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Synthesis and performance of methacrylic ester based polycarboxylate superplasticizers possessing hydroxy terminated poly(ethylene glycol) side chains

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Abstract

The synthesis and performance of new methacrylate ester based polycarboxylate superplasticizers is shown. These new superplasticizers possess hydroxy termination of the poly(ethylene glycol) side chains instead of conventional methoxy termination. Properties of the new superplasticizers in cement paste were compared to those of conventional ones. For this comparison, methacrylic acid–poly(ethylene glycol) methacrylate ester copolymers having three different side chain lengths and either hydroxyl or methoxy terminated graft chains were synthesized. For characterization of the superplasticizers, gel permeation chromatography (GPC) as well as anionic charge density determination was carried out. The performance of the polymers in cement was tested by measuring paste flow, adsorption as well as zeta potential. Additionally, retardation of the copolymers possessing side chains of 45 ethylene oxide units was investigated by heat calorimetry. According to the data, macromonomers based on hydroxy terminated poly(ethylene glycol) methacrylate ester chemistry allow to produce superplasticizers of high quality.

Keywords: Adsorption; Admixture; Polymers; Portland cement; Superplasticizer

1. Introduction

The use of superplasticizers (SPs) is an absolute necessity to achieve high quality concrete as construction material [1]. Superplasticizers (dispersants) reduce the amount of water necessary to obtain an acceptable workability of the fresh concrete. Furthermore, water reduction generally leads to a higher strength of the product. This enables special applications such as ultra high performance concrete (UHPC). As an example, without these admixtures it would not be possible to build extremely high concrete based buildings with adequately sized concrete pillars exhibiting sufficient strength. The term superplasticizer first came up with the invention of polycondensate admixtures mainly represented by poly(melamine sulfonate) (PMS) and poly(naphthalene sulfonate) (BNS). They are more efficient than plasticizers based on lignosulfonate technology. In the middle of the 1980s, Nippon Shokubai together with Nippon Master Builder Technologies invented a new class of superplasticizers based on polycarboxylate (PC) chemistry having poly(ethylene oxide) (PEO) side chains. Though being in general not as robust or tolerant to different cements or admixtures like polycondensates [2], much lower water to cement ratios can be achieved with PC, especially in precast concrete. Also, specific PC molecules provide excellent slump retention of ready-mix concrete without imposing retardation on the cement. Generally, the performance of PC is determined by parameters such as side chain length, side chain density (and therefore amount of negatively charged groups) and main chain length [3,4]. Because of their advantages, these superplasticizers, synthesized by radical copolymerization, are still replacing conventional polycondensates [5], especially in high performance applications such as self compacting concrete or UHPC.

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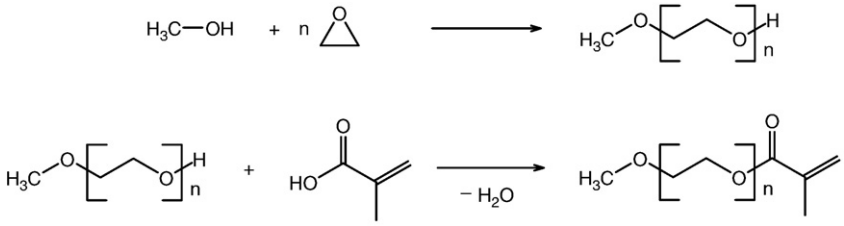

Fig. 1. Synthesis of the methoxy terminated MPEG-methacrylate macromonomer.

This work deals with the synthesis and performance of modified polycarboxylate superplasticizers by using newly synthesized monomers. The most commonly used PC superplasticizers are manufactured from the monomers methacrylic acid and ω-methoxy poly(ethylene oxide) methacrylate (MPEG-MA) in a radical copolymerization reaction. The obtained "comb-like" structured polymers, in which the PEO side chains allow for the steric stabilization of dispersed particles, are not only used as superplasticizers for cement, but also e.g. as dispersants for pigments [6]. The macromonomer MPEG-MA is commonly synthesized in a two step process (Fig. 1). The first step involves the synthesis of α-methoxy-ω-hydroxy-poly(ethylene glycol) (MPEG) as a precursor. In the second step, the MPEG is reacted with methacrylic acid or methyl methacrylate to form the methoxy terminated ester MPEG-MA [7].

An alternative route involving only one instead of two reaction steps leads to ω-hydroxy poly(ethylene glycol) methacrylate (HPEG-MA). It is obtained through direct reaction of methacrylic acid or methacrylic esters with ethylene oxide. A similar structure as for the MPEG-MA macromonomer is obtained. However, this new macromonomer differs from the conventional monomer in the termination of the PEO side chain. Instead of a methoxy termination, a hydroxy termination is obtained (Fig. 2).

The hydroxy terminated monomer has the advantage that it can be produced in a more efficient synthesis than the conventional methoxy poly(ethylene oxide) methacrylates, mainly due to the avoidance of a second reaction step. Additionally, it contains less by-products and impurities.

Hydroxy modification of the side chain termination could have an influence on the interaction of the polymer with cement, and thus impact its performance as superplasticizer. In contrast to the methoxy group, the hydroxy functionality can partially deprotonate at the highly alkaline pH (≥12.5) of the cement paste. Therefore, not only the polymer trunk, but also the side chain possessing a coiled structure may adsorb on the surface of cement [8,9]. This effect may cause a reduction of the steric effect of PC and thus decrease its dispersing power. It is also known that methacrylate based PC superplasticizers may partially intercalate into hydrating C_3A [10]. The tendency to intercalate depends on the specific anionic charge density and steric size of the PC and the SO_3/C_3A ratio in the cement. Thus, the intercalated SP is not available for acting as a dispersant for the cement particles. The intercalation behaviour might also be influenced by chemical modification of the side chain end groups because –OH functionalities may coordinate with Ca atoms in the $[Ca_2Al(OH)_6]^+$ main layer of C_3A hydrates. Thus, superplasticizer effectiveness could be reduced.

Based upon these considerations, we tested the new HPEG-MA macromonomers in comparison to MPEG-MAs for the applicability to the superplasticizer synthesis. Macromonomers with three different chain lengths resulting from 17, 24 and 45 ethylene oxide units (EOUs) were used to synthesize polymers with either hydroxy or methoxy termination. Subsequently, the hydroxy terminated poly(HPEG-MA-*co*-Na-methacrylate) SPs were tested for their superplasticizing effect in comparison with the conventional SPs having methoxy termination of the side chains. Most importantly, the plasticizing (dispersing) effect was tested utilizing a "mini slump test". Furthermore, different methods for characterizing the interaction between the superplasticizers and the cement particles, such as adsorption, zeta potential or heat calorimetry, were carried out.

2. Experimental

2.1. Materials

All superplasticizers were synthesized by radical copolymerization of methacrylic acid and hydroxy or methoxy terminated poly(ethylene oxide) methacrylate. Methacrylic acid (MAA) as well as the initiator sodium persulfate was obtained from the company VWR International. The hydroxyl or methoxy terminated poly(ethylene oxide) methacrylates (HPEG-MA, MPEG-MA) were supplied by Clariant Produkte (Deutschland) GmbH, Burgkirchen (Germany). The polymer chain transfer agent methallyl sulfonic acid (sodium salt) (MASA) was obtained from Aldrich.

2.2. Synthesis of the polycarboxylates

100 mL of deionized water was placed in a reaction vessel after which methacrylic acid, the macromonomer (HPEG-MA or MPEG-MA) and the chain transfer agent dissolved in 263 mL of deionized water were added. Subsequently, the pH was set to ~9 and an aqueous solution of 2.5 g initiator in 15 mL of deionized

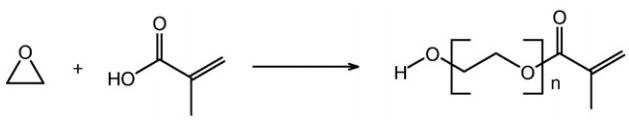

Fig. 2. One-step synthesis of the hydroxy terminated HPEG-methacrylate macromonomer.

water was added to start the polymerization which was carried out at 80 °C for 1 h. The reaction mixture was then allowed to cool down to room temperature. The superplasticizer solution was used without further purification. In Table 1, the exact amounts of starting materials used for the different syntheses and the molar composition of the prepared PCs are shown.

The denomination of the synthesized PCs is as follows: the number denotes the number of ethylene oxide units in the side chain. OH stands for hydroxy and OMe for methoxy termination of the side chains.

2.3. Characterization of cement

The cement chosen for the experiments was an ordinary portland cement OPC (CEM I 32.5 R from HeidelbergCement, Rohrdorf plant) which contains approximately 9 wt.% C_3A and therefore requires a high dosage of SP. The phase composition determined by XRD is given in Table 2. Its average particle size (d_{50} value) is 14.6 µm and its density is 3.15 g/cm^3 (Helium pycnometer). The Blaine value is 3419 cm^2/g.

The particle size was determined by laser granulometry (Cilas 1064, Cilas company). These values are necessary for the calculation of the zeta potential. Filtrates for the anionic charge detection were collected from a cement slurry with $w/c=0.485$ by vacuum percolation using a diaphragm vacuum pump (Vaccubrand company) with filter paper (Schleicher und Schuell company, Grade: 589/3, classification 2d according to DIN 53 135) at a vacuum of ~50 mbar.

2.4. Methods of evaluation

For the determination of the paste flow, a "mini slump test" according to DIN EN 1015 was utilized and carried out as follows: first, the water to cement (w/c) ratio of the paste without polymer was set to give a spread of 18 ± 0.5 cm. At this w/c ratio, the dosages of superplasticizers required to reach a spread of 26 ± 0.5 cm were determined. The superplasticizer was added to the required amount of batch water in a porcelain casserole. 300 g of cement was added and agitated for 1 min, then stayed for 1 min without stirring and then again stirred for 2 min. Immediately after the stirring, the cement paste was poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) on a glass plate and the cone was vertically removed. The resulting spread of the paste was measured twice, the second measurement being in a 90° angle to the first and averaged to give the spread value. For the mini slump test over time, 400 g of cement and 185 g of water were used. After each measurement, the slurry was put back in the casserole and covered with a wet towel in order to avoid drying. Before each subsequent measurement, the paste was stirred again for 2 min. For testing delayed addition of superplasticizer, the cement was added and dispersed for 30 s. After this, the slurry was rested unagitated for 30 s. Then, superplasticizer was added over the course of 30 s. After this, the slurry rested again for 30 s without stirring. Finally, the mixture was stirred for 1 min and the cone was filled. The w/c ratio of the paste used to study the influence of delayed addition was slightly higher ($w/c=0.49$, Table 6) compared to the first mini slump measurements ($w/c=0.45$, Table 5), because a different batch of cement was used. For all measurements, no bleeding or segregation of the paste was observed. The specific anionic charge density of the PC molecules was determined by a particle charge detector PCD 03 pH (Mütek Analytic company, Herrsching, Germany). This method allows the experimental determination of the charge of polymers. Here, an aqueous solution of the anionic SP was titrated with the cationic polymer poly-diallyl dimethyl ammonium chloride (polyDADMAC) until charge neutralization (zero potential) was reached. From the amount of polyDADMAC used to reach a zero potential, the amount of negative charge per gram of SP can be calculated. Gel permeation chromatography (also known as size exclusion chromatography), where large molecules pass the column faster than small molecules, was performed on a Waters 2695 Separations Module equipped with Ultrahydrogel™ columns (Waters company, Eschborn, Germany) with subsequent light scattering detector ("mini Dawn" from Wyatt Technology Corp., Santa Barbara, CA, USA). Total organic carbon (TOC) adsorption measurements were carried out using a "High TOC II" from Elementar Analysensysteme Company, Hanau, Germany. Zeta potentials were determined using a model "DT 1200 Electroacoustic Spectrometer" (Dispersion Technology, Inc., Bedford Hills, NY, USA). This instrument measures a vibration current induced by an acoustic wave which causes the aqueous phase to move relative to the cement particles. From that, a potential difference results which can be measured and is designated as zeta potential. Contrary to other methods used to determine zeta

Table 1
Starting materials and molar compositions of synthesized polycarboxylates

Copolymer	EOUs	Molar ratio M(H)PEG-MA/MAA/MASA	Amounts of raw materials			
			MAA [g]	M(H)PEG-MA [g]	MASA [g]	H_2O [g]
PC 17 OMe	17	1/3/0.4	12.9	37.5	3.26	263
PC 17 OH	17	1/3/0.4	12.9	43.9	3.26	263
PC 24 OMe	24	1/3/0.4	12.9	55.0	3.26	263
PC 24 OH	24	1/3/0.4	12.9	87.3 [a]	3.26	236
PC 45 OMe	45	1/3/0.4	12.9	100.0	3.26	263
PC 45 OH	45	1/3/0.4	12.9	155.2 [b]	3.26	216

[a] Aqueous solution containing 27 g of water.
[b] Aqueous solution containing 47 g of water.

Table 2
Phase composition of cement sample (CEM I 32.5 R) determined by XRD with Rietveld refinement

Phase	wt.%
C_3S, m	54.5
C_2S, m	20.6
C_3A, c	6.1
C_3A, o	2.8
C_4AF, o	8.5
Free lime (Franke)	0.2
Periclase (MgO)	2.7
Anhydrite	2.4
Hemihydrate	2.2
Dihydrate	0.0

potentials such as electrophoresis or osmosis, the electroacoustic device allows to measure even in very concentrated solid suspensions such as cement paste, provided the particle sizes range between 200 nm and 100 μm. Isothermal heat calorimetry measurements were carried out using a TAM air Thermostat (Thermometric, Järfälla, Sweden).

3. Results and discussion

The comparison of the new hydroxy side chain terminated superplasticizers with the conventional methoxy terminated polymers included firstly the characterization of the synthesized polymers, and secondly a study of potential differences regarding their performance in cement.

3.1. Superplasticizer characterization

The SP solutions obtained in the syntheses were compared regarding their solids content, pH and the anionic charge of the polymers (Table 3). SPs with the same side chain length but varying termination (–OMe, –OH) lie in the same range. The measured anionic charge densities are typical for superplasticizers with a 3:1 molar ratio of methacrylic acid (charge carrying group):MPEG-MA macromonomer.

Furthermore, molar masses and polydispersities of the SPs were determined by means of GPC (eluent: 0.1 mol/L $NaNO_3$ solution, pH=12 adjusted with 30 wt.% aqueous NaOH) and light scattering (Table 4). The polydispersity index (PDI) is obtained by dividing the weight average molecular weight (M_w) by the number average molecular weight (M_n). It describes the uniformity of a polymer with respect to molecular mass distribution. The minimum value of the PDI is 1, which would correspond to only exactly one molecular length being present in the polymer. In general, this setup allows for direct determination of the number as well as the weight average molar masses without the need of a reference substance. For the PC polymers studied here, the lower limit for mass detection using this device lies at approximately 3000–8000 Da depending on the molecular weight of the sample.

Table 3
Physical properties of the synthesized polymers

Property	PC 17 OMe	PC 17 OH
Solids content [wt.%]	15.0	14.8
pH	7.6	7.7
Anionic charge in H_2O [μeq/g]	2730	2872
Anionic charge in cement paste filtrate [μeq/g]	3019	3458
Property	**PC 24 OMe**	**PC 24 OH**
Solids content [wt.%]	19.4	20.7
pH	7.5	7.7
Anionic charge in H_2O [μeq/g]	1750	1845
Anionic charge in cement paste filtrate [μeq/g]	2676	2758
Property	**PC 45 OMe**	**PC 45 OH**
Solids content [wt.%]	28.9	27.3
pH	7.6	7.4
Anionic charge in H_2O [μeq/g]	1800	1128
Anionic charge in cement paste filtrate [μeq/g]	2822	2965

Table 4
Molar masses, polydispersities (PDIs) and degrees of polymerization (DP) of the synthesized polymers

Polymer	M_w [Da]	M_n [Da]	PDI (M_w/M_n)	DP (M_n/M_{unit})
PC 17 OMe	74,920	12,130	6.1	10.4
PC 17 OH	71,350	9 020	7.9	7.7
PC 24 OMe	127,200	26,510	4.7	18
PC 24 OH	133,600	52,780	2.5	36
PC 45 OMe	405,300	46,200	8.7	19
PC 45 OH	206,400	73,250	2.8	30.5

Since the synthesis conditions remained the same for all polymerizations, apart from the side chain length of the macromonomers being varied, the mean polymer weight rises accordingly from SPs with short side chain length (PC 17) to SPs with long side chain length (PC 45). It appears to be significant that PC 24 OH and PC 45 OH have a much lower polydispersity than their methoxy terminated counterparts (PC 24 OMe and PC 45 OMe). Both macromonomers, the methoxy and hydroxyl terminated PEG-MA which are used as starting materials, possess a PDI of <1.2. Therefore, the synthesis of the hydroxy terminated SP appears to proceed in a more controlled way.

In Fig. 3, the GPC chromatogram of PC 45 OH is shown as an example. The light scattering signal, in combination with the refractive index signal and the refractive index increment (for this type of compound: $dn/dc=0.135$ mL/g), allows for direct determination of the molar mass distribution [11]. For PC 45 OH, a narrow polymer distribution (PDI=2.8) with only small amounts of unreacted monomers or by-products formed can be observed at higher elution times.

The chromatograms (refractive index detection) of all synthesized polymers are compared in Fig. 4. Each pair of PC OH/PC OMe polymers possessing the same side chain length shows similar mass distribution. It can also be seen that polymer molecules with higher molecular weight elute earlier from the chromatography column.

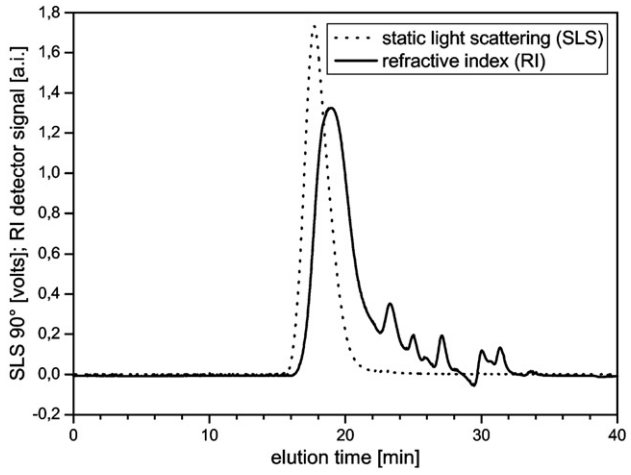

Fig. 3. GPC chromatogram of PC 45 OH with refractive index and static light scattering detection.

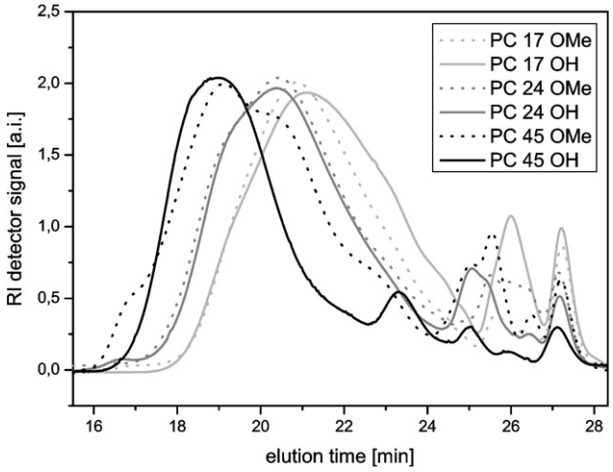

Fig. 4. GPC chromatograms (refractive index detection) of all synthesized PC polymers.

3.2. Superplasticizer performance

For each superplasticizer, the specific dosage (corresponding to the solid part of the SP solution) by weight of cement (bwoc) to reach a paste flow of 26 ± 0.5 cm in the "mini slump" test was experimentally determined. The *w*/*c* ratio of the paste without SP was set to produce a flow of 18 ± 0.5 cm (*w*/*c* = 0.485). As pointed out by Roussel et al., the mini slump (or mini cone) test not only represents an empirical test, but at low viscosity also a real rheological tool that allows its user to access an intrinsic property (yield stress) of the tested material instead of only measuring a test geometry and material density dependant slump value [12]. However, here we leave it at comparing the dosages for a spread geometry of 26 ± 0.5 cm. The results for the SPs are shown in Table 5. Considering the accuracy of the method, approximately the same dosages are necessary for the SPs with hydroxy and methoxy termination in order to reach the required spread of 26 ± 0.5 cm.

These results indicate that there is no difference in the performance of hydroxy and methoxy terminated SPs. However, one has to bear in mind that we only investigated one type of cement without further additives or aggregates. The compatibility with other systems still needs to be looked at.

It is well known that some superplasticizers show a great difference in performance when they are added a few minutes after the concrete has been mixed (delayed addition) instead of being contained in the mixing water (early addition). Effectiveness of these polymers is much enhanced upon delayed addition. It is assumed that intercalation (chemical absorption) of the polymers into layered calcium aluminate hydrate phases is the reason behind the poor performance at early addition [13]. To investigate the behaviour of the PCs with respect to intercalation, mini slump tests were carried out with early and delayed addition of the polymers. The results are presented in Table 6. For all SPs, a significant difference in performance can be observed when comparing early and delayed addition. Generally, a much higher spread is achieved upon delayed addition. This result shows again that –OH or $–OCH_3$ termination of the PC side chain has no impact on the behaviour of the polymer with respect to the time of addition to concrete.

Additionally, for PC 45 OMe and PC 45 OH, the mini slump test was carried out over a time period of 2 h to study slump retention over time (Fig. 5). For PC 45 OMe, the plasticizing effect decreases relatively quickly within the first 30 min. This behaviour is known from PCs made with –OMe terminated side groups at molar ratios of MAA:MPEG-MA of 3:1. PC 45 OH does not loose its effectiveness as fast as PC 45 OMe. It provides better slump retention, particularly within the first 60 min. After

Table 5
SP dosages to reach a paste flow of 26 ± 0.5 cm in the "mini slump" test

	PC 17 OMe	PC 17 OH
Dosage [%]	0.16	0.15
Spread [cm]	26.1	25.5
	PC 24 OMe	PC 24 OH
Dosage [%]	0.15	0.19
Spread [cm]	25.9	26.4
	PC 45 OMe	PC 45 OH
Dosage [%]	0.12	0.11
Spread [cm]	25.8	25.7

Table 6
Cement paste flow achieved with SPs at early and delayed addition

	PC 17 OMe		PC 17 OH	
	Early addition	Delayed addition	Early addition	Delayed addition
Dosage [%]	0.16		0.15	
Spread [cm]	25.5	29.0	26.0	28.6
	PC 45 OMe		PC 45 OH	
	Early addition	Delayed addition	Early addition	Delayed addition
Dosage [%]	0.12		0.11	
Spread [cm]	24.0	27.0	24.1	28.1

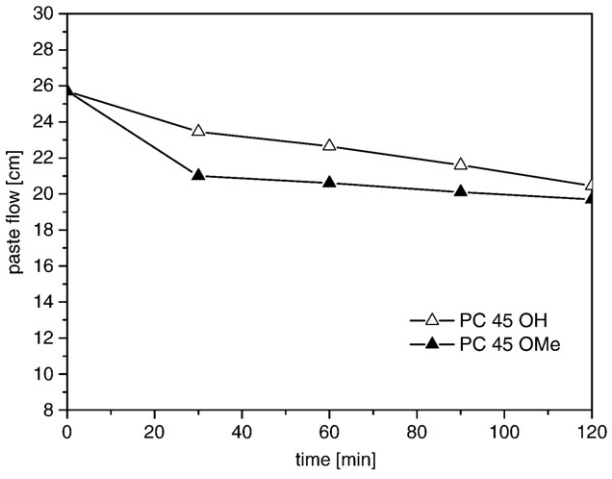

Fig. 5. Cement paste flow over time after addition of –OH and –OMe terminated PC 45.

120 min, however, both pastes show approximately the same paste flow of around 20 cm.

3.3. Superplasticizer adsorption

For the dispersing effect it is generally accepted that the superplasticizer molecules have to adsorb onto the cement grain surface [14,15]. The preferred hydration phase for adsorption of superplasticizer is ettringite [16]. Here, the superplasticizers were tested for their adsorption onto cement using the TOC method. Table 7 shows the adsorbed amounts of the SPs as well as the adsorption ratios. The measurements were carried out at the previously determined dosages necessary for a paste flow of 26 ± 0.5 cm (Table 5).

All superplasticizers adsorb in substantial amounts onto the cement grain surface. The ratio between added dosage and adsorbed amount of the different superplasticizers ranges from 48 to 67%. The adsorption ratio of PC 45 OH is much lower than for PC 45 OMe, again confirming that the –OH terminated version of this PC should provide better slump retention properties than the –OMe terminated polymer.

3.4. Zeta potential of cement slurries with superplasticizers

For gaining more insight into the interaction of the superplasticizers with the cement particles, zeta potential measurements were carried out. Utilizing the electroacoustic method based on the work by Dukhin et al., the zeta potential of concentrated cement slurries may be measured [17]. This method has the great advantage that cement slurries with application relevant water to solid ratios can be investigated and not only a dilute suspension. The zeta potential (or potential at the shear plane between particle and solution) was measured for each SP at increasing dosages of up to 1% by weight of cement. Again, as for the paste flow measurements, the *w*/*c* ratio was set to 0.485. All zeta potential measurements were carried out by titrating the aqueous polymer solution to the cement paste. This procedure corresponds to the delayed addition of SP to concrete. In all other experiments, the polymers were always contained in the mixing water.

Depending on the side chain length of PCs, different characteristic curves are obtained (Fig. 6). With respect to the zeta potential values, it should be taken into account that, for the low voltages produced by the pastes prepared here, systematic deviations of roughly ± 1 mV may occur due to very slight variations in preparation or measuring conditions and from the accuracy of the instrument in general. All SPs show an increase of the zeta potential up to approximately the dosage required for a paste flow of 26 ± 0.5 cm. Such an increase towards the isoelectric point (0 mV) is typical for SPs which disperse cement due to a steric stabilization effect [18]. This is in contrast to the electrostatic repulsion effect observed for polycondensates where the zeta potential becomes highly negative.

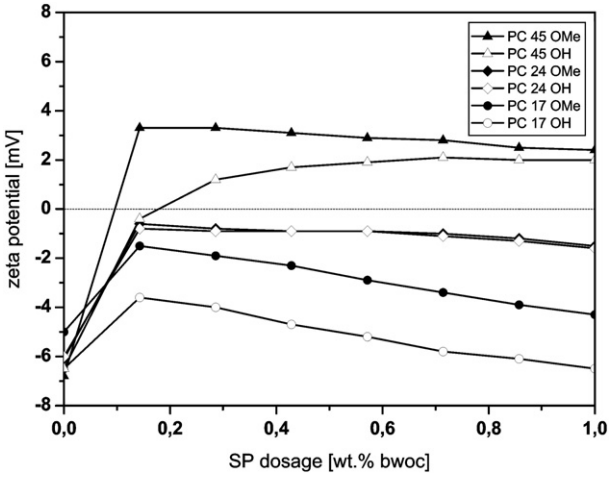

Fig. 6. Zeta potentials of cement slurries containing different SPs as a function of SP dosage.

The zeta potential curves for PC 17 and PC 24 are quite similar and independent of the side chain termination (–OH or –OMe group). The rise of the zeta potential to the isoelectric point may be explained by the steric effect caused by the poly (ethylene oxide) side chains which move the shear plane away from the charged particle surface into the solution [19]. For both PC 45 polymers, a change of sign to a positive potential is observed. We recently published a model trying to explain this behaviour by adsorption of positively charged calcium ions onto a layer of perpendicularly adsorbed allyl ether type PC [20,21]. Alike the paste flow and adsorption tests, the zeta potential curve of PC 45 OH differs slightly from that of PC 45 OMe. At higher dosages, though, they become identical. In

Table 7
Adsorbed amounts and adsorption ratios of synthesized SPs

Superplasticizer	Dosage [%]	Adsorbed amount [mg SP/g cement]	Adsorption ratio [%]
PC 17 OMe	0.16	0.84	56.3
PC 17 OH	0.15	0.80	56.4
PC 24 OMe	0.15	0.67	55.6
PC 24 OH	0.19	0.81	47.8
PC 45 OMe	0.12	0.81	67.4
PC 45 OH	0.11	0.54	48.8

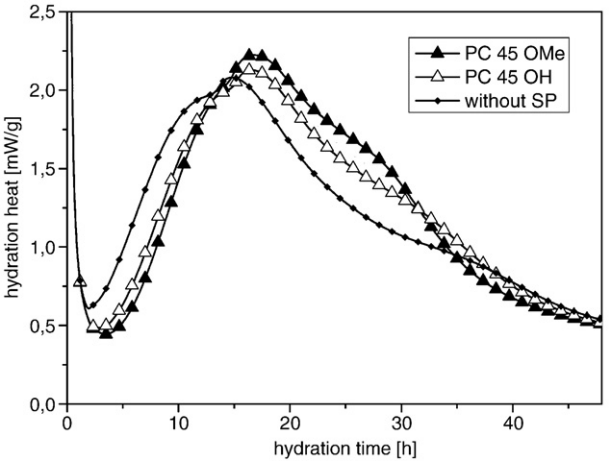

Fig. 7. Isothermal heat flow calorimetry for the –OH and –OMe terminated PC 45 SPs in cement paste (*w*/*c*=0.485).

accordance with its low adsorption ratio, PC 45 OH does not reach the plateau level at a dosage between 0.1 and 0.2 wt.%, but at around 0.6 wt.%. This observation is in line with the fact that this polymer is by far the bulkiest (according to M_n). This high molecular weight limits its adsorption to the surface. However, it is important to note that no significant change in the curve type is obtained when comparing –OH to conventional –OMe termination of the side chains. Therefore, the zeta potential measurements also indicate that in cement, the new –OH side chain terminated SPs should behave similar to the –OMe terminated polymers.

3.5. Influence of superplasticizers on the hydration of CEM I 32.5 R

As a final investigation, the influence of the two PC 45 superplasticizers on the heat development of hydrating cement was tested. Fig. 7 shows the heat evolution over 48 h. Again, SP dosages were the same as determined previously for a paste flow of 26 ± 0.5 cm. Both PC 45 containing samples retard the hydration only little compared to the control sample without SP. This behaviour is normal for PCs of such molar composition [22]. The two PC 45 superplasticizers studied differ more than the other synthesized polymers regarding their polydispersity, but still show the same effect on cement hydration. Therefore, it is evident that the –OH modification of the PC side chain has no negative impact on cement hydration.

4. Conclusions

The influence of hydroxy termination of the poly(ethylene oxide) side chains in poly{carboxylate-g-(ethylene glycol)-ether} type superplastizers on their performance in cement was studied. Compared to superplasticizers possessing conventional methoxy termination, similar properties were observed. Due to similar molecular weights and anionic charge densities for the methoxy and hydroxy terminated polymers, the copolymerization itself should have led to similarly structured comb copolymers. When comparing the properties as superplasticizer, especially in terms of superplasticizer dosage and effectiveness, the hydroxy terminated superplasticizers performed as well as the methoxy terminated polymers. Their slump retention behaviour over time is slightly better than for the same –OMe terminated polycarboxylate. The measured adsorption values correlate well with the dosages required to achieve high paste flow. Zeta potential measurements reveal similar trends for both the hydroxy and methoxy modified copolymers. Isothermal heat flow calorimetry for the superplasticizers in cement also does not show significant differences.

The results suggest that for the preparation of polycarboxylate admixtures, –OH terminated poly(ethylene glycol) methacrylate macromonomers offer an attractive alternative to –OMe terminated methacrylates. By using appropriate polymerization technique, superplasticizers of high quality can be synthesized.

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