Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes

Yan-Rong Zhang, Xiang-Ming Kong, Zhen-Bao Lu, Zi-Chen Lu, Shan-Shan Hou

Abstract

The traditional polycarboxylate (PC) superplasticizers are usually negatively charged polymers, in which the carboxylate functionalities are responsible for their adsorption on cement surface driven by electrostatic interaction. This paper investigates the impacts of the charge characteristics of PC co-polymers on their adsorption behaviors and the retardation effects on cement hydration. PC co-polymers with variation of their charge species were synthesized by co-polymerizing the macro-monomer with selected anionic and cationic monomers. Adsorption and retardation effects on cement hydration of the monomers, their homo-polymers and the PC co-polymers were studied in cement pastes by total organic carbon tests and calorimetry respectively. Results show that in cement pastes, no adsorption and retardation were observed for the monomers while for their corresponding homo-polymers, different extents of adsorption and retardation were found. Charge characteristics of PC co-polymers strongly determine their adsorption behaviors and retardation effects, in the order of -COO⁻ > -SO₃⁻ > -N+O⁻. © 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Superplasticizers are nowadays commonly used to improve the workability of concrete in practice, and are becoming indispensable components in concrete to modify the workability of fresh concrete and/or to reduce the water demand. The working mechanism of superplasticizers in concrete is to disperse the flocculated cement grains and to release entrapped water by creating a repulsive force among them [1]. It is widely accepted that the dispersing function of superplasticizers in cement pastes is achieved through adsorption on the surface of cement grains. With the surface of heterogeneous charge distribution originating from different mineral phases, cement grains can considerably adsorb charged superplasticizer molecules due to the electrostatic interaction between cement surface and superplasticizers [2,3]. For polycarboxylate based superplasticizers (PCs), the strong electrostatic interaction of anionic carboxylate groups located in the polymer backbone with the Ca²⁺ bound as counter-ions on the mineral surfaces also facilitates the adsorption of PC molecules on cement grains [4,5]. Usually, the adsorbed superplasticizer molecules could bring about certain effects on cement hydration, generally retardation [6,7]. Their coverage on surface of cement grains is thought to hinder the exchange of water and ions at the cement–solution interface, thereby decelerating cement hydration [8]. In addition, the nucleation and growth kinetics and the morphology of hydration products may also be altered by addition of superplasticizers [9–11]. Different superplasticizers exhibit different adsorption behaviors and retardation effects, closely correlating with their specific molecular architecture.

Extensive research has been carried out for better understanding and explaining the structure–property relationship of superplasticizers. Burgos-Montes et al. [12] found that the traditional admixtures such as lignosulfonate and sulfonated naphthalene-type superplasticizers had high adsorption values on cement and they supposed that the adsorption was related to the charge density and the configuration of the adsorbed molecules. Houst et al. [13,14] reported that the PCs with long side chains presented stronger dispersing ability than lignosulfonates and sulfonated naphthalene-type superplasticizers in spite of the lower adsorption amount. More specifically, Winnefeld et al. [7] investigated the effects of superplasticizers with varied structures and found that PCs with higher molecular weight, lower side chain density and shorter side chains were favorable to a high adsorption amount on cement surface. Pourchet et al. [15] reported that not only the content of the carboxyl groups, but also their repartition along the polymer backbone would significantly affect the adsorption behaviors and the retardation effects of the carboxyl groups containing polymers. Additionally, Zingg et al. [16] and Pourchet et al. [8] pointed out that the retarding effects of PCs were related to the backbone charge density and the number of –COO⁻ groups in the adsorbed superplasticizer molecules, while Yamada et al. [17] supposed that higher concentrations of the remaining carboxylic and sulfonic groups in the aqueous phase could effectively delay the setting of cement paste.
Previous insights mainly concerned the effects of polymer architecture on the adsorption, zeta potential, rheological and hydration behaviors of cement paste. There is so far no study dedicated to the effects of the various functional groups and the charge specie of backbone in PCs on the adsorption and cement hydration. This study aims at elucidating the correlations of charge characteristics of the backbone of PC superplasticizers with their adsorption behaviors and retardation effects in cement pastes. The typical backbone of PC molecules is mainly composed of acrylic acid (AA) repeating units, which makes the polymer anionically charged in alkaline solution. In order to disclose the influences of the charge feature of molecules on the adsorption and the retardation effects in cement pastes, organic monomers possessing different charges in aqueous solution, including AA, sodium p-styrene sulfonate (SSS), sodium methylpropanesulfonic acid (AMPS), ammonium persulfate (APS) and sodium methyl acryl sulfonate (SMAS), were used as received (all analytical grade of chemicals, acrylic acid (AA), sodium p-styrene sulfonate (SSS) as well as 3-(methacryloylamino)propyltrimethyl ammonium chloride (MAPTAC), and their corresponding homo-polymer, were chosen to investigate their adsorption behaviors in cement pastes by total organic carbon (TOC) tests and their impacts on cement hydration by means of isothermal calorimetry.

Self-synthesized amphoteric comb-shaped PC co-polymers with variation of charging species by replacing AA monomer in the preparation of PC co-polymers with the monomer of MAPTAC, were employed to study the influences of the negative charges and the positive charges on the behaviors of PC co-polymers in cement system. The impacts of the carboxyl and sulfonic groups with the same negative charge density were also compared by adjusting the molar ratios of carboxyl to sulfonic groups in backbones. This research is expected to bring new insights about the influences of PC superplasticizers on cement hydration and to lay the theoretical basis for the development of new superplasticizers with more efficient and robust performance.

2. Experimental

2.1. Materials

2.1.1. Cement

Two batches of Portland cement 42.5R complying with the Chinese standard GB175-2007 were used, whose composition are listed in Table 1. The composition of the cement was obtained according to the Chinese Standard GB/T176-2008 “Chemical Analysis of Cement”, which is consistent with the European standard EN 196-2:2005. The contents of oxides were measured by X-ray fluorescence. The Franke method and the Bogue method were respectively used to analyze the contents of f-CaO and mineral phases. The fineness of cement I is 2.3% and the density is 3.10 g·cm$^{-3}$ with a Blaine value of 350 m$^2$/kg. For cement II, the fineness, density and Blaine value are 2.5%, 3.09 g·cm$^{-3}$ and 346 m$^2$/kg respectively. Fineness of cement is measured by sieving it on a sieve with a mesh size of 0.08 mm. The proportion of the remaining cement with size larger than the mesh size is thus determined according to the British standard BS EN 196-6:2010.

2.1.2. Organic materials

Analytical grade of chemicals, acrylic acid (AA), sodium p-styrene sulfonate (SSS), 3-(methacryloylamino)propyltrimethyl ammonium chloride (MAPTAC), sodium methyl acryl sulfonate (SMAS), 2-acrylamide-2-methylpropanesulfonic (AMPS) acid, ammonium persulfate (APS) and 3-mercaptopropionic (MPA) acid, were used as received (all purity). Deionized water was used in all experiments in this study including synthesis of polymers and preparation of cementitious mixtures. Poly(acrylic acid) (PAA) with weight average molecular weight (Mw) of ca. 5000 was provided by Beijing Chengzheng Yongchang Chemicals Co. Ltd. Analytical grade of poly(sodium-p-styrene sulfonate) (PSSS) with Mw of 70,000 was purchased from Acros Organics. Cationic polymer, poly[3-(methacryloylamino)propyltrimethyl ammonium chloride] (PMAPTAC) was synthesized via semi-batch radial polymerization by using APS as initiator at 80 °C. 45.0 g of water was pre-charged into a flask vessel equipped with two feeding pipes. The flask was firstly washed by using nitrogen gas for 3 times and then the mixture was heated up to 80 °C in oil bath. 335.0 g of MAPTAC solution with a mass concentration of 32.8% and 65.0 g of APS solution with a mass concentration of 1.7% were then separately fed into the vessel dropwise in 2.5 h and 3.0 h respectively. After completion of both feedings, the reactant mixture was kept at 80 °C under stirring for another 2.0 h to complete the polymerization. An aqueous solution of PMAPTAC with solid content of ca. 25.0% was obtained. The synthesized PMAPTAC sample was purified via dialysis and then analyzed by size exclusion chromatography (SEC) to measure the molecular weight distribution (as described in Sections 2.2.1 and 2.2.2.). From the dialysis experiment, it was found that the polymer fraction in the solid part of the synthesized PMAPTAC sample was as high as 95.0%, suggesting successful polymerization. The Mw and polydispersity of the purified PMAPTAC were 59,030 and 2.436 respectively. The chemical structures of AA, SSS, and MAPTAC are presented in Fig.1.

Self-synthesized amphoteric comb-shaped PC co-polymers with variation of charging species by replacing AA monomer in the preparation of PC co-polymers with the monomer of MAPTAC, were employed to study the influences of the negative charges and the positive charges on the behaviors of PC co-polymers in cement system. The impacts of the carboxyl and sulfonic groups with the same negative charge density were also compared by adjusting the molar ratios of carboxyl to sulfonic groups in backbones. This research is expected to bring new insights about the influences of PC superplasticizers on cement hydration and to lay the theoretical basis for the development of new superplasticizers with more efficient and robust performance.

Table 1

<table>
<thead>
<tr>
<th>Chemical composition (mass %)</th>
<th>Mineral composition (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>I</td>
<td>22.10</td>
</tr>
<tr>
<td>II</td>
<td>21.56</td>
</tr>
</tbody>
</table>

Note: The composition was obtained according to EN 196-2:2005 and the Chinese Standard GB/T176-2008 “Chemical Analysis of Cement”. This research is expected to bring new insights about the influences of PC superplasticizers on cement hydration and to lay the theoretical basis for the development of new superplasticizers with more efficient and robust performance.

A detailed description of the preparation procedure of the above-mentioned polymers (PAM and PAS series) is summarized as following. Monomers with mixed proportion as described in Table 2, together with the chain transfer agent, were dissolved in deionized water and an aqueous solution with a mass concentration of 55.0% was prepared. An initiator solution with a mass concentration of 2.0% was prepared.

Table 2

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>1.0:0.47:0.13</td>
</tr>
<tr>
<td>SSS</td>
<td>1.0:0.25</td>
</tr>
<tr>
<td>MAPTAC</td>
<td>1.0:0.25</td>
</tr>
<tr>
<td>PMAPTAC</td>
<td>1.0:0.25</td>
</tr>
</tbody>
</table>

The comb-shaped PC superplasticizer was prepared via semi-batch free radical polymerization at 80 °C by co-polymerizing the monomers of AA, MPEGMA and SMAS with a monomer molar ratio of 1.0:0.47:0.13, based on the basic recipe PAS100-0, given in Table 2 [18]. The initiator for polymerization was APS and MPA was used as chain transfer agent to control the molecular weight. By partly replacing the monomer AA with AMPS in the polymerization recipes, the ratio of the −COO$^-$ groups to the −SO$_3$H groups can be adjusted without changing the charge density in the synthesized PC molecules. Thus, the effects of the −COO$^-$ and −SO$_3$H groups in PC molecules on their behaviors in cementitious system can be studied. The synthesis formula of the comb-shaped PC polymers is presented in Fig. 2.

Amphoteric PC co-polymers were synthesized based on the basic recipe PAM100-0 (Table 2), in which the molar ratio of monomer AA to MPEGMA and SMAS was fixed at 1.0:0.25. Cationic charges can be introduced into the PC molecules by simply replacing the monomer AA with MAPTAC at a certain ratio and the synthesized PC molecules become amphoteric. Complete replacement of AA with MAPTAC makes the produced PC molecule turn to a cationic one (PAM0-100). The synthesis formula of the amphoteric PC polymers is presented in Fig. 3.
by dissolving APS in deionized water. In the polymerization process, 350.0 g of monomer solution was used and the molar ratio of initiator to total monomers was fixed at 1.0%. A flask vessel filled with 35.0 g of water and 35.0 g of monomer solution as pre-charge and equipped with two feeding pipes, was firstly washed by using nitrogen gas for 3 times and heated up to 80 °C in an oil bath. Then the initiator solution and the rest of the monomer solution were separately fed into the vessel dropwise over 2.5 h and 2.0 h respectively. The inside temperature was kept constant at 80 ± 2 °C during polymerization. After complete dosing, the whole reactant mixture was kept at 80 °C for an additional post-polymerization time of 30 min under stirring to complete polymerization and then was allowed to cool down to room temperature at 25 °C. The obtained products appeared to be yellowish transparent solutions with solid contents in a range of 36.0–38.0 wt.%.

2.2. Characterization of the synthesized polymers

2.2.1. Size exclusion chromatography

SEC has been a standard method for polymer fractionation and analysis of molecular weight distribution of polymers based on separation of polymer fractions with different molecular sizes, i.e. hydrodynamic volume. Integration of a light scattering instrument in the SEC system allows obtaining absolute molecular weights that do not rely on calibration with standards of known molecular mass. In this study, SEC equipped with a multi-angle laser light scattering (LS) detector (DAWN HELEOS II, Wyatt Technology, USA) and a refractive index (RI) detector (Optilab rEX, Wyatt Technology, USA) was used to determine the Mw, number average molecular weight (Mn) and the polydispersity (PDI) of the prepared polymers. Meanwhile, polymer content in the prepared polymer solution can be estimated by separation of polymers and oligomers with relatively high molecular weight from the synthesized product, which contains polymers, oligomers, macro-monomers (Mw of ca. 1300) and probably residual monomers with molecular weight lower than 1000. For all polymers, 0.1 mol/L NaNO₃ solution at a pH of 7 was used as the eluent in SEC measurement. The synthesized polymers were diluted to a concentration of 5 mg/mL (10 mg/L for samples of PAM0-100, PAS0-100, PMAPTAC) and directly injected into a 0.2 mL loop with a spectra system autosampler. Temperature during measurement was kept constant at 25 °C and the flow rate was adjusted to 0.5 mL/min. SEC columns of SB-804 HQ connected with SB-802.5 HQ (OHpak, Shodex, USA) were used for SEC measurement of all polymers.

2.2.2. Purification of synthesized polymers

As it is well understood that the synthesis of PC co-polymers cannot reach a conversion of 100% and known from the result of SEC measurement, the obtained samples from the synthesis of the PC co-polymers contain fractions of polymer, oligomer, un-reacted macro-monomer and those monomers with smaller molecular weights, and a tiny amount of salts from the decomposition of the initiator. In this study, the dialysis technique was adopted to remove un-reacted monomers, salts and a part of oligomers with small molecular weights from the samples and to obtain purified PC co-polymer solutions. A cellulose ester semipermeable membrane MD44-7 with nominal molecular weight cut-off of 7000 Da provided by Beijing Ruida Henghui Science and Technology Development Co. Ltd was used, which allows globulin with a molecular weight of 7000 and smaller molecules to pass through. The synthesized product was firstly diluted to 10.0 wt.% and then 40 mL of the diluted polymer solution was introduced into a dialysis bag with a diameter of 25 mm and a length of 300 mm, which is made of the semipermeable membrane. Subsequently, 10 completely sealed dialysis bags filled with the polymer solutions were placed into a container filled with 5000 mL deionized water as dialysate. In order to accelerate the diffusion process of the monomers and salts across the semipermeable membrane, the water bath was kept at 40 °C under stirring and renewed every 3 h. The electrical conductivity of the dialysate was

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**Table 2**

Monomer combination in synthesis of the PC co-polymers.

<table>
<thead>
<tr>
<th>NO.</th>
<th>AA</th>
<th>MPEGMA1300</th>
<th>SMAS</th>
<th>AMPS</th>
<th>MAPTAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM100-0</td>
<td>1</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>PAM80-12</td>
<td>0.88</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>PAM75-25</td>
<td>0.75</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>PAM50-50</td>
<td>0.5</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>PAM0-100</td>
<td>0</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>PAS100-0</td>
<td>1</td>
<td>0.47</td>
<td>0.13</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>PAS70-30</td>
<td>0.7</td>
<td>0.47</td>
<td>0.13</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>PAS50-50</td>
<td>0.5</td>
<td>0.47</td>
<td>0.13</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>PAS0-100</td>
<td>0</td>
<td>0.47</td>
<td>0.13</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

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**Fig. 1.** Schematic drawing of chemical structure of the monomers used in this study (a) AA, (b) SSS and (c) MAPTAC.

**Fig. 2.** Synthesis formula of the PC polymers containing both the carboxyl and sulfonic groups.
measured by using a conductivity meter (FE30, Mettler Toledo, Switzerland) every 3 h before the dialysate was renewed. It is noticed in Fig. 4 that the electrical conductivity of the dialysate sharply decreased at the beginning of the dialysis (first 24 h), which indicated a fast diffusion of the salts and monomers from the sample inside the dialysis bag to the water bath. With continuous dialysis for 4 days, the electrical conductivity of dialysate kept slowly decreasing. Knowing that the electrical conductivity of deionized water was about 10 μS/cm, we ended the dialysis process when the electrical conductivity of dialysate dropped below 30 μS/cm. Thus, most of the salts, residual monomers and oligomers that are able to pass across the semipermeable membrane were effectively removed from the sample. After purification by dialysis, the solid content of the obtained solution was measured. From this value, information about the polymer content in the original synthesized product can be calculated. In this manner, the synthesized products, including the PMAPTAC homo-polymer, and PAM and PAS co-polymers were purified for Fourier transform infrared (FTIR) spectrum analysis and for all the following investigations on their behaviors in cementitious system.

2.2.3. Fourier transform infrared (FTIR) spectrum

The chemical structures of the purified co-polymers were characterized by a FTIR (Nicolet 6700 FTIR, Thermo Fisher Scientific, USA) instrument with a resolution of 4 cm⁻¹. The purified PC solution was homogeneously mixed with KBr salt and completely dried in a vacuum oven at 80 °C. The mixture was pressed into a tablet and then scanned in the transmission mode from 400 to 4000 cm⁻¹ at a room temperature of 25 °C.

2.3. Cement paste preparation

The adsorption of the abovementioned monomers, homo-polymers and the purified PC co-polymers as well as their influences on cement hydration was studied in cement pastes. For the investigation on organic monomers AA, SSS, MAPTAC and the corresponding homo-polymers, the cement pastes were prepared with a fixed water to cement ratio (W/C) of 0.4 and the addition of the monomers/polymers was 16.5 μmol/g cement with identical molar quantity of the functional groups. The quantity of the monomers was counted by mole of the substance and the quantity of the homo-polymers was measured by mole of the repeating units. Thus, the influences of the functional groups of COO⁻, SO₃⁻ and N⁺ on the adsorption on cement surface and on cement hydration were studied. Their mass to cement ratios are also listed in Table 3.

For investigation on the organic monomers AA, SSS, MAPTAC and the corresponding homo-polymers, cement I was used, while for the study on those comb-shaped PC co-polymers, cement II was employed as a different batch from the same type as cement I. The W/C of the cement pastes was adjusted to 0.35 in order to avoid bleeding phenomenon because of the water reducing effect of those PC co-polymers. The addition of the purified PC co-polymers in cement pastes was varied as 0.1%, 0.2% and 0.4% by weight of cement (bwoc), respectively.

All the cement pastes were prepared in accordance with the Chinese standard GB/T8077. Water and chemicals were firstly added into a mixer, and then cement was gradually introduced over a time span of 2 min into the mixer at 62 rpm. After a 10 sec interval, mixing was resumed for an additional 2 min at 125 rpm. The freshly mixed cement pastes were instantly subjected to the following measurements.

2.4. Measurements on cement paste

2.4.1. Adsorption amount

The adsorption amounts of the chemicals on cement grains were determined by total organic carbon (TOC) measurement using a TOC analyzer (Shimadzu, TOC-VCPH, Japan), the measurement range of which is from 4 ppb to 4000 ppm. After it was well mixed with a mixing time of 4 min, the fresh cement paste was immediately centrifuged at 3000 rpm for 10 min. A clear supernatant solution was then collected by using a membrane filter with a pore diameter of 0.22 μm. Subsequently, the supernatant solution was diluted with deionized water to a suitable concentration for TOC measurement, which should be located in the range of 20–60 mg/L in order to match the 100 mg/L standard curve.

Fig. 3. Synthesis formula of the amphoteric PC polymers containing the cationic group \(\text{\textsc{N}^+} \cdot\).
used in the TOC analyzer. The 100 mL diluted solution was used for the measurement of concentration of carbon element. Finally, the adsorption amount on cement of per unit mass could be calculated by subtracting the amount of the organic chemicals remaining in the aqueous solution from the amount initially added in cement paste. It should be mentioned that a tiny amount of carbon (ca. 0.014 mg/g cement) can be detected in the blank cement paste and it should be subtracted in the calculation of the adsorption amounts of the chemicals in cement pastes. Given that the different molecular weights for AAA, SSS and MAPTAC and the corresponding homo-polymers, their adsorption amounts in cement pastes were expressed in the form of molar amount of the functional groups (μmol/g cement) for the purpose of comparing the effects of charge properties on the adsorption behaviors. For the comb-shaped PC co-polymers, their adsorption mass on cement of per unit mass (mg/g cement) was discussed.

2.4.2. Precipitation measurement

It has been well established that the –COO⁻ groups may chelate the Ca²⁺ ions in solution [4,8,17]. Consequently, when AA or PAA is added into fresh cement paste, complexes, which are either water soluble or water insoluble may be formed due to the reaction between –COO⁻ and Ca²⁺ in aqueous phase of the fresh cement paste. If water insoluble products are formed, which are then precipitated from the solution phase, the adsorption measurement as described in Section 2.4.1 may give wrong results because the carbon contained in the precipitates is falsely considered as the adsorbed carbon on cement surface. Thus, the adsorption amounts of chemicals on cement surface will be overestimated. In order to con rm whether precipitates were formed when the chemicals were added into cement pastes, precipitation experiments were conducted by mixing cement pore solution with AA, SSS, MAPTAC, PAA, PSSS and PMAP TAC respectively.

A blank cement paste with W/C of 0.4 was prepared with the same mixing procedure as described in Section 2.3. After mixing for 4 min, supernatant pore solution of the blank cement paste was obtained by centrifuging in accordance with the method described in Section 2.4.1. Subsequently, a 100 mL pore solution was taken and a selected chemical was added into the fresh cement paste, complexes, which are either water soluble or water insoluble may be formed due to the reaction between –COO⁻ and Ca²⁺ in aqueous solution from the amount initially added in cement paste. It should be mentioned that a tiny amount of carbon (ca. 0.014 mg/g cement) can be detected in the blank cement paste and it should be subtracted in the calculation of the adsorption amounts of the chemicals in cement pastes. Given that the different molecular weights for AAA, SSS and MAPTAC and the corresponding homo-polymers, their adsorption amounts in cement pastes were expressed in the form of molar amount of the functional groups (μmol/g cement) for the purpose of comparing the effects of charge properties on the adsorption behaviors. For the comb-shaped PC co-polymers, their adsorption mass on cement of per unit mass (mg/g cement) was discussed.

2.4.3. Zeta potential

Zeta potential of cement pastes containing different chemicals was measured by using an acoustic & electroacoustic spectrometer (Dispersion Technology, DT1201, USA), with a measuring range of −3000 mV to +3000 mV. The amplitude of error in zeta potential measurement is in the vicinity of 5 mV. Because of the poor fluidity of cement pastes at W/C of 0.4, some of which showed spread diameters as small as 60 mm, the W/C in all the cement pastes was heightened to 0.5 in order to ensure the operability and the accuracy of the zeta potential measurement. Prior to the measurement, a zeta probe was calibrated by using the pore solution of cement paste as ionic background for the zeta potential measurements of the corresponding cement paste. After a mixing time of 4 min, 40 mL fresh paste was immediately transferred into a 50 mL sample cell equipped in DT1201. The probe was dipped into the well mixed fresh cement paste and the zeta potential was then measured. During the measurement, the cement paste was kept stirring by using a magnetic mixer at 200 rpm in order to keep the mixture homogeneous. The measurement of zeta potential was repeated 7 times over 10 min for each sample and an average of these zeta values was recorded.

2.4.4. Iso-thermal calorimetry

TAM-air micro-calorimeter (Thermometric AB, Sweden) was employed to monitor the heat evolution during cement hydration. The measurement error is approximately 20 μW. Before tests, the calorimeter was regulated at a constant temperature of 25 ± 0.02 °C and then equilibrated for 24 h. Thereafter, the freshly mixed samples were promptly decanted to an ampoule of 20 mL and then placed into the channels. The heat evolution within 80 h was recorded.

2.4.5. Fluidity

A fluidity test was conducted to evaluate the plasticizing efficiency of the synthesized PC co-polymers in cement pastes with W/C of 0.35. The fluidity of the fresh cement pastes with the addition of various PC co-polymers (PAM series and PAS series) was characterized by spread diameter in a mini-cone test, where a copper cone with a top diameter of 36 mm, bottom diameter of 60 mm and height of 60 mm was used. After well mixed, the fresh paste was poured into the cone and then, the cone was quickly lifted up. After the paste stopped flowing, the average value of four crossing spread diameters of the cement paste was recorded.

3. Results and discussion

3.1. AA, SSS, and MAPTAC and their corresponding homo-polymers

The adsorption amounts of the organic monomers including AA, SSS, MAPTAC as well as the corresponding polymers on cement grains were
obtained by TOC measurement in combination with the precipitation experiments. As shown in Fig. 5, it is clearly seen that only the addition of PAA results in precipitation in the pore solution, while the pore solutions with addition of other chemicals keep transparent. The precipitation ratio of PAA was measured as 15.0% in the pore solution and this portion of PAA should be deducted to obtain the real adsorption amount, marked as the corrected adsorption amount in Table 3.

Table 3 presents the adsorption amount of each chemical as well as the variation of zeta potential of cement pastes. It is clearly seen that the monomers, AA, SSS and MAPTAC are hardly adsorbed on the surface of cement grains. Correspondingly, the zeta potential of cement paste is just slightly changed with the addition of these organic monomers within ±5 mV, which is regarded as the measuring error. On the other hand, significant adsorption of PAA, PSSS and PMAPTAC on cement grains is found and their adsorption amounts vary in the circumstance of identical initial addition of molar amount. Specifically, large proportions of PAA and PSSS added in cement paste are adsorbed on cement grains, while only a minor part of PMAPTAC is adsorbed. Meanwhile, the adsorption of these polymers leads to notable changes on the zeta potentials of the fresh cement pastes. PAA and PSSS remarkably decrease the zeta potential from 6.3 mV to large negative values, whereas higher positive zeta potential is observed in the presence of PMAPTAC in fresh cement paste. Comparing the adsorption behavior of PAA with that of PSSS, it is interesting to note that PSSS more significantly decreases the zeta potential than PAA although less PSSS is adsorbed on cement grains.

It has been well reported that the adsorption of chemical admixtures on cement grains is related to the charge types and the charge density in the molecules of the admixtures [19]. The higher charge density usually brings stronger interaction of admixtures with the mineral surfaces and consequently facilitates the adsorption on cement grains. However, when those organic monomers and the corresponding homo-polymers are compared, the monomers AA, SSS and MAPTAC fail to adsorb on cement grains although they possess the same charge density as their corresponding homo-polymers. This indicates that there must exist another factor influencing the adsorption capability of the chemical admixtures. Plank [19,20] stated that conformation of macromolecule, intermolecular forces and entropic effects also determined the adsorbed amount of chemical admixtures due to their contributions to the changes in free energy. The adsorption of chemicals on a solid surface is an entropy reduction process, which is unfavorable to the free energy reduction. Thus, the monomers are much more difficult to be adsorbed on cement surface than their corresponding homo-polymers due to their larger entropic loss upon the adsorption. In conclusion, the results in Table 3 confirm that the monomers are hardly adsorbed on cement surface while the adsorption of their corresponding homo-polymers is quite obvious, although the electrostatic interactions are quite similar in the two cases.

With regard to the different adsorption behaviors of PAA and PSSS from PMAPTAC, it should be attributed to the heterogeneous charge distribution on the surface of hydrating cement grains originating from different hydrating phases [20]. When cement grains come into contact with water, the fast dissolution and the early hydration of cement build surface charges on cement grains. Silicate phases are found to possess a negatively charged surface whereas aluminate hydrates are usually positively charged. The positive zeta potential value of blank cement paste as seen in Table 3 confirms that the positively charged area covers a larger part in fresh cement paste, which is due to the faster reaction of the aluminate phases at the early stage. As a consequence, the hydrating cement grains provide more adsorption sites for the

Fig. 5. Solubility examination of the organic monomers and the homo-polymers in pore solution of fresh cement paste: pore solution of blank cement paste (a), pore solutions mixed with AA (b), with PAA (c), with SSS (d), with PSSS (e), with MAPTAC (f) and with PMAPTAC (g).

Fig. 6. Schematic drawing of the adsorption of (a) PAA and (b) PSSS on the surface of cement grains.
negatively charged ions than the positively charged ones. This is the reason why the adsorption amounts of PAA and PSSS with anionic charges are prominently larger than that of PMAPTAC with cationic charges. Such way, the addition of PAA and PSSS decreases the zeta potential of the pastes to larger negative values whereas PMAPTAC increases the zeta potential from the initial value of 6.3 mV to 25.2 mV.

Aside from being adsorbed on the positively charged aluminate surface under electrostatic attraction forces, PAA is also able to be adsorbed on the negatively charged silicate surface through the bridging ions Ca\(^{2+}\) due to the complexation between the COO\(^{-}\) groups and Ca\(^{2+}\) as illustrated in Fig. 6 [20]. In contrast, PSSS does not have such an effect with Ca\(^{2+}\). Thus, the adsorbed amount of PAA is higher than that of PSSS as seen in Table 3. In the same way, the adsorption of PAA on the negatively charged mineral surfaces via Ca\(^{2+}\) bridging leads to less reduction of the zeta potential of cement paste due to the coverage on the anionic surface and the extension of the shear plane. In addition, the adsorbed PAA molecules may further catch Ca\(^{2+}\) in solution to form complexes (shown in Fig. 6), which may also weaken the capability of PAA to decline the zeta potential value of the cement paste to some extent. A similar phenomenon has been reported by Yoshioka [21]. He proposed that the adsorption of anionic admixtures on the silicates through chelation effects had little influence on the zeta potential of cement paste. Thus, in the premise of owning the same charge density, PAA leads to less reduction of zeta potential of cement paste than PSSS does, although the adsorption ratio of PAA on cement surface is higher than that of PSSS.

<table>
<thead>
<tr>
<th>Item</th>
<th>(t_A) (h)</th>
<th>(\frac{dQ}{dt}_A) (mW/g)</th>
<th>(Q_A) (J/g)</th>
<th>(K_{A-B}) (mW/(g·h))</th>
<th>(\frac{dQ}{dt}_C) (mW/g)</th>
<th>(Q_{A-C}) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.94</td>
<td>0.52</td>
<td>1.51</td>
<td>0.364</td>
<td>2.95</td>
<td>49.71</td>
</tr>
<tr>
<td>PMAPTAC</td>
<td>2.21</td>
<td>0.47</td>
<td>1.85</td>
<td>0.382</td>
<td>3.03</td>
<td>50.11</td>
</tr>
<tr>
<td>PSSS</td>
<td>3.39</td>
<td>0.33</td>
<td>5.31</td>
<td>0.297</td>
<td>2.75</td>
<td>50.09</td>
</tr>
<tr>
<td>PAA</td>
<td>6.14</td>
<td>0.18</td>
<td>9.09</td>
<td>0.128</td>
<td>2.54</td>
<td>71.86</td>
</tr>
</tbody>
</table>

Fig. 7. Influences of AA, SSS and MAPTAC on the exothermic heat flow of cement hydration.

Fig. 8. Influences of PAA, PSSS, MAPTAC and MPEGMA on the exothermic heat flow of cement hydration.

Fig. 9. A typical exothermic heat flow curve of cement hydration.

Fig. 10. SEC chromatograms of the PAM co-polymers (LS: light scattering, RI: refractive index).
3.1.2. Cement hydration

Usually, the adsorption of admixtures on cement grains leads to visible changes in the hydration kinetics of cement [6,7]. Figs. 7 and 8 present the exothermic heat flow of cement hydration in the cement pastes with incorporation of the monomers AA, SSS, and MAPTAC and their corresponding homo-polymers. In Fig. 7, it is noted that the monomers AA, SSS, and MAPTAC have little influence on cement hydration, which is fully consistent with the adsorption results in Table 3 that no adsorption occurs as organic monomers are added in cement pastes. Fig. 8 shows that the addition of the corresponding homo-polymers leads to a prolonged induction period, a delayed and lowered heat flow peak in the acceleration period of cement hydration, which is the so-called retardation effect. To analyze the influence of these polymers on the hydration kinetics in detail, six parameters are extracted from the heat evolution curves in Fig. 8 based on the illustration in Fig. 9. As shown in Fig. 9, tA represents the ending time point of the induction period, tB the inflection point between A and C on the heat evolution curve, reflecting point between A and C on the heat evolution curve, representing the nucleation effect on cement hydration, which is considered as a period when cement hydration is proceeding at a very low rate and in the meantime, various ions slowly diffuse from the mineral phases of cement grains to the aqueous phase [2]. It is reported that the hydration rate in the induction period and the duration of the induction period tA are related to the diffusion rate of various ions from the mineral phases to the aqueous phase. And the ions diffusion rate is mainly governed by the contact surface of the mineral phases with water. The adsorbed polymers undoubtedly hinder the exchange of water and ions between the hydrating cement grains and the aqueous phase due to their coverage on cement surface [8], thereby decreasing the hydration rate and prolonging the induction period. As it is noted in Table 4, slight influences on the heat evolution parameters of cement hydration are found when PMAPTAC is added, which is due to its low adsorption amount on cement surface. PAA and PSSS evidently prolong the induction period and depress the hydration rate (dQ/dt)A in the induction period, implying the decelerated ion diffusion caused by the prominent adsorption of PAA and PSSS on cement surface. In addition, PAA brings about more evident retardation on cement hydration than PSSS, which is in very good agreement with the fact that the adsorption amount of PAA is larger than that of PSSS.

After the induction period, cement hydration steps into the acceleration period with rapid nucleation and growth of hydrates. On the assumption that the growth rate of C–S–H remains constant, the hydration rate in the acceleration period is in proportion to the amount of growth active sites of C–S–H. Namely, the hydration rate at any time in the acceleration period is solely determined by the total amount of hydrate nuclei at that moment [22,23]. Thus, KA,B reflects the nucleation rate of C–S–H at the early stage of the acceleration period. In Table 4, it can be seen that KA,B and (dQ/dt)C visibly drop with the incorporation of PAA while a slight reduction is found when PSSS is added in cement paste, suggesting that PAA has a marked impact on depressing the nucleation of hydrates during the acceleration period, which may be ascribed to the chelation effects of PAA with Ca2+ [20].

With the growth of hydrates, a hydrate layer is gradually formed over the surface of cement grains, which further hinders the exchange of water and the ions and eventually brings about the deceleration period of cement hydration (diffusion controlled reaction) at time point tC. The maximum hydration rate is mainly determined by the number of nuclei formed during the time periods A to C. The lower hydration peak (dQ/dt)C is related to fewer nuclei formed during A to C. Thus, from the lower hydration peak (dQ/dt)C, it can be deducted that the total nuclei number is significantly reduced when PAA is added into cement paste. Moreover, PAA obviously increases the cumulative heat flow QA–C during the acceleration period. This result again accords with the

Table 5
SEC analysis for the samples of PAM and PAS series and the polymer fraction in the solid part of the synthesized samples obtained from dialysis results.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Polymer fraction Mw</th>
<th>Mw/Mn</th>
<th>Mass fraction (%)</th>
<th>Oligomer fraction Mw</th>
<th>Mw/Mn</th>
<th>Mass fraction (%)</th>
<th>Polymer (Mw = 7000) fraction in the solid part of the synthesized samples obtained from dialysis results (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPEGMA</td>
<td>24,860</td>
<td>1.297</td>
<td>66.1</td>
<td>1093</td>
<td>1.071</td>
<td>95.1</td>
<td>–</td>
</tr>
<tr>
<td>PAM100-0</td>
<td>43,920</td>
<td>1.680</td>
<td>83.9</td>
<td>6729</td>
<td>1.132</td>
<td>31.5</td>
<td>78.0</td>
</tr>
<tr>
<td>PAM88-12</td>
<td>40,490</td>
<td>1.643</td>
<td>83.3</td>
<td>4496</td>
<td>1.189</td>
<td>13.6</td>
<td>53.2</td>
</tr>
<tr>
<td>PAM57-25</td>
<td>45,910</td>
<td>1.541</td>
<td>77.4</td>
<td>4769</td>
<td>1.218</td>
<td>13.9</td>
<td>51.3</td>
</tr>
<tr>
<td>PAM50-50</td>
<td>72,510</td>
<td>1.045</td>
<td>37.4</td>
<td>2726</td>
<td>1.304</td>
<td>19.6</td>
<td>75.9</td>
</tr>
<tr>
<td>PAM0–100</td>
<td>15,840</td>
<td>1.232</td>
<td>60.6</td>
<td>20,040</td>
<td>1.106</td>
<td>18.3</td>
<td>49.3</td>
</tr>
<tr>
<td>PAS100-0</td>
<td>19,060</td>
<td>1.496</td>
<td>55.7</td>
<td>5593</td>
<td>1.096</td>
<td>23.1</td>
<td>65.3</td>
</tr>
<tr>
<td>PAS70-30</td>
<td>20,580</td>
<td>1.358</td>
<td>43.7</td>
<td>2417</td>
<td>1.146</td>
<td>31.0</td>
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</tr>
<tr>
<td>PAS50-50</td>
<td>21,680</td>
<td>1.190</td>
<td>30.7</td>
<td>1531</td>
<td>1.146</td>
<td>39.5</td>
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<td>PAS0–100</td>
<td>9513</td>
<td>1.251</td>
<td>63.9</td>
<td>37.2</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
reduced nuclei number during A to C with addition of PAA, because a thicker hydrate layer, namely higher hydration degree is required with fewer nuclei in order to reach full coverage of hydration products on cement surface and to switch the hydration into the deceleration period. One may conclude that PAA prolongs the induction period, delays and depresses the hydration peak due to its higher adsorption amount on cement surface. The high adsorption amount of PAA reduces the diffusion rate of ions and water crossing the interface between the cement and aqueous phases, and further depresses the nucleation process of cement hydration. Our results about the adsorption and retardation of AA and PAA in cement pastes indirectly confirm the results of Pourchet et al. [15]. They found that the interaction between Ca$^{2+}$ and the carboxyl groups depended on the distance separating the anionic groups. The isolated or diad carboxyl groups were less efficient to drive the adsorption of polymer on cement and thus less effective for retardation of cement hydration than triad, tetrad, pentad, etc.

On the basis of the above results, it is not hard to find that a polymer with positive charges (PMAAPTAC) has a slight influence on the hydration kinetics of cement while the polymers with negative charges (PSSS and PAA) retard cement hydration to different extents. In spite of the same negative charge density in the molecules, PAA with carboxyl groups exerts a stronger retardation effect than PSSS with sulfonic ones due to its larger adsorption amount and strong complexation effect with Ca$^{2+}$ ions.

3.2. Comb-shaped PC co-polymers

The different adsorption behaviors of PAA, PSSS and PMAAPTAC linear polymers without side chains and their impacts on cement hydration originating from the different functional groups $-\text{COO}^-$, $-\text{SO}_3^-$ and $\equiv\text{N}^+$ have been elucidated in Section 3.1. As it is well known, the typical PC superplasticizer is a comb-shaped polymer with polycarboxylate chain as backbone and poly(ethylene oxide) (PEO) as side chain. A large number of carboxyl groups ($-\text{COO}^-$) and sometimes a certain amount of sulfonic groups ($-\text{SO}_3^-$) are usually contained in the main chain, which makes the PC molecules negatively charged in alkaline solution. By changing the molar ratio of monomer AA to AMPS during polymerization, the ratio of the $-\text{COO}^-$ groups to the $-\text{SO}_3^-$ groups can be adjusted without changing the charge density in the synthesized PC co-polymers. Thus, the effects of the $-\text{COO}^-$ and $-\text{SO}_3^-$ groups in PC superplasticizer on its performance in cementitious system can be studied. In the same way, cationic charges can be introduced into the PC molecules by simply replacing the monomer AA with MAPTAC at a certain ratio and the synthesized PC co-polymers become amphoteric. Cationic PC polymers can be produced by complete replacement of AA with MAPTAC. In the following part, the effects of the various functional groups $-\text{COO}^-$, $-\text{SO}_3^-$ and $\equiv\text{N}^+$ on the behaviors of PC molecules are investigated.

3.2.1. Characterization of the synthesized PC co-polymers

3.2.1.1. SEC measurement and dialysis results. SEC equipped with a laser light scattering (LS) detector and a refractive index (RI) detector was employed to determine the molecular weight of the prepared polymer and to roughly estimate the fraction of the desired polymer in the synthesized sample. SEC chromatograms of the samples of PAM series and PAS series before purification are given in Figs. 10 and 11 respectively. It is seen in Figs. 10 and 11, the SEC chromatograms of the synthesized samples often exhibit multi-peaks. This indicates that rather than pure polymer, the synthesized product contains many components with different molar masses, which might be either the desired PC co-polymer, or the un-polymerized macro-monomer and even the residual monomers with smaller molar mass. In the SEC chromatograms, a combination of LS signals with RI signals allows a qualitative analysis for individual fraction in the synthesized PC samples. The LS signals are used for calculation of molecular weight, including Mw, Mn and molecular weight distribution Mw/Mn, and the RI signals can be used for estimation of the concentration of each fraction in the sample by integration of the area for each peak. The analysis results of SEC for samples of both PAM series and PAS series are listed in Table 5.
As shown in Fig. 11 and Table 5, it is found that for the synthesized macro-monomer MPEGMA, the weight average molecular weight Mw is about 1093, the polydispersity is 1.071 and the mass content of macro-monomer is about 95.1%. In Fig. 10, it is seen that the synthesized PAM samples mainly contain two fractions, indicated as peak I and peak II. The fraction of peak I presents high molecular weight of Mw above 10,000 and peak II shows relatively lower Mw, which should be recognized as oligomers. It is noted that the molecular mass of fraction II in the samples of PAM series, which is obtained from the LS signals, is not located around 1100, that is the average molecular weight of the macro-monomer MPEGMA (as given in Fig. 11), and varies from samples, although the elution times of peak II are quite close. A single peak with a molar mass of about 1100 is not observed. This implies that the fraction of peak II is not the unreacted macro-monomers, but would rather be oligomers that may be composed of several macro-monomer units linked by a few monomer units. The absence of the macro-monomer peak indicates that the conversion of monomers is relatively high. Knowing that the polymerization rates for the monomers such as AA are much higher than that of the macro-monomer MPEGMA and the latter is hardly able to form homo-polymer [24], we believe that the fraction of peak II in the samples might be produced after the main consumption of the monomers like AA and MAPTAC.

The condition of relatively high concentration of macro-monomer and low concentration of monomers at the late stage of the polymerization, i.e. after complete dosage of monomers, produces these oligomers with molecular weights of several thousands. In the case of the PAS series, two peaks (peak I and peak II) are similarly found in the chromatograms as seen in Fig. 11. Peak I represents the fraction of polymers in the samples with high molecular weights of 10,000–25,000 and peak II should be assigned as oligomers.

From the SEC data presented in Table 5, it is found that the obtained products are not pure and the polymer contents in the PAM and PAS samples present a significant difference. Before we start to investigate the influences of these synthesized polymers on cement hydration, all the prepared samples were purified by the dialysis technique. As described in Section 2.2.2, residual monomers, salts and oligomers with Mw < 7000 were removed from the samples by dialysis. After purification, the polymer (Mw > 7000) fraction in the solid part of the synthesized product can be calculated as listed in Table 5. It can be seen that the polymer fractions obtained from the SEC analysis and from the dialysis experiment are quite comparable. Thus, in the following part of this paper, the characterization of the obtained PC co-polymers by FTIR and the investigation of the PC co-polymers in cement pastes were carried out by using the purified PC co-polymers to avoid any disturbance from the remaining monomers, oligomers and salts.

3.2.1.2. FTIR analysis. In order to confirm the co-polymerization of the various monomers in the synthesis of the PC co-polymers (PAM and PAS series) as designed in Table 2, FTIR analysis was performed on the purified PC co-polymers and the spectra are given in Fig. 12. The broad peak around 3485 cm\(^{-1}\) and the sharp peak at 2873 cm\(^{-1}\) are respectively assigned to the O–H and C–H stretching bands. The absorption peak at 1652 cm\(^{-1}\) corresponds to the amine-carboxyl group which derives from the monomer MAPTAC and AMPS. The peak of the N–H amine band can be found at 1540 cm\(^{-1}\) for the PAS series. The peak at 1726 cm\(^{-1}\) is assigned to the overlapping of C=O in AA repeating units and the macro-monomer MPEGMA units. Moreover, the characteristic band of MPEGMA also appears at 1109 cm\(^{-1}\) for the C–O–C asymmetric stretching. The presence of these characteristic peaks in the FTIR spectra of the purified PAM and PAS samples demonstrates the successful co-polymerization of the involved monomers. On the other hand, with the increasing proportion of MAPTAC in the synthesis of the PAM series, the peak of amino-carboxyl at 1652 cm\(^{-1}\) in the polymers becomes more intense while that of C=O at 1726 cm\(^{-1}\) from AA units gets lower when the height of peak at 1109 cm\(^{-1}\) for C–O–C is fixed constant, as seen in Fig. 12b. This indicates that the molar ratio of MAPTAC to AA in the PAM molecules increases as expected. A similar trend has been also found in the PAS series (Fig. 12c). Thus, the ratio of repeating units of MAPTAC to AA in the PAM co-polymers (or AMPS to AA for the PAS co-polymers) can be semi-quantitatively determined by comparing the heights of the characteristic peaks from both monomers. The peak at 1726 cm\(^{-1}\) is used as the characteristic peak of AA units and the peak at 1652 cm\(^{-1}\) is adopted to represent MAPTAC (or AMPS) units, when the peak at 1109 cm\(^{-1}\) assigned to MPEGMA is fixed. The variations of the two peaks in the PAM and PAS co-polymers are listed in Table 6, which provides a clear evidence of the co-polymerization of various monomers and the variation trend of their corresponding repeating units in the obtained co-polymers, when monomer proportions are changed in synthesis.

3.2.2. PC co-polymers with positive charges and negative charges (PAM) in cement paste

The charge types of the PC co-polymer could be adjusted from anionic to cationic by co-polymerization of AA, MAPTAC and MPEGMA with a variation of molar ratio of AA to MAPTAC, as the samples of the PAM series, which is confirmed by the FTIR analysis shown in Fig. 12b. Purified PAM co-polymers are used to investigate the effects of charge types in polymer chains on the adsorption behaviors of the co-polymers on cement surface. Fig. 13 exhibits the adsorption behaviors of the PC co-polymers with varied ratios of AA repeating units to MAPTAC units and the zeta potential of cement pastes. It is clearly seen that at a fixed polymer to cement ratio, the adsorption amounts of the PC co-polymers dramatically decline as more cationic MAPTAC repeating units are incorporated in PC molecules. The adsorption amount of the fully cationic PAM0-100 is far lower than that of the anionic PC co-polymer PAM100-0. This means that the adsorption capability of the negatively charged PC co-polymers is much higher than that of the positive ones, which is certainly attributed to the fact that the positively charged aluminates hydrates are dominant in an early hydrating cement paste. Besides, the chelating effect of \(\text{COO}^-\) with \(\text{Ca}^{2+}\) also contributes to the higher adsorption amount of the PC molecules containing more AA repeating units on cement grains.
With the adsorption of PC molecules on the surface of cement grains, the zeta potential is bound to be changed, as indicated in Fig. 13. The addition of PAM100-0 bearing only anionic charges effectively decreases the zeta potential of cement pastes from +7.2 mV to −2 mV at a dosage of P/C = 0.2%. With the increasing molar ratio of cationic charges to anionic charges in PC molecules, a notable growth on zeta potential is observed in the presence of the PC co-polymers in cement pastes. When monomer AA is completely replaced by MAPTAC (PAM0-100), the inclusion of PC in cement paste enables the zeta potential to increase to 23.8 mV, which is far higher than the value of 7.2 mV for the blank cement paste.

The various purified PAM co-polymers are mixed into cement pastes to investigate the impacts of the charge types in PC co-polymers on cement hydration by calorimetry, as presented in Fig. 14a. It is seen that more polymer addition generally leads to stronger retardation effect on cement hydration. At a fixed polymer dosage, a higher molar ratio of \(\text{N}^+\) – groups to \(\text{COO}^-\) groups in PC molecules brings about a lower retardation effect on cement hydration. PAM100-0 retards the cement hydration most significantly in terms of prolonging the induction period and reducing the maximum hydration rate. By contrast, the positively charged PAM0-100 has little influence on the cement hydration compared to the blank cement paste. These phenomena could be fully interpreted from the viewpoint of their adsorption behaviors on cement grains. Fig. 14b presents the variations of \(t_\text{i}\) and \((dQ/dt)_\text{c}\) with adsorption amount. It is evidently seen that larger adsorption amount of polymers on cement surface leads to an increase of \(t_\text{i}\) and a decrease of \((dQ/dt)_\text{c}\) due to the hindrance to the diffusion of various ions across the adsorption layer during the cement hydration process. Additionally, the strong complexation effect of \(\text{COO}^-\) with Ca\(^{2+}\) is also responsible for the retardation because of the effect of depressing nucleation process [22].

One of the main expected functions of the PC co-polymers is the cement dispersing effect indicated by either fluidizing effect in cement pastes or water-reducing effect in concrete [14,25,26]. In order to compare the performance of the synthesized PC co-polymers, the fluidity of the fresh cement pastes with the addition of various purified PAM co-polymers is measured as shown in Fig. 15. It is apparently seen that the fluidity of the cement paste in the presence of PAM88-12 is slightly higher than that with addition of PAM100-0, which indicates that incorporation of a certain amount of cationic charges in the conventional anionic PC co-polymer (such as PAM100-0) could improve the plasticizing efficiency of PC co-polymers to some extent. Similar results have also been reported in literatures [27,28], where amphoteric PC co-polymers were investigated in cementitious systems. On the other hand, when more AA units are replaced by MAPTAC units in the PAM
co-polymers (PAM50-50 and PAM0-100), the fluidizing efficiency of the PC co-polymers becomes lower, which could be understood that the adsorption amount drastically decreases as shown in Fig. 13.

3.2.3. PC co-polymers with negative charges provided by carboxyl or sulfonic groups (PAS) in cement paste

The effects of the carboxyl and sulfonic groups in PC molecules on their adsorption behaviors and on the cement hydration are shown in Figs. 16 and 17 at varied P/Cs. It is found in Fig. 16 that a marked decrease in adsorption amount is recorded as more AA is replaced by AMPS in the preparation of PC co-polymers, implying that the adsorption capability of carboxyl groups on cement surface is stronger than the sulfonic groups, which is fully in agreement with the result in Table 3. As previously discussed in Section 3.1.1, the adsorption driving force of sulfonic groups on cement surface is only the electrostatic attraction, whereas carboxyl groups promote the adsorption of the PC co-polymers by the combined effects of electrostatic force and more importantly the complexation with Ca$^{2+}$ ions, as illustrated in Fig. 6. Thus, in the premise of the same negative charge density, the PC molecules with more carboxyl groups could adsorb in a more considerable amount on cement surface.

Based on the abovementioned adsorption behaviors, the finding that the higher molar ratio of sulfonic groups to carboxyl groups in PC molecules results in less prolongation of the induction period is in accordance with expectation, as presented in Fig. 17. From the measurement of fluidity of the cement pastes with addition of the purified PAS samples (Fig. 18), it is interestingly found that the plasticizing performance of the PAS co-polymers is not greatly changed by the incorporation of a certain amount of sulfonic groups in the PC co-polymers, when PAS100-0 and PAS70-30 are compared. More replacement of AA units by AMPS units in the PAS co-polymers reduces the dispersing capability, as observed in the case of PAS50-50. The very low fluidizing effect of PAS0-100 must be caused by the decreased adsorption amount of the PC polymer on cement grains, as shown in Fig. 16.

4. Conclusions

In this study, organic monomers possessing different charges in aqueous solution, including AA, SSS as well as MAPTAC, and their corresponding homo-polymers were employed to investigate the influences of the charge feature of molecules on their adsorption behaviors in cement pastes and their impacts on cement hydration. Comb-shaped amphoteric PC co-polymers were also synthesized by simply replacing AA monomer with the monomer of MAPTAC in the PC co-polymers in order to study the effect of the negative charges as well as the positive charges...
on the behaviors of PC-co-polymers in cement system. Moreover, the impacts of carboxyl and sulfonic groups with the same negative charge density were also compared by adjusting the molar ratios of the carboxyl to sulfonic groups in PC co-polymer backbones. Based on the aforementioned results, the correlations of charge characteristics of the backbone of PC superplasticizers with their adsorption behaviors and retardation effects in cement paste were disclosed.

(1) Organic monomers AA, SSS and MAPTAC do not show visible adsorption on cement surface due to the large entropic loss upon adsorption. Correspondingly, no changes on the zeta potential and the cement hydration kinetics are found when they are added into cement paste. On the other hand, the corresponding homo-polymers PAA, PSSS and PMAAPTAC are able to be adsorbed on cement surface to different extents, no matter what charges are contained in these polymers. The adsorption ratios of PAA and PSSS added in cement paste are higher than 60% while only a minor part of PMAAPTAC is adsorbed, which is related to the fact that the positively charged aluminated hydrates are dominant in an early hydrating cement paste. In addition, PAA and PSSS remarkably decrease the zeta potential from positive to negative value whereas a higher positive zeta potential is observed in the presence of PMAAPTAC in cement paste. Compared with PSSS, PAA less significantly decreases the zeta potential in spite of its relatively higher adsorption ratio on cement surface, which is ascribed to the complexation effect of −COO − in PAA with Ca2+.

(2) Polymer with positive charges (PMAAPTAC) has a slight influence on the hydration kinetics of cement while the negatively charged polymers (PSSS and PAA) retard cement hydration to different extents. PAA with carboxyl groups presents a stronger retardation effect than PSSS with sulfonic ones due to its larger adsorption amount and strong complexation effect with Ca2+.

(3) For the comb-shaped PC co-polymers with negative charges, both the adsorption capacity and the retardation effect are stronger than those with positive charges. With the increasing molar ratio of cationic charges to anionic charges in the PC molecules, notable decreases in adsorption amount and lower retardation effect are observed in the presence of the PC co-polymers in cement paste. Moreover, incorporation of a certain amount of cationic charges in anionic PC co-polymers is beneficial for improvement of plasticizing efficiency. On the other hand, in the premise of the same negative charge density, the PC co-polymers with more carboxyl groups show stronger impacts in term of adsorption on cement surface and retardation on cement hydration.

Acknowledgments

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References