. Such coprecipitation is not uncommon in cement and has been reported before, for example, for the combination of an AMPS[®]-co-NNDMA FLA with a lignosulfonate-based retarder.³⁰ Here, the high amount of AA present in the shell of the branched molecule represents numerous docking sites for Ca²⁺ ions which can chelate the carboxylate functionalities. As carboxylate groups are only monovalent anions, a positive charge remains after coordination with calcium and this is then compensated by tartrate anions. Through this specific mechanism, coprecipitation of the polymer with tartrate retarder is facilitated. The coprecipitate forms a layer on the surface of the

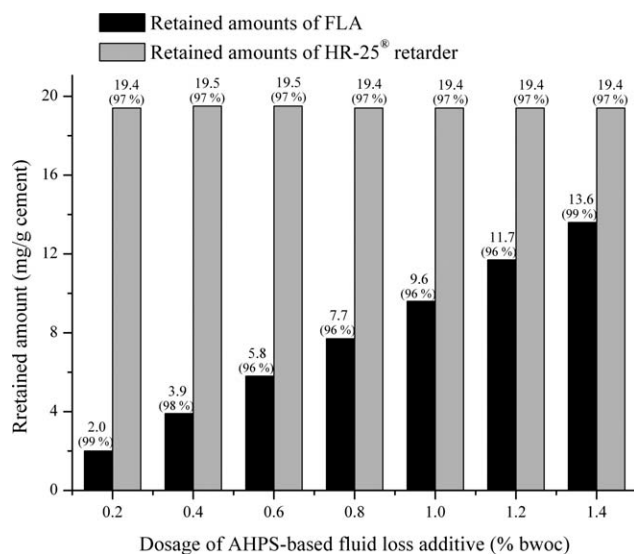


Figure 4. Retained amounts of AHPS-based FLA and HR-25[®] retarder, measured at 200°C in cement slurries containing different dosages of FLA and 2.0% bwoc retarder; () = retained amounts in percentage of dosage added.

Table VIII. Precipitated Amounts of AHPS-Based Fluid Loss Additive, of HR-25[®] and of a Combination of Both in Presence of 1.8 g/L Ca²⁺, Measured at pH = 13

Additive	Amount of additive found after Ca ²⁺ addition			
	AHPS-based FLA		Retarder	
	g/L	Reduction (%)	g/L	Reduction (%)
AHPS-based FLA (10 g/L)	9.5	5	-	-
HR-25 [®] retarder (10 g/L)	-	-	3.7	63
Retarder (10 g/L) + FLA (10 g/L)	7.5	25	5.3	47

cement particles which reduces the pore space in the filtercake. Through this mechanism, the loss of water from the cement slurry is hindered and fluid loss control is achieved.

CONCLUSION

A novel FLA based on AHPS as a new building block was synthesized. For this purpose, a forpolymer composed of a very slightly crosslinked AHPS/AMPS[®]/NNDMA terpolymer as a core and an AA shell was prepared. The forpolymer was enquired such as to fulfill several requirements. AMPS[®] monomer was incorporated for water solubility yet high calcium stability of the polymer while NNDMA was chosen to obtain a relatively stiff, linear polymer chain which is beneficial for fluid loss control. AHPS monomer was included to enhance high temperature stability while the function of AA was to provide anionic character and hence cement dispersion. Last, the NNMB crosslinker was used to boost the molecular weight of the polymer which improves fluid loss performance. Successful copolymerization of AHPS monomer with AMPS[®], NNDMA, and AA was proven by ¹H NMR and FTIR spectroscopy. Its molar amount was quantified by elemental analysis. The polymer exhibits excellent fluid loss performance under the extreme conditions of 200°C and 70 bar pressure. In addition, the FLA does not viscosify cement which is highly desirable in high temperature well cementing.

The working mechanism of the AHPS-based FLA in presence of a retarder was found to rely on a reduction of filtercake permeability. This reduction is achieved by coprecipitation of the FLA with tartaric acid retarder as a result of concomitant interaction with Ca²⁺ ions present in cement pore solution. The precipitate obstructs the pore space in the filtercake and thus reduces the flow of water through the pores.

Thermal treatment of the FLA showed a change in polymer conformation from branched to a linear structure and a decrease in molecular weight. However, the fluid loss performance was not much affected by this alteration.

The study demonstrates that a specific modification of the polymer composition allows to improve its functionality under the extreme environments of HTHP drilling. Further modifications will be necessary to push the envelope at which these synthetic polymers work to even higher temperatures such as 260°C. Furthermore, it will be helpful to study the degradation mechanisms of the polymers occurring under those conditions. This should allow to identify improved polymer structures which can satisfy the demands for even ultra-high temperature drilling.

ACKNOWLEDGMENTS

C. Tiemeyer wishes to thank the Jürgen Manchot Foundation for financial support of the study which enabled him to write this paper. Furthermore, Lubrizol Company is thanked for the supply of AMPS[®] monomer, and BIMAX company for providing the AHPS monomer. Finally, supply of API Class G “black label” cement from Dyckerhoff AG and of HR-25[®] from Halliburton GmbH is acknowledged.

REFERENCES

1. Fink, J. K. *Oil Field Chemicals*; Gulf Professional Publishing: Burlington, MA, **2003**.
2. Nelson, E. B.; Guillot, D. *Well cementing*, 2nd ed.; Schlumberger Dowell: Sugar Land, TX, **2006**.
3. Smith, D. K. *Cementing*; Society of Petroleum Engineers; SPE Monograph: New York, NY, **1990**.
4. Desbrières, J. *Cem. Concr. Res.* **1993**, *23*, 347.
5. Desbrières, J. *Cem. Concr. Res.* **1993**, *23*, 1431.
6. Audebert, R.; Janca, J.; Maroy, P.; Hendriks, H. U. S. Pat. 5 594 050, **1997**.
7. Plank, J.; Dugonjić-Bilić, F.; Lummer, N. R.; Salami, T. *J. Appl. Polym. Sci.* **2010**, *117*, 2290.
8. Hook, F. E. U. S. Pat. 3 483 007, **1969**.
9. Raines, R. H. U. S. Pat. 4 629 573, **1986**.
10. Vijn, J. P.; Dao, B.; Melbouci, M. U. S. Pat. 6 730 636, **2004**.
11. Bülichen, D.; Plank, J. SPE International Symposium on Oilfield Chemistry; The Woodlands/TX SPE paper 141182, USA **2011**.
12. Bülichen, D.; Plank, J. *J. Appl. Polym. Sci.* **2012**, *124*, 2340.
13. Brake, B. G.; Chatterji, J.; King, B.; Brennels, C. U. S. Pat. 5 340 860, **1994**.
14. Dugonjić-Bilić, F.; Plank, J. *J. Appl. Polym. Sci.* **2011**, *121*, 1262.
15. Chatterji, J.; Zamora, E.; King, B. J.; Mckinley, R. J. U. S. Pat. 6 268 406, **2001**.
16. Engelhardt, F.; Riegel, U.; Hille, M.; Wittkus, H. U. S. Pat. 4 309 523, **1982**.
17. Stephens, M. U. S. Pat. 5 294 651, **1994**.
18. Rao, P. S.; Burkhalter, J. F. U. S. Pat. 4 555 269, **1985**.
19. Plank, J.; Brandl, A.; Zhai, Y. N.; Franke, A. *J. Appl. Polym. Sci.* **2006**, *102*, 4341.
20. Salami, O. T.; Plank, J. *J. Appl. Polym. Sci.* DOI 10.1002/app.36725 2011, to appear.
21. American Petroleum Institute. API Specification 10A, 24th ed.; American Petroleum Institute: Washington, **2010**.
22. Franke, B. *Z. Anorg. Allgem. Chem.* **1941**, *247*, 180.
23. McCusker, L. B.; VonDreele, R. B.; Cox, D. E.; Louër, D.; Scardi, P. *J. Appl. Cryst.* **1999**, *32*, 36.
24. Huglin, M. B. In *Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E., Eds.; Wiley: New York, **1989**.
25. Plank, J.; Sachsenhauser, B. *Cem. Concr. Res.* **2009**, *39*, 1.
26. American Petroleum Institute. API Recommended Practice 10B-2, 1st ed.; American Petroleum Institute: Washington, **2005**.
27. Burchard, W. *Adv. Polym. Sci.* **1983**, *48*, 1.
28. Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience Publishers: New York, **1968**.
29. Lummer, N. R.; Dugonjić-Bilić, F.; Plank, J. *J. Appl. Polym. Sci.* **2011**, *121*, 1086.
30. Lummer, N. R.; Plank, J. *Cem. Concr. Res.* **2012**, *42*, 728.