Impact of the Steric Position of Phosphonate Groups in Poly(*N,N*-dimethylacrylamide-*co*-2-acrylamido-2-methylpropanesulfonate-*co*-2-x-phosphonate) on its Adsorbed Conformation on Cement: Comparison of Vinylphosphonic Acid and 2-Acrylamido-2-methylpropanephosphonate Modified Terpolymers

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ABSTRACT: For phosphonated copolymers, the effect of distance of the phosphonate group from the polymer backbone on the Ca^{2+} chelating capability and the adsorption behavior on cement was studied. For this purpose, 2-acrylamido-2-methylpropane phosphonic acid (AMPPA) and vinyl phosphonic acid (VPA), respectively, were reacted in an aqueous free-radical polymerization with *N,N*-dimethylacrylamide (NNDMA) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS®) to give poly(*N,N*-dimethylacrylamide-*co*-2-acrylamido-2-methylpropanesulfonate-*co*-2-acrylamido-2-methylpropanephosphonate) (CaAMPS®-*co*-NNDMA-*co*-CaAMPPA) and poly(*N,N*-dimethylacrylamide-*co*-2-acrylamido-2-methylpropanesulfonate-*co*-vinylphosphonate) (CaAMPS-*co*-NNDMA-*co*-CaVPA), respectively. Adsorption behavior and thus performance of the terpolymers strongly depend on their calcium binding capacity. Ca^{2+} selective conductivity measurements show that the AMPPA modified terpolymer chelates less calcium than the VPA polymer. Therefore, it interacts less with surfaces containing calcium atoms/ions. To investigate the consequences for practical applications adsorbed amounts on cement surface and effectiveness as water retention agent (fluid loss additive, FLA) in oil well cement slurries with and without acetone-formaldehyde-sulfite (AFS) dispersant were determined. CaAMPS-*co*-NNDMA-*co*-CaAMPPA and AFS adsorb simultaneously whereas CaAMPS-*co*-NNDMA-*co*-CaVPA does not allow dispersant adsorption. The reason is that affinity of phosphonate functions towards Ca^{2+} ions is reduced with increasing distance from the polymer backbone. Thus, AMPPA is a weaker anchor group than VPA. Zeta potential measurements indicate that the increased length of the side chain holding the phosphonate function decreases the anionic charge density of the polymer. Accordingly, CaAMPS-*co*-NNDMA-*co*-CaAMPPA appears to develop weaker bonds with the cement surface. Upon addition of AFS, the AMPPA modified FLA can change its adsorbed conformation from "train" to "loop" or "tail" mode and thus provide space for the dispersant to adsorb as well. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1758–1768, 2010

Key words: polymer; adsorption; cement; calcium binding capacity; 2-acrylamido-2-methylpropane phosphonate

INTRODUCTION

In oil well cementing, additives are applied to adjust the properties of cement slurries.[1] Fluid loss additives (FLAs) reduce uncontrolled water loss from the slurry pumped along the porous formation of the bore hole.[2,3,4] Dispersants ensure the pumpability of the cement slurry over a distance of several kilometers. Occasionally, combinations of different additives lead to malfunction of the cementing system, resulting in poor slurry properties or even in a complete failure of the cementation. Previous studies revealed an adsorptive working mechanism for poly(*N,N*-dimethylacrylamide-*co*-2-acrylamido-2-methylpropanesulfonate) (CaAMPS®-*co*-NNDMA) cement FLA and also for acetone-formaldehyde-sulfite (AFS) polycondensate dispersant.[5] In binary admixture systems, the two admixtures generally compete for a limited number of adsorption sites available on the surface of hydrating cement. Because of this competitive adsorption, CaAMPS-*co*-NNDMA is displaced by strongly adsorbing AFS from the cement surface. Thus, the fluid loss control of the slurry declines with increasing AFS dosage. Recently, it has been shown that incorporation of minor amounts of vinyl phosphonic acid as supplementary anchor group into CaAMPS-*co*-NNDMA-polymer produces a FLA (CaAMPS-*co*-NNDMA-*co*-CaVPA) which still adsorbs in the presence of AFS and maintains its effectiveness.[6] In this terpolymer, however, the affinity of the phosphonate anchor groups toward calcium present on the surface of hydrating cement is so strong that it no longer

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

C_3S^a (wt %)	C_2S^b (wt %)	$C_3A_c{}^c$ (wt %)	C_4AF^d (wt %)	Free CaO (wt %)	$CaSO_4 \cdot 2H_2O$ (wt %)	$CaSO_4 \cdot 1/2\ H_2O$ (wt %)	$CaSO_4$ (wt %)	Specific density (kg/L)	Specific surface area (m²/kg)	d_{50} value (μm)
59.6	22.8	1.2	13.0	<0.3	2.7[e]	0.0[e]	0.7	3.18	305.8	9.8

[a] C_3S: tricalcium silicate ($Ca_3(SiO_4)O$).
[b] C_2S: dicalcium silicate (Ca_2SiO_4).
[c] C_3A_c: cubic modification of tricalcium aluminate ($Ca_9Al_6O_{18}$).
[d] C_4AF: tetra calcium aluminate ferrite ($Ca_4Al_2Fe_2O_{10}$).
[e] Measured by thermogravimetry.

allows the simultaneous adsorption of AFS dispersant. Hence, this cement dispersant cannot work. It is incompatible with this FLA.

In a previous study, McCormick and Elliott have shown for carboxylated and sulfonated copolymers that moving the anionic functionality away from the polymer backbone reduces the charge density in the polymer trunk.[7] This way, precipitation in the presence of Ca^{2+} ions was suppressed or even prevented. Differences were found between carboxylated and sulfonated polymers: For example, the NaAMPS homopolymer does not precipitate in $CaCl_2$ solution while the homopolymer of sodium 3-acrylamide-3-methylbutanoate (NaAMB) does. The interaction of these polymers with Ca^{2+} depends not only on the length of the side chain bearing the anionic group, but also on the acidity and the local microstructure of the terpolymer.

Goal of our investigation was to study the effect of the steric distance of a phosphonate functionality from the polymer trunk on its calcium binding capability and adsorption behavior. Phosphonates are known to be much stronger anchor groups than sulfonates or carboxylates.[6,8] For this purpose, vinylphosphonic acid contained in CaAMPS-co-NNDMA-co-CaVPA was substituted by another monomer possessing a phosphonate functionality with a greater distance to the polymer trunk. Ideally, this different

steric position of the phosphonate functionality should reduce its strength as an anchor group to an extent that simultaneous adsorption of FLA and AFS is possible. Thus, 2-acrylamido-2-methylpropane phosphonic acid (AMPPA) monomer was incorporated into CaAMPS-co-NNDMA. The resulting terpolymer (CaAMPS-co-NNDMA-co-CaAMPPA) possesses phosphonate functions which are several bond lengths away from the backbone. Fluid loss and rheology of cement slurries containing CaAMPS-co-NNDMA-co-CaVPA or CaAMPS-co-NNDMA-co-CaAMPPA and AFS were measured and compared. The impact of the distance of the phosphonate groups from the polymer trunk on charge density, calcium binding capacity and adsorption of this polymer on cement were investigated.

EXPERIMENTAL

Materials

Oil well cement

An API Class G cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) according to American Petroleum Institute (API) Specification 10A was used.[9] Phase composition, specific density,
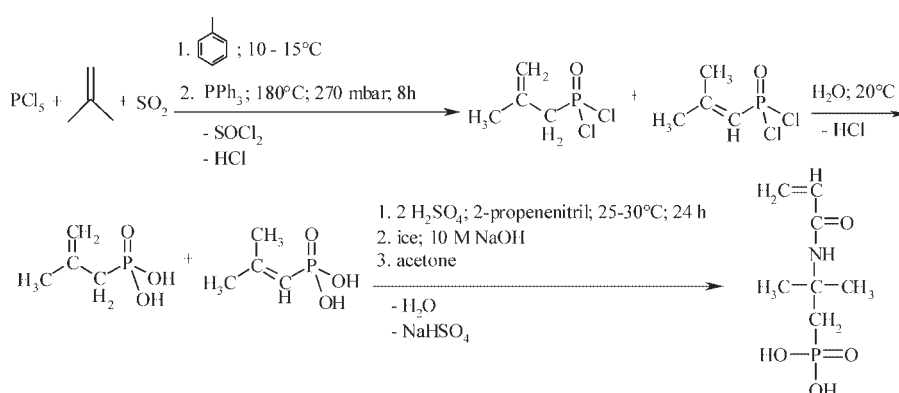
Scheme 1 Reaction scheme for the three step synthesis of 2-acrylamio-2-methylpropane phosphonic acid (AMPPA) monomer.
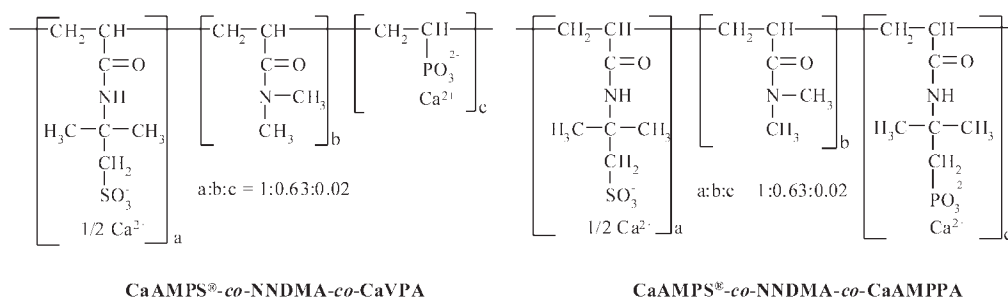
Figure 1 Chemical structures of synthesized CaAMPS-co-NNDMA-co-CaVPA and CaAMPS-co-NNDMA-co-CaAMPPA.

particle size (d_{50} value), and specific surface area of the sample are presented in Table I.

2-Acrylamido-2-methylpropane phosphonic acid

The monomer AMPPA was prepared in a three step synthesis according to Scheme 1. The procedure described by Finke and Rupp was applied.[10] (1) In the first step, the isomers of 2-methyl-2-propenyl-phosphonic dichloride were synthesized by reacting sulfur dioxide with a mixture of phosphorous pentachloride and isobutene (25% yield). ^{1}H-NMR (CDCl$_3$), isomer 1: δ (ppm) 1.23 (s, 3H, CH_3), 1.91 (d, 2H, CCH_2P), 3.30 + 5.10 (2x dd, 2H, H_2C=C), isomer 2: δ (ppm) 1.97 (s, 3H, CH_3), 2.18 (d, 3H, CH_3), 5.85 (d, 1H, C=CHP). ^{13}C-NMR (CDCl$_3$), isomer 1: δ (ppm) 28.1 (CH$_3$), 52.4 (CCH$_2$P), 77.3 (H_2C=C), 121.5 (H_2C=C); isomer 2: δ (ppm) 21.5 (CH$_3$), 33.5 (CH$_3$), 120.0 (C=CHP), 163.7 (C=CHP). ^{31}P-NMR (CDCl$_3$), isomer 1: δ (ppm) 30.5; isomer 2: δ (ppm) 40.6. (2) In the second step, 2-methyl-2-propenylphosphonic dichloride was hydrolyzed with water. The yield of the resulting 2-methylpropenylphosphonic acid isomers was 96%. ^{1}H-NMR (D$_2$O) isomer 1: δ (ppm) 1.04 (s, 3H, CH_3), 1.82 (d, 2H, CCH_2P), 4.91 (d, 2H, H_2C=C); isomer 2: δ(ppm) 1.58 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 5.18 (d, 1H, C=CHP). ^{13}C-NMR (D$_2$O) isomer 1: δ (ppm) 27.5 (CH$_3$), 41.0 (CCH$_2$P), 69.5 (H_2C=C), 113.5 (H_2C=C); isomer 2: δ (ppm) 21.2 (CH$_3$), 29.5 (CH$_3$), 111.7 (C=CHP), 160.6 (C=CHP). ^{31}P-NMR (D$_2$O) isomer 1: δ (ppm) 18.1; isomer 2: δ (ppm) 27.2. (3) In the third step, 2-propenenitrile was transformed to 2-acrylamido-2-methylpropane phosphonic acid (30% yield) via Ritter reaction using the synthesized 2-methylpropenylphosphonic acid isomers as alkylating reagents. ^{1}H-NMR (D$_2$O): δ (ppm) 1.48 [s, 6H, NC(CH_3)$_2$], 2.41 (d, 2H, NCCH_2), 5.68 (d, 1H, H_2C=CH, ^{3}J (H,H) = 10.04 Hz), 6.12 (d, 1H-[syn-], H_2C=CH, ^{2}J (H,H) = 17.06 Hz), 6.22 (dd, 1H-[anti-], ^{2}J (H,H) = 17.08 Hz, ^{3}J (H,H) = 10.04Hz). ^{13}CNMR (D$_2$O): δ (ppm) 27.9 (NC(CH$_3$)$_2$), 35.8 + 37.1 (2C, C(CH$_3$)$_2$), 51.8 (NCCH$_2$), 126.8 (H_2C=C), 131.3 (H_2C=C), 168.1 (CO). ^{31}P-NMR (D$_2$O): δ (ppm) 26.6.

Elemental analysis (calculated/found): C (40.58%/40.25%); H (6.81%/6.96%), N (6.76%/6.62%), P(14.95%/14.32%). ESI-MS (70 eV): m/z 208 [m+H]$^+$, 453 [2m+K]$^+$, 660 [3m+K]$^+$.

Fluid loss polymers

Terpolymers of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N,N-dimethylacrylamide (NNDMA), vinyl phosphonic acid (VPA) or 2-acrylamido-2-methylpropane phosphonic acid (AMPPA) were synthesized by aqueous free-radical polymerization as previously reported.[5,6] The aqueous solutions of the polymers composed of molar ratios 1 : 0.63 : 0.02 of AMPS:NNDMA:AMPPA or VPA were drum dried at 150°C, yielding a white powder. AMPS and VPA were obtained from Merck-Schuchardt (Darmstadt, Germany). NNDMA was obtained from Sigma-Aldrich Chemical (Munich, Germany). AMPPA was prepared as described earlier. Figure 1 shows the chemical structures of the synthesized FLAs.

AFS Polycondensate

Synthesis of the acetone-formaldehyde-sulfite polycondensate (molar ratios of acetone:formaldehyde:sodium sulfite 1 : 3 : 0.5) was carried out according to Aignesberger and Plank which is reported in previous work.[5,11,12] A structure of AFS derived from IR and ^{1}H-NMR data is proposed in Figure 2.

Poly(DADMAC)

A 0.001N solution of poly(diallyl dimethyl ammonium-chloride) obtained from BTG Mytek GmbH (Herrsching, Germany) was used as cationic polyelectrolyte.
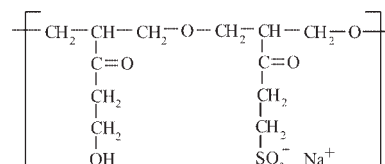

Figure 2 Proposed chemical structure of acetone-formaldehyde-sulfite (AFS) dispersant.

Reagents

$CaCl_2$ was obtained from Merck-Schuchardt (Darmstadt, Germany). NaOH was supplied by VWR International GmbH (Darmstadt, Germany).

Instruments

GPC

A Waters Alliance 2695 (Waters, Eschborn, Germany) separation module equipped with RI detector 2414 (Waters, Eschborn, Germany) and a dynamic light scattering detector (Dawn EOS, Wyatt Technologies, Clinton) was used. AFS separation was performed by using Ultrahydrogel 500, 250, and 120 columns (Waters, Eschborn, Germany) and a three angle dynamic light scattering detector, whereas FLA was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). For FLA, an 18 angle dynamic light scattering detector was used.

NMR spectroscopy

NMR spectra were obtained using a JEOL JMN-GX-270 spectrometer (JEOL GmbH, Eching bei Munich, Germany) with multinuclear (^{1}H (270.17 MHz), ^{13}C (67.94 MHz), ^{31}P (270.17 MHz)) probe. ^{1}H, ^{13}C-NMR and ^{31}P spectra were referenced internally to the used solvent, d-chloroform or deuterium oxide. The NOESY and the ^{31}P spectra of the polymers and the monomers (2-acrylamido-2-methylpropane phosphonic acid and vinyl phosphonic acid) were recorded on a 600 MHz Bruker DMX-600 spectrometer using deuterium oxide as the solvent in 5 mm TXI NMR tubes. Here, D_2O was also used as reference.

Elemental analysis

C,H,N,P analyzes were carried out on a Perkin Elmer 2400 analyzer (Perkin Elmer, Massachusetts).

Gas chromatography

The analysis was carried out on an HP 5970 mass selective detector (Hewlett-Packard, Palo Alto, CA), linked to an HP 5890 gas chromatograph equipped with a split-splitless injector (Cooled Injection System, Brielle, The Netherlands).

pH measurement

The pH values were measured at 25°C with a SCHOTT pH mV meter (Schott Geräte GmbH, Mainz, Germany) equipped with a SCHOTT A161 pH electrode (Schott Geräte GmbH, Mainz, Germany). The meter was standardized by a two-point calibration method.

Calcium concentration

Measurement of solved Ca^{2+} was carried out at 25°C using the calcium selective electrode ionmeter pH/ION 340i (WTW, Weilheim, Germany).

Charge titration

PCD 03 pH (Mütek Analytic, Herrsching, Germany) and a blue ribbon filter paper obtained from Whatman® (Dassel, Germany) were used.

Cement testing

Phase composition of the cement sample was determined using an XRD instrument (D8 Advance, Bruker AXS, Karlsruhe, Germany) with Bragg-Bretano geometry. The diffractometer is equipped with a scintillation detector using CuK_α ($\lambda = 1.5406$ A) radiation with a scanning range between 5 and 80° 2θ at a scanning speed of 0.5 s/step (with 0.008°/step). Specific density of the cement was measured on an Ultrapycnometer1000 (Quantachrome Instruments, Florida). The average particle size (d_{50}) measurement was carried out using a laser-based particle size analyzer (Cilas 1064, Marseille, France). The specific surface area was determined with a Blaine instrument (Toni Technik, Berlin, Germany). A blade type laboratory blender manufactured by Waring (Torrington) was used to prepare the cement slurry. The slurry was homogenized in an atmospheric consistometer (Model 1250, Chandler Engineering, Oklahoma).

API filtration cell

A 500 mL OFITE high temperature high pressure filter press (Part No. 171-00-C, OFI Testing Equipment, Houston) was used.

Rheology

A Couette type coaxial cylinder rotational viscometer, FANN 35SA (Fann Instruments Company, Houston) equipped with R1 rotor sleeve (rotor radius: 1.84cm), B1 bob (bob radius: 1.7245 cm, bob height: 3.8 cm) and F1 torsion spring was used.

Adsorption

High TOC II (Elementar, Hanau, Germany) with CO_2 and NO detector was used.

Zeta potential measurements

The zeta potential was measured using a combined acoustic and electroacoustic spectrometer (Model

DT-1200, Dispersion Technology, Mount Kisco, NY). This instrument has separate sensors for measuring acoustic and electroacoustic signals and allows to measure zeta potentials of highly solids loaded suspensious such as cement slurries.

Procedures

GPC separation

AFS: Molecular weights (M_w, M_n) of the synthesized AFS samples were determined by GPC. Aqueous $0.1M$ NaNO$_3$ (adjusted with NaOH to pH 12) was used as an eluant at a flow rate of 1.0 mL/min. The AFS solutions were filtered through a 0.2-µm filter and measured. A dn/dc of 0.177 mL/g [value for poly(sodium 4-styrene sulfonate)] was applied. Thus, all measured molecular weights are relative to poly (sodium 4-styrene sulfonate).[13] CaAMPS-co-NND MA: M_w and M_n of the copolymer were determined using a $0.2M$ NaNO$_3$ aqueous solution (adjusted with NaOH to pH = 9) as an eluant at a flow rate of 1.0 mL/min. FLA solution was filtered through a 5-µm filter. The value of dn/dc used to calculate M_w and M_n was 0.156 mL/g (value for polyacrylamide).[14] Thus, the molecular weights measured are relative to polyacrylamide.

pH measurement

The pH values of vinyl phosphonic acid and 2-acrylamido-2-methylpropane phosphonic acid monomer were measured at 0.04 mol/L concentration in deionized water.

Calcium binding capacity

Concentration of freely solved, nonbound Ca^{2+} was determined using a calcium selective electrode. Procedure for AMPPA and VPA monomers: An aqueous $0.01M$ CaCl$_2$ solution (50 mL) was added stepwise (1 mL) to 30 mL of a stirred 5 mmol/L monomer solution (adjusted with NaOH to pH 11). Procedure for CaAMPS-co-NNDMA-co-CaAMPPA and CaAMPS-co-NNDMA-co-CaVPA: An aqueous $0.07M$ CaCl$_2$ solution (60 mL) was added stepwise (1 mL steps) to 30 mL of a stirred 2 mmol/L solution of each polymer (adjusted with NaOH to pH 11). After waiting until readings from the sensor were stable (20 s), concentration of solved calcium (displayed in mg/L) was recorded. Subtracting the amount of solved calcium from the known amount of Ca^{2+} contained in CaCl$_2$ added produces the amount of calcium which is bound.

Cement slurry preparation

Cement slurries were prepared in accordance with the test procedure set forth in Recommended Prac-

tice for Testing Well Cements, API Recommended Practice 10B, issued by the American Petroleum Institute, using API Class G oil well cement and deionized water.[15] The cement slurry was mixed at a water-to-cement ratio of 0.44 using the Waring blender. First, 700 g cement and 3.5 g (0.5% by weight of cement, bwoc) FLA (e.g., CaAMPS-co-NNDMA-co-VPA powder) were dry blended. Next, 2.8 g (0.4% bwoc) AFS were dissolved in 308 g water and siffed into the 1500 mL cup of the Waring Blender. Then, the cement/FLA blend was added within 15 s to the aqueous AFS solution and mixed for 35 s at 12,000 rpm. To ensure homogeneous consistency, all slurries were poured into the 500 mL slurry container of an atmospheric consistometer and stirred for 20 min at 27°C.

API static fluid loss

Static fluid loss was determined at 27°C following API RP 10B procedure using a 500 mL HTHP filter press.[15] After pouring the homogenized cement slurry into the filter cell, a differential pressure of 70 bar (N$_2$) was applied at the top of the cell. Filtration proceeded through a 3.5 sq. in. mesh metal sieve placed at the bottom of the cell. The filtrate produced by the differential pressure was collected for 30 min (V_{30}). As described by API RP 10B, the collected filtrate volume was doubled and designated as API fluid loss of the corresponding cement slurry.

Rheology

Rheology of the cement slurry was determined following API RP 10B procedure using the FANN 35SA rotational viscometer.[15] The homogenized cement slurry obtained after stirring in the atmospheric consistometer was poured into the 300 mL cup of the FANN rheometer. Shear stress (lbs/100ft^2) was measured at shear rates of 600, 300, 200, 100, 6, and 3 rpm. The initial instrument dial reading was taken 1 min after continuous rotation at 300 rpm. The following readings were taken in ascending order after continuous rotation of 20 s at each speed. Finally, the reading at 600 rpm was taken.

Charge titration

The specific anionic charge amounts of AFS and FLA, respectively, in cement pore solution were determined by charge titration using poly(diallyl dimethyl ammoniumchloride) as cationic polyelectrolyte. Cement pore solution was prepared by vacuum filtration of the cement slurry without additives using a blue ribbon filter paper. Charge titration was performed with a solution prepared from 9 mL cement pore solution and 1 mL of a 0.2 g/L solution

TABLE II
Characteristic Properties of Synthesized FLA Terpolymers and AFS Dispersant

Polymer	Molecular weight		Poly dispersity index M_w/M_n	Radius of gyration Rg_z (nm)	Specific anionic charge amount ε (C/g)	Molar anionic charge density Θ (C/mol/nm^3)
	M_w (g/mol)	M_n (g/mol)				
CaAMPS-co-NNDMA-co-CaVPA	1,728,000	1,170,000	1.5	69.5	381	217
CaAMPS-co-NNDMA-co-CaAMPPA	1,794,000	1,239,000	1.5	69.7	366	215
AFS	64,000	16,000	4.0	9.0	243	2222

of either AFS or FLA. Using the procedure of Lechner,[16] the molar anionic charge density for each polymer was calculated as follows: Assuming that the polymers are hard spheres, their molecule radius can be obtained from $R = (5/3 \cdot Rg_z^2)^{0.5}$, where Rg_z is the experimentally determined radius of gyration (Table II). As a next step, the volume of the molecules can be calculated according to $V = 4/3 \cdot \pi \cdot R^3$. Further, the molar anionic charge amount $\varepsilon_m = \varepsilon \cdot M_w$ is derived from the experimentally measured values of the specific anionic charge amount ε and the weight average molecular weight M_w of the polymers. Finally, the molar anionic charge densities Θ are obtained according to $\Theta = \varepsilon_m/V$. The results for the FLA polymers and AFS are listed in Table II.

Adsorption

The amount of admixture adsorbed on cement was determined from the filtrate collected in the fluid loss test. Achievement of adsorption equilibrium was checked by comparing polymer adsorption in cement slurry stirred for 20 min in the atmospheric consistometer with a slurry which was not stirred. In both cases, the same values for adsorbed amount of polymers were found. The adsorbed amount was calculated from the difference in the equilibrium concentrations of the polymers in the liquid phase before and after adsorption. When only AFS was present in the cement filtrate, its concentration was measured by TOC analysis. When both admixtures were present, FLA concentration was determined by TN analysis. The adsorbed amount of AFS was calculated by subtracting the adsorbed amount of FLA measured by TN analysis from the sum of adsorbed amounts of FLA and AFS obtained by TOC analysis. For TN analysis, the alkaline cement filtrate containing the unadsorbed polymers obtained from the fluid loss test was adjusted to neutral pH by adding 0.01M phosphoric acid.

Zeta potential measurements

Cement slurries were prepared as mentioned earlier.[15] As zeta potentials were measured as a function of time, the cement slurry was used immediately after preparation in the Warring Blender, without stirring in the atmospheric consistometer. The ionic background of the cement filtrate without polymer was determined at a w/c ratio of 0.44 and was substracted from the zeta potential values obtained for the slurries containing the polymers.

RESULTS AND DICUSSION

Characterization of the phosphonated copolymers

Molecular weight, polydispersity index, gyration radius, and molar anionic charge density of each FLA polymer were found to be comparable (Table II). The incorporation of AMPPA and VPA into the copolymers was evidenced by ^{31}P-NMR [for AMPPA: δ (ppm) 21; for VPA: δ (ppm) 26]. Molar composition of the terpolymers was confirmed by ^{1}H-NMR spectroscopy (Fig. 3). For CaAMPS-co-NNDMA-co-CaAMPPA, based on the integrals of methyl protons present in the monomers AMPS, AMPPA, and NNDMA, a molar ratio of 1.02 : 0.63 was found for (AMPS + AMPPA):NNDMA, indicating that 0.02 mol % of AMPPA were incorporated into the copolymer. In contrast, CaAMPS-co-NNDMA-co-CaVPA revealed a molar ratio of 1:0.63 for AMPS:NNDMA. This is in perfect agreement
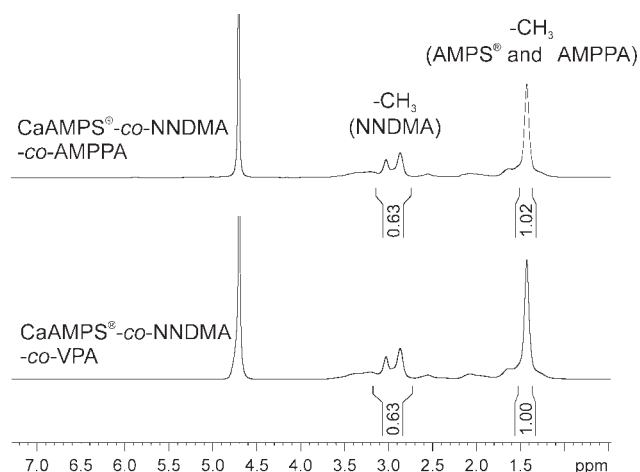

Figure 3 ^{1}H-NMR spectra of CaAMPS-co-NNDMA-co-CaAMPPA and of CaAMPS-co-NNDMA-co-CaVPA, measured in D$_2$O.

TABLE III
Q and *e* Values of the Monomers Used for Preparation of the FLAs[17]

Monomer	*Q*	*e*
AMPS	0.39	0.22
NNDMA	0.41	−0.26

with the monomer ratio which was used in the synthesis. Because of the absence of any methyl protons in VPA, it does not contribute to the signal intensity. Additionally, NOESY experiments performed for both polymers show ^{1}H signals of high intensity due to the interaction of the geminal dimethyl groups present in AMPS [δ(ppm) 1.4–1.5] and the methyl groups contained in NNDMA [δ(ppm) 2.8–3.1]. They indicate either a statistic or alternating distribution of these monomers along the polymer trunk. This can also be expected from their polarity (*e* value) and resonance stability (*Q* value).[17] Because of the similar *Q* values and different signs of e values (see Table III), AMPS and NNDMA show an alternating arrangement along the trunk of the molecule. Previously, we found that CaAMPS-*co*-NNDMA-*co*-CaVPA is a statistical terpolymer with phosphonate anchor groups distributed statistically along the polymer trunk.[6] From the similarity of the NOESY spectra of CaAMPS-*co*-NNDMA-*co*-CaVPA and CaAMPS-*co*-NNDMA-*co*-CaAMPPA we conclude that minor amounts of VPA or AMPPA present in the terpolymers do not significantly change the polymer architectures. Thus, the major structural difference between the two terpolymers lies in the type of side chain holding the phosphonate group.

Calcium binding capacity of VPA and AMPPA

Apparently, adsorption of the FLA copolymers occurs by interaction between the anionic anchor groups of these copolymers with calcium atoms present on the surface of hydrating cement. To investigate this interaction, the calcium chelating ability of the phosphonated monomers VPA and AMPPA was investigated by using a calcium selec-

tive electrode. To compare their acidities, the pH values of vinyl phosphonic acid and 2-acrylamido-2-methylpropane phosphonic acid monomer were measured at 0.04 mol/L concentration in deionized water. For VPA, a slightly lower pH value (1.9) was determined than for AMPPA (2.2). Thus, VPA is a stronger acid, it dissociates more (32%) than AMPPA (17%). Consequently, at pH 12.5–13.5 (pH range of cement slurries), VPA produces more phosphonate anions which can interact with Ca^{2+}. Hence, it can be expected to bind Ca^{2+} ions more readily than AMPPA.

To verify this, the concentration of freely solved Ca^{2+} present at 25°C in 5mmol/L solutions of each monomer titrated with increasing amounts of CaCl$_2$ was determined. The calcium uptake of the monomers was calculated by subtracting the displayed free calcium concentration from the amount of Ca^{2+} added (Table IV). At all CaCl$_2$ additions, VPA shows lower concentrations of freely solved Ca^{2+} than AMPPA. The calcium binding capacity of VPA monomer was found to be about 90% which is significantly higher than for AMPPA (calcium binding capacity 55–69%). The result allows to conclude that vinylphosphonic acid interacts stronger with calcium ions than 2-acrylamido-2-methylpropane phosphonic acid.

Calcium binding capacity of CaAMPS-*co*-NNDMA-*co*-CaAMPPA and CaAMPS-*co*-NNDMA-*co*-CaVPA

Similar to the experiments with the monomers, the calcium uptake of aqueous CaAMPS-*co*-NNDMA-*co*-CaAMPPA and CaAMPS-*co*-NNDMA-*co*-CaVPA solutions was determined at 25°C and pH 11. Again, the calcium binding capacity of the polymers was calculated by subtracting the displayed concentration of free calcium in the polymer solutions from the amount of Ca^{2+} added. The results are shown in Table V.

Both polymer solutions already contain some calcium ions before CaCl$_2$ addition. This is owed to the use of Ca(OH)$_2$ in the neutralization step of the

TABLE IV
Calcium Binding Capacity of Aqueous 2-Acrylamido-2-methylpropane Phosphonic Acid and Vinylphosphonic Acid Solutions (*c* = 5 mmol/L) at Different CaCl$_2$ Concentrations and pH 11

Addition of 0.01*M* CaCl$_2$ (mL)	Ca^{2+} added (10^{-3} mg/L)	Free Ca^{2+} (10^{-3} mg/L) AMPPA	Free Ca^{2+} (10^{-3} mg/L) VPA	Uptake of Ca^{2+} (10^{-3} mg/L) AMPPA	Uptake of Ca^{2+} (10^{-3} mg/L) VPA	Calcium binding capacity (%) AMPPA	Calcium binding capacity (%) VPA
1	0.4	0.2	0.0	0.2	0.4	50	100
5	2.0	0.9	0.2	1.1	1.8	55	90
10	4.0	1.5	0.4	2.5	3.6	63	90
15	6.0	1.9	0.7	4.1	5.3	68	88
20	8.0	2.5	0.8	5.5	7.2	69	90
50	20.1	6.3	2.5	13.8	17.6	69	88

TABLE V
Calcium Binding Capacity of Aqueous CaAMPS-*co*-NNDMA-*co*-CaAMPPA and CaAMPS-*co*-NNDMA-*co*-CaVPA Solutions (c = 2 mmol/L) at Different CaCl$_2$ Concentrations and pH 11

Addition of 0.07M CaCl$_2$ (mL)	Ca^{2+} added (10^{-3} mg/L)	CaAMPS-*co*-NNDMA-*co*-CaAMPPA		CaAMPS-*co*-NNDMA-*co*-CaVPA		Calcium binding capacity (% of Ca^{2+} added with CaCl$_2$)	
		Free Ca^{2+} (10^{-3} mg/L)	Uptake of Ca^{2+} (10^{-3} mg/L)	Free Ca^{2+} (10^{-3} mg/L)	Uptake of Ca^{2+} (10^{-3} mg/L)	CaAMPS-*co*-NNDMA-*co*-CaAMPPA	CaAMPS-*co*-NNDMA-*co*-CaVPA
0	0	22.8	–	13.1	–	–	–
1	2.8	25.4	0.2	15.3	0.6	7	21
6	16.8	38.0	1.6	22.7	7.2	10	43
7	19.6	40.3	2.1	24.4[a]	8.3	11	42
8	22.4	42.1	3.1	15.0[b]	20.5	14	92
10	28.1	47.3	3.6	20.7	20.5	13	–
20	56.1	73.5	5.4	48.6	20.6	10	–
50	140.0	148.1[a]	14.7	132.2	20.9	11	–
55	154.3	159.1[b]	18.0	–	–	12	–
60	168.3	172.7	18.4	–	–	–	–

[a] Solution turns opaque.
[b] Polymer precipitates.

polymer synthesis. Although the same amount of Ca(OH)$_2$ was added in the preparation of both polymers, the quantity of free calcium ions found in the presence of CaAMPS-*co*-NNDMA-*co*-CaAMPPA is higher than that measured in CaAMPS-*co*-NNDMA-*co*-CaVPA solution. Similar to the VPA monomer, the VPA-modified terpolymer shows a higher uptake of Ca^{2+} than the terpolymer containing AMPPA. In aqueous solution, the polymers are assumed to possess a completely stretched conformation due to intramolecular repulsion among the negative charges along the trunk chain.[18,19] Owing to the vicinity of the phosphonated groups to the polymer backbone, the anionic charge of CaAMPS-*co*-NNDMA-*co*-CaVPA is located more along the polymer trunk chain. This effect which has been described earlier by McCormick et al. for copolymers bearing sulfonate groups results in a higher uptake of calcium ions.[7]

The effect was confirmed when more Ca^{2+} in the form of CaCl$_2$ was added to the polymer solutions (Table V). As expected, CaAMPS-*co*-NNDMA-*co*-CaVPA shows a higher uptake of calcium and a higher calcium binding capacity than CaAMPS-*co*-NNDMA-*co*-CaAMPPA. Because of the charge neutralization from this chelating process, it precipitates at a lower calcium concentration (19.6 × 10^{-3} mg Ca^{2+}/L) than the AMPPA modified terpolymer (50 × 10^{-3} mg Ca^{2+}/L). Thus, it is confirmed that CaAMPS-*co*-NNDMA-*co*-CaVPA interacts stronger with calcium than CaAMPS-*co*-NNDMA-*co*-CaAMPPA.

Zeta potential measurements

Zeta potential measurements of cement pastes are an effective method to investigate the charge of colloidal cement particles.[20,21] A strong decline of zeta potential to more negative values indicates electrostatic repulsion between the particles. They become more negatively charged due to adsorbed polymer molecules which carry anionic functional groups. The higher the charge of adsorbed polymer and its adsorbed amount, the more negative is the zeta potential of the suspended solids particles.[20] Figure 4 demonstrates that, in presence of the FLA polymers, the zeta potential is not much dependant on the progress of cement hydration, which may result in different concentrations of ions (especially Ca^{2+} and SO$_4^{2-}$) in the pore solution over time.[20] Accordingly, equilibrium of the polymer adsorption is accomplished within the first minutes. It shows that, despite almost the same adsorbed amounts found for both FLAs (see next chapter), the zeta potential for CaAMPS-*co*-NNDMA-*co*-CaVPA is slightly more negative than that for CaAMPS-*co*-NNDMA-*co*-
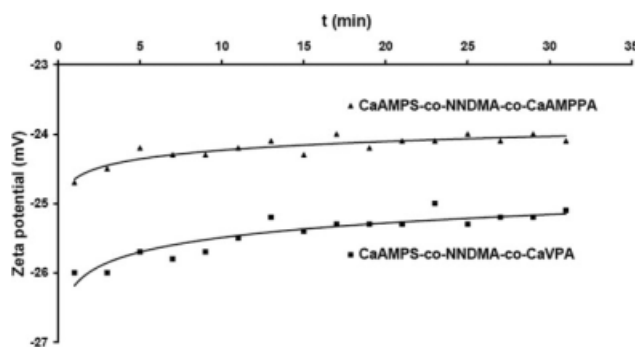

Figure 4 Time-dependant zeta potentials of cement slurries containing AMPS-*co*-NNDMA-*co*-AMPPA and AMPS-*co*-NNDMA-*co*-VPA, respectively (dosages of each FLA: 0.5%bwoc).
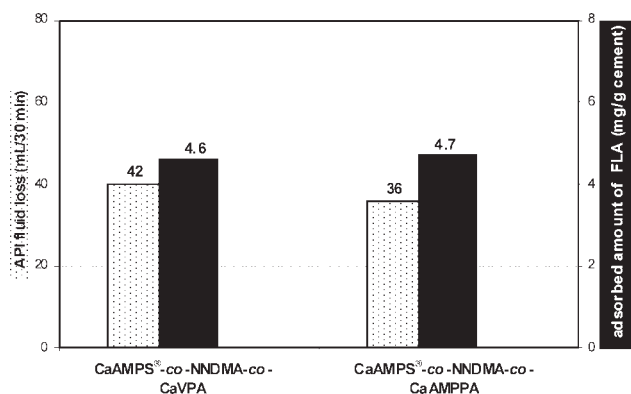
Figure 5 API fluid loss (dotted bars) and adsorbed amount (black bars) of cement slurries containing the synthesized FLA polymers (FLA dosage: 0.5% bwoc).

CaAMPPA. Hence, increased distance of the functional group diminishes the anionic charge density of the polymer which adsorbs in a stretched conformation on cement particles. Thus, the negative charge of cement particles carrying CaAMPS-*co*-NNDMA-*co*-CaAMPPA is less than when the same amount of VPA copolymer is adsorbed. Consequently, the lower calcium binding capacity of the AMPPA terpolymer may be attributed to a lower anionic charge density of the phosphonate group present in AMPPA compared to the one in VPA.

Fluid loss performance and adsorption of FLAs

Static cement fluid loss volumes and the amount of terpolymers adsorbed on cement were determined. Static fluid loss volume represents the effectiveness of the FLA. The higher the amount of terpolymers adsorbed on cement, the lower the fluid loss and the more effective is the FLA. Figure 5 shows that, at a dosage of 0.5% bwoc, both FLAs perform similar. CaAMPS-*co*-NNDMA-*co*-CaVPA produces a slightly higher API fluid loss (42 mL/30min) than CaAMPS-*co*-NNDMA-*co*-CaAMPPA (36 mL/30min). Correspondingly, the adsorbed amount of the first terpolymer (4.6 mg/g) is slightly lower than the adsorbed amount of the polymer containing the monomer with the longer side chain (4.7 mg/g). This is in line with previous work in which a direct relationship between the volume of fluid loss and the adsorbed amount of FLA polymer was found.[5]

FLA behavior in the presence of AFS

For combinations of 0.5% bwoc FLA and 0.4% bwoc AFS, API fluid loss, adsorbed amount of each admixture and cement slurry rheology were measured. The relationship between API fluid loss volumes and adsorbed amounts of FLA and AFS are shown in Figure 6. In presence of AFS, the adsorbed

amount and effectiveness of CaAMPS-*co*-NNDMA-*co*-CaVPA remain unchanged whereas CaAMPS-*co*-NNDMA-*co*-CaAMPPA even slightly improves its efficiency. The difference is induced by additional adsorption of the dispersant. CaAMPS-*co*-NNDMA-*co*-CaVPA does not allow AFS adsorption whereas in presence of CaAMPS-*co*-NNDMA-*co*-CaAMPPA, the dispersant can adsorb as well. Adsorption of AFS also is evident from a lower rheology of the cement paste as shown in Table VI.

Generally, water-soluble polymers adsorbed onto mineral surfaces can adopt different conformations. These are "train" type (all functional groups positioned along the trunk chain of the polymer are bound to the surface), "loop" or "tail" type (only partial binding of the polymer to the surface).[19,22,23] A change in the adsorbed conformation of CaAMPS-*co*-NNDMA-*co*-CaAMPPA in the presence of AFS can be assumed to explain the dispersant adsorption (Fig. 7). In absence of AFS, both CaAMPS-*co*-NNDMA-*co*-CaVPA and CaAMPS-*co*-NNDMA-*co*-CaAMPPA assume a flat adsorbed conformation on cement particles ("train" type), resulting in a maximum number of contact points between polymer segments and the surface of cement. This way, the stretched FLA molecules occupy maximum surface area. Because of its strong interaction with calcium on the cement surface, the adsorbed conformation of CaAMPS-*co*-NNDMA-*co*-CaVPA does not change in presence of AFS dispersant. Thus, AFS cannot adsorb. No adsorption and consequently ineffectiveness of the AFS dispersant was confirmed by rheological measurements of the cement slurry (Table VI).

In contrast, CaAMPS-*co*-NNDMA-*co*-CaAMPPA allows simultaneous adsorption of dispersant (2.0 mg/g) and FLA (4.7 mg/g). The reason is a change of its adsorbed conformation from "train" in absence of AFS to "loop" or "tail" in presence of AFS. This
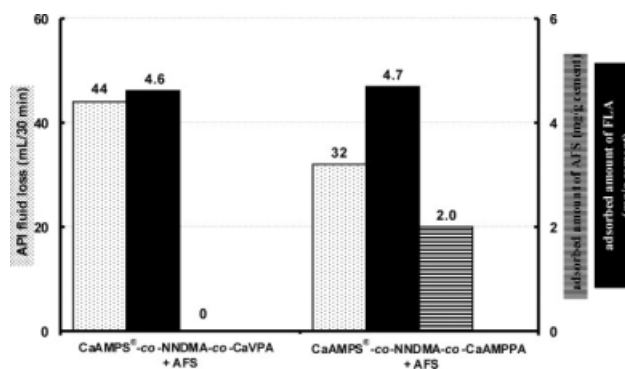

Figure 6 API fluid loss (dotted bars), adsorbed amount of FLA (black bars), and AFS (lined bars), respectively, for cement slurries containing the synthesized FLA polymers (dosages: FLA 0.5%bwoc, AFS 0.4%bwoc).

effect is owed to its lower calcium chelating tendency and a weaker bond to the surface. It allows the macromolecule to assume an adsorbed conformation with fewer contact points to calcium atoms on the surfaces of hydrating cement. Thus, only a fraction of the FLA polymer functionalities actually adsorb onto the surface, with the remainder protruding freely into the cement pore solution in the form of loops and tails.[24] Apparently, complexation and ion condensation between freely protruding, unadsorbed terpolymer segments and Ca^{2+} ions result in a more effective plugging of the pores between cement particles, thus reducing the water loss from the slurry. Because of its high adsorbed amount, the AFS also can become effective as dispersant (Table VI).

CONCLUSIONS

The calcium binding capacity of polymers appears to be a key parameter which determines their adsorption behavior on cement surfaces and thus their performance as admixture in cement-based systems. According to calcium chelating and adsorption measurements as well as the slightly higher value of the molar anionic charge density, the phosphonate anchor groups present in CaAMPS-co-NNDMA-co-CaVPA have a higher affinity towards Ca^{2+} ions than those in CaAMPS-co-NNDMA-co-CaAMPPA. Obviously, the ability of these macromolecules to bind Ca^{2+} ions is strongly affected by the steric position of the phosphonate and their neighboring groups. When incorporated into the copolymer, the phosphonate groups of AMPPA are present at a distance of several bonds to the backbone. This diminishes the charge density along the chain and gives the macromolecule more flexibility and conformational freedom. This way, interaction with Ca^{2+} is reduced. It also results in a higher number of poten-

TABLE VI
Rheology(Shear Stress) of Cement Slurries Containing Combinations of FLA (0.5% bwoc Dosage) and AFS Dispersant (0.4% bwoc), Measured at Different Shear Rates

Admixture combination	Shear stress(lbs/100 ft²) at shear rate 600-300-200-100- 6- 3 rpm
Blank	122- 83- 69- 54-23-17
AFS	41- 17- 11- 6- 3- 1
CaAMPS-co-NNDMA-co-CaVPA	>300-212-159- 98-20-18
CaAMPS-co-NNDMA-co-CaVPA + AFS	>300-225-168-105-25-21
CaAMPS-co-NNDMA-co-CaAMPPA	293-176-127- 72- 7- 4
CaAMPS-co-NNDMA-co-CaAMPPA + AFS	276-156-110- 61- 5- 3

a) CaAMPS®-co-NNDMA-co-CaVPA b) CaAMPS®-co-NNDMA-co-CaAMPPA
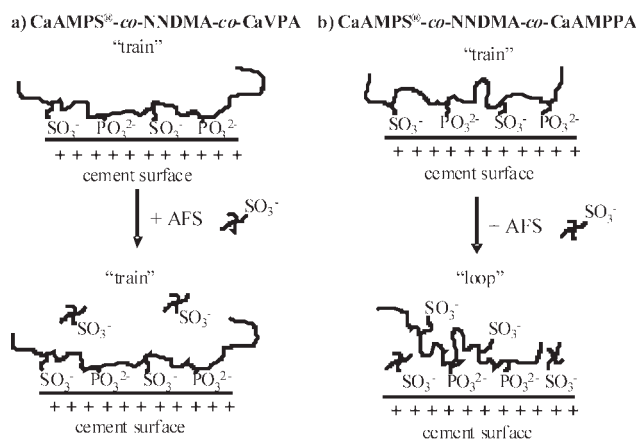
Figure 7 Schematic illustration of the proposed adsorbed conformations of synthesized FLA polymers on cement surface in absence and presence of AFS dispersant.

tial adsorbed conformations on cement surface. Hence, when competing with another adsorbate such as e.g., AFS, CaAMPS-co-NNDMA-co-CaAMPPA does not adsorb in stretched but in "loop" or "tail" mode. Simultaneous adsorption of FLA and AFS is possible by a change of its adsorbed conformation.

As a result of the greater distance of the phosphonate group from the backbone of the polymer and the higher conformational flexibility of 2-acrylamido-2-methylpropane phosphonate, the binding capability of its phosphonate groups towards Ca^{2+} ions diminishes and hence its strength as anchor group. In contrast, the vicinal position of the phosphonate group in VPA to the hydrophobic methyl groups present in AMPS or NNDMA increases the electrostatic attraction between the polymer and Ca^{2+} ions on the binder surface.

Our study demonstrates that relatively minor modifications in the composition of a functional polymer can severely impact its performance in presence of other admixtures. "Incompatibility" problems between admixtures can be eliminated by fine-tuning their molecular architectures with respect to the distance of the anionic functionalities from the backbone which leads to a different adsorption behavior. Understanding the processes occurring between the macromolecule and the mineral surface at the molecular level can help to develop concepts for improved admixture systems to be used in cement and concrete.

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