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Synthesis, Characterization and Dispersing Properties of Anionic and Zwitterionic Polycarboxylate Superplasticizers Prepared *Via* Different Synthetic Methods

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Ein Vogel hat niemals Angst davor,

dass der Ast unter ihm brechen könnte.

Nicht weil er dem Ast vertraut,

sondern seinen eigenen Flügeln.

(Author unbekannt)

Being a scientist is like being an expolorer.

You have this immense curiosity, this stubbornness,

this resolute will that you will go forward

no matter what other people say.

(Sara Seager, astrophysicist)

List of articles

Journal Article with Peer-Review:

Chomyn, C., Plank, J.

Impact of different synthesis methods on the dispersing effectiveness of isoprenol ether-based zwitterionic and anionic polycarboxylate (PCE) superplasticizers

Cement and Concrete Research *119*, **2019**, 113 - 125.

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Impact of Different pH-Values of Polycarboxylate (PCE) Superplasticizer Solutions on their Dispersing Effectiveness

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Another Journal Article, developed within the framework of a cooperation:

Fröhlich, D. R., Koke, C., Maiwald, M. M., Chomyn, C., Plank, J., Panak, P. J.

A spectroscopic study of the complexation reaction of trivalent lanthanides with a synthetic acrylate based PCE-superplasticizer

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 207, **2019**, 270 - 275.

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List of abbreviations

AA	Acrylic acid
AA:MM	Molar ratio of acrylic acid : macromonomer
	(x mol AA denotes polymers with ratios of x mol AA : 1 mol MM)
AFS	Acetone-formaldehyde-sulfite polycondensate
Alite	Tricalcium oxy silicate ($Ca_3O(SiO_4)$ or C_3S)
Aluminate	Tricalcium aluminate ($Ca_9(Al_6O_{18})$ or C_3A)
APEG	α-Allyl-ω-methoxy poly(ethylene glycol) ether
APS	Ammonium persulfate
ATRP	Atom transfer radical polymerization
Belite	Dicalcium silicate ($Ca_2(SiO_4)$ or C_2S)
BPO	Benzoyl peroxide
bwoc	By weight of cement
c	Concentration
°C	Degree Celsius
C_3A_o	Orthorombic C_3A
CEM I	Portland Cement after DIN EN 197-1 [34]
CRP	Controlled radical polymerization
d.n.a.	Data not available
EO	Ethylene oxide
Ferrit	Tetracalcium alumina ferrite ($Ca_4Al_2Fe_2O_{10}$ or $C_4A_xF_{1-x}$)
DLS	Dynamic light scattering
g	Gram
h	Hour
HPEG	α-Methallyl-ω-methoxy poly(ethylene glycol) ether
IPEG	Isoprenyl oxy poly(ethylenglycol) ether
L / mL	Litre / millilitre
LS	Light scattering
µeq/g	Microequivalent per gram
µm	Micrometer
m	Meter
M	Molar (mol per litre)
(M)	Monomer

MPEG	ω-Methoxy-poly(ethylene glycol) ester
M_w	Weight average molecular weight
MWCO	Molecular Weight Cut Off
N_2	Nitrogen
n_{EO}	Amount of ethylenoxide units
nm	Nanometer
OSi modified PCEs	Organo-silane modified PCEs
PAA	Poly(acrylic acid)
PCE	Polycarboxylate ether
PDI	Polydispersity index
PMS	Polymelamine sulfonate formaldehyde
PNS	Polynaphthalene sulfonate formaldehyde
PolyDadmac	Poly(diallyl dimethyl ammoniumchlorid)
ppm	Parts per million
R·	Radical
RI	Refractive index
RM·	Radical-monomer-molecule
RAFT	Reversible addition-fragmentation chain transfer polymerization
rpm	Rotations per minute
SCPS	Synthetic cement pore solution
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
s.t.	Short time adsorption measurement
T	Temperature
TOC	Total organic carbon
VPEG	Vinyl poly(ethylene glycol) ether
w/c ratio	Water to cement ratio
w/o	Without
wt.-%	Weight percent
XPEG	Crosslinked PCE polymers
XRD	X-Ray diffraction
ζ-potential	Zeta potential

Common cement chemistry notation

Notation	Chemical formula	Mineral name
A	Al_2O_3	Aluminium oxide
C	CaO	Calcium oxide
F	Fe_2O_3	Iron oxide
H	H_2O	Water
S	SiO_2	Silicon dioxide
s	SO_3	Sulfur trioxide
C_3S	$Ca_3O(SiO_4)$	Tricalcium oxy silicate
C_2S	$Ca_2(SiO_4)$	Dicalcium silicate
C_3A	$Ca_9(Al_6O_{18})$	Tricalcium aluminate
$C_4A_xF_{1-x}$	$Ca_4Al_2Fe_2O_{10}$	Tetracalcium alumino ferrite
Cs	$CaSO_4$	Calcium sulfate
$C_3A \cdot 3Cs \cdot H_{32}$ (AF_t)	$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot 26\ H_2O$	Ettringite
$C_3(A,F) \cdot 3Cs \cdot H_{32}$ (AF_t)	$[Ca_3(Al_xFe_{1-x})(OH)_6]_2(SO_4)_3 \cdot 26\ H_2O$	Iron ettringite
$C_3A \cdot Cs \cdot H_{12}$ (AF_m)	$[Ca_2Al(OH)_6]_2(SO_4) \cdot 6\ H_2O$	Monosulfoaluminate
C-S-H	$Ca_5[Si_6O_{18}H_2] \cdot 8\ H_2O$	Tobermorite } Calcium silicate hydrate
	$Ca_9[Si_6O_{18}H_2(OH)_8] \cdot 6\ H_2O$	Jennite } Calcium silicate hydrate
CH	$Ca(OH)_2$	Calcium hydroxide / Portlandite

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1 Introduction

Concrete is not only one of the most favored materials worldwide to construct buildings, but also to create objects of prestige. The versatility of cement even allows its use in art and decoration. Due to these almost unlimited possibilities of application, it is not surprising that about 4,100 million tons of cement were produced worldwide in 2018. As can be seen in **Figure 1**, the absolute leader was China with approx. 2,370 million tons, followed by India (290 million tons) and the United States (88.5 million tons) [1].

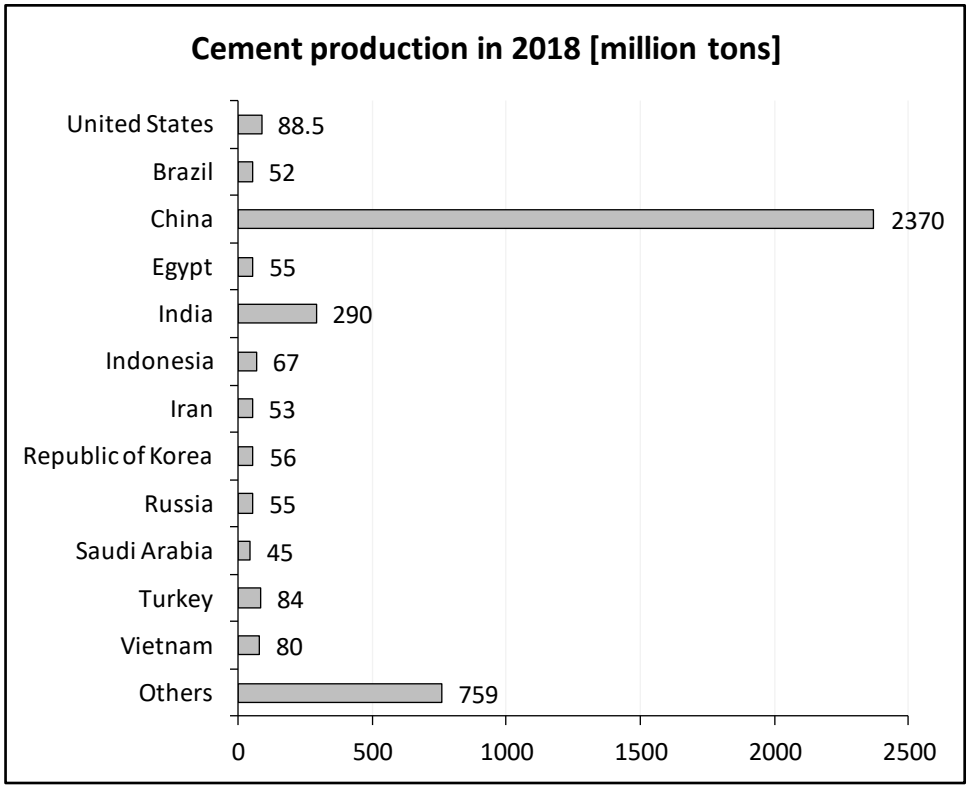


Figure 1. Worldwide cement production in 2018 estimated by the U.S. Department of the Interior U.S. Geological Survey [1].

Admixtures are used to equip the concrete with properties required to improve its workability and durability. One of the most important types of admixtures are polycarboxylate superplasticizers (PCEs). They guarantee high fluidity of cement paste and therefore easy pumping of concrete and allow the transportation of freshly mixed concrete over hours from the concrete factory to the construction sites with stable consistency and workability through slump-retaining effects. Furthermore, they allow lower water amounts in the concrete maintaining a consistent processibility at the same time enhancing the strength and freeze/thaw resistance. All these properties are based on

the ability of PCE superplasticizers to adsorb on the surface of cement particles or its hydration products, which leads to an electrostatic and steric repulsion between these particles resulting in desagglomeration and therefore dispersing effectiveness [2-4].

A characteristic feature of the PCE superplasticizers is that they can be used for both precast and ready-mix concrete due to their adjustable molecular structure [5]. Furthermore, many different kinds have been developed for a wide variety of special applications since the company *Nippon Shokubai* invented the first PCE [6-8]. To date, PCEs are considered the most effective class of plasticizers. Nevertheless, they need to be constantly redeveloped to meet the ever-changing challenges of modifying cement compositions and contaminated materials with for instance clay. Moreover, the desires for multifunctional products possessing additional properties such as a dispersing and defoaming ability or a reduced concrete stickiness are becoming more important [9]. Especially this area is subject of current research. However, the following images of *Burj Khalifa* and *The Dancing House* (see **Figure 2**) reflect all about ultra-high performance concrete (produced with PCEs) and serves as an example on what can be realized with concrete and its admixtures.

Figure 2. Burj Khalifa (Dubai, United Arab Emirates) [10] and The Dancing House (Prague, Czech Republic [11].

2 Aim and scope of this thesis

The application of PCE superplasticizers is essential for today's construction industry. The steady decline of raw materials for cement production already means that only contaminated materials (for example with clay) are available in some areas. Furthermore, special properties of the PCEs are desired such as less air entrainment, an increasing flow speed or reduced stickiness of the concrete [9]. In order to meet these challenges, a great amount of research is being conducted in the field of PCEs. The aim is to develop dispersing agents which can cope with the properties mentioned above. Most research groups focus on the invention of new structures of PCEs by (1) incorporating an additional monomer to already known PCE structures [12-16] or (2) by investigating completely new chemical structures [17-21].

Only few investigations have been carried out so far to improve already existing superplasticizers (common PCEs) by changing their synthesis method. Modifications in the PCE synthesis that have already been tested aimed to polymerize block copolymers instead of random PCEs [22-25]. For instance, Weidmann et al. [26,27] studied the difference between conventional PCEs with a random order of side chains and carboxylic groups and PCEs with a well-defined block structure (separate blocks of side chains or carboxylic acids). They found an improved dispersing effect in alkali-activated binders as well as reduced mixing times for concrete when using the block copolymers. In addition, Wang et al. [28] and Pourchet et al. [29] found improved sulfate tolerance of their block copolymers. The decisive disadvantage of these polymers however lies in their expensive synthesis, which can only be achieved by "controlled radical polymerization" (CRP), respectively reversible addition-fragmentation chain transfer polymerization (RAFT) or atom transfer radical polymerization (ATRP). Additional chemicals are usually necessary for these polymerization processes [30,31].

The aim of this study was to improve common PCEs by changing details in the synthesis process. However, unlike in the previous works, the polymerization process should continue to rely on the "free radical copolymerization" mechanism and use only easily accessible chemicals. Therefore, zwitterionic and anionic isoprenol ether-based polycarboxylate superplasticizers (IPEG PCEs) with a uniform chain length of 52 ethylene oxide units and a molar ratio of acrylic acid to macromonomer (= AA:MM) of 2:1, 3:1, 4.5:1 and 6:1 were synthesized in different manners. The synthesis methods compared to those of the anionic PCEs synthesized according to a well established, conventional standard procedure [32] were changed using a redox initiator system (Fe(II)-salt, Rongalit® and H_2O_2) instead of ammonium

persulfate initiator and the addition process of the chemicals during the synthesis was modified. By means of size exclusion chromatography (SEC) and ionic charge amount measurements, the compositions of the synthesized superplasticizers were determined. Furthermore, the dispersing effectiveness was compared to those of the conventional PCEs. One PCE per synthesis process was additionally tested for its clay and sulfate tolerance.

In a next step, the most promising synthesis method with the shortest polymerization process developed in the sections before was evaluated in more detail. Now, pure anionic isoprenol ether-based polycarboxylate superplasticizers with 23 and 52 ethylene oxide units in the side chains and a molar ratio of AA:MM of 2:1 were prepared. To capture the impact of polymerization time in the applied synthesis process on the polymers formed, the syntheses were repeated with a prolonged polymerization time and polymer formation was observed via SEC during the polymerization processes. All resulting PCEs were compared with respect to their composition and dispersing effectiveness. In order to get a particularly detailed impression of the specific properties of these PCEs, their dispersing performance was investigated in cement and mortar with different water to cement ratios (w/c ratio) in presence and absence of montmorillonite clay and additional sulfate ions. Additionally, the superplasticizers were tested for slump retention.

The simplest way to improve the dispersing effectiveness of standard PCEs is to change their pH value to be more acidic. Based on this observation, the last part of this research included the influence of the pH value of a PCE superplasticizer solution on its dispersing effectiveness. Therefore, the dispersing performance of conventional isoprenol ether-based (IPEG PCEs), α-methallyl-ω-methoxy-based (HPEG PCEs) as well as α-allyl-ω-methoxy-based (APEG PCE) superplasticizers with a pH value of 1.5 and 7.0 was determined according to a standard “mini slump” test and a modified procedure in which the superplasticizer was added to the cement slurry later. To capture the impact of cement composition, three different types of cement were established, which differ strongly in their orthorhombic C_3A (C_3A_o) and hemihydrate contents. In order to shed light on the reason for different dispersing abilities of some PCEs dependent on the pH value, nano ettringite was extracted from cement slurries admixed with PCE solutions (pH = 1.5 or 7.0). Moreover, the impact of an acidic or neutralized PCE solution on synthetic ettringite precipitation was investigated by means of dynamic light scattering (DLS) and scanning electron microscopic (SEM) imaging. Afterwards, the adsorption behaviors of acidic and neutralized PCE solutions on cement paste were determined by means of

TOC measurements from cement paste centrifuged after 20 seconds (immediate adsorption) or after 2 minutes.

3 Theoretical background and state of the art

3.1 Portland cement and its hydration

The raw material for Portland cement clinker is raw meal, a grinded mixture of claystones and limestones, which are won by querry mining. In addition to the main component $CaCO_3$ (calcium carbonate), SiO_2 (silicon dioxide), Al_2O_3 (aluminium oxide) and Fe_2O_3 (iron oxide) are present. In order to gain cement clinker, the calcination of the raw materials in a rotary kiln is required at a temperature of ~ 1450 °C. Inside, $CaCO_3$ is converted to CaO (calcium oxide) at lower temperatures, from which calcium aluminates and calcium silicates are formed in regions of higher temperatures together with the other components [33]. The resulting main clinker phases are alite ($Ca_3O(SiO_4)$, C_3S, tricalcium oxy silicate) and belite ($Ca_2(SiO_4)$, C_2S, dicalcium silicate) which have a negative ζ-potential, whereas aluminate ($Ca_9(Al_6O_{18})$, C_3A, tricalcium aluminate) and ferrite ($Ca_4Al_2Fe_2O_{10}$, $C_4A_xF_{1-x}$, tetracalcium aluminate ferrite) possess a positive ζ-potential. For anionic PCEs, the C_3A is most important as its surface allows the adsorption of the negative anchoring groups of the PCE superplasticizers (see **Section 3.3.1.4**). Furthermore, on $C_4A_xF_{1-x}$ and the hydration product ettringite, the superplasticizer adsorption is rather high [2,5].

In order to use the cement clinker, it must be ground to cement powder, to which usually additives such as sulfate carriers (gypsum, hemihydrates or anhydrite) are then added. They make the rapid hydration reaction of the tricalcium aluminate clinker (C_3A) more controllable by limiting the immediate formation of platelet-shaped C_2AH_8 and C_4AH_{13} crystals and instead enable the reaction to ettringite crystals which only occurs in the presence of sufficient sulfate ions [2,5,33].

According to DIN EN 197-1 [34], cement is a hydraulic binder, which means a finely ground, inorganic raw material. Combined with water, a cement paste is produced which sets (cement paste has lost plasticity, but possesses almost no strength) and hardens (intergrowing hydrate phases → measurable compressive strength) through hydration – even under water. Once hardened, it keeps its shape and strength and cannot be dissolved [35]. Moreover, the hydration products arising during cement hydration are essential for cement properties and dictate the mode of action for many additives and admixtures like for example superplasticizers.

In terms of time, according to Stark and Wicht [36], the cement hydration proceeds in 5 steps, with the *pre-induction period* being the first one. Especially C_3A, C_3S and sulfate carriers dissolve quickly until saturation is reached. Dissolving C_3A results in the formation of ettringite (AF_t phase) on the surface of clinker particles. Furthermore, metastable syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) and first metastable C-S-H are formed. In the following step, the so-called *induction (dormant) period* the dissolution of e.g. C_3S and further hydration reactions are prevented [33,35-37]. In general, there are two different theories for this behavior: according to the “protective membrane theory”, precipitated, amorphous C-S-H gel prevents further dissolution by surrounding and shielding the C_3S, whereas, according to the “dissolution theory”, the dissolution rate of C_3S considerably decreases when the system is close to a solution equilibrium [38,39]. However, the sulfate ion concentration in the solution remains rather uniform in spite of the consumption caused by the formation of ettringite crystals because of the additional dissolution of calcium sulfate. As soon as osmosis decomposes the layers blocking precipitation or the slow dissolution is overcome, the *acceleration period* can start. The highest heat release can be observed here. Now, “second-stage” C-S-H is formed by the hydration of C_3S and C_2S. Moreover, portlandite ($Ca(OH)_2$) is produced and the metastable syngenite is decomposed to secondary gypsum, which promotes the formation of ettringite. As long as the concentration of sulfate is three times the amount of aluminate, ettringite is still formed. But whenever the concentration decreases, ettringite is converted to monosulfoaluminate (AF_m) in the presence of C_3A and $C_4A_xF_{1-x}$. This happens in the so-called *deceleration period*, in which all hydration reactions slow down due to the decreasing amount of cement clinkers. However, the ongoing hydration of C_3S and C_2S leads to further C-S-H. In the *final hydration period*, the increasing amount of the already formed cement hydrate products severely limit all reactions due to diffusion control. The only reactions still occurring are condensation reactions between SiO_4 tetrahedrons, a so-called aging process of hydrate phases [33,35-37].

To investigate the hydration reactions from a chemical point of view, the reaction equations for the most important components are given in the following paragraphs.

When silicate hydration reactions are taking place (C_3S and C_2S), portlandite and amorphous C-S-H layers will always be formed (see **Equation 1**, **2**). Only a general formula for C-S-H is given because of its varying composition.

$$\underbrace{Ca_3O(SiO_4)}_{\mathbf{C_3S}} + x\ H_2O \rightarrow \underbrace{y\ CaO \cdot SiO_2 \cdot (y\text{-}(3\text{-}x))\ H_2O}_{\mathbf{C\text{-}S\text{-}H}} + \underbrace{(3\text{-}y)\ Ca(OH)_2}_{\mathbf{Portlandite}}$$

Equation 1. Reaction of C_3S with water to C-S-H and portlandite [5].

$$\underbrace{Ca_2(SiO_4)}_{\mathbf{C_2S}} + x\ H_2O \rightarrow \underbrace{y\ CaO \cdot SiO_2 \cdot (y\text{-}(2\text{-}x))\ H_2O}_{\mathbf{C\text{-}S\text{-}H}} + \underbrace{(2\text{-}y)\ Ca(OH)_2}_{\mathbf{Portlandite}}$$

Equation 2. Reaction of C_2S with water to C-S-H and portlandite [5].

Aluminate hydration reactions depend on the amount of sulfate available. These amounts are adjusted through addition of sulfate carriers, which enable hydration reactions of C_3A and $C_4A_xF_{1-x}$ to ettringite or monosulfoaluminate (see **Equation 3**, **4**).

$$C_3A + \underbrace{3\ CsH_2}_{\mathbf{Gypsum}} + 26\ H \rightarrow \underbrace{C_3A \cdot 3\ Cs \cdot H_{32}}_{\mathbf{Ettringite\ (AF_t)}}$$

Equation 3. Reaction of C_3A with gypsum, water and high SO_4^{2-} concentration to ettringite [5].

$$3\ C_4A_xF_{1-x} + \underbrace{12\ CsH_2}_{\mathbf{Gypsum}} + 110\ H \rightarrow \underbrace{4\ [C_3(A,F) \cdot 3\ Cs \cdot H_{32}]}_{\mathbf{Iron\ ettringite\ (AF_t)}} + \underbrace{2\ [(A,F)H_3]}_{\mathbf{Aluminum\text{-}\ and\ iron\ hydroxide}}$$

Equation 4. Reaction of $C_4A_xF_{1-x}$ with gypsum, water and high SO_4^{2-} concentration to iron ettringite [5].

In presence of fewer sulfate ions, mainly monosulfoaluminate is formed (see **Equation 5**).

$$C_3A + \underbrace{CsH_2}_{\mathbf{Gypsum}} + 10\ H \rightarrow \underbrace{C_3A \cdot Cs \cdot H_{12}}_{\mathbf{Monosulfoaluminate\ (AF_m)}}$$

Equation 5. Reaction of C_3A with gypsum, water and low SO_4^{2-} concentration to monosulfoaluminate [5].

At the end of the acceleration period, when the concentration of sulfate ions is very low, ettringite is able to react with C_3A or $C_4A_xF_{1-x}$ to monosulfoaluminate (see **Equation 6**, **7**).

$$2\ C_3A + \underbrace{C_3A \cdot 3\ Cs \cdot H_{32}}_{\mathbf{Ettringite\ (AF_t)}} + 4\ H \rightarrow \underbrace{3\ C_3A \cdot Cs \cdot H_{12}}_{\mathbf{Monosulfoaluminate\ (AF_m)}}$$

Equation 6. Reaction of C_3A with ettringite to monosulfoaluminate [5].

$$3\ C_4A_xF_{1-x} + \underbrace{2\ [C_3(A,F) \cdot 3\ Cs \cdot H_{32}]}_{\textbf{Iron ettringite } (AF_t)} + 14\ H \rightarrow \underbrace{6\ [C_3(A,F) \cdot Cs \cdot H_{12}]}_{\textbf{Monosulfoaluminate } (AF_m)} + \underbrace{2\ [(A,F)H_3]}_{\textbf{Aluminum and iron hydroxide}}$$

Equation 7. Reaction of $C_4A_xF_{1-x}$ with iron ettringite to monosulfoaluminate [5].

Figure 3 shows the cement hydration depending on the hydration time according to Stark et al. [40] and modified by Plank et al. [5].

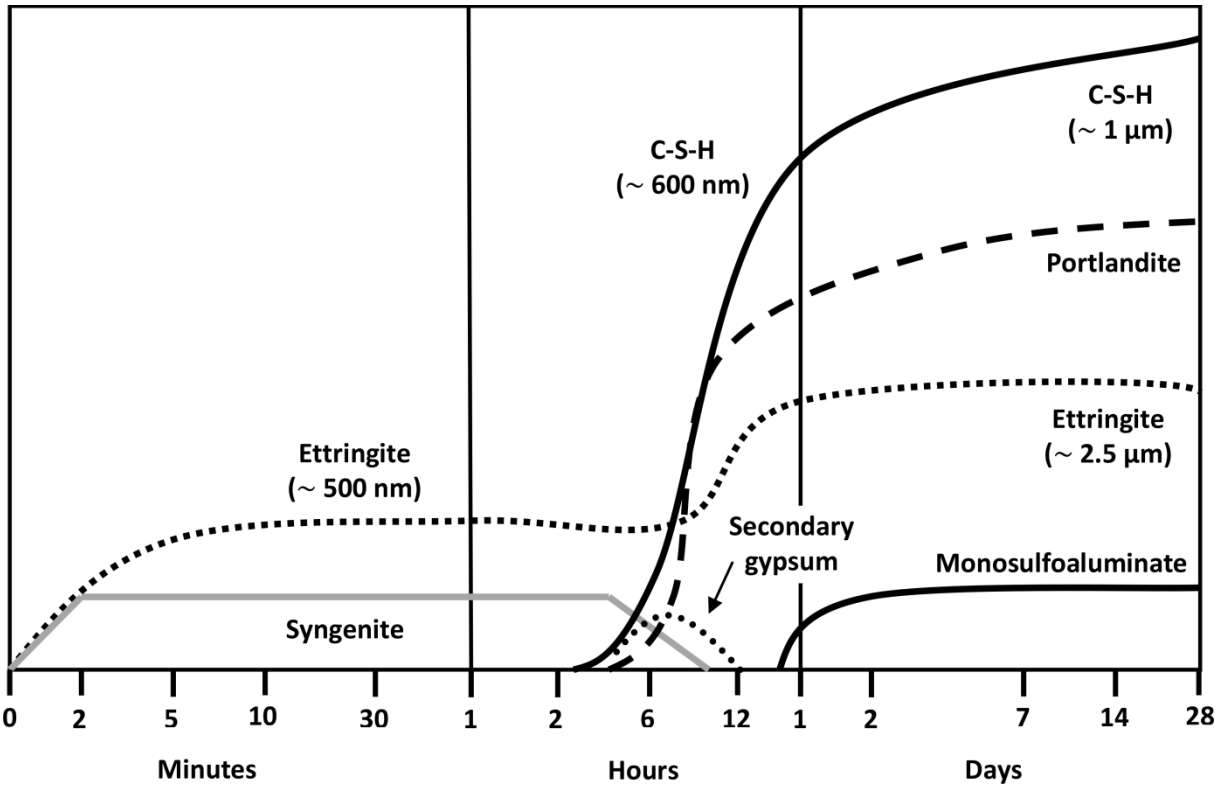


Figure 3. Cement hydration depending on the hydration time [40] modified from [5].

3.2 Structure, composition and properties of ettringite

Ettringite is one of the first hydration products formed almost immediately when cement is mixed with water [41]. One important condition is an excess of sulfate ions in the system, which is usually ensured by means of a sulfate carrier [5] as otherwise, monosulfoaluminate will be produced (see **Section 3.1**). Due to the positive ζ-potential of ettringite, it plays a role for PCE superplasticizer adsorption in cement pastes. As it impacts the dispersing performance to a high degree, ettringite is highlighted in the following sections.

3.2.1 Structure and composition of ettringite

In general, ettringite crystals have a characteristic hexagonal prismatic (needle-like) shape and consist of two structural components. On the one hand, there are columns with the formula $[Ca_6[Al(OH)_6]_2 \cdot 24H_2O]^{6+}$, on the other hand, there are channels (the voids between the columns) composed of $[(SO_4)_3 \cdot 2H_2O]^{6-}$. Octahedral $Al(OH)_6$ units fill the inside of the columns which alternate with three connected (edge-sharing) CaO_8 polyhedra. The Ca^{2+} coordinates four OH^- ions, which are also part of the $Al(OH)_6$ octahedra. In addition, four water molecules are coordinated by the Ca^{2+} and represent the outside of the column. Four of the columns form a rhombus. The channels are filled with 3 SO_4^{2-} ions and 2 water molecules [42-45]. The crystal structure of ettringite is shown in **Figure 4**.

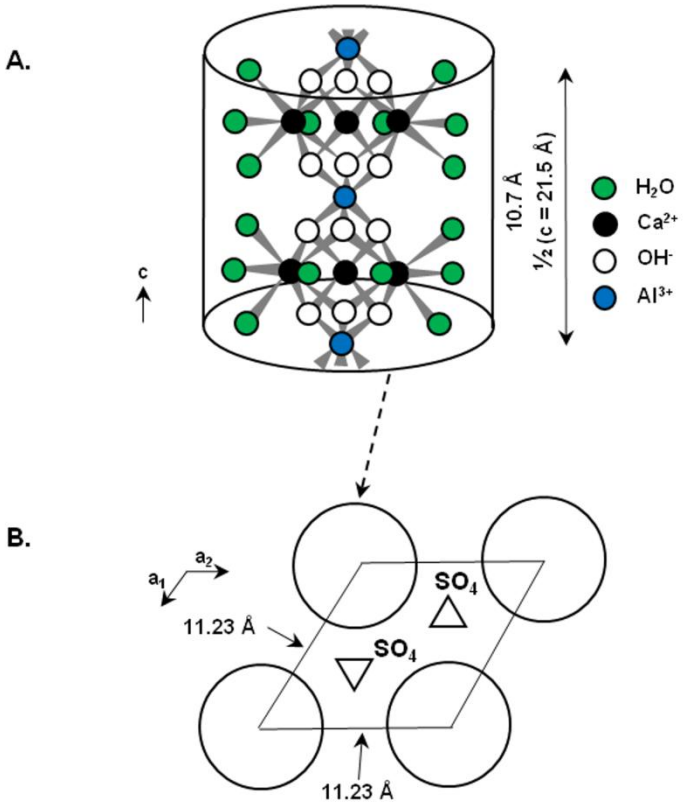


Figure 4. Crystal structure of ettringite after Tailor [42] modified from [46] with c = crystallographic axis and a_1 and a_2 = unit cell spacings. (A) Structure of ½ ettringite column. (B) Arrangement of ettringite columns (circles) and channels (region between columns).

Goetz-Neunhoeffer et al. [47] found that the pH value has a strong influence on the ettringite crystal morphology. With an increasing pH value of 9.5 to 12.5, the so-called aspect ratio (length/width of the crystals) decreased. Kreppelt et al. [48] investigated the ettringite formation in a synthetic pore solution

with a pH value of only 12.5 instead of the usual value ≥ 13 and with higher SO_4^{2-} but less Ca^{2+}- concentration. The resulting ettringite exhibited slim crystals.

3.2.2 Influence of PCEs on ettringite formation

As already discussed in literature [41,49], ettringite is formed during early cement hydration. Several studies investigated the influence of PCEs on the ettringite formation. Due to the positive ζ-potential of ettringite caused by the cationic character of the columns that cover anions oriented towards inside (see **Section 3.2.1**), the columns represent a main adsorption surface for anionic PCEs [2,50-52]. For example, Lange et al. [53] found that in presence of PCEs, the morphology of ettringite changed. They referred to the PCEs as "morphology modifying agent", which is responsible for the significantly smaller size of the formed ettringite needles (only nano sized instead of meso sized). This change in crystal size results in a higher PCE polymer consumption due to additional surfaces which had to be covered. Moreover, an "interlocking effect" caused through a large number of small ettringite needles reduces the fluidity of the system [54]. Additionally, more water is required to wet the extra surfaces, which leads to a higher water demand of the system. According to Meier et al. [55], strongly anionic PCEs influence the morphology of synthetic ettringite during precipitation more (→ smaller crystals) because they adsorb in higher amounts on the ettringite crystals resulting in stronger modifications. A change in the aspect ratios of the ettringite crystals was observed as well. In contrast to the findings for PCEs, Cody et al. [46] detected that most carboxylic acids cannot influence the morphology of ettringite crystals. Only those which are able to chelate Ca^{2+} showed an effect. Furthermore, Dalas et al. [56] investigated PCEs with different anionic charge in a system which was more similar to a cement slurry (paste consisting of synthetic cement pore solution, C_3A, gypsum, hemihydrates, $CaCO_3$) than to synthetic ettringite. They revealed that a stronger delay in ettringite precipitation occurred with an increasing charge and dosage of PCE. Additionally, the surface area of the ettringite crystals was increased within the first 5 minutes of hydration which proved that (1) smaller crystals were formed in presence of PCE and (2) the interaction of PCE and ettringite takes place at the very beginning of hydration. Moreover, Meier et al. [55] supposed that the influence of the superplasticizer on the ettringite crystals depends on the kind of macromonomer in the PCE. These findings were confirmed by Shi et al. [57].

In addition, PCE superplasticizers do not only influence the ettringite morphology, but also impact the entire cement hydration. It is already known that PCEs cause a delay in aluminate hydration because they can complex Ca^{2+} ions resulting in a smaller amount of precipitates. Furthermore, PCEs can adsorb on the surfaces of hydration products and stop their growth by shielding the surface [58].

3.3 Superplasticizers

3.3.1 Superplasticizers – chemical structure and mode of action

After the previous sections were devoted to cement and its hydration, the group of "superplasticizer" admixtures is now explained in more detail. In general, two different kinds of superplasticizers – the polycondensates and the polycarboxylates – are commonly used. In the following sections, they are introduced.

3.3.1.1 Chemical structure of polycondensates

Polycondensate superplasticizers are linear, short-chained macromolecules or oligomers with a high anionic charge density which originates from sulfonic acid groups contained in the molecule [59]. As shown in **Figure 5**, a polycondensate can be schematically represented as a chain (main chain) possessing anionic charges. These types of superplasticizers are synthesized through a condensation reaction which is a kind of organic addition reaction and always results in an addition product and water [60]. As raw material α`-methylol β-naphthalene sulfonic acid, dimethylol melamine methylene sulfonic acid sodium salt or the combination of acetone, formaldehyde and sodium sulfite is used [5].

Figure 5. Schematic representation of the basic structure of a polycondensate superplasticizer; modified from [5].

3.3.1.2 Chemical structure of polycarboxylates (PCEs)

Polycarboxylate-based superplasticizers (PCEs) are synthetic, organic polymers synthesized through a radical copolymerization processes with very good dispersing effectiveness in cement, mortar, or concrete. In contrast with polycondensate superplasticizers, they always possess a comb structure composed of a main chain, the so-called backbone, and side chains (see **Figure 6**). The main chain bears the ionic charge: for anionic charge, carboxylic acid groups are directly integrated in the backbone chain. Deprotonation of these carboxyl groups at high pH value, which exists in cement paste, mortar, or concrete, leads to anionic charge.

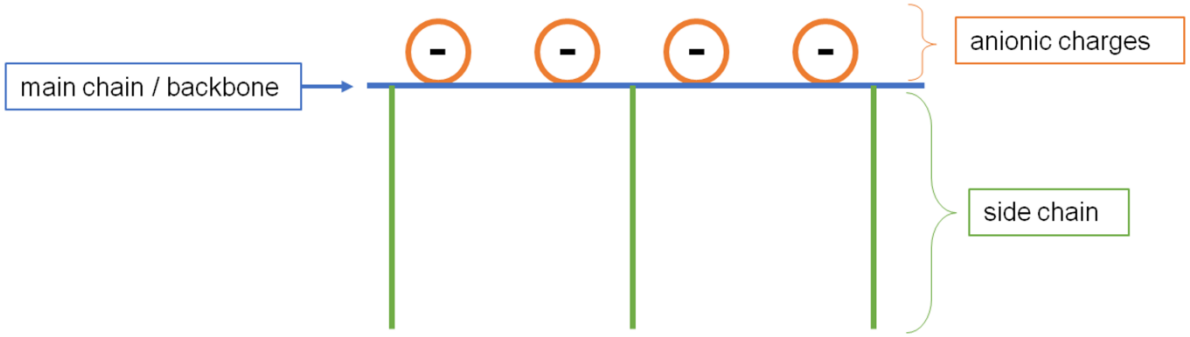


Figure 6. Schematic representation of the basic structure of an anionic PCE superplasticizer; modified from [5].

However, through (quarternary) ammonium-bearing monomers involved in the main chain, cationic charge can be established as well. Side chains are connected to the main chain by ester or ether (sometimes amide or imide) bonds and mainly consist of poly(ethylene glycol) which gives them the typical hydrophilic and uncharged character [5,59].

3.3.1.3 Mode of action of polycondensates

The dispersing effect of a polycondensate exclusively relies on an electrostatic stabilization as shown in **Figure 7**. The sulfonic acid groups contained in the polycondensate enable an adsorption on positively charged surface areas of cement clinker phases like C_3A and cement hydration products like ettringite or monosulfoaluminate. The resulting anionic charge of the whole cement particles and hydration products lead to electrostatic repulsion between them and therefore to a desagglomeration which provides dispersing effectiveness [3,61,62].

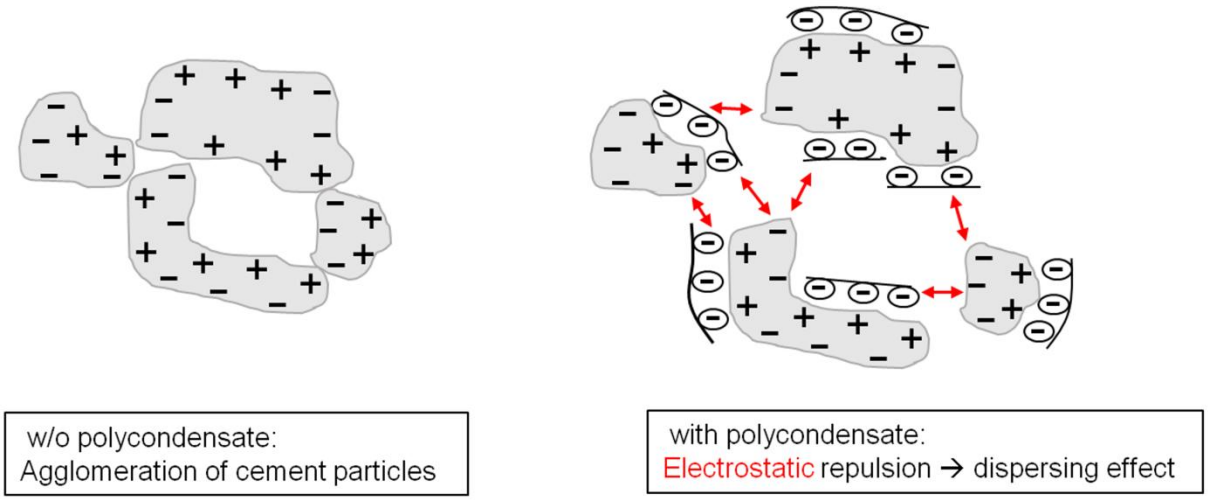


Figure 7. Schematic representation of the mode of action of a polycondensate superplasticizer. Agglomeration of clinker particles and hydration products due to different surface charges (left) and dispersing effect with a polycondensate through electrostatic repulsion (right); modified from [63].

3.3.1.4 Mode of action of polycarboxylate superplasticizers using the example of anionic PCEs

The dispersing effectiveness of PCE superplasticizers is based on a mixture of electrostatic and steric stabilization as can be seen in **Figure 8** [4].

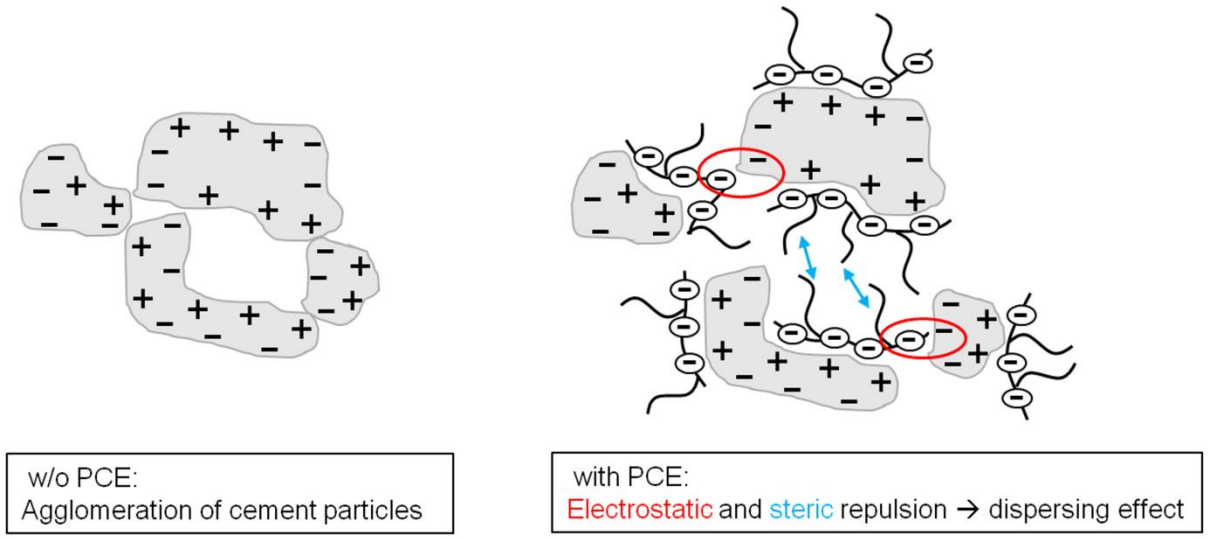


Figure 8. Schematic representation of the mode of action of an anionic PCE superplasticizer. Agglomeration of clinker particles and hydration products due to different surface charges (left) and dispersing effect with an anionic PCE through electrostatic and steric repulsion (right); modified from [63].

The adsorption of the PCEs through their negatively charged backbone on positively charged cement clinker or hydration surfaces (C_3A, ettringite, monosulfoaluminate) lead to charge neutralization resulting in an exclusive negatively charged clinker and hydration surface [2]. The arising electrostatic repulsion between the clinker particles and hydration products contributes to dispersing effectiveness. Furthermore, the adsorbtion of the PCE superplasticizer lead to a radial protrusion of the side chains into the cement pore solution [3]. The outcome of this is a steric repulsion between such clinker particles or hydration products and therefore an increase of the dispersing effect of the cement slurry.

Depending on the length of the side chains used in the PCE, the main mechanism of dispersion changes: Short side chains cause only minor steric repulsion as these PCEs are mostly based on electrostatic repulsion. Meanwhile, the dispersing effect of PCEs which contain long-side chains is dominated by steric repulsion. Here, the anionic charge only enables adsorption on the clinker and hydration particles [64].

In addition, non-adsorbed particles such as uncharged polyglycols or polymer molecules, can improve the steric repulsion in the cement pore solution, especially at low water to cement ratios [65,66]. Lange et al. [65] assumed that the non-adsorbed particles “form a thin film which acts as a lubricant reducing the friction between adjacent cement particles” [65]. The model is shown in **Figure 9**.

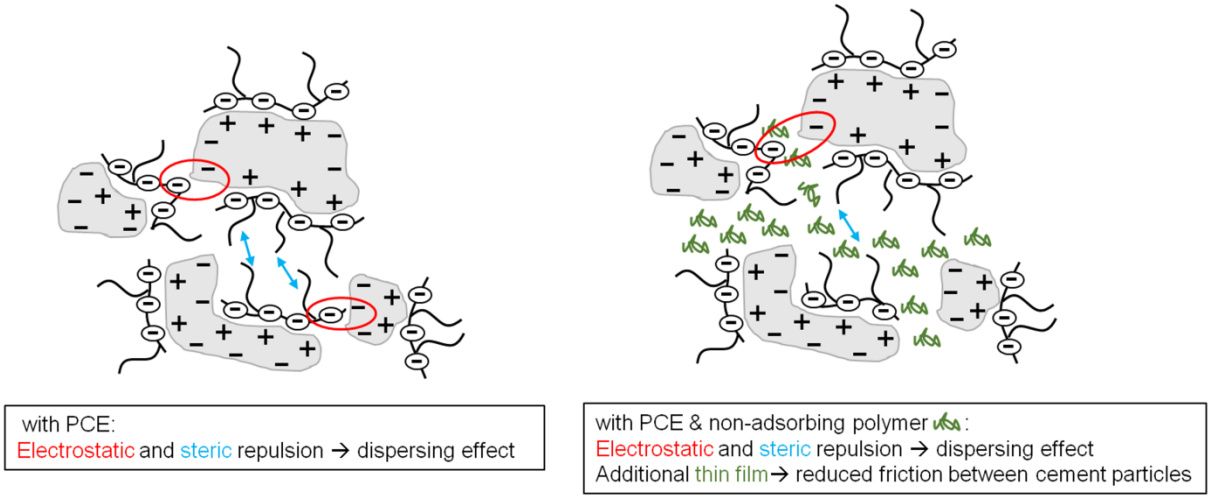


Figure 9. Model explaining the dispersing effect of non-adsorbed particles at low water to cement ratios; modified from [65].

The following section addresses the multiple uses of PCE superplasticizers depending on their molecule structure.

3.3.1.5 Dependency of plastification on the PCE molecular structure

A special characteristic of PCEs is their variability in molecular structure. For most kinds of PCEs, it is possible to modify the side chain density or rather the ionic charge density, which in turn affects the dispersing effectiveness of the superplasticizer. In general, the more side chains are contained per unit length in a PCE polymer (= high side chain density), the lower its ionic charge amount and the longer the dispersing effectiveness over time will be. This makes PCEs with high side chain density ideal for ready-mix concrete, while PCEs with low side chain densities are especially used for precast concrete as is illustrated in **Figure 10**. The origin of the different time-delayed dispersing abilities lies in the different adsorption rates on clinker or hydration surfaces. A PCE with low anionic charge amount adsorbs only to 20 - 50 % directly after the mixing procedure. This results in (1) a low dispersing effectiveness directly in the beginning (can be compensated with higher dosage) and (2) in a superplasticizer reservoir in the mixing water which has not already adsorbed and therefore is still available after a certain amount of time. In contrary, a PCE with high ionic charge amount adsorbs almost completely after the mixing procedure on the clinker or hydration particles. An excellent dispersing effect is reached immediately, but loses its effect quite fast [5].

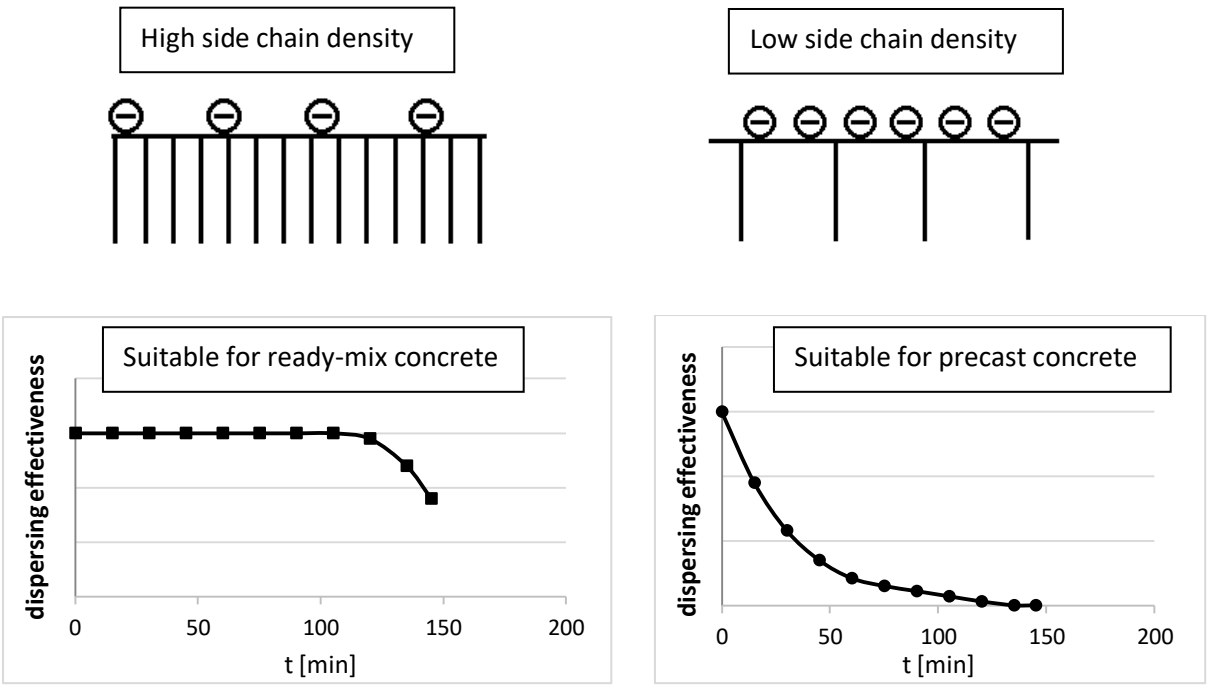


Figure 10. Relationship between PCE structure and dispersing effectiveness; modified from [5].

It is worth noting that an overdosis of PCEs will cause segregation of the cement paste, with heavy particles sinking to the bottom and the mixing water accumulating at the top (surface). This process is referred to as “bleeding” and is undesirable [59].

3.3.1.6 Susceptibility of PCEs to clay und sulfate ions

Most concretes contain impurities of clay which are introduced to the system through aggregates such as sand and gravel. The problem, however, is that clay – especially montmorillonite – can considerably reduce the dispersing effect of the PCEs. Chemisorption of the PCE between the anionic alumosilicate layers of montmorillonite leads to a smaller amount of superplasticizers which is available for adsorption on clinker particles and hydration products and results in a decreased dispersing performance. This intercalation is based on hydrogen bonds. They are formed between the poly(ethylene glycol) side chains of the PCE and water molecules which are fixed by the silanol groups placed on the surface of the aluminosilicate layers of the clay as shown in **Figure 11** [67,68]. Moreover, physisorption on the surface of clays over Ca^{2+} bridges also diminishes the amount of PCE available for adsorption on clinker particles and hydration products [67,69-73].

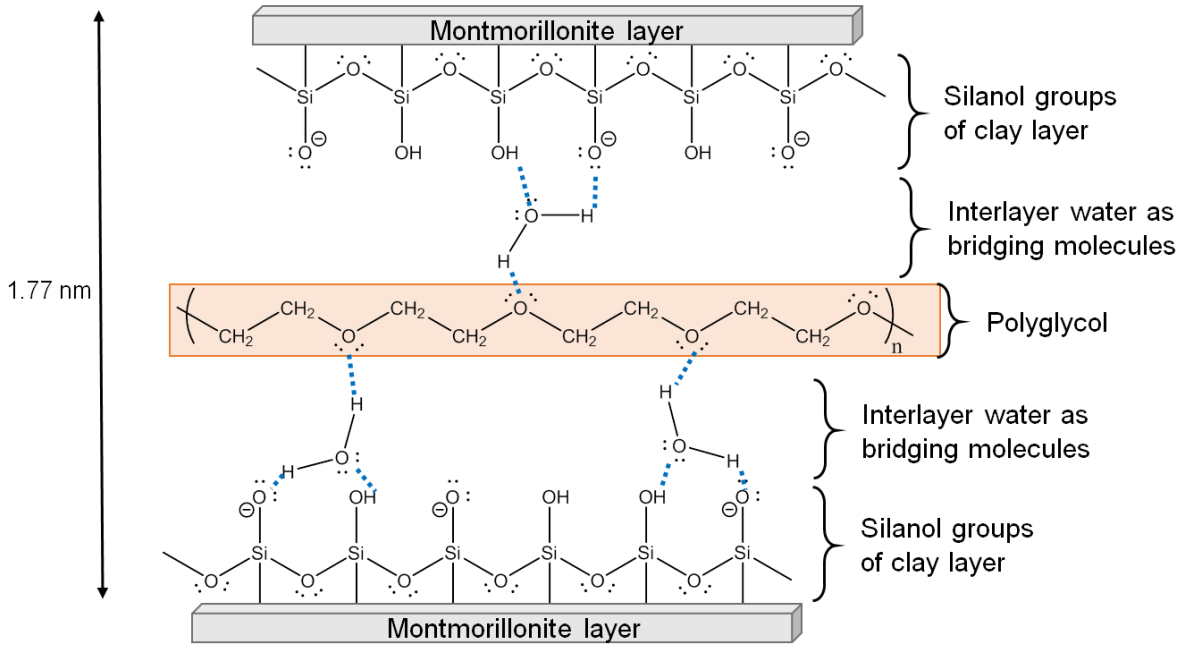


Figure 11. Intercalation of poly(ethylene glycol) between the alumosilicate layers of montmorillonite; modified from [67].

Another component which can influence PCE effectiveness are sulfate ions. They have a large influence especially in “over-sulfated cements”. The amount of PCE polymers is reduced through competitive adsorption with SO_4^{2-} ions on the clinker particles and hydration products which leads to lower dispersing effectiveness. As strongly negative PCEs cannot be easily displaced, the effect does not have a big impact on these types [74,75].

3.3.2 Synthesis of polycarboxylate superplasticizers

The superplasticizers synthesized in this study were exclusively prepared by free radical copolymerization. Therefore, the principle of this type of reaction is introduced in the following.

3.3.2.1 Basic principle of free radical copolymerization

In this reaction, a minimum of 2 different monomers were connected to a polymer chain in an alternating or statistic sequence according to the mechanism of a *radical polymerization.* This consists of three steps starting with the “initiation”. **Equation 8** shows the decomposition of the initiator molecule (I) (e.g. through temperature) in two radicals (R·) which react with a monomer (M) to a radical monomer molecule (RM·) [76,77].

$$\mathrm{I} \xrightarrow{\Delta T} 2\,\mathrm{R}\cdot \xrightarrow{2M} 2\mathrm{RM}\cdot$$

Equation 8. Initiation of a radical polymerization [76,77].

In the second step, the “propagation”, the polymer chain is growing. Therefore, the radical monomer molecule (RM·) reacts with further monomers (M) untill a macromolecular chain has been formed. In this step, the highest conversion of monomers takes place and the amount of radicals does not decline because the functionality is always propagated (see **Equation 9**). The more stabilized a monomer (e.g. resonance stabilization) is, the more slowly the polymer chain grows [76,77].

$$\mathrm{RM}\cdot \xrightarrow{n\,M} \mathrm{R(M)_nM}\cdot$$

Equation 9. Propagation of a radical polymerization [76,77].

The last step is called “termination”. Here, the radical polymer chains are able to combine with each other as presented in **Equation 10** or undergo a disproportionation reaction as demonstrated in

Equation 11. Only in case of a combination is the polymerization degree doubled, while it remains constant in a disproportionation reaction. Furthermore, every second polymer chain exhibits a double bond when a disproportionation has taken place. Usually, the combination reaction is favored due to smaller activation energy needed. However, other factors such as the viscosity of the reaction mixture also influence the actually occurring reaction [76,77].

$$2\ \mathrm{R(M)_nM^{\cdot}} \quad \rightarrow \quad \mathrm{R(M)_nM-M(M)_nR}$$

Equation 10. Combination of two polymer chains [76,77].

$$2\ \mathrm{R(M)_nCH_2CH_2^{\cdot}} \quad \rightarrow \quad \mathrm{R(M)_nCH_2CH_3} \quad + \quad \mathrm{CH_2=CH(M)_nR}$$

Equation 11. Disproportionation reaction of one polymer chain [76,77].

Based on the monomers used in the copolymerization reaction, different arrangement sequences in the macromolecular chain are possible. The copolymerisation parameter of each monomer determines whether the monomer preferentially reacts with itself or with the other monomer. For instance, in case of APEG PCEs (see **Figure 21**), alternating sequences are always obtained. For those PCEs, where both monomers can polymerize with each other, the ratio between the monomers used plays a role for the sequence, too. However, in most cases, a gradient copolymer is obtained due to the different reactivities of the monomers. In contrast, the “grafting process” (see description of MPEG PCEs) leads to very uniform (random) polymer chains (see **Figure 12**).

Figure 12. Schematic structure of a gradient and random copolymer; modified from [78].

3.3.2.2 Initiator systems for the free radical copolymerization

The three different initiator systems used in this work are specified here. Generally, an initiator is a molecule which decomposes in two equal parts with the shared electron binding pair being divided in two radicals. There are different classes of initiators depending on the activation of the decomposition [76,77].

Both ammonium persulfate (APS) and benzoyl peroxide (BPO) belong to the class of inorganic peroxides decomposing through thermal heat (~ 40 – 70 °C). Due to its water solubility, APS is suitable for polymerizations in aqueous solutions, whereas BPO is not water-soluble and is therefore mainly used for reactions in bulk [76,77]. **Figures 13** and **14** represent the thermal decomposition of APS and BPO.

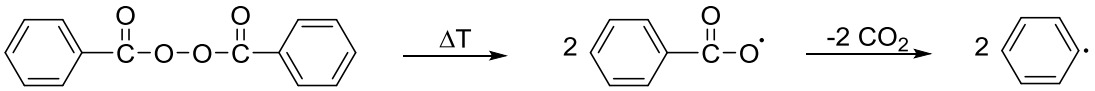


Figure 13. Thermal decomposition of benzoyl peroxide (BPO) [76].

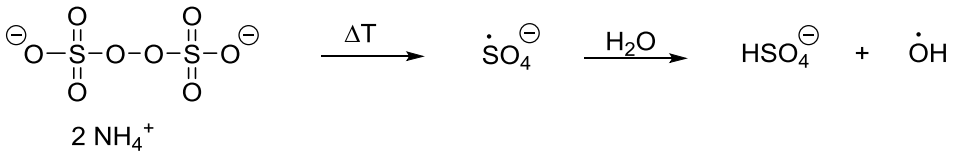


Figure 14. Thermal decomposition of ammonium persulfate (APS) [77].

As an alternative, a redox-initiator system can be used at 20 – 30 °C if low temperatures during synthesis are preferred to prevent the decomposition of monomers or autoinitiation (= formation of radicals by reaction of two monomers with themselves). The system applied here consisted of hydrogen peroxide, iron(II)sulfate heptahydrate, and Rongalit®. Using the latter, the amount of iron to be used in the system can be reduced [79]. However, as a first step, iron (II) is oxidized to iron (III) with the hydrogen peroxide decomposing in a hydroxide ion and a hydroxyl radical. Rongalit® reduces Fe(III) to Fe(II) and reacts as a radical with hydrogen peroxide to a hydroxyl radical and hydroxymethane sulfonic acid. Next, the hydroxyl radical reacts with hydrogen peroxide to water and a hydroperoxyl radical. Recombining of the hydroperoxyl radical with the Rongalit® radical results in sulfuric acid and formaldehyde [79,80]. In **Figure 15**, the whole redox process is described.

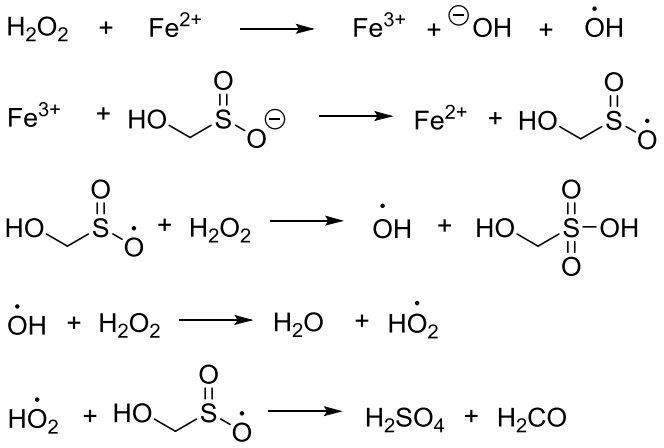


Figure 15. Reaction of the initiator redox system with hydrogen peroxide, iron(II)sulfate heptahydrate and Rongalit® [80].

Especially the synthesis of zwitterionic PCEs and the synthesis methods with very short reaction times of 5, 15, or 30 minutes for anionic and zwitterionic PCEs were performed with this system (see **Sections 5.1** - **5.4**). Two patents [81,82] served as general templates for these synthesis procedures with this initiator system. At this point, it should be mentioned that zwitterionic or cationic PCEs can also be prepared with other initiator systems like APS [83].

3.3.3 Superplasticizers and their variability

The following sections explain different kinds of superplasticizers and give an overview about the diverse product range. For this purpose, examples of polycondensates, the first type of superplasticizers, are discussed in **Section 3.3.3.1** followed by a selection of the later invented polycarboxylates described in more detail in **Section 3.3.3.2**.

3.3.3.1 Polycondensate superplasticizers

The first conventional superplasticizers were polycondensates. In 1962, the company Kao Soap (Japan) invented sulfonated naphthalene formaldehyde polycondensates (polynaphthalene sulfonate = PNS) while in the same year the company SKW Trostberg AG (Germany) established sulfonated melamine formaldehyde resins (polymelamine sulfonate = PMS) [84,85]. Later, in 1981, a third kind, the acetone formaldehyde sufite polycondensate (AFS) was developed by SKW Trostberg AG (Germany) [86,87].

3.3.3.1.1 Naphthalene sulfonate formaldehyde (PNS) & melamine formaldehyde sulfite resins (PMS)

In order to produce a PNS superplasticizer, three different reaction steps are required: At first, the raw material naphthalene is sulfonated to a β-naphthalene sulfonic acid. A methylolation with formaldehyde results in α`-methylol-β-naphthalene sulfonic acid, which then reacts to the PNS through a condensation reaction. **Figure 16** presents the reaction process [5].

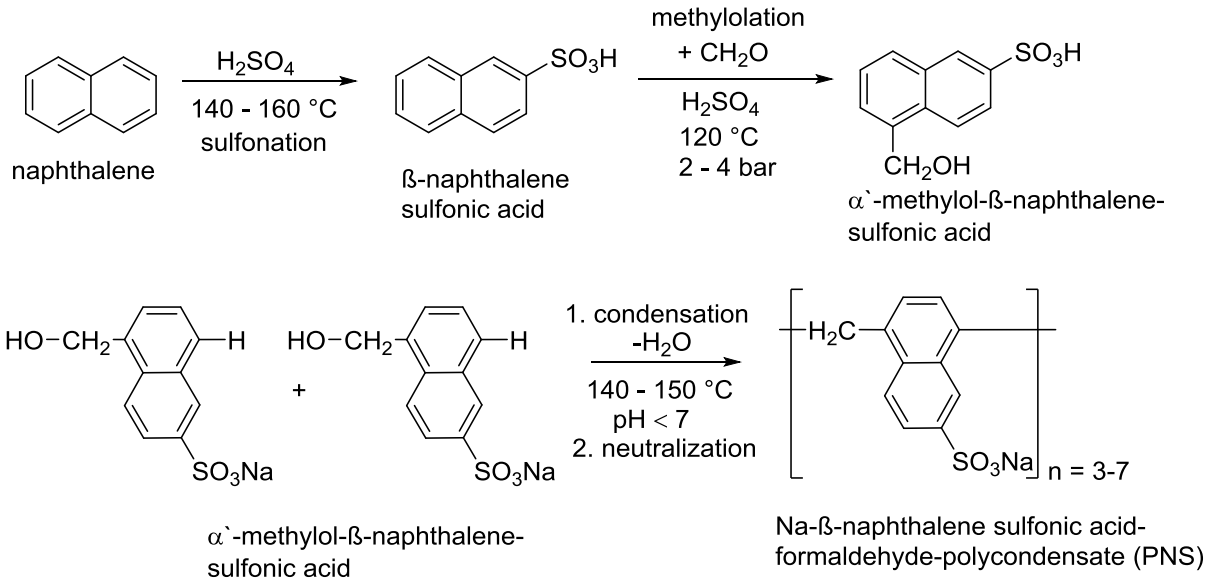


Figure 16. Reaction process for sulfonated naphthalene formaldehyde polycondensates (PNS).

The raw material for the PMS superplasticizer is melamine. However, similar to PNS, three different reactions are necessary to produce this polycondensate as shown in **Figure 17** [5].

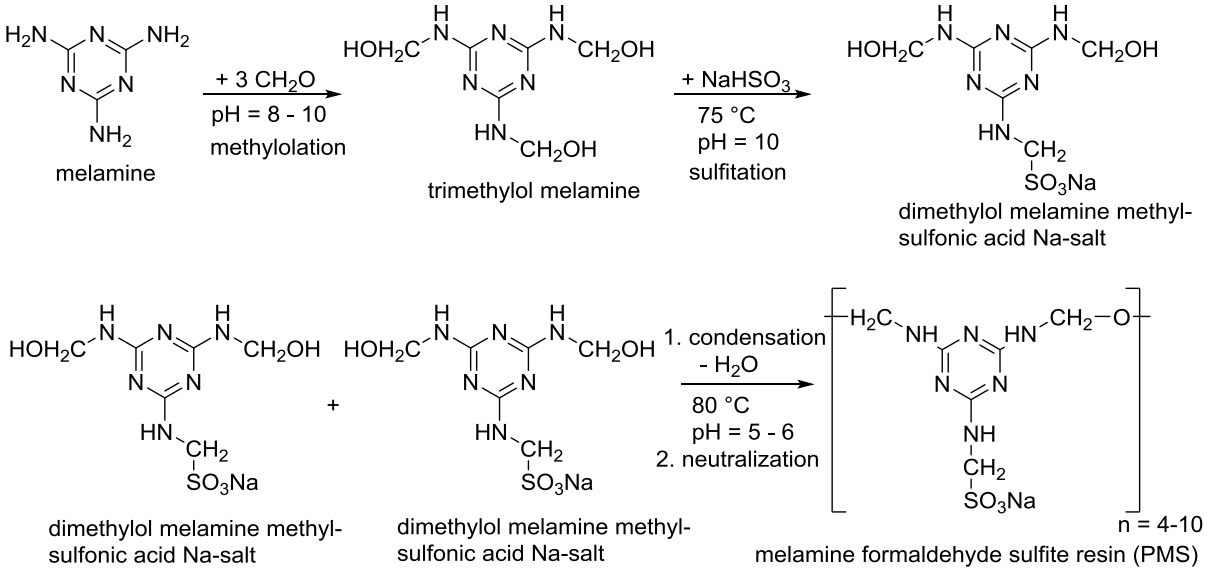


Figure 17. Reaction process for melamine formaldehyde sulfite resins (PMS).

Methylolation of melamine leads to trimethylol melamine which subsequently is sulfitized. The PMS is produced by the condensation reaction shown in **Figure 17**.

3.3.3.1.2 Acetone formaldehyde sufite polycondensate (AFS)

An advantage of the AFS superplasticizer is its easier synthesis compared to the previously mentioned products: thanks to an adol condensation of acetone, formaldehyde and sulfite, only one synthesis step is necessary for preparation as shown in **Figure 18**. However, the red color of the superplasticizer considerably limits its use [86,87]. To overcome this disadvantage, other components can be used for this synthesis. A similar, but less colored polycondensate superplasticizer consisting of sulfanilic acid, phenol and formaldehyde was for example invented in China [88].

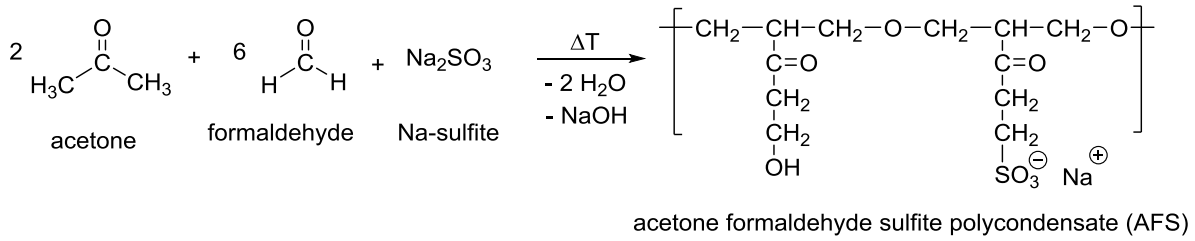


Figure 18. Reaction process for acetone formaldehyde sulfite polycondensate (AFS) [86,87].

In general, all polycondensates have a good initial dispersing effectiveness at low dosages of 0.1 - 0.3 % bwoc which make them preferable for precast concrete. However, their poor slump-retaining behaviour (loss of dispersing effectiveness after ~ 30 min) exclude them for ready-mix applications [89,90]. Additionally, their dispersing effect in high strength concrete (low w/c ratio) is insufficient as high dosages of polycondensates and long mixing times are required [66]. Due to their hardly variable chemical structure, these disadvantages cannot be overcome. Furthermore, the harmful formaldehyde is involved in all resins. Post-treatment with the *Cannizzaro* reaction or post-sulfiting reduces the content of free formaldehyde in the solutions, nevertheless, a small amount always remains [5,91].

These disadvantages of polycondensates were decisive for further research in the field of superplasticizers. Therefore, polycarboxylate superplasticizers were established which showed improved properties and which allowed more diverse fields of application.

3.3.3.2 Polycarboxylate superplasticizers (PCEs)

Table 1 gives an overview of the most important types of PCEs and their special characteristics. These PCE superplasticizers are explained in detail in the following sections.

Table 1. Overview of the most important PCE superplasticizers and their special characteristics.

Superplasticizer	Special characteristics of the PCEs
Carboxylic acid based PCEs	
MPEG PCE	- First generation of PCEs - Esterbond in macromonomer involved → can decompose at pH ≥ 12 - 2 different synthesis methods possible (grafting/esterification or free radical copolymerization in solution)
APEG PCE	- Second generation of PCEs - Always alternating copolymer - Synthesis in bulk or in aqueous solution - Etherbond in macromonomer involved→ no decomposition at pH ≥ 12
Amide-/Imide-type PCE	- Costly and rarely used
VPEG PCE	- Macromonomer is highly reactive →synthesis requires a redox initiator system at room temperature →macromonomer can polymerize with many different monomers which results in high diversity of the superplasticizer
IPEG PCE	- Reactive macromonomer → easy to polymerize - Room temperature synthesis possible - Etherbond in macromonomer involved→ no decomposition at pH ≥ 12 - PCE has excellent dispersing performance, especially at low w/c values
HPEG PCEs	- Very similar to IPEG PCEs - Main PCE kind in China
XPEG PCE	- Crosslinked polymer structure→ low dosages required
PCE from macroradicals	- Alternative to synthesize a PCE without a macromonomer
PCE with reduced sensitivity to clay	- PCEs without a poly(ethylene glycol) side chain
PCEs combined with defoamer	- PCE is connected with a defoamer molecule which is released at pH ≥ 12
PCEs with other anchoring groups	
Organo-silane modified PCE	- Chemical bond between the PCE and the C-S-H-surface can occur → increased sulfate tolerance
Phosphate superplasticizers	- PCE contains phosphate instead of carboxylic acid anchoring groups - Stronger adsorption of the phosphate group than a carboxylate group - PCE reduces stickiness in concrete, less retardation of cement hydration
Amphoteric and zwitterionic superplasticizers	- PCE bears anionic and cationic charge - Increased adsorption for these PCEs, often improved clay tolerance

Based on the comb structure of polycarboxylate superplasticizers, which is necessary for their mechanism of cement dispersion, two different kinds of modifications are possible to increase the diversity and enhance the specific functionality: on the one hand, the ratio of macromonomer to monomer amount in the polymer can be varied. Furthermore, the order of macromonomer and monomer in one polymer chain can be determined through controlled reaction conditions. On the other hand, variation of the PCEs is achieved by different chemical educts (macromonomers and monomers). The most frequent chemical difference is a variation between the macromonomers. For instance, ester or ether groups can be used as linking units to the poly(ethylene glycol) side chains. However, a change in the anchoring group is also possible without destroying the specified framework. Interestingly, 98 % of these groups are represented by olefinic carboxylic acids like acrylic, methacrylic, maleic, or itaconic acid [14], but also sulfonate groups or phosphonate groups are possible [92,93].

3.3.3.2.1 Carboxylic acid based PCEs

3.3.3.2.1.1 MPEG PCEs: Acrylic or Methacrylic acid – ω-Methoxy poly(ethylene glycol) methacrylate ester copolymers

The first superplasticizer containing poly(ethylene glycol) side chains was invented in 1981 by Dr. T. Hirata, a researcher at Nippon Shokubai company [6-8]. A few years later, in 1986, this copolymer composed of methacrylic acid and ω-methoxy poly(ethylene glycol) methacrylate ester (MPEG-MA) was sold as “FC 600” [94]. Compared to the subsequently developed superplasticizers, the poly(ethylene glycol) side chains in MPEG PCEs are fixed by ester bonds which can lead to an offsplitting at high temperatures or high pH values due to hydrolysis [95].

Two different synthesis methods for MPEG PCEs have been well established:

(1) Esterification of poly(methacrylic acid) with ω-methoxy poly(ethylene glycol) [96,97]

In this process, a poly(meth)acrylic acid polymer is used as anionic backbone for the superplasticizer. In order to insert side chains, ω-methoxy poly(ethylene glycol) is anchored via esterification to this backbone, which leads to a grafted copolymer as shown in **Figure 19**. Depending on the molar ratio of backbone to side chains, the anionic charge density and therefore the dispersing properties of the PCEs can be controlled. A special characteristic of grafted polymers is their regular statistical distribution of side chains along the back bone. Furthermore, this confers a very narrow M_w distribution

of the polymer provided that the M_w of the used backbone is also uniform. However, to conduct the reaction with high conversion rates, temperatures of 120 – 150 °C and catalysts (e.g. LiOH, H_2SO_4, *p*-toluol sulfonic acid or hypophosphite) are necessary. Furthermore, the nascent reaction water has to be removed through azeotropic distillation [97,98]. Due to the remaining, non-reacted macromonomer in the reaction mixture, which is based on low conversions of only ~ 70 %, increased foaming is obtained for the synthesized superplasticizer solution [99].

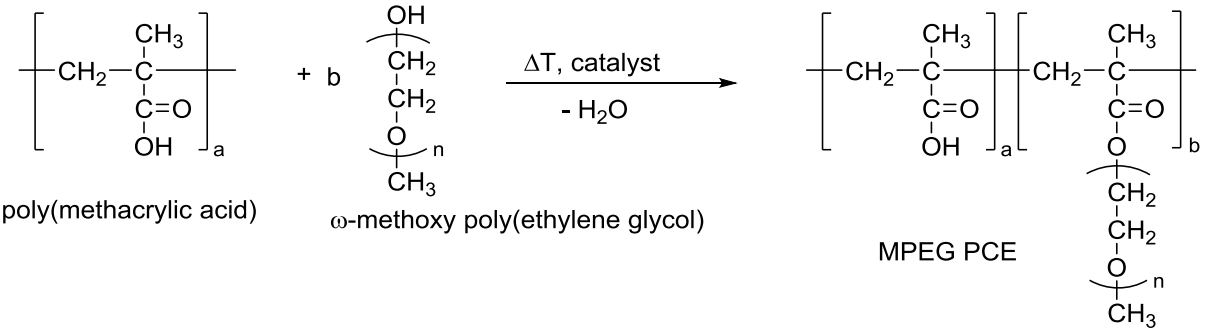


Figure 19. Synthesis procedure of an MPEG PCE via grafting [97,98].

(2) Free radical copolymerization (in solution)

In this synthesis process, acrylic or methacrylic acid (the monomer carrying the anionic charge) and ω-methoxy poly(ethylene glycol) methacrylate ester (the macromonomer introducing the side chain) are copolymerized (see **Figure 20**) [100]. In case of a batch polymerization, both educts are dissolved in a solvent (mostly water) and the reaction is started through adding an initiator to this mixture over a period of time. By conducting a continuing polymerization process, the initiator as well as the monomers are steadily mixed together in the reaction vessel [100-103]. A broad assortment of initiator systems is available as specified in **Section 3.3.2.2**. However, depending on which system is chosen, reaction temperatures of 25 - 80 °C are sufficient to reach macromonomer conversions of ~ 90 % [104,105]. Chain transfer agents (e.g. 3-mercaptopropionic acid) regulate the length of the polymer chain which is formed corresponding to the length of the superplasticizer backbone [106,107]. However, different polymerization rates of the monomer and macromonomer led to non-statistic gradient polymers. Therefore, the side chain density along the backbone is not uniform (see **Section 3.3.1.5**). Moreover, polymers synthesized via free radical copolymerization are characterized by a broad M_w distribution.

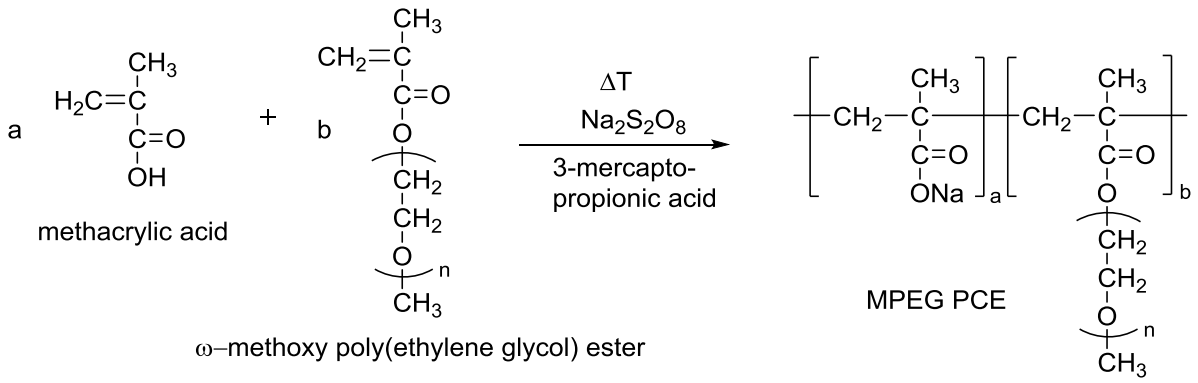


Figure 20. Synthesis procedure of an MPEG PCE via free radical copolymerization [100].

It is important in both synthesis routes to prevent crosslinking between two PCE polymers because such connected molecules do not or only contribute very little to the dispersing effectiveness. Crosslinking can occur when a diol (from poly(ethylene glycol)) is present in the grafting process where it can connect two poly(methacrylic acid) backbones [78,108].

3.3.3.2.1.2 APEG PCEs: maleic anhydride – α-allyl-ω-methoxy or ω-hydroxy poly(ethylene glycol) ether copolymer

The second generation of PCE superplasticizers was invented by the company Nippon Oil & Fats in 1989. The copolymer consists of the monomer maleic anhydride/maleic acid and the macromonomer α-allyl-ω-methoxy or ω-hydroxy poly(ethylene glycol) ether [109,110]. The special property of the used allyl macromonomer is its inability to homopolymerize due to allylic rearrangement and the resulting resonance stability of the radical. This causes slow reaction rates for this allyl ether and always results in a strictly alternating copolymer. Moreover, the stability of the allyl radical leads to degradative chain transfers making the addition of chain transfer agents to the reaction mixture unnecessary [111-113]. The high side chain density and backbone rigidity of the alternating copolymer causes a good dispersing effect over time but simultaneously leads to a delay in unfolding the whole dispersing force within the first 30 min. Hence, overdosed amounts of APEG PCEs which lead to bleeding, decomposition, and segregation of concrete are a common problem. However, this effect can be eliminated by adding additional copolymers, so-called “spacer molecules”, like allyl maleate or styrene, due to a reduced flexibility of the original main chain resulting in a faster adsorption of the polymer on the cement particles or hydration products and therefore in a less delayed dispersing effect [78,95,104,114].

Similar to MPEG PCEs there are two synthesis methods. While the first one represents the already presented free copolymerization in an aqueous solution, the second one is carried out without any solvent, the so-called radical copolymerisation in bulk as indicated in **Figure 21**. A homogeneous reaction mixture of monomer and macromonomer is ensured by melting both chemicals at a reaction temperature of 70 °C. As there is no water available for solving the initiator, the water-insoluble dibenzoyl peroxide is applied instead of sodium or ammonium persulfate. Furthermore, polymers with higher M_w than for the free radical copolymerization in solution are obtained due to the occurring *Trommsdorff-Norrish* effect [95,110,115].

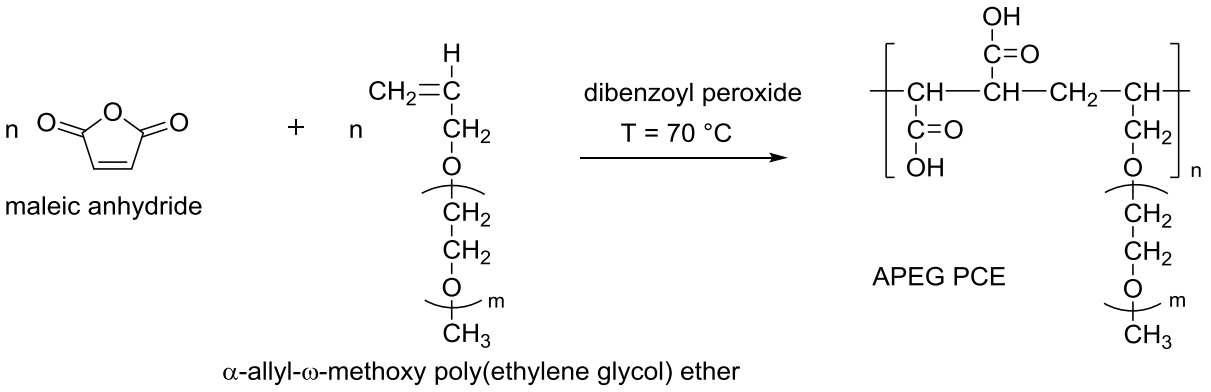


Figure 21. Synthesis procedure of an APEG PCE [109,110].

The criterion for which synthesis process is chosen is the length of the side chains of the macromonomer. An increasing amount of poly(ethylene glycol) units in the side chains leads to a stronger hydrophobic macromonomer which is insoluble in water due to unstable hydrogen bonds at higher temperatures (reaction temperature) and therefore is not suitable for the free radical copolymerisation in solution. As a summary, the free radical copolymerisation in solution is only performable for those macromonomers which are soluble in water. Usually APEG PCEs with ≤ 34 poly(ethylene glycol) units are appropriate for both methods while macromonomers with 70 poly(ethylene glycol) units can be exclusively synthesized in bulk [78,95,115].

3.3.3.2.1.3 Amide / Imide type PCE

In this type of PCE, so-called Jeffamines® (polyethylene oxide or propylene oxide amines) were grafted as side chains to the backbone consisting of poly acrylic- or methacrylic-acids as shown in **Figure 22**. This type of PCE was invented by the company W.R. Grace. Due to higher costs of the side chains, this superplasticizer is rarely used [5,116,117].

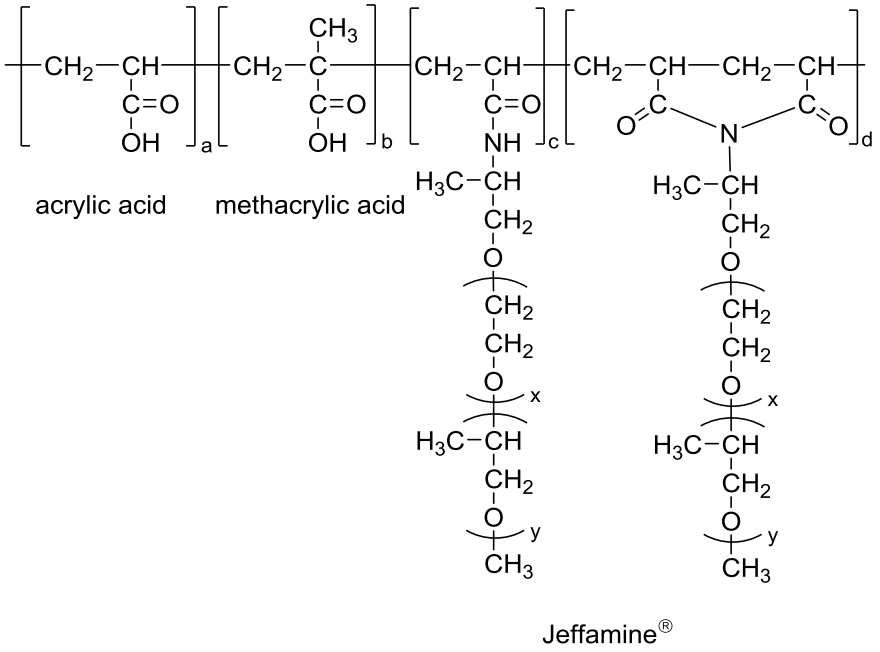


Figure 22. Chemical structure of amide and imide based PCEs [5,116,117].

3.3.3.2.1.4 VPEG PCEs: maleic anhydride – vinyl poly(ethylene glycol) ether copolymer

In 1995, BASF developed a superplasticizer copolymerized from maleic anhydride or acrylic acid and a vinyl ether macromonomer like 4-hydroxy butyl poly(ethylene glycol) vinyl ether. The synthesis procedure is given in **Figure 23**. Still today, they are almost exclusively produced by BASF [118,119]. Compared to the APEG macromonomer, the vinyl ether-based monomer is clearly more reactive, which facilitates high macromonomer conversions during polymerization. However, the risk of decomposition and the high reactivity of the vinyl ether monomer require low reaction temperatures of < 30 °C and therefore adapted initiator systems like Vazo 50® (2,2´-Azo-bis (2-methyl propionamidine) dihydrochloride) [15,120].

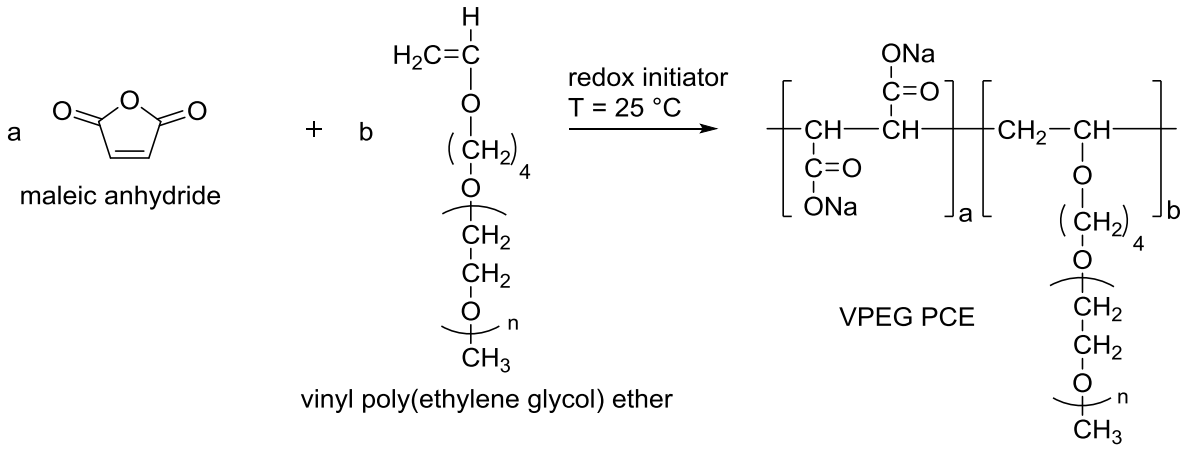


Figure 23. Synthesis procedure of a VPEG PCE [118].

3.3.3.2.1.5 IPEG PCEs: acrylic acid – isoprenyl oxy poly(ethylene glycol) ether copolymer

Between 2000 and 2002, the company Nippon Shokubai designed PCE superplasticizers based on isoprenol ether [121,122]. This kind of macromonomer does not include unstable ester bonds as MPEG monomers do and is more reactive than APEG monomers because no radical resonance stabilization takes place. Therefore, high macromonomer conversions in the free radical copolymerization process between acrylic acid and isoprenyl oxy poly(ethylene glycol) ether are common. In addition, no special initiator system is necessary – the free radical copolymerization reaction in solution can take place at moderate temperatures of ~ 60 °C as demonstrated in **Figure 24**. Furthermore, variations in side chain density or side chain length are easily realized by adding the required monomers in the desired ratios [15,120]. IPEG PCEs feature an excellent dispersing performance, especially in systems containing a small amount of water [120,123]. However, IPEG monomers can decompose into isoprene, glycol and water in an elimination reaction when stored in bulk. Therefore, it is necessary to keep them in aqueous solution [124].

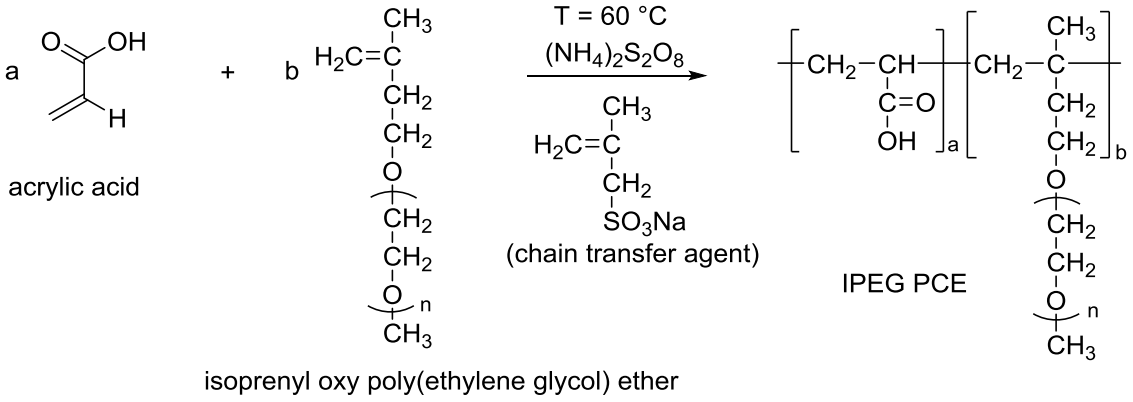


Figure 24. Synthesis procedure of an IPEG PCE [121,122].

3.3.3.2.1.6 HPEG PCEs: acrylic acid – α-methallyl-ω-methoxy poly(ethylene glycol) ether copolymer

HPEG PCEs were established in 2000 by Nippon Shokubai [125] and are very similar to IPEG PCEs regarding their performance and advantages over earlier PCE generations. They are synthesized through free radical copolymerization in solution of acrylic acid and α-methallyl-ω-methoxy or ω-hydroxy poly(ethylene glycol) ether even at room temperature as presented in **Figure 25** [105,125]. No decomposition in bulk is possible which makes them more favourable than IPEG PCEs [125]. Their main area of application is Asia (China) [15,120].

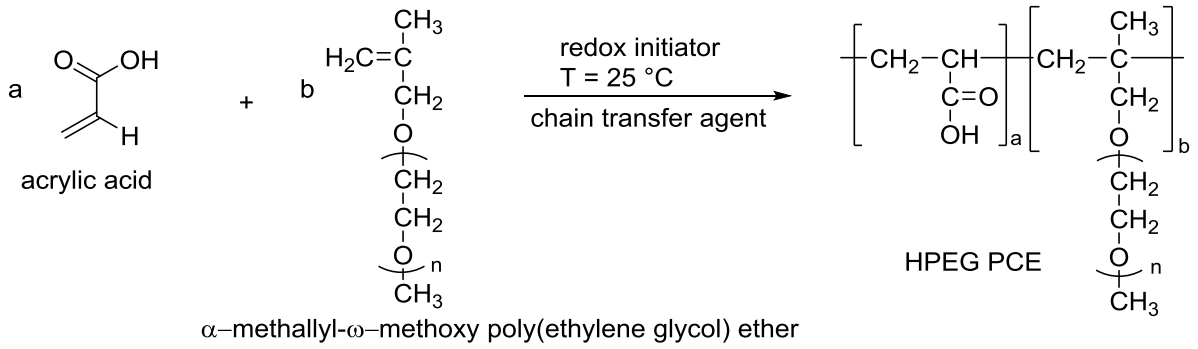
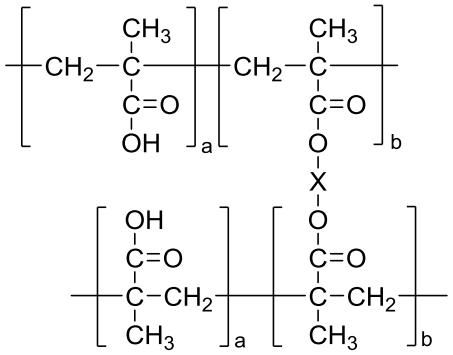


Figure 25. Synthesis procedure of an HPEG PCE [105,125].

3.3.3.2.1.7 XPEG PCEs

Slightly crosslinked polymers were designated as XPEG PCEs (see **Figure 26**). For synthesis, monomers containing diester groups were utilized. It was hoped to achieve a higher coverage of the surface of cement particles and hydration products than with conventional PCEs and therefore to require a lower dosage for the same dispersing effectiveness [120,126,127]. Furthermore, according to the same mode of action, polycarboxylated poly(glycerols) forming dendrimeric or hyperbranched polymers were investigated. They possessed stronger adsorption compared to the conventional PCEs [17].



XPEG PCE

Figure 26. Chemical structure of a XPEG PCE [126].

3.3.3.2.1.8 PCEs from macroradicals

In case no conventional macromonomer (e.g. MPEG, APEG, IPEG, HPEG, etc.) for polymerization or no appropriate poly(methacrylic acid) for esterification (MPEG PCEs, grafting) is available, this synthesis method represents an alternative to obtain a PCE superplasticizer. **Figure 27** shows the

reaction scheme. In this synthesis process, the side chains as well as the back-bone of the superplasticizer consisted of poly(ethylene glycol). Therefore, a mono maleate ester was formed by esterification of maleic anhydride with ω-methoxy poly(ethylene glycol). Grafting of maleic anhydride and the mono maleate ester onto a ω-methoxy poly(ethylene glycol) macroradical which was formed during the synthesis process provided the PCE superplasticizer [104,128].

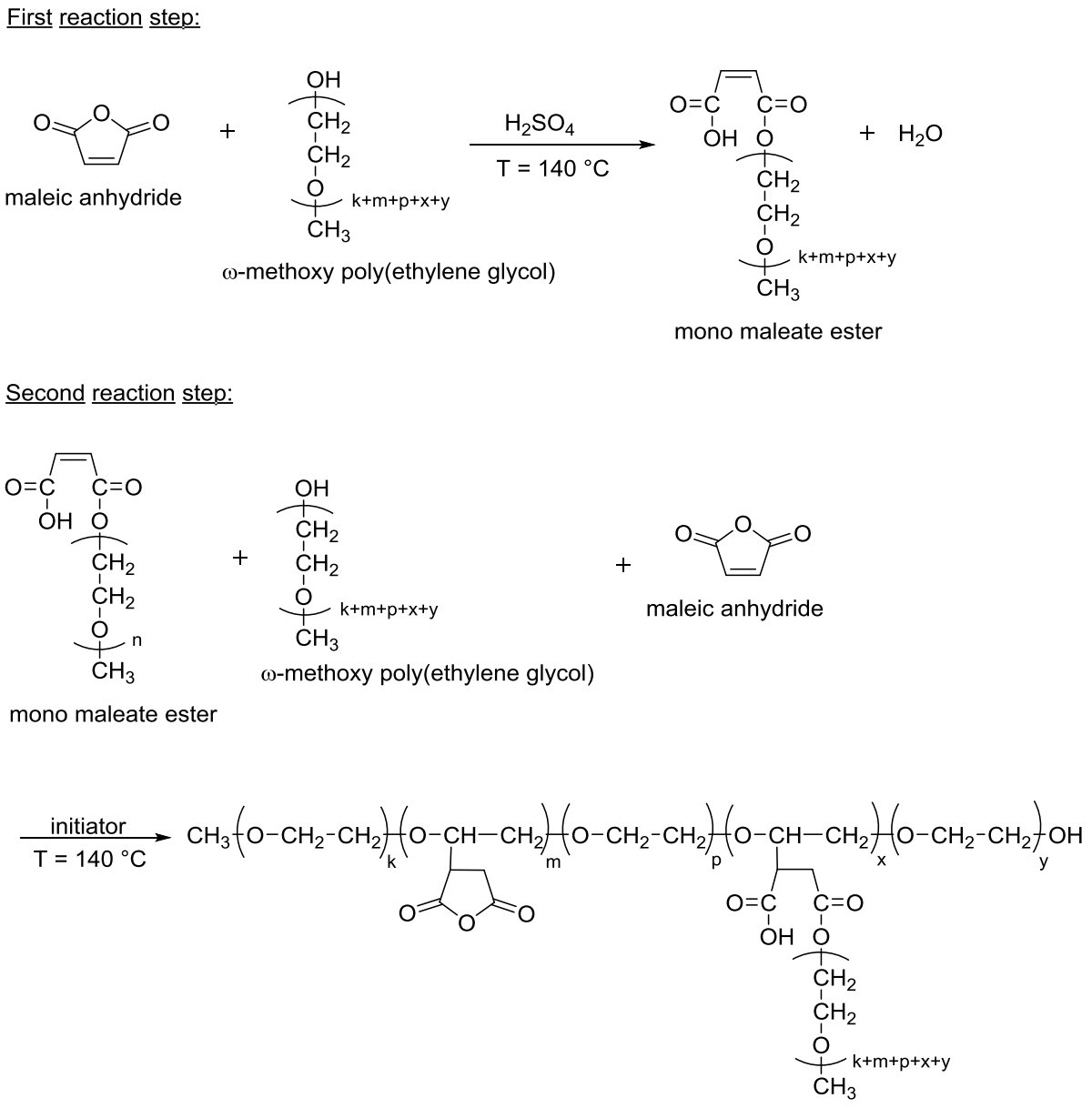
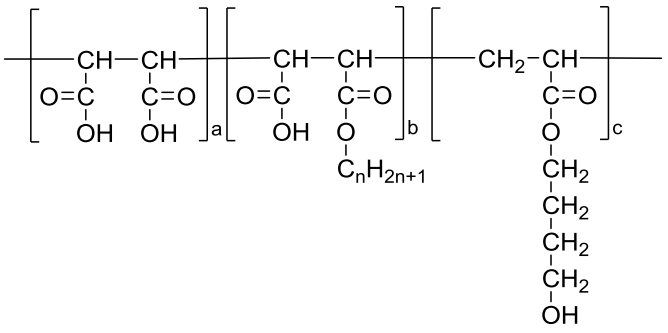


Figure 27. Synthesis procedure of a macroradical based PCE; modified from [128].

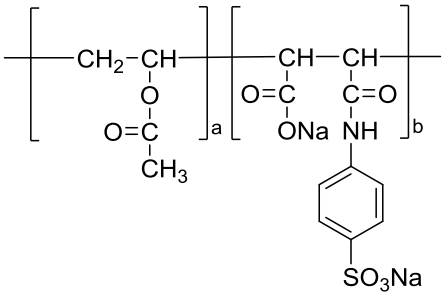
3.3.3.2.1.9 PCEs with reduced sensitivity to clay

Intercalation of PCEs in the clay structure reduces the dispersing effectiveness. Since the sorption is favored by hydrogen bonds between the poly(ethylene glycol) side chains of the PCE, water

molecules and silanol groups of the clay (see **Section 3.3.1.6**), it was tried to develop PCEs which do not contain these side chains. **Figure 28** shows two successful examples [9].



Terpolymer of maleic anhydride, monoalkyl maleate and 4-hydroxy butyl vinyl ether (HBVE)



Copolymer of vinyl acetate and adduct of sulfanilic acid with maleic anhydride

Figure 28. PCEs with reduced sensitivity to clay according to [129] (left) and [20] (right).

3.3.3.2.1.10 PCEs with combined defoamer

In order to avoid air entrainment in concrete, a defoamer is always added to the mixture when PCEs are present [99]. PCEs which make this addition redundant already contain a defoamer in their own structure. Therefore, the defoaming component is coupled either via an ester bond which decomposes in the cement slurry (pH > 12) or it is connected by an electrostatic attraction which breaks down by deprotonation in the alkaline environment and thus liberates the defoamer [9]. **Figure 29** presents PCEs each containing one possible mechanism.

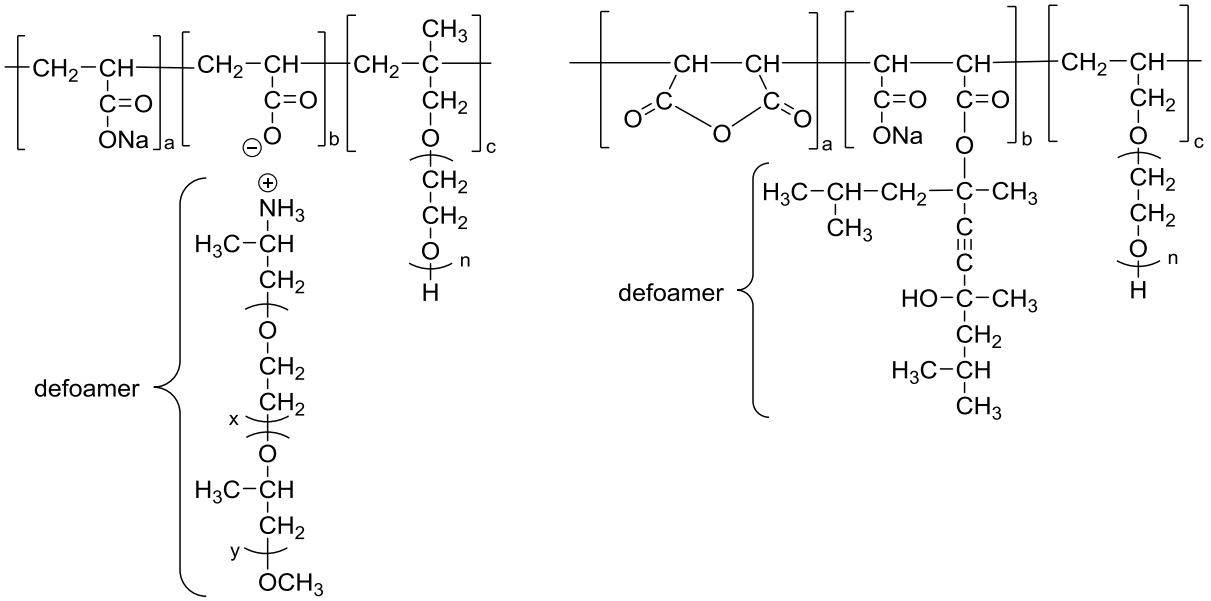


Figure 29. PCE with integrated defoamer. Left: ion pair system; right: ester-bond system [9].

3.3.3.2.2 PCEs with other anchoring groups

The mechanism of the dispersing ability of superplasticizers is based on the adsorption of the polymers on the cement particle and hydration product surfaces. In order to achieve this, charged chemical groups like carboxylic acids are always involved in the polymer chains to ensure electrostatic attraction with the clinker and hydration surfaces which are charged as well. The different adsorption behavior of diverse anchoring groups leads to specific dispersing effectiveness.

Sulfonate, carboxylate and phosphonate/phosphate groups have been established as anionic anchoring groups. They differ in their strength of adsorption, with sulfonate groups being the weakest and phosphonate groups being the strongest [92,93]. However, cationic anchoring groups are also potential anchoring groups. They can be used solely or in combination with anionic groups – the so-called amphoteric or zwitterionic polymers. Furthermore, silylated PCEs can even form a chemical bond with the C-S-H surface of cement.

3.3.3.2.2.1 Organo-silane (OSi) modified PCEs

In order to strengthen the adsorption of the PCE molecules to the cement particle and hydration product surfaces, silylated polymers were applied as can be seen in **Figure 30** [120].

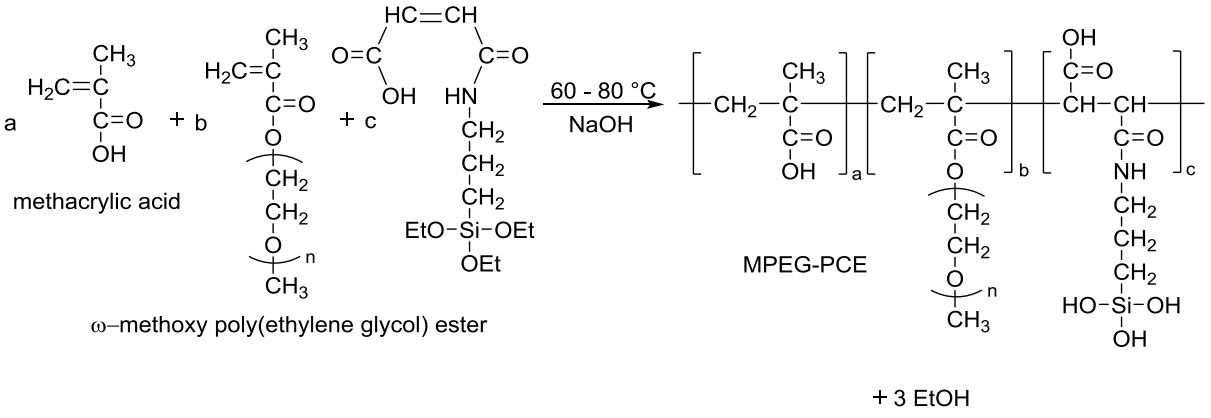


Figure 30. Synthesis procedure of an organo-silane modified PCE [130].

Through a condensation reaction of silanol groups (-Si-OH), a chemical bond can arise between the superplasticizer and the C-S-H surfaces accomplishing an irreversible anchor, resulting in an increased sulfate tolerance of the PCEs. For synthesis of such superplasticizers, copolymers like 3-trimethoxysilyl propyl methacrylate or *N*-maleic γ-amidopropyl triethoxy silane were used [130,131].

3.3.3.2.2.2 Phosphate superplasticizers

This kind of superplasticizer contains phosphate instead of (or additionally to) carboxylic acid anchoring groups as shown in **Figures 31** and **32**. Monomers for such polymers can be produced through esterification of hydroxyethyl methacrylate with phosphoric acid [78]. There are only a few examples of these superplasticizers even though it is assumed that they adsorb almost instantly on cement [14,132,133]. **Figure 31** presents a comb polymer synthesized via a polycondensation reaction with phosphate ester anchoring groups, poly(ethylene glycol) side chains and a polyaromatic backbone [90,133].

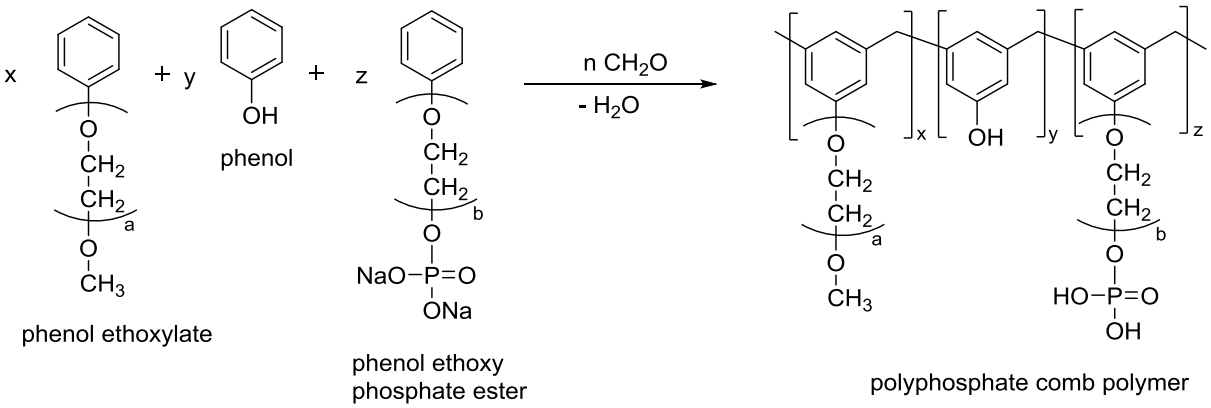


Figure 31. Synthesis procedure of a phosphate comb polymer [133].

Furthermore, Dalas et al. [134] tested a methacrylate ester-based PCE with phosphate anchoring groups. These superplasticizers were less sensitive to the adsorption competition with sulfate ions. In addition, Stecher et al. [14] confirmed that compared to carboxylic acid-based PCEs their superplasticizers (see **Figure 32**) were characterized by an extremely good dispersing ability in cement paste, less retardation of cement hydration, a remarkable high calcium binding capacity as well as a good flow rate (reduced stickiness) of concrete at a low water to cement ratio (< 0.30).

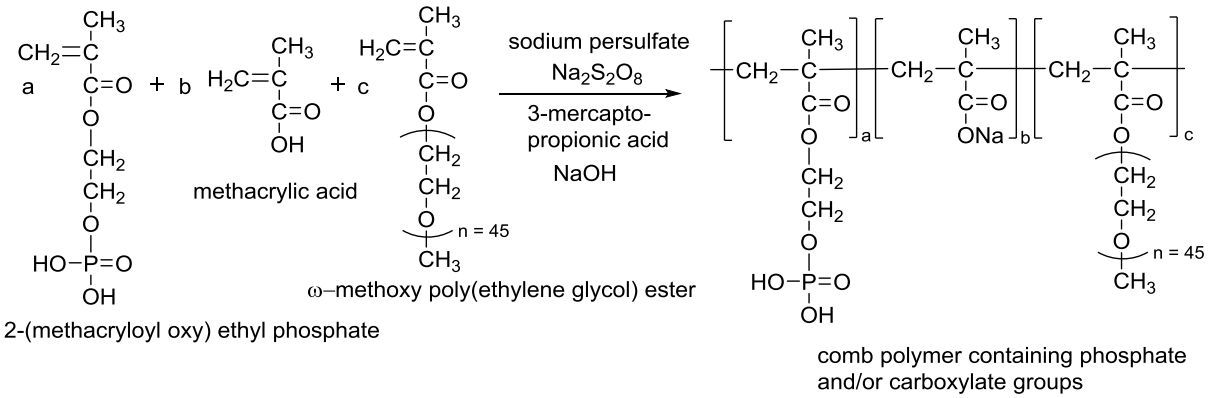


Figure 32. Synthesis procedure of a phosphate PCE [14].

3.3.3.2.2.3 Amphoteric and zwitterionic superplasticizers

Amphoteric or zwitterionic superplasticizers include cationic and anionic charges. The superplasticizers can be distinguished by the position of the ionic charges in the molecules. For instance, the charges can be placed in the backbone or in the side chains of the superplasticizer. The reason for combining differently charged anchoring groups in one polymer was to allow a higher adsorption of the superplasticizer on the cement particle and hydration product surfaces. Furthermore, it was hoped to integrate the desired properties of cationic polymers in the anionic superplasticizer. For instance, cationic polymers have a high clay tolerance because they can occupy the interlayers of bentonite clay [67] and prevent the clay from swelling [135,136].

The PCE superplasticizer developed in 2000 by Sika (Switzerland) and Toho (Japan) companies contained poly(ethylene glycol) as well as poly(amido amine) side chains as demonstrated in **Figure 33**. Due to the similarity of MPEG PCEs, the anionic charge was provided in the backbone while the cationic charge was present in the side chains (pH dependent). This property provided a dispersing effectiveness even at very low water to cement ratios of 0.12 [15,137,138].

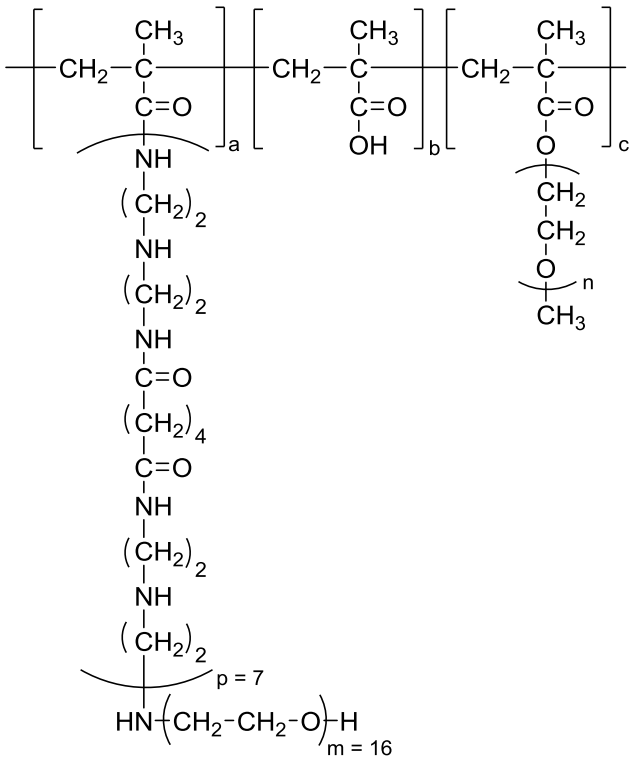
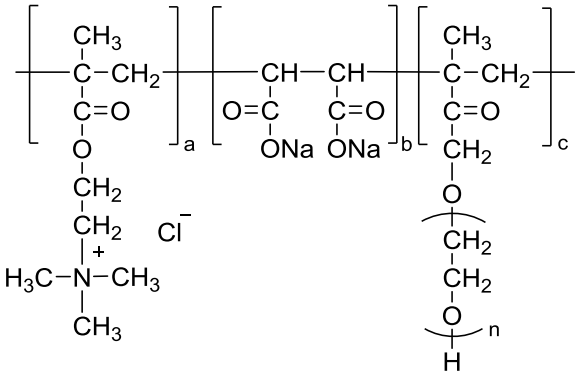
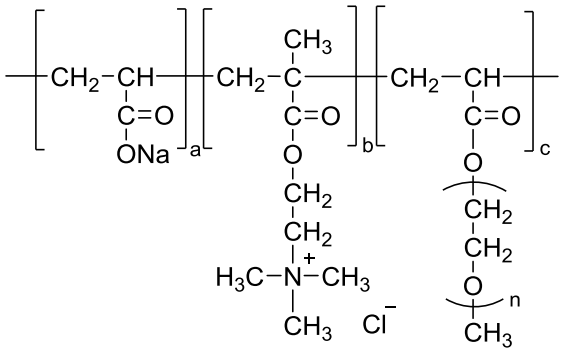


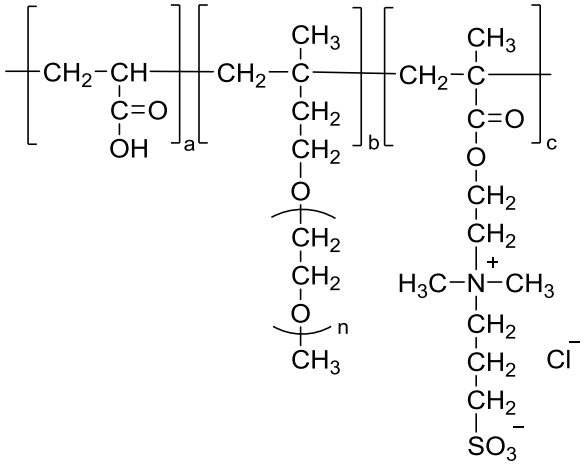
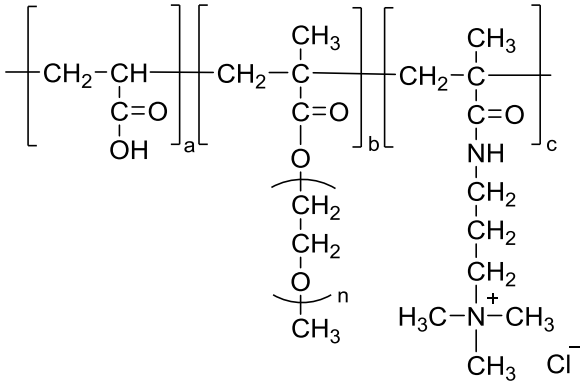
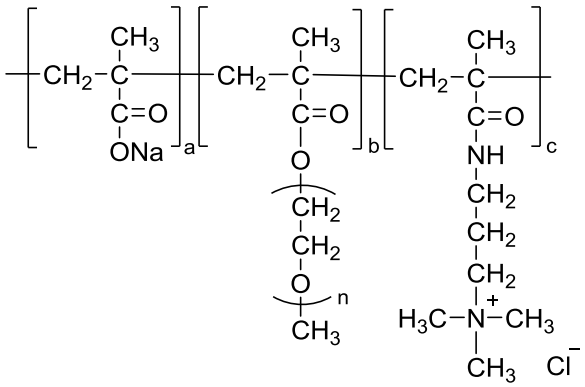
Figure 33. Chemical structure of a polyamidoamine superplasticizer [15].

Another possibility for zwitterionic PCE molecule structures are cationic and anionic anchoring groups in the backbone or in very short side chains without any repeating units (no PEO units). In most cases, quarternary ammonium ions and carboxylic acid groups provide the charge of the polymer. The cationic and anionic charge is mainly found on two different monomers (see [139-142]), but both charges can also be located on one monomer (see [83,143-145]).

For instance, Hsu et al. prepared a linear copolymer consisting of acrylamide and α-N,N-dimethyl-N-(3-(β-carboxylate) acrylamino) propyl ammonium ethanate, in which the anionic as well as the cationic anchoring group were part of the backbone. Compared to a commercial β-naphthalene sulfonate formaldehyde (BNS) superplasticizer, a lower dosage for the same spread flow as well as an improved slump retention was obtained [146]. However, amphoteric superplasticizers with a similar structure as common PCEs (MPEG, IPEG, APEG, etc.) were also established. **Table 2** lists some examples and the advantages of these polymers.

Table 2. Examples for amphoteric superplasticizers and their special advantages.

Research group	Polymer structure
Guo et al. [140]	 - Larger adsorbed amount than anionic PCEs - Good dispersing and slump retaining behavior
Miao et al. [141]	 - High water reducing capacity - Increased early strength - No retardation of cement hydration - Increased compressive strength of hardened concrete at early and final stages - Decreased porosity and reduced average pore size

Li et al. [143] Chen et al. [83]	 - Adsorbs more easily on the surface of clay but without incorporation into the layer structure of clay
Jiang et al. [139]	 - Lower retardation effect on cement hydration - Higher early strength of cement mortar
Schmid et al. [147]	 - No retardation of early hydration of cement - Good dispersing performance in cement blended with calcined clay

4 Materials and methods

4.1 Materials

4.1.1 Chemicals

All chemicals were used without further purification. **Table 3** lists the utilized chemicals.

Table 3. Chemicals used in this work.

Chemical	Provided by
α-Allyl-ω-methoxy poly(ethylene glycol) ether; M_w = 1596 Da (= 34APEG)	Nippon Oil & Fats Corporation, Tokyo, Japan
Isoprenyl oxy poly(ethylene glycol) ether; M_w = 1100 Da (= 23IPEG)	Jilin Zhongxin Chemical Group Co., Ltd, Jilin, China
Isoprenyl oxy poly(ethylene glycol) ether; M_w = 2400 Da (= 52IPEG)	Jilin Zhongxin Chemical Group Co., Ltd, Jilin, China
α-Methallyl-ω-methoxy poly(ethylene glycol) ether; M_w = 2300 Da (= 50HPEG)	Kelong Fine Chemical Co., Liaoning, China
Acrylic acid (pure) (= AA)	BASF, Ludwigshafen, Germany
Maleic anhydride	Merck KGaA, Darmstadt, Germany
2-Trimethylammonium ethylmethacrylate chloride 75 wt.-% aqueous solution (= TMAEMC)	Evonik Performance Materials GmbH, Darmstadt, Germany
Ammonium persulfate (= APS)	Sigma Aldrich, St. Louis, Missouri
Benzoyl peroxide 75 wt.-% (= BPO)	Merck KGaA, Darmstadt, Germany
Rongalit® (hydroxymethane sulfinic acid sodium salt hydrate) 95 wt.-%	Alfa Aesar GmbH & CoKG, Karlsruhe, Germany
Iron(II)sulfate heptahydrate [$FeSO_4 \cdot 7\ H_2O$]	VWR, Radnor, Pennsylvania
Aqueous hydrogen peroxide [H_2O_2] 30 wt.-%	VWR, Radnor, Pennsylvania
Sodium hypophosphite (NaH_2PO_2)	Sigma Aldrich, St. Louis, Missouri
Sodium methallyl sulfonate 98 wt.-%	Sigma Aldrich, St. Louis, Missouri
Aluminum sulfate octadecahydrate [$Al_2(SO_4)_3 \cdot 18\ H_2O$]	Sigma Aldrich, St. Louis, Missouri
Calcium hydroxide [$CaOH_2$]	Merck KGaA, Darmstadt, Germany
Sodium montmorillonite	BYK Chemie GmbH, Wesel, Germany
Surfynol MD-20	Defoamer, Air Products, the Netherlands
Acetone (> 99.9 %)	Merck KGaA, Darmstadt, Germany
Deionized water	Synergy® Water Purification system (Millipore GmbH, Germany).

For the dialysis of polymer samples, a SpectraPor (Spectrum Laboratories Inc., USA) dialysis membrane was used with a molecular weigth cut off (MWCO) of 10,000 Da.

4.1.2 Cement

To study the behavior of the synthesized superplasticizers in cement, three different cement types were used. The ordinary Portland cements CEM I 52.5 R and 42.5 R were received from HeidelbergCement (Burglengenfeld plant, Germany) and the API Class G cement (~ CEM I 32.5 N) was obtained from Dyckerhoff (Lengerich plant, Germany). All used cements strongly differ in their orthorhombic C_3A (C_3A_o) and hemihydrate contents.

Table 4. Phase compositions and *Blaine* values of CEM I 52.5 R, 42.5 R and API Class G as obtained by Q-XRD using *Rietveld* refinement, thermogravimetry, and the *Franke method.*

	CEM I 42.5 R Heidelberg	**CEM I 52.5 R Heidelberg[1]**	**CEM I 52.5 R Heidelberg[2]**	**API Class G**
Phase	**wt.- %**	**wt.- %**	**wt.- %**	**wt.- %**
C_3S, m	56.64	59.64	64.31	59.30
C_2S, m	15.08	16.99	11.18	19.50
C_3A_c	7.72	2.33	2.99	1.70
C_3A_o	3.18	1.88	2.54	< 0.01
C_4AF_o	6.98	12.79	10.83	14.10
Free lime (*Franke*)	0.53	0.16	0.91	< 0.30
Free lime (*Rietveld*)	0.31	0.31	0.96	---
Periclase (MgO)	0.56	0.22	0.15	---
Anhydrite	1.85	1.64	2.41	0.00
Hemihydrate*	2.24	2.08	1.66	0.20
Gypsum*	0.00	0.00	0.00	4.60
Calcite	3.78	0.78	0.83	---
Quartz	0.90	0.42	0.47	---
Dolomite	0.23	0.75	0.76	---
Total	**100.00**	**100.00**	**100.00**	**100.00**
d_{50} [µm]	16.03	3.78	6.31	11.00
Density [g/cm^3]	3.16	3.17	3.15	3.18
Blaine [cm^2/g]	3,553	5,720	5,634	3,058

* determined by thermogravimetry
1: this batch of cement was used for the experiments from **Sections 5.1** - **5.4**
2: this batch of cement was used for the experiments of **Section 5.5**

Their phase compositions (see **Table 4**) were quantified via X-ray diffraction (Bruker axs Advance D8 diffractometer) with the help of *Rietveld* refinement [148]. Additionally, free lime was determined according to the *Franke* method [149]. The median particle size (d_{50} value) was specified with a laser granulometer (Cilas 1064, Cilas, Marseille, France) and the density was measured via helium

pycnometry. The *Blaine* method was applied to calculate the specific surface areas (*Blaine* instrument, Toni Technik, Berlin, Germany).

4.2 Experimental and analytical methods

4.2.1 Denomination of the synthesized superplasticizer samples

Generally, all synthesized PCE samples were designated according to the scheme aBP(x:y:z)_M, with **a** representing the amount of ethylene glycol units in the side chain of the macromonomer and **BP** indicating the kind of macromonomer used in the synthesis. **(x:y:z)** specified the molar ratios between the monomer (**x**) (acrylic acid or maleic anhydride), the macromonomer (**y**) and the cationic monomer TMAEMC (**z**). Thus, the following designations were used:

HPEG PCE: → 50HP(x:y:z)_M

APEG PCE: → 34AP(x:y:z)_M

IPEG PCE: → 52P(x:y:z)_M [= P(x:y:z)_M] and 23P(x:y:z)_M

As in the first three sections of the discussion (see **Sections 5.1** to **5.3**) only IPEG with 52 ethylene glycol units was used, the number (**a = 52**) was not included → P(x:y:z)_M

The synthesis method was described through the key parameter **M**, with **M** being defined as:

- → C = synthesis method for conventional PCEs (see **Sections 5.1.1.1**, **5.4.1.3**, **5.5.1.1**, **5.5.1.2**)
- → M1 = short time synthesis method for anionic and amphoteric PCEs (see **Section 5.1.2.1**)
- → M2 = synthesis method for amphoteric PCEs (see **Section 5.1.3.1**)
- → M3 = 2-step synthesis method for amphoteric PCEs (see **Section 5.2.1.1**)
- → 5M = synthesis method with a polymerization time of 5 minutes (see **Section 5.2.1.2**, **5.4.1.2**)
- → 30M = synthesis method with a polymerization time of 30 minutes (see **Section 5.4.1.1**)

4.2.2 Solid content

To measure the solid content of the synthesized PCE solutions an infrared balance (Sartorius, Germany) was used. Therefore, approx. 1.0 g of polymer solution was dropped on the balance and

dried at 90 °C for 15 minutes. The weight of the residual solid is used as polymer content of the PCE solution. High macromonomer conversions allow the use of the value because only small amounts of non-reacted macromonomer (solid!) are contained in the polymer solution and only slightly adulterates the value. In **Section 5.5**, acidic and neutralized PCE solutions were compared requiring the additional following step for those polymers: In order to subtract the weight of the NaOH used for neutralization from the polymer content of the PCE sample, the added amount of NaOH was determined and thus the original polymer content was calculated.

4.2.3 Size exclusion chromatography

The molecular weight (M_w), the polydispersity index (PDI), and the macromonomer conversion was determined for each synthesized PCE via size exclusion chromatography (SEC). A PCE solution with a concentration of 10 g/L was prepared. The filtered (0.2 µm) sample was separated in a *Waters 2695 separation module* by particle size with three *Ultrahydrogel*^{TM} colums (120, 250, 500) and a *Ultrahydrogel*^{TM} guard colum (Waters, Eschborn, Germany). The prepared sample solution was pumped (flow rate = 1.0 mL min^{-1}) through the system with a 0.1 N $NaNO_3$ solution which was treated with 0.2 g/L NaN_3 and NaOH to reach a pH value of 12. The refractive index detector (2414 RI, Waters, Eschborn, Germany) and the 3-angle light scattering detector (Dawn EOS from Wyatt Technology, Santa Barbara, CA/USA) allowed the characterization. The absolute molar masses were calculated based on the dn/dc value of poly(ethylene oxide) (0.135 mL/g [150]). The data collection and evaluation was carried out via the software programs *Empower* (Waters Deutschland GmbH) and *Astra 4.9.8* (Wyatt Technologies).

To observe the **polymer formation over time**, samples were removed from the reaction vessel and analyzed via SEC during the reaction process, not after the synthesis process had completely finished.

4.2.4 Ionic charge amount via polyelectrolyte titration

The anionic charge amount of the polymers was determined by means of a *particle charge detector PCD 03 pH* (Mütek Analytic, Herrsching, Germany). 10 mL of a 0.1 g/L PCE solution was titrated with a 0.001 N cationic PolyDadmac (Poly(diallyl dimethyl ammonium chloride)) solution (= 0.001 eq/L). The medium for the PCE solution can be represented through deionized water, 0.1 M NaOH solution

or synthetic cement pore solution (SCPS). To prepare the SCPS, 1.72 g/L $CaSO_4 \cdot 2\ H_2O$, 6.959 g/L Na_2SO_4 and 4.757 g/L K_2SO_4 were gradually dissolved in 1 L of deionized water. The pH value was adjusted with 7.12 g/L KOH to pH ~ 13. Based on the consumption of PolyDadmac for the titration, the anionic charge was calculated according to **Equation 12**.

$$anionic\ charge\ amount\ \left[\frac{eq}{g}\right] = \frac{consumption\ of\ polyDadmac\ solution\ [L] \cdot concentration\ of\ polyDadmac\ [\frac{eq}{L}]}{mass\ of\ PCE\ in\ the\ sample\ [g]}$$

Equation 12. Formula to calculate the ionic charge amount of the synthesized PCEs [151].

4.2.5 Theoretical ionic charge amount

When calculating the theoretical anionic charge amount of a PCE, complete deprotonation of the contained carboxylic acid groups is assumed. Therefore, the value can be compared with experimentally determined values in 0.1 M NaOH. According to literature [151], **Equation 13** allows the calculation.

$$theoretical\ anionic\ charge\ amount\ \left[\frac{eq}{g}\right] = \frac{n_{COO^-}}{M_u}$$

$$n_{COO^-} = number\ of\ COO^-\ functionalities\ per\ repeating\ unit\ of\ the\ polymer$$

$$M_u = molar\ mass\ of\ one\ repeating\ unit\ of\ the\ polymer$$

Equation 13. Formula to calculate the theoretical anionic charge amount of the synthesized PCEs [151].

4.2.6 Dispersing performance in cement

To determine the dispersing ability of the PCEs, “mini slump” tests were carried out at 20 °C and 40 % rel. humidity. The dosage, which is sufficient to cause a spread flow of the cement slurry of 26 ± 0.5 cm, was determined for each PCE tested. This dosage can be understood as a measure of effectiveness of a superplasticizer.

The **standard procedure** is a modified test (without sand) according to DIN EN 1015 [152] and was performed for all sections as follows, unless explicitly stated otherwise: The mixing water (deionized water) and the polymer solution were filled in a porcelain cup. In order to consider the water still contained in the polymer solution, it was subtracted from the mixing water. After homogenization by stirring, 300 g of cement were added uniformly over a period of 1 minute to the solution. After a soaking time of 1 minute, a homogenous cement slurry was prepared by manually stirring the mixture with a spoon for 2 minutes. A *Vicat* cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm), which was placed on a glass plate, was quickly and completely filled with the cement slurry. Then, the cone was lifted up to allow the cement slurry to spread. Holding the cone for 2 seconds over the spreading cement paste allowed leftovers to drip. The polymer dosage was adjusted so that the average value of the diameter of two perpendicular axes was 26 ± 0.5 cm.

For **slump-retaining** experiments, the dispersing performance was determined every 20 minutes in the first 2 hours and afterwards every hour. After the measurement, the cement slurry was put back into the porcelain cup and covered with a moist cloth. Before each measurement, the mixture was stirred for 2 minutes.

To determine the **clay tolerance** of PCEs in cement paste, 300 g of montmorillonite blended cement was utilized in the “mini slump” tests. The content of clay in the cement mixture was 3.0, 6.0, 9.0, or 15.0 g which corresponds to 1, 2, 3 or 5 % of the whole mixture.

By dissolving 3.0, 6.0 or 9.0 g Na_2SO_4 in the mixing water of the “mini slump” tests, the **sulfate tolerance** of the PCEs was tested.

For the “mini slump” tests with a “**delayed PCE addition**”, the PCE was not added to the porcelain cup at the beginning of the procedure. It was dropped to the cement slurry within 20 seconds when the 2-minute mixing process started (after soaking time).

The water – to - cement (w/c) ratios varied depending on the cement used and on the experiments carried out. For the first given w/c value for each cement in **Table 5**, the pure cement paste without any PCE admixture reached a spread flow of 18 ± 0.5 cm.

Table 5. Water to cement (w/c) ratios used in the experiments.

Cement	(w/c) ratio	water amount for 300 g cement [g]
CEM I 42.5 R	0.50	150
CEM I 52.5 R	0.62, 0.45, 0.35 and 0.30	186 / 135 / 105 / 90
API Class G	0.40 and 0.30	120 / 90

4.2.7 Dispersing performance in mortar

Mortar tests were performed to further characterize the dispersing performance of the synthesized PCEs. According to DIN EN 196-1, a mixture of cement (450 g, CEM I 52.5 R), PCE solution, *Surfynol MD-20* (defoamer, Air Products, the Netherlands) and mixing water (w/c ratio = 0.5 → 225 g water or w/c ratio = 0.4 → 180 g water) was filled into a mixing bowl and stirred automatically for 30 seconds at low speed (ToniMix, Toni Technik, Berlin, Germany). During stirring for another 30 seconds, 1,350 g CEN standard sand was added to the mixture and mixed again for 30 seconds at a fast rate. The subsequent mixing stop of 90 seconds allowed to manually homogenize the mixture for approx. 5 seconds. The process ended after another 60 seconds of mixing at high speed. The spread flow was achieved via flow table test, where the mortar was filled and manually compacted in the *Haegermann funnel* placed on a *Haegermann vibration table*. Afterwards, the funnel was lifted to allow spreading of the mortar and 15 hubs (1 hub per second) of the vibration table were carried out. The polymer dosage was adjusted so that the average value of the diameter of two perpendicular axes was 18 ± 0.5 cm. In some experiments (see **Section 5.4.6.2**), a fixed dosage of 0.43 % bwoc of the PCEs was chosen.

To prove **clay tolerance**, 445.5 g of pure cement and 4.5 g of montmorillonite clay were blended and used.

Sulfate tolerance was determined by solving 4.5 g Na_2SO_4 in the mixing water.

For **slump-retaining** experiments, the dispersing performance was determined over 4 hours every 30 minutes. After a measurement, the mortar paste was put back into the mixing bowl and covered with a moist cloth. Before each measurement, the mixture was stirred for 1 minute.

4.2.8 Crystallization of synthetic ettringite

To further investigate the impact of neutralized and acidic PCE solutions on the ettringite crystallization, synthetic ettringite was precipitated in solutions containing superplasticizers as well as in solutions without. The precipitation was conducted according to Struble's method [153]. 25 mL of a saturated aqueous $Ca(OH)_2$ solution (concentration 1.70 g/L) and 3 mL of an $Al_2(SO_4)_3 \cdot 18\ H_2O$ solution (concentration 21.25 g/L) were simultaneously poured together (pH ~ 11.5) in a vessel filled with 3 mL of deionized water and equipped with a stir bar and, if desired 0.025, 0.050 or 0.075 g of PCE (the amount of water contained in the PCE solution was considered). The dosage of the PCEs added correspond to 3.5, 6.9, and 10.4 % of the maximum amount of ettringite that can be formed when calculating the value from the experimentally inserted educts.

4.2.9 Dynamic light scattering

A *Zetasizer Nano ZS apparatus* (Malvern Instruments, Workestershire, United Kingdom) was utilized to determine the particle size of precipitated ettringite. For sample preparation, the crystals were dispersed in acetone and equilibrated at 25 °C for 10 seconds directly in the cell. Afterwards, each sample was measured 6 times and averaged.

4.2.10 Scanning electron microscopy imaging

For characterization of the morphology and crystal size of the precipitated ettringite, scanning electron microscopy (SEM) images were taken with a *FEI XL 30 FEG* environmental scanning electron microscope. An accelerating voltage of 10 - 20 kV at a working distance of 8.9 - 9.1 mm was used. For sample preparation, the crystals were washed in acetone and dried at room temperature directly on the sample holder which was prepared with a conductive carbon paint (Planocarbon N 650, plano GmbH, Wetzlar, Germany). Furthermore, the sample was sputtered with carbon to achieve higher conductivity and therefore more precise images. A minimum of 4 different sample regions was investigated and images at magnifications of 5,000 x, 10,000 x, 20,000 x, and 40,000 x were analyzed. The *XL Doku software* (version 3.1, Soft Imaging System GmbH, Münster, Germany) allowed to determine the crystal length and width. Approx. 150 crystals were analyzed per sample. The small amount of crystals for the samples "52P(10:1:0)_C; pH = 7; 0.075 g PCE" and "50HP(10:1:0)_C; pH = 7; 0.075 g PCE" (see **Section 5.5.5.2.3**) only allowed ~ 100 / 30 crystals (only

one sample region for the latter) to be examined. Furthermore, some crystals were picked for elemental analysis via EDX measurement.

4.2.11 Polymer adsorption

Dosage-dependent polymer adsorption was carried out according to the **standard procedure** as follows: At first, a solution of the desired amount of PCE and 14 mL of deionized water (w/c ratio = 0.35) was prepared. The amount of water contained in the PCE solution was considered. Then, 40 g of cement (CEM I 52.5 R) were added to this solution and homogenized to a cement slurry for 2 minutes at 2,500 rpm with a vortex mixer (VWR International, Radnor, Pennsylvania). Subsequent centrifugation over 15 minutes at 8,500 rpm resulted in a supernatant which was filtered (0.2 µm, VWR International, Darmstadt, Germany) and diluted in 0.1 M HCl. As a reference, the pure polymer solution was diluted in 0.1 M HCl, too. The carbon content was determined by means of a *LiquiTOC* analyzer (Elementar, Hanau, Germany). By applying the depletion method, where the difference between the carbon content of the reference and the supernatant was calculated, the adsorbed amount of PCE per gram of cement was obtained. To ensure correct values, the carbon value of the pure cement was also considered.

The mixing procedure was shortened during sample preparation to determine early adsorption (**short time adsorption**). In this case, the cement and the PCE water solution were manually stirred for 20 seconds with a spoon instead of 2 minutes with a vortex mixer. All subsequent steps remained the same as described in the standard procedure.

4.2.12 Extraction of nano ettringite gel

In order to prove if nano ettringite was formed in cement pastes dispersed with PCE, “mini slump” pastes with a PCE dosage were prepared according the standard procedure (see **Section 4.2.6**) to reach a spread flow of 26 ± 0.5 cm. Depending on the cements used, the following w/c ratios were utilized: CEM I 52.5 R: w/c ratio = 0.35; CEM I 42.5 R: w/c ratio = 0.5 and API Class G: w/c ratio = 0.4. To extract the nano ettringite gel, 30 g of the prepared cement slurry was first mixed with 16 g acetone and then centrifuged at 8,500 rpm for 20 minutes. In presence of nano ettringite, a white top layer above the cement residue was obtained.

4.2.13 Amount of precipitated ettringite crystals

To determine the amount of precipitated ettringite crystals when combining 25 mL of saturated $Ca(OH)_2$ solution and 3 mL of an $Al_2(SO_4)_3 \cdot 18\ H_2O$ solution (concentration 21.25 g/L) in presence or absence of PCE (see **Section 4.2.8**), the turbid suspension was centrifuged for 15 minutes at 8500 rpm. The clear centrifugate was discarded and the white residue was mixed with acetone and centrifuged again (15 min, 8500 rpm) to clean the ettringite powder. The centrifugate was disposed and the cleaning procedure was repeated. Afterwards, the ettringite crystals were dried at room temperature under atmospheric pressure and weighted.

4.2.14 Powder X-ray diffraction

X-ray diffraction measurements were carried out on a *D8 Advanced instrument* (Bruker AXS, Karlsruhe, Germany) to determine the formed precipitates from the crystallization and centrifugation tests (see **Sections 4.2.8** and **4.2.12**). It was equipped with *Bragg-Brentano* geometry and a Cu K_α source (30 kV, 35 mA). Due to the very small volume of the precipitates, they were washed with acetone and dried under atmospheric pressure at room temperature directly on the sample holder. This type of preparation can cause higher irregularities in the intensities caused by crystal morphology. During measurement, all samples were scanned in the range of 5 - 70° 2θ.

5 Results and discussion

5.1 Impact of different synthesis methods on the polymer composition of isoprenol ether-based zwitterionic and anionic polycarboxylates (PCEs)

The results presented in **Section 5.1** were published 2019 in the publication “Impact of different synthesis methods on the dispersing effectiveness of isoprenol ether-based zwitterionic and anionic polycarboxylate (PCE) superplasticizers” by C. Chomyn and J. Plank in the journal “Cement and Concrete Research” [154].

The idea of this study was to clarify how different synthesis methods influence PCE superplasticizers regarding their composition, dispersing effectiveness and properties. Isoprenol ether-based zwitterionic and anionic PCE superplasticizers with 52 ethylene oxide units per side chain were chosen for these experiments. Similar to the anionic PCEs, the zwitterionic samples always contained acrylic acid as anionic monomer and additionally 2-trimethylammonium ethylmethacrylate chloride (TMAEMC) as cationic monomer. Furthermore, three different synthesis methods were applied, where an increasing acrylic acid content for the polymers (2, 3, 4.5 or 6 mol) was used for each method. The SEC result measured for each sample was related to the specific dispersing effectiveness of the PCE determined in cement paste via “mini slump” test with a CEM I 52.5 R at a w/c ratio of 0.62.

The following section describes and discusses the synthesis method, the SEC results as well as the dispersing performance for each PCE obtained. A general formula for the PCEs received is given in **Section 9.1**. The **Sections 5.1.1** - **5.1.4** (results, figures and tables) closely follow the paper published by C. Chomyn and J. Plank [154].

5.1.1 Synthesis and characterization of conventional anionic PCEs (standard preparation method and reference)

The first synthesis method was conducted according to a conventional (C), state-of-the-art industrial process described in literature [32]. Particular attention has been paid to creating a monodisperse polymer with a low PDI. Acrylic acid, the initiator, and the chain transfer agent were fed into the reaction vessel over **3 hours**, in which the macromonomer was placed at 60 °C for polymerization.

The reaction was completed after stirring for 2 hours at this temperature. For this well-established process, ammonium persulfate (APS) as an initiator and sodium methallyl sulfonate as a chain transfer agent were used. A series of PCEs designated as polymer P(x:1:0)_C with x = 2, 3, 4.5 and 6 were prepared for testing.

5.1.1.1 Synthesis of conventional anionic PCEs P(2 - 6:1:0)_C

The synthesis of conventional PCEs following the industrial process is specified using the example P(2:1:0)_C. The monomer quantities and amounts of APS and sodium methallyl sulfonate for preparation of P(3 - 6:1:0)_C are listed in **Tables 6** and **7**.

36.0 g (15.0 mmol) of 52IPEG solved in 48 mL of deionized water were filled into a 500 mL five-neck round-bottomed flask and purged with nitrogen. Next, the mixture was warmed up to 60 °C and two solutions (A = 2.16 g AA (29.98 mmol) and 0.86 g of sodium methallyl sulfonate (5.44 mmol) dissolved in 20 mL of deionized water; B = 0.70 g APS (3.07 mmol) dissolved in 30 mL of deionized water) were simultaneously added over a period of 180 minutes utilizing peristaltic pumps. Afterwards, the polymer mixture was stirred for 2 hours at 60 °C. A colorless, slightly viscous PCE solution (28 wt.-%, pH ~ 2) was received.

Table 6. Designation, composition, and solution properties of the synthesized anionic comb polymers P(2 - 6:1:0)_C.

Polymer sample	Synthesis method	Molar ratio AA:IPEG:TMAEMC	Monomer quantities [g]			Solid content of solution [wt.-%]
			AA	52IPEG	TMAEMC	
P(2:1:0)_C	conventional	2:1:0 [2:0.74:0]	2.16	36.0	0.00	28.2
P(3:1:0)_C	conventional	3:1:0 [3:0.79:0]	3.24	36.0	0.00	29.3
P(4.5:1:0)_C	conventional	4.5:1:0 [4.5:0.85:0]	4.86	36.0	0.00	30.5
P(6:1:0)_C	conventional	6:1:0 [6:0.77:0]	6.48	36.0	0.00	32.2

[ ] molar ratios actually present in the polymers as calculated from SEC measurements

Table 7. Amounts of APS and sodium methallyl sulfonate used in the synthesis for polymers P(2 - 6:1:0)_C.

Polymer designation	Amount of APS	Amount of sodium methallyl sulfonate
P(2:1:0)_C	0.70 g (3.07 mmol)	0.86 g (5.44 mmol)
P(3:1:0)_C	0.93 g (4.08 mmol)	1.14 g (7.21 mmol)
P(4.5:1:0)_C	1.28 g (5.61 mmol)	1.57 g (9.93 mmol)
P(6:1:0)_C	2.97 g (13.02 mmol)	3.73 g (23.58 mmol)

5.1.1.2 SEC analysis of anionic conventional PCEs P(2 - 6:1:0)_C

Figure 34 shows the SEC spectra of the superplasticizers P(2 - 6:1:0)_C produced according to the conventional method.

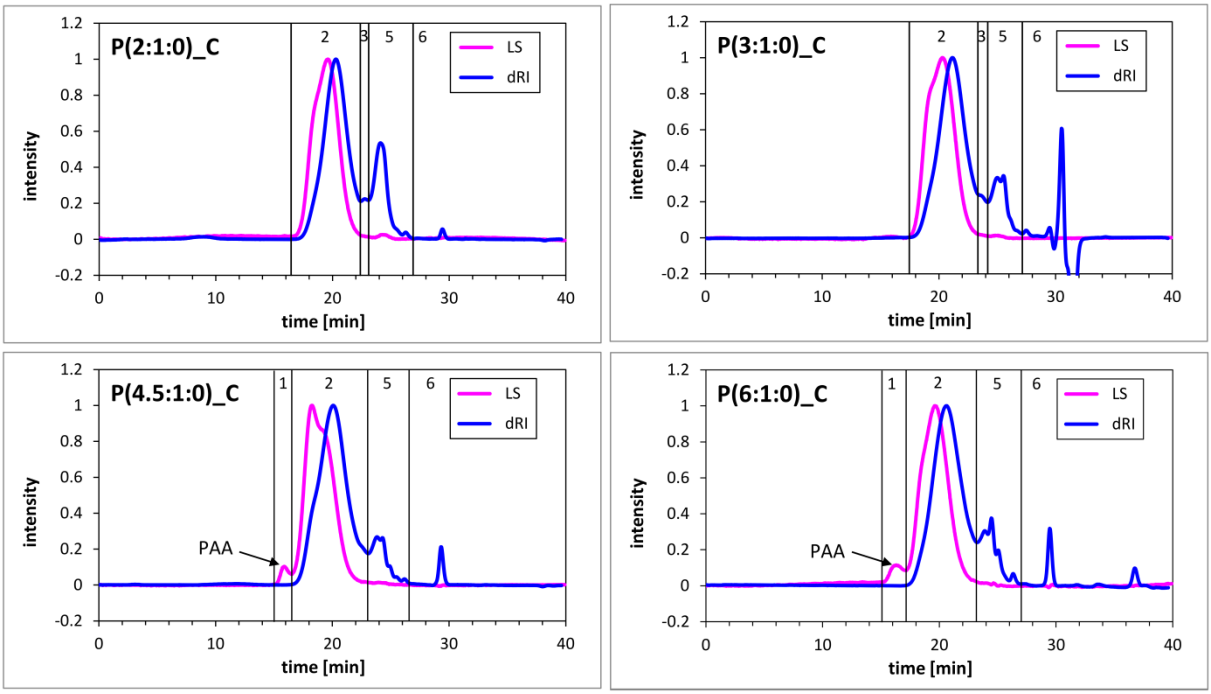


Figure 34. SEC spectra of the anionic reference polymers P(2 - 6:1:0)_C, prepared according to the conventional synthesis method.

Particularly striking was the relatively uniform molecular weight distribution occurring for all synthesized PCEs independent of their AA:MM ratio. To be more precise, a satisfying macromonomer conversion of 75 – 84 % and only one major polymer peak (fraction 2) were found. These results were in accordance with the rather well-controlled polymerization conditions, where acrylic acid was dropped constantly over 3 hours to the macromonomer. However, with an increasing amount of AA in

the synthesis (4.5 and 6 mol), poly(arylic acid) (PAA) was formed (see peak 1) suggesting an unnecessary excess of AA. In case of minor AA amounts (2 or 3 mol), a low molecular weight polymer fraction (peak 3) occurred beside the main polymer peak (peak 2), which indicated a shortage of AA. Moreover, unreacted macromonomer (not polymerized) was identified in peak 5. Salt and water from the eluent were represented in peak 6 and can be neglected as these two components are included in all superplasticizer samples.

In **Table 8**, the molecular parameters of the anionic reference polymers P(2 - 6:1:0)_C are listed. The main polymer peak (peak 2) was characterized by molar masses (M_w) of 33,000 - 69,000 g mol^{-1}, while peak 1 representing the poly(acrylic acid) was characterized by a very high molecular weight of ~ 4 mio g mol^{-1}. Furthermore, the PDIs of 2.2 - 3.3 of the main polymer fractions showed a moderate monodispersity. The macromonomer conversion of ~ 84 % reflected an acceptable polymerization rate except for P(2:1:1)_C, where a slightly lower conversion of 75 % was achieved.

Table 8. Molecular parameters and macromonomer conversion for the anionic reference polymers P(2 - 6:1:0)_C.

Polymer sample	M_w [g mol^{-1}]					PDI [M_w/M_n]	MM conversion [%]
	Peak 1	Peak 2	Peak 3	Peak 4*	Peak 5	(Peak 2 - 4)	(Peak 1 - 4)
P(2:1:0)_C	---	44,190	6,400	---	4,382	2.6	75.0
P(3:1:0)_C	---	55,330	3,107	---	1,407	3.3	84.1
P(4.5:1:0)_C	4,097,000	68,990	---	---	5,122	2.2	87.4
P(6:1:0)_C	---**	33,060	---	---	4,802	2.7	83.2

*Peak 4 represents a main polymer fraction between peak 3 and peak 5. No values are given for this peak because it does not occur for the reference polymers P(2 - 6:1:0)_C
**M_w was not determinable by SEC measurement (insufficient amount)

5.1.1.3 Dispersing effectiveness of anionic conventional PCEs P(2 - 6:1:0)_C

The dispersing performance of the synthesized conventional superplasticizers was determined on cement paste via “mini slump” tests with a CEM I 52.5 R and a w/c ratio of 0.62. **Table 9** lists the required dosages [% bwoc] to reach a spread flow of 26 cm for each polymer.

Compared to P(3 - 6:1:0)_C, approx. twice the amount of superplasticizer (0.20 % bwoc) was necessary for sample P(2:1:0)_C to obtain a spread flow of 26 cm. This significantly lower dispersing ability was attributed to the lower anionic charge (AA content). Interestingly, the small amounts of high-

molecular-weight poly(acrylic acid) in P(4.5:1:0)_C and P(6:1:0)_C seemed to have no negative effect on the dispersing performance of these PCEs.

Table 9. Dosages [% bwoc] of the anionic reference polymers P(2 - 6:1:1)_C required to reach a spread flow of 26 cm (CEM I 52.5 R, w/c ratio = 0.62).

Anionic conventional polymers (C)				
Theor. molar ratio of AA:IPEG:TMAEMC	2:1:1	3:1:1	4.5:1:1	6:1:1
Dosage [% bwoc] required to reach a spread flow of 26 cm	0.20	0.11	0.09	0.10

5.1.2 Synthesis and characterization of anionic and zwitterionic PCEs according to synthesis method M1 (all monomers mixed together)

As an alternative synthesis method to the conventional process (see **Section 5.1.1.1**), a time-saving, one-pot procedure with a redox initiator system was performed which allowed polymerization at only 30 °C. Therefore, all monomers (macromonomer, acrylic acid and, where appropriate, TMAEMC), the chain transfer agent (NaH_2PO_2) as well as a part of the initiator system ($FeSO_4 \cdot 7\ H_2O$) were filled into the reaction flask and heated to 30 °C. By dropping the initiator solutions (30 wt.-% H_2O_2 and Rongalit®) over **15 minutes** to this mixture, polymerization took place. Subsequent stirring for 1 hour at this temperature completed the reaction.

5.1.2.1 Synthesis of anionic and zwitterionic PCEs P(2 - 6:1:0)_M1 or P(2 - 6:1:1)_M1 according to synthesis method M1

In the following section, the synthesis procedure for the zwitterionic polymer solution P(2:1:1)_M1 is specified. For the pure anionic PCEs P(2 - 6:1:0)_M1 the same method was used, except that the monomer TMAEMC was omitted.

As a preparation for the polymerization process, a clear solution was produced consisting of 1.80 g of AA (24.98 mmol), 30.0 g of 52IPEG (12.5 mmol), 3.46 g of TMAEMC (75 wt.-%; 12.49 mmol), 0.75 g of NaH_2PO_2 (8.53 mmol), 0.08 g of $FeSO_4 \cdot 7\ H_2O$ (0.29 mmol) and 30 mL of deionized water. All components were stirred for ~ 10 min in a 500 mL five-neck round-bottomed flask. Subseqeuently, the solution was purged with N_2 and heated to a temperature of 30 °C. To start the reaction, two solutions

(solution A = 3.00 g of 30 wt.-% H_2O_2 (26.46 mmol) and 5 mL of deionized water and solution B = 1.60 g of Rongalit® (12.87 mmol) and 10 mL of deionized water) were dropped into the flask at the same time over 15 minutes. Peristaltic pumps were used for this procedure. To compensate the heat release of the reaction, the flask was cooled by a water bath to keep the temperature below 38 °C. After solutions A and B had been completely added, 1 hour of stirring at 30 °C finished the reaction. A colorless, slightly viscous polymer solution (43 wt.-% solid content, pH ~ 2) was received.

All other zwitterionic PCEs (P(3 - 6:1:1)_M1) as well as the pure anionic PCEs P(2 - 6:1:0) were synthesized in the same way. The molar amounts of the monomers required for each individual PCE are listed in **Table 10**.

The preparation of PCE P(6:1:1)_M1 required 50 mL of deionized water (instead of 30 mL) in the round-bottomed flask.

Table 10. Designation, composition, and solution properties of the synthesized anionic and zwitterionic polymer solutions P(2 - 6:1:0)_M1 and P(2 - 6:1:1)_M1.

Polymer solution	Synthesis method	Molar ratio AA:IPEG:TMAEMC	Monomer quantities [g]			Solid content of solution [wt.-%]
			AA	IPEG	TMAEMC	
P(2:1:0)_M1	M1 comp.	2:1:0 [2:0.80:0]	1.80	30.0	0.00	40.3
P(3:1:0)_M1	M1 comp.	3:1:0 [3:0.81:0]	2.70	30.0	0.00	41.1
P(4.5:1:1)_M1	M1 comp.	4.5:1:0 [4.5:0.85:0]	4.05	30.0	0.00	40.8
P(6:1:1)_M1	M1 comp.	6:1:0 [6:0.83:0]	5.40	30.0	0.00	35.3
P(2:1:1)_M1	M1	2:1:1 [2:0.80:0.64]	1.80	30.0	3.46	41.8
P(3:1:1)_M1	M1	3:1:1 [3:0.81:0.65]	2.70	30.0	3.46	39.5
P(4.5:1:1)_M1	M1	4.5:1:1 [4.5:0.80:0.72]	4.05	30.0	3.46	46.0
P(6:1:1)_M1	M1	6:1:1 [6:0.83:0.67]	5.40	30.0	3.46	38.7

[ ] molar ratios actually contained in the polymer solutions calculated from SEC measurements

5.1.2.2 SEC analysis of anionic and zwitterionic PCEs P(2 - 6:1:0)_M1 or P(2 - 6:1:1)_M1 according to synthesis method M1

Figures 35 and **36** present the SEC spectra of the superplasticizers P(2 - 6:1:0)_M1 and P(2 - 6:1:1)_M1 which are synthesized according to the time-saving, one-batch method M1. In **Table 11**, the molecular parameters of the polymer solutions are listed.

Table 11. Molecular parameters and macromonomer conversion for the synthesized amphoteric and anionic comb polymer solutions “M1”.

Polymer solution	M_w [g mol^{-1}]					PDI [M_w/M_n]	MM conversion [%]
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	(Peak 2 - 4)	(Peak 1 - 4)
P(2:1:0)_M1	741,600	56,840	4,306	2,484	1,866	4.2	83.1
P(3:1:0)_M1	1,619,000	179,400	3,624	3,426	1,955	4.0	84.0
P(4.5:1:0)_M1	2,339,000	209,900	34,670	3,265	1,750	4.1	87.0
P(6:1:0)_M1	1,621,000	326,800	37,860	4,788	2,657	4.1	86.5
P(2:1:1)_M1	2,196,000	43,640	6,948	3,533	2,222	3.8	82.5
P(3:1:1)_M1	7,564,000	166,300	31,490	3,935	2,081	3.9	83.0
P(4.5:1:1)_M1	4,929,000	149,000	28,450	4,429	2,171	3.8	83.0
P(6:1:1)_M1	14,990,000	219,400	31,270	4,810	2,426	4.0	85.0

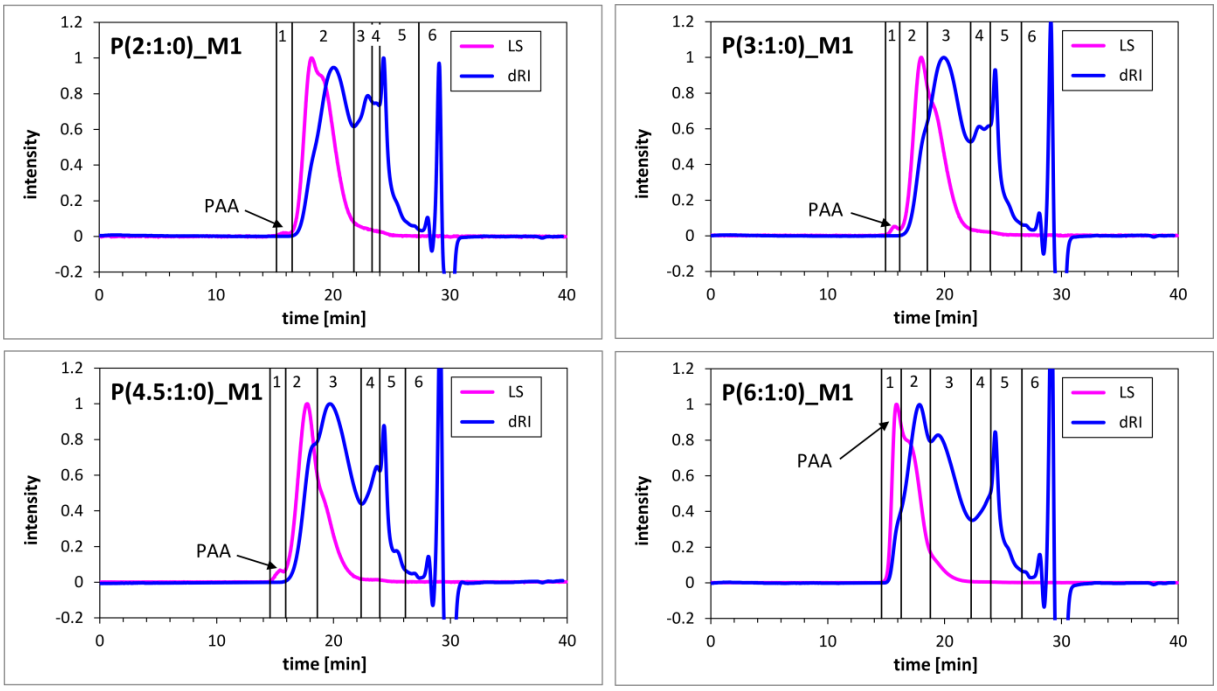


Figure 35. SEC spectra of the anionic reference polymer solutions P(2 - 6:1:0)_M1 prepared according to synthesis method M1.

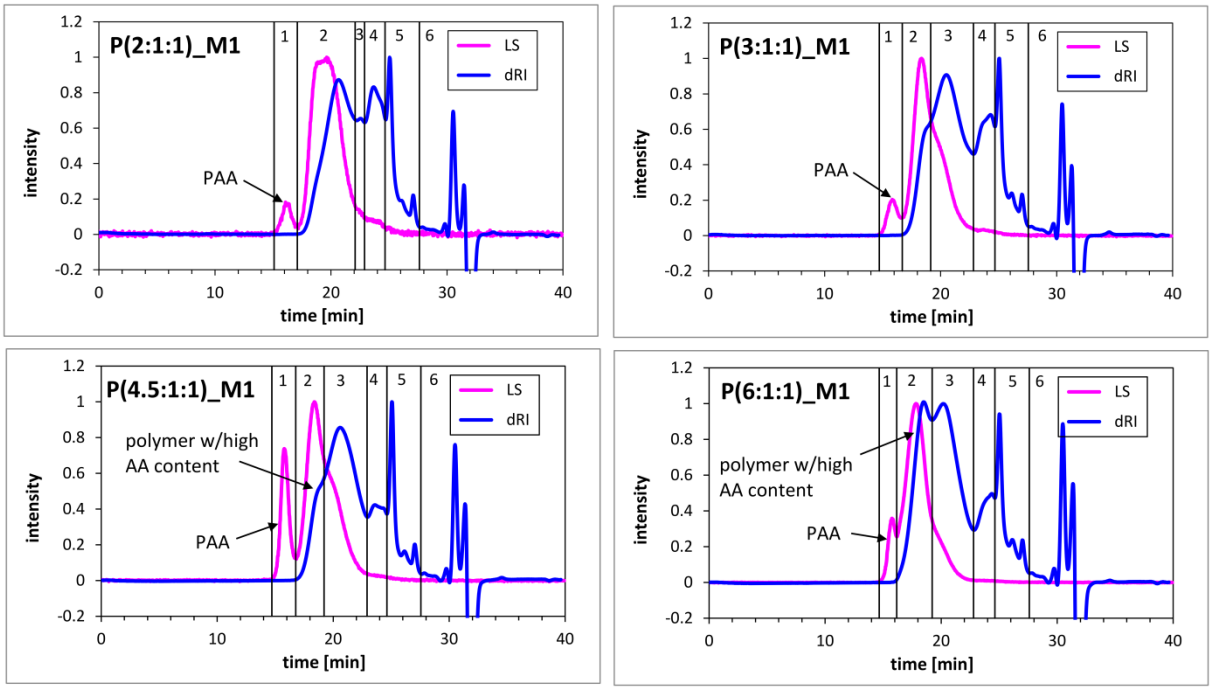


Figure 36. SEC spectra of the zwitterionic polymer solutions P(2 - 6:1:1)_M1 prepared according to synthesis method M1.

The most noticeable result was the multiplicity of different polymer fractions (peaks) contained in each prepared PCE for the anionic as well as the zwitterionic PCEs. Based on this insight, these PCEs clearly present mixtures of several different polymers. Thus, reaction method M1 seemed to produce PCEs, consisting of a polymer fraction as obtained in the conventional method, as well as of additional polymer fractions. This only slightly controlled polymerization process led to a highly complex polymer mixture with up to four different polymer fractions of different molecular weights or monomer compositions each. In general, M_w values of about 4,000 Da, 30,000 Da and 150,000 Da and a macromonomer conversion of ~ 85 % were found.

The peaks 2 to 4 in the SEC spectra (**Figures 35** and **36**) represented the main polymer fractions and account for ~ 80 - 90 wt.-% of the entire reaction product. As was the case in the conventional PCEs, Peak 1 described a fraction consisting of high molecular weight poly acrylic acid (PAA) and occurred to an higher extent when the amount of AA was increased in the synthesis procedure (e.g. P(6:1:0)_M1). However, contrary to the conventional PCEs P(2 - 6:1:0)_C, this fraction already appeared for the “M1” superplasticizers with a low acrylic acid amount like P(2:1:0)_M1 or P(2:1:1)_M1. Furthermore, peak 5 still displayed residual, non-polymerized IPEG macromonomer and, in case of the zwitterionic polymer solutions presumably, also the homopolymer of the cationic

monomer TMAEMC. Those fractions were identified in a prestudy via SEC (see **Section 9.2**). The higher the amount of AA in the polymerization procedure (P(2:1:1)_M1 → P(6:1:1)_M1) was, the larger the amount of high-molecular weight fraction which was formed (peak 2). Surprisingly, this first main polymer fraction increased at the expense of fraction 4, which represented the last main polymer fraction, but not at the expense of fraction 5, which signified still unreacted macromonomer. Peak 6, the salt and water from the eluent, can be neglected.

5.1.2.3 Dispersing effectiveness of anionic and zwitterionic PCEs P(2 - 6:1:0)_M1 or P(2 - 6:1:1)_M1 according to synthesis method M1

As known from a previous study [32], a certain amount of the poly acrylic acid with a high molecular weight (SEC, peak 1) can significantly reduce the dispersing effectiveness of a superplasticizer. However, it was very surprising that the polymer samples containing a mixture of polymer fractions required only low dosages to obtain a spread flow of 26 cm. They were in the same range (see **Table 12**) as the conventional anionic PCEs (see **Section 5.1.1.3**) and performed even better when less AA was present (P(2:1:0)_M1 or P(2:1:1)_M1). This proved that a polymer mixture consisting of several different polymer fractions can exhibit the same or even better dispersing performance than a superplasticizer containing only one kind of very uniform polymer. Furthermore, it was noticeable that there was no big difference between the zwitterionic and the anionic superplasticizers synthesized according to method “M1”.

Table 12. Dosages [% bwoc] of the anionic and zwitterionic polymer solutions P(2 - 6:1:0)_M1 and P(2 - 6:1:1)_M1 required to reach a spread flow of 26 cm (CEM I 52.5 R, w/c ratio = 0.62).

Anionic and zwitterionic polymer solutions according to method “M1”					
Theor. molar ratio of AA:IPEG:TMAEMC		2:1:1	3:1:1	4.5:1:1	6:1:1
Dosage [% bwoc] required to reach a spread flow of 26 cm	**anionic polymer solutions according to method “M1”**	0.11	0.11	0.11	0.13
	zwitterionic polymer solutions according to method “M1”	0.14	0.12	0.10	0.12

5.1.3 Synthesis and characterization of zwitterionic PCEs according to synthesis method M2 (AA fed to IPEG/TMAEMC)

To expand the spectrum of the zwitterionic synthesis method M1 (see **Section 5.1.2.1**), a second type was developed to create such superplasticizers. Here, as already used in method M1, a redox initiator system was applied allowing a reaction temperature of only 30 °C and a short reaction time of 60 minutes. In contrast to method “M1”, only the IPEG macromonomer and the cationic monomer TMAEMC (but not the monomer acrylic acid) as well as a part of the initiator system ($FeSO_4 \cdot 7\ H_2O$) and the chain transfer agent NaH_2PO_2 were placed in the reaction flask and heated to 30 °C. By dropping the initiator solutions (30 wt.-% H_2O_2 and Rongalit®) as well as acrylic acid to this mixture over **60 minutes**, polymerization took place. Subsequent stirring for 1 hour at this temperature completed the reaction.

5.1.3.1 Synthesis of the zwitterionic PCEs P(2 - 6:1:0)_M2 according to synthesis method M2

A description of the synthesis method M2 for the example P(2:1:1)_M2 is given in the following. In **Table 13**, the amounts of all monomers required for the PCEs P(2 - 6:1:1)_M2 are listed.

As a first step, a clear solution consisting of 30.0 g of 52IPEG (12.5 mmol), 3.46 g of TMAEMC (75 wt.-%; 12.49 mmol), 0.75 g of NaH_2PO_2 (8.53 mmol), 0.08 g of $FeSO_4 \cdot 7\ H_2O$ (0.29 mmol), and 30 mL of deionized water was prepared by stirring all components in a 500 mL five-neck round-bottomed flask for ~ 10 min. Afterwards, the solution was purged with N_2 and heated to a temperature of 30 °C. Simultaneously dropping three solutions to the mixture with peristaltic pumps over 60 minutes started the polymerization process. While solution A completed the addition of the monomer ingredients in the reaction (solution A = 1.80 g AA (24.98 mmol)), solutions B and C provided the initiator (solution B = 3.00 g of 30 wt.-% H_2O_2 (26.46 mmol) and 10 mL of deionized water and solution C = 1.60 g Rongalit® (12.87 mmol) and 10 mL of deionized water). To compensate the heat release of the reaction, the flask was cooled by a water bath in order to keep the temperature below 38 °C. After the three solutions had been completely added, 1 h of stirring at 30 °C finished the reaction. A yellow, slightly viscous polymer solution (38 wt.-% solid content, pH ~ 2.2) was received.

For the polymer solutions P(4.5:1:1)_M2 and P(6:1:1)_M2, 50 mL of deionized water instead of 30 mL were used to generate a clear solution at the beginning of the procedure.

Table 13. Designation, composition, and solution properties of the synthesized zwitterionic comb polymer solutions “M2”.

Polymer solution	Synthesis method	Molar ratio AA:IPEG:TMAEMC	Monomer quantities [g]			Solid content of solution [wt.-%]
			AA	IPEG	TMAEMC	
P(2:1:1)_M2	M2	2:1:1 [2:0.80:0.64]	1.80	30.0	3.46	38.5
P(3:1:1)_M2	M2	3:1:1 [3:0.86:0.69]	2.70	30.0	3.46	39.3
P(4.5:1:1)_M2	M2	4.5:1:1 [4.5:0.87:0.78]	4.05	30.0	3.46	29.6
P(6:1:1)_M2	M2	6:1:1 [6:0.88:0.79]	5.40	30.0	3.46	29.6

[ ] molar ratios actually contained in the polymer solutions calculated from SEC measurements

5.1.3.2 SEC analysis of the zwitterionic PCEs P(2 - 6:1:1)_M2 according to synthesis method M2

Figure 37 shows the SEC spectra of the zwitterionic superplasticizers P(2 - 6:1:1)_M2 which were synthesized according to method “M2” – which was the better controlled reaction process compared to “M1”. The molecular parameters of the polymer solutions are specified in **Table 14**.

Table 14. Molecular parameters and macromonomer conversion for the synthesized amphoteric comb polymers P(2 - 6:1:1)_M2.

Polymer solution	M_w [g mol^{-1}]					PDI [M_w/M_n]	MM conversion [%]
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	(Peak 2 - 4)	(Peak 1 - 4)
P(2:1:1)_M2	---*	---	24,390	3,743	2,544	2.9	80.9
P(3:1:1)_M2	2,297,000	145,900	21,460	3,549	2,787	4.1	86.9
P(4.5:1:1)_M2	5,115,000	426,200	67,000	26,470	20,090	3.7	87.1
P(6:1:1)_M2	4,039,000	359,000	46,050	20,530	17,030	3.7	90.3

*M_w was not determinable by SEC measurement (insufficient amount)

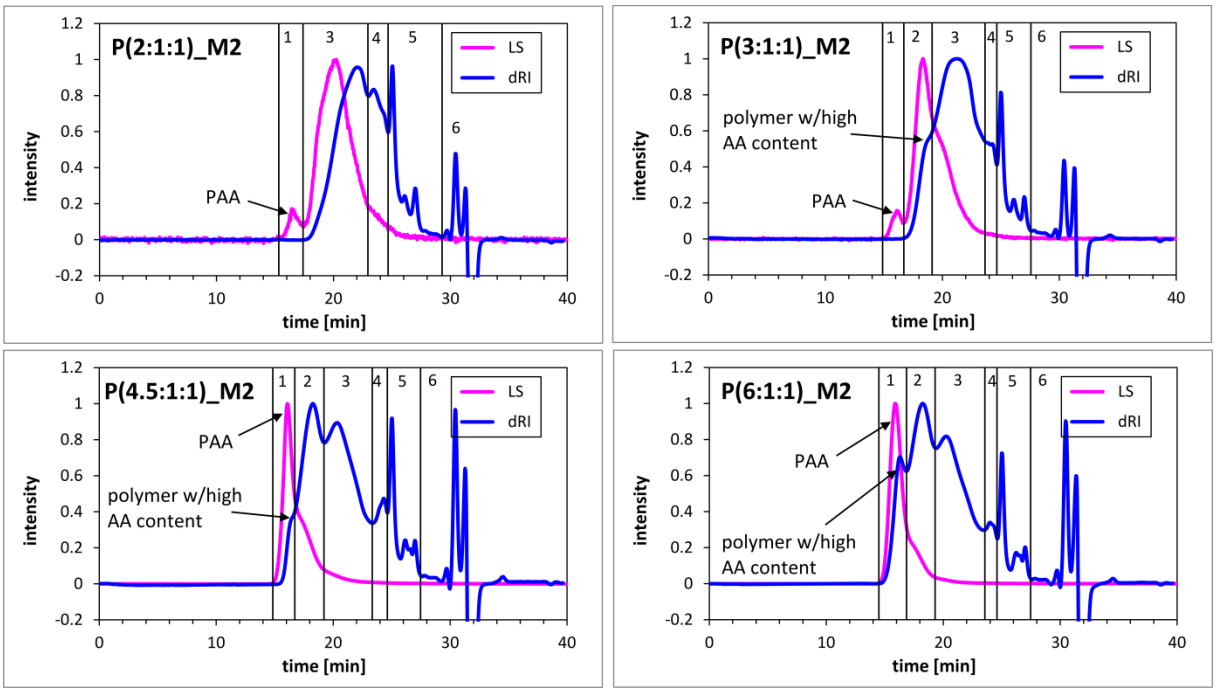


Figure 37. SEC spectra of the zwitterionic polymer solutions P(2 - 6:1:1)_M2 prepared according to synthesis method M2.

This polymerization process is subject to a much higher degree of reaction control than was the case for the “M1” method. In fact, the “M2” principle also was a batch synthesis equal to “M1”, but here, the highly reactive monomer acrylic acid was only dropped in the reaction flask and not added completely at the beginning, which allowed significantly more control, as it is not possible for the acrylic acid to co- or homopolymerize all at once. However, according to the SEC spectra in **Figure 37**, again different main polymer fractions (peak 2 - 4) with different molecular weights were received. Furthermore, as with synthesis process “M1”, higher amounts of poly(acrylic acid) (peak 1) were formed with increasing AA contents in the polymer solutions. As already discussed for the “M1” polymer solutions, peak 5 still represents cationic homopolymer and non-polymerized macromonomer and peak 6 represents salt and water from the eluent.

Moreover, the fractions thus formed were very similar to the polymer fractions formed in “M1” except for their molecular weights. Here, the polymer samples from “M2” exhibited a much higher M_w (~ 20,000 Da for peak 4, ~ 40,000 Da for peak 3, and ~ 300,000 Da for peak 2). Due to this special property, a decrease in the dispersing performance was expected because an excessive molecular weight may impair their effectiveness [32]. Therefore, common superplasticizers usually show a M_w of ~ 20,000 to 120,000 Da only.

5.1.3.3 Dispersing effectiveness of the zwitterionic PCEs P(2 - 6:1:1)_M2 according to synthesis method M2

As already described in literature, the dispersing ability of the zwitterionic "M2" polymer solutions were much reduced compared to those synthesized by the "M1" process (see **Table 15**). Apparently, the high M_w of these superplasticizers lowered the dispersing performance. In addition, the polymer solutions with very low or high acrylic acid amount (P(2:1:1)_M2 and P(6:1:1)_M2) performed worst. Similar to all other synthesis processes (conventional, M1), the polymer sample with 4.5 mol of AA again constituted the best suitable ratio in order to achieve the best dispersing effectiveness.

Table 15. Dosages [% bwoc] of comb polymer solutions P(2 - 6:1:1)_M2 required to reach a spread flow of 26 cm (CEM I 52.5 R, w/c ratio = 0.62).

Zwitterionic polymer solutions according to method "M2"				
Theor. molar ratio of AA:IPEG:TMAEMC	2:1:1	3:1:1	4.5:1:1	6:1:1
Dosage [% bwoc] required to reach a spread flow of 26 cm	24.0 cm[a]	0.40	0.22	1.00

[a] here, a polymer dosage of 1.0 % bwoc was not sufficient to reach 26 cm; therefore the spread flow achieved at 1 % dosage is given in cm

5.1.4 Summary of Section 5.1

In this section the impact of different synthesis methods for isoprenol ether-based PCE superplasticizers (52IPEG PCEs) was investigated. Therefore, three different methods, including the conventional process (C), a very uncontrolled, easy and short-time synthesis method (M1) as well as a slightly more controlled type (M2) were tested. For the "M1" process, strictly anionic as well as zwitterionic polymer solutions were prepared, while for "M2" exclusively zwitterionic PCEs and for the conventional method only anionic superplasticizers were synthesized. The molar ratio of AA:MM varied between 2:1, 3:1, 4.5:1 and 6:1 for each method. Utilizing the "mini slump" test allowed to study the connection between molecular properties and the dispersing effectiveness of the PCEs. **Table 16** provides an overview of the characteristics of the obtained PCEs**.**

It was found that the conventional synthesis process led to polymers with a very uniform molecular weight distribution. At the most one side fraction was identified. In contrast, the "M1" and "M2" methods resulted in polymer mixtures with about three main polymer fractions. These results showed

that rather uncontrolled reaction conditions led to polymer mixtures instead of one main polymer fraction.

Table 16. Properties of the resulting PCEs according the “conventional”, “M1” or “M2” polymerization process.

Synthesis method	Reaction time & temperature	Amount of main polymer fractions	M_w for main polymer fraction(s)	Best AA:MM feeding ratio for dispersing effectiveness and dosage for 26 cm
P(2 - 6:1:0)_C conventional	3 h + 2 h 60 °C	1 - 2	~ 5,000 Da (peak 3) ~ 50,000 Da (peak 2)	4.5:1 0.09 % bwoc
P(2 - 6:1:0)_M1 Method M1	15 min + 1h 30 °C	3	~ 3,500 Da (peak 4) ~ 35,000 Da (peak 3) ~ 200,000 Da (peak 2)	4.5:1 0.11 % bwoc
P(2 - 6:1:1)_M1 Method M1	15 min + 1h 30 °C	3	~ 4,000 Da (peak 4) ~ 30,000 Da (peak 3) ~ 150,000 Da (peak 2)	4.5:1 0.10 % bwoc
P(2 - 6:1:1)_M2 Method M2	1 h + 1h 30 °C	2 - 3	~ 20,000 Da (peak 4) ~ 40,000 Da (peak 3) ~ 300,000 Da (peak 2)	4.5:1 0.22 % bwoc

Furthermore, no big differences were observed concerning the polymer fractions between the anionic and zwitterionic “M1” polymer solutions. This proved that the synthesis method used has a greater influence on the formation of the PCEs than the monomers. However, the molecular weight of the polymer fractions obtained for “M1” and “M2” strongly differed: the M_w for P(2 - 6:1:1)_M2 polymer samples was much higher than for those synthesized with method “M1”.

Independent of the synthesis process, the PCEs containing 4.5 mol AA performed best in regard to the dispersing effectiveness. Furthermore, it was striking that the conventional and strictly anionic or zwitterionic “M1” polymer solutions showed almost the same dispersing performance. The higher macromonomer conversion of the polymer solutions “M1” and “M2” when only 2 mol AA were present was also remarkable. In case of the “M1” polymer solutions (AA:MM ratio of 2:1), this led to a better dispersing performance than was reached for the conventional PCEs.

Therefore, it could be shown that a polymer solution consisting of several polymer fractions can perform equally well to a conventional polymer with only one main fraction. In addition, the synthesis procedure for polymers consisting of a mixture of polymer fractions is much simpler and faster than that of the conventional polymer. However, exceptionally high molecular weights for polymer solutions seemed to hinder their dispersing ability and have to be avoided.

5.2 Impact of different synthesis methods on the dispersing effectiveness of isoprenol ether-based zwitterionic and anionic polycarboxylate (PCE) superplasticizers

Parts of **Section 5.2** were published in the publication “Impact of different synthesis methods on the dispersing effectiveness of isoprenol ether-based zwitterionic and anionic polycarboxylate (PCE) superplasticizers” by C. Chomyn and J. Plank in the journal “Cement and Concrete Research” [154].

As shown in **Section 5.1**, the ratio of 4.5 mol of acrylic acid and 1 mol of macromonomer turned out to produce the optimal polymer solutions for dispersing effectiveness in cement. Based on these results, properties like the anionic charge amount of the polymer solutions and the dispersing effectiveness in cement were analyzed for the zwitterionic and strictly anionic polymer samples P(4.5:1:1)_M1, P(4.5:1:1)_M2, P(4.5:1:0)_C and P(4.5:1:0)_M1 previously presented in **Section 5.1**. In addition, two more superplasticizers P(4.5:1:1)_M3 and P(4.5:1:0)_5M were tested. Their synthesis methods and molecular properties (SEC spectra) were specified in the following section (**Section 5.2.1**). Finally, an analysis of their actual composition with regard to the different polymer fractions is provided. **Sections 5.2.2** to **5.2.4** (results, figures and tables) closely follow the paper published by C. Chomyn and J. Plank [154].

5.2.1 Synthesis method and molecular properties of the PCEs P(4.5:1:1)_M3 and P(4.5:1:0)_5M

5.2.1.1 Synthesis of the zwitterionic PCE P(4.5:1:1)_M3 according to synthesis method M3

According to this method, first the cationic monomer TMAEMC (solution A) as well as one part of the initiator (solution B) were separately fed into the IPEG macromonomer in the reaction flask. Subsequently, the anionic monomer acrylic acid (solution C) and the second part of the initiator (solution D) were dropped into the reaction mixture which was obtained in the first step to start polymerization. With respect to the polymerization type used (no living polymerization, but free radical copolymerization), not only one zwitterionic polymer was expected to be formed, but also a mixture of exclusively cationic comb polymers and strictly anionic comb polymers (see **Figure 39**).

In the first step, a solution of 30.0 g of 52IPEG (12.5 mmol), 0.02 g of $FeSO_4 \cdot 7\ H_2O$ (0.07 mmol) as well as 30 mL of deionized water was prepared and placed in a 500 mL five-neck round-bottomed flask. Next, the reaction mixture was flushed with N_2 and heated to 30 °C. When the desired temperature had been reached, 3.00 g of 30 wt.-% H_2O_2 (26.46 mmol) was added, and then immediately, solution A and B (solution A = 3.46 g of TMAEMC (75 wt.-%, 12.49 mmol) and 7 mL of deionized water, solution B = 1.60 g of Rongalit® (12.87 mmol) and 10 mL of deionized water) were separately fed with peristaltic pumps to the reaction flask during **1 hour**. To finish the first reaction step, the reaction mixture was kept at 30 °C and stirred for 1 hour.

For the second step, a solution consisting of the reaction product from step one, 4.05 g of AA (56.20 mmol), 0.75 g of NaH_2PO_2 (8.53 mmol) and 0.08 g of $FeSO_4 \cdot 7\ H_2O$ (0.29 mmol) were filled into the 500 mL five-neck round-bottomed flask and heated to 30 °C. After flushing with N_2, solution C and D were separately fed with peristaltic pumps to the reaction flask during **15 minutes**. Solution C consisted of 1.80 g of 30 % H_2O_2 (15.88 mmol) and 5 mL of deionized water, solution D consisted of 1.60 g of Rongalit® (12.87 mmol) and 10 mL of deionized water. After complete dosing, the reaction mixture was kept at 30 °C and stirred for 1 hour. A yellow, slightly viscous polymer solution (31.5 wt.-% solid content, pH value ~ 1.5) was received.

5.2.1.2 Synthesis of the anionic PCE P(4.5:1:0)_5M according to synthesis method 5M

The basic principle of the synthesis method “5M” was described in the bachelor study “Synthesis and Characterization of different IPEG-PCE polymers” from Lai Hsiao Yu who was supervisied by C. Chomyn and J. Plank [155].

This synthesis method is identical to the time-saving, uncontrolled batch polymerization process “M1” (see **Section 5.1.2.1**), except that (1) the reaction time was **5 minutes** only and (2) the **polymerization process was stopped** after initiator addition by cooling the reaction mixture immediately to 7 °C and performing dialysis.

A solution of 60.0 g of 52IPEG (25.0 mmol), 8.11 g of AA (112.55 mmol), 0.15 g of $FeSO_4 \cdot 7\ H_2O$ (0.54 mmol), 1.50 g of NaH_2PO_2 (17.05 mmol), and 185 mL of deionized water was prepared. After purging the solution with N_2 and heating the mixture to 30 °C, solution A and B (solution A = 0.60 g of 30 % H_2O_2 (5.29 mmol) and 2 mL of deionized water, solution B = 0.27 g of Rongalit® (2.17 mmol)

and 2 mL of deionized water) were fed in with two peristaltic pumps over 5 minutes. Immediately after dosing was complete, the reaction product was cooled for 5 minutes in ice and afterwards for 1 hour at 7 °C. Subsequent dialysis for 24 hours ensured that non-reacted acrylic acid was flushed out. A colorless, slightly viscous polymer solution (15 wt.-% solid content, pH value ~ 1.9) was received.

Table 17 summarizes the required monomer amounts as well as the composition of the synthesized zwitterionic polymers P(4.5:1:1)_M3 (see **Section 5.2.1.1**) and the anionic polymer P(4.5:1:0)_5M.

Table 17. Designation, composition, and solution properties of the synthesized zwitterionic polymer solution P(4.5:1:1)_M3 and the anionic polymer P(4.5:1:0)_5M.

Polymer solution	Synthesis method	Molar ratio AA:IPEG:TMAEMC	Monomer quantities [g]			Solid content of solution [wt.-%]
			AA	IPEG	TMAEMC	
P(4.5:1:1)_M3	M3	4.5:1:1 [4.5:0.75:0.60]	4.05	30.0	3.46	31.5
P(4.5:1:0)_5M	5M	4.5:1:0 [4.5:0.75:0]	8.11	60.0	---	15.0

[ ] molar ratios actually contained in the polymer solutions calculated from SEC measurements

5.2.1.3 SEC analysis of the zwitterionic PCE P(4.5:1:1)_M3 and the anionic polymer P(4.5:1:0)_5M

According to the SEC spectra (see **Figure 38**), synthesis method “M3” led to a polymer solution with three different main polymer fractions (peak 2 - 4) as already obtained for the “M1” and “M2” polymer solutions (see **Sections 5.1.2.2** and **5.1.3.2**).

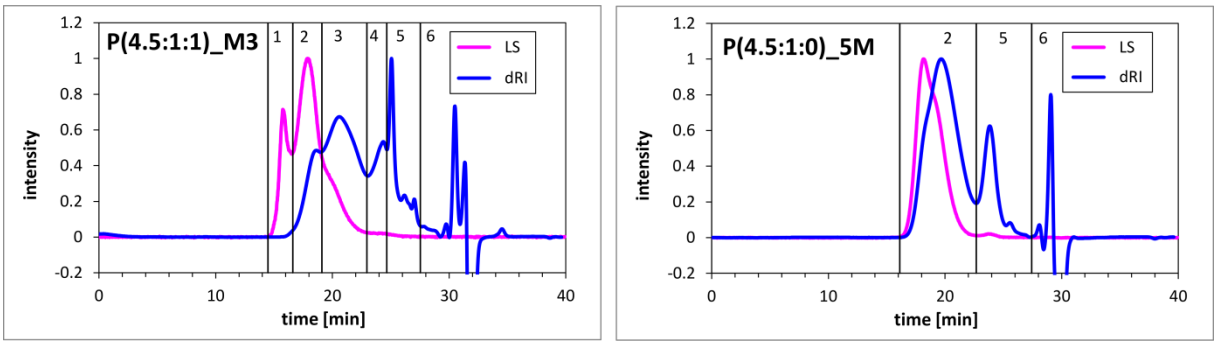


Figure 38. SEC spectra of the zwitterionic polymer solution P(4.5:1:1)_M3 and the anionic polymer P(4.5:1:0)_5M.

The molecular weights of the main polymer fractions were similar to those of the “M1” polymer solutions. Additionally, peak 1 indicated small amounts of poly(acrylic acid). In contrast, the anionic polymer P(4.5:1:0)_5M consisted of only one uniform polymer fraction (peak 2) which showed a high

similarity to the conventional PCEs. In addition, its molecular weight was in the same order as for those polymers (C) with only a 10 % lower macromonomer conversion. In both SEC spectra, Peak 5 represents non-reacted macromonomer and for the "M3" PCE a homopolymer of TMAEMC, while peak 6 indicates salt and water from the eluent. **Table 18** lists the molecular details of the obtained PCEs.

Table 18. Molecular parameters and macromonomer conversion for the synthesized amphoteric polymer solution P(4.5:1:1)_M3 and the anionic polymer P(4.5:1:0)_5M.

Polymer solution	M_w [g mol^{-1}]					PDI [M_w/M_n]	MM conversion [%]
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	(Peak 2 - 4)	(Peak 1 - 4)
P(4.5:1:1)_M3	4,473,000	209,000	27,100	4,193	2,120	5.3	79.6
P(4.5:1:0)_5M	---	64,280	---	---	3,102	2.4	78.0

5.2.1.4 Dispersing effectiveness of the zwitterionic PCE P(4.5:1:1)_M3 and the anionic polymer P(4.5:1:0)_5M

As for all polymer solutions described in **Section 5.1**, the dispersing effectiveness of these two superplasticizers was tested via "mini slump test". The required dosage to reach a spread flow of 26 cm (CEM I 52.5 R, w/c ratio = 0.62) is given in **Table 19**.

Table 19. Dosages [% bwoc] of polymer solutions P(4.5:1:1)_M3 and P(4.5:1:0)_5M required to reach a spread flow of 26 cm (CEM I 52.5 R, w/c ratio = 0.62).

Superplasticizer	Dosage to reach a spread flow of 26 cm [% bwoc]
P(4.5:1:1)_M3	0.20
P(4.5:1:0)_5M	0.08*

* value for purified (dialysed) product

A high similarity between the polymer solutions P(4.5:1:1)_M2 (required dosage = 0.22 % bwoc) and P(4.5:1:1)_M3 was observed, while P(4.5:1:0)_5M was similar to P(4.5:1:0)_M1 (required dosage = 0.11 % bwoc) and P(4.5:1:0)_C (required dosage = 0.09 % bwoc). However, P(4.5:1:0)_5M required purification via dialysis.

5.2.2 Short overview of the tested PCE samples

Now that two more polymers and their synthesis method have been presented (see **Section 5.2.1**), all superplasticizers that are used for detailed dispersing performance tests are compared. **Table 20** represents the superplasticizers and their specific characteristics which were chosen for tests providing more details on the correlation between the synthesis procedure and the properties, especially the dispersing behavior.

Table 20. Properties of the tested PCEs.

Polymer solution	Charge character & initiator system	Reaction time & temperature	Number of main polymer fractions	M_w for main polymer fraction(s)	Dosage [% bwoc] to reach 26 cm (CEM I 52.5 R, w/c ratio = 0.62)
P(4.5:1:0)_C Conventional	anionic APS	3 h + 2 h 60 °C	1	~ 69,000 Da (peak 2)	0.09 % bwoc
P(4.5:1:0)_5M 5 minute method	anionic redox	5 min* 30 °C	1	~ 64,000 Da (peak 2)	0.08 % bwoc
P(4.5:1:0)_M1 Method M1	anionic redox	15 min + 1 h 30 °C	3	~ 3,500 Da (peak 4) ~ 35,000 Da (peak 3) ~ 200,000 Da (peak 2)	0.11 % bwoc
P(4.5:1:1)_M1 Method M1	zwitterionic redox	15 min + 1 h 30 °C	3	~ 4,400 Da (peak 4) ~ 28,500 Da (peak 3) ~ 150,000 Da (peak 2)	0.10 % bwoc
P(4.5:1:1)_M2 Method M2	zwitterionic redox	1 h + 1 h 30 °C	3	~ 26,500 Da (peak 4) ~ 67,000 Da (peak 3) ~ 430,000 Da (peak 2)	0.22 % bwoc
P(4.5:1:1)_M3 Method M3	zwitterionic redox	2x15 min + 2x1 h 30 °C	3	~ 4,000 Da (peak 4) ~ 27,000 Da (peak 3) ~ 210,000 Da (peak 2)	0.20 % bwoc

*Additionally reaction termination and dialysis required

As mentioned above, all PCEs possessed a feeding molar ratio of 4.5 mol of acrylic acid and 1 mol of 52IPEG macromonomer. The zwitterionic polymer solutions additionally contained 1 mol of TMAEMC. A redox initiator system was used for all samples except for the conventional polymer (C). Furthermore, all zwitterionic polymer solutions contained 3 different main polymer fractions.

Comparing the molecular weights of the PCEs, the polymer solution “M2” clearly had a higher M_w than the “M1” and “M3” polymer solutions. The anionic uniform PCEs “C” and “5M” were similar to each other with ~ 66,000 Da. The anionic polymer P(4.5:1:0)_5M was dialyzed due to the necessity during the synthesis process (see **Section 5.2.1.2**). This likely contributes to its superior dispersing effectiveness compared to all other PCEs.

Considering the chosen synthesis method, the used monomers as well as the analyzed SEC spectra of the PCEs, a very general prediction of the formed polymer fractions in each PCE could be made and are shown in **Figures 39** and **40**.

According to SEC analysis, small amounts of poly(acrylic acid) and cationic homopolymer were present as well as the main polymer fractions of the amphoteric PCEs “M1” and “M2” consisting of zwitterionic terpolymers with varying AA content (see **Figure 39**). Furthermore, with an increasing amount of AA in the PCEs, byproducts like copolymers with a high AA content and an anionic comb polymer were assumed to have formed. In contrast, mainly a mixture of cationic and anionic polymers was expected for the main polymer fractions of the “M3” PCE due to the two-stage synthesis process performed with free radical polymerization.

Poly(acrylic acid) as well as anionic comb polymers were expected for all strictly anionic PCEs (“C”, “5M”, “M1”). Since the “M1” PCEs have several main polymer fractions (polymer mixture), various kinds of polymers with different AA contents were hypothesized (see **Figure 40**).

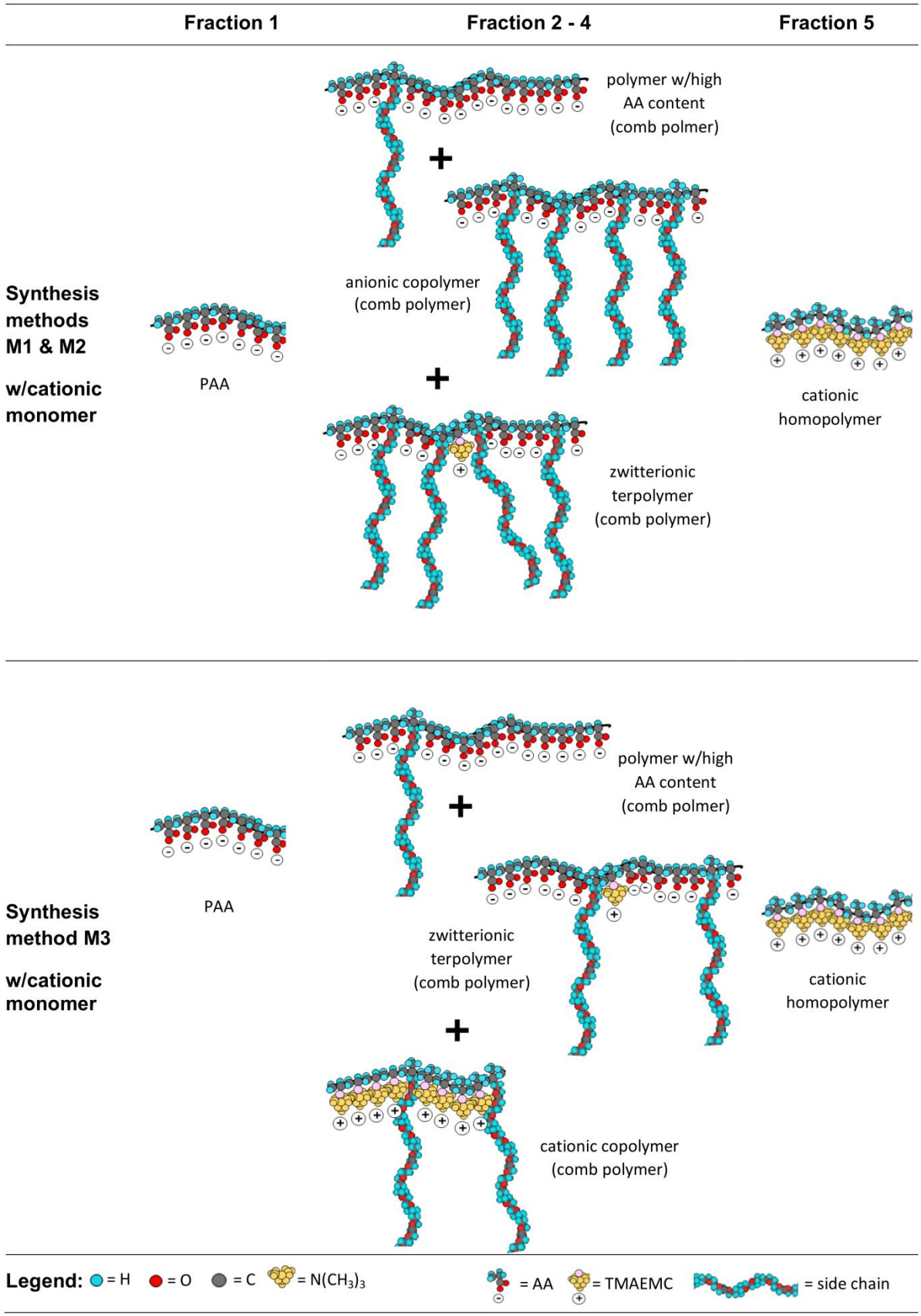


Figure 39. Polymer fractions present in the PCEs containing the cationic monomer TMAEMC prepared according to the synthesis method “M1”, “M2” or “M3”.

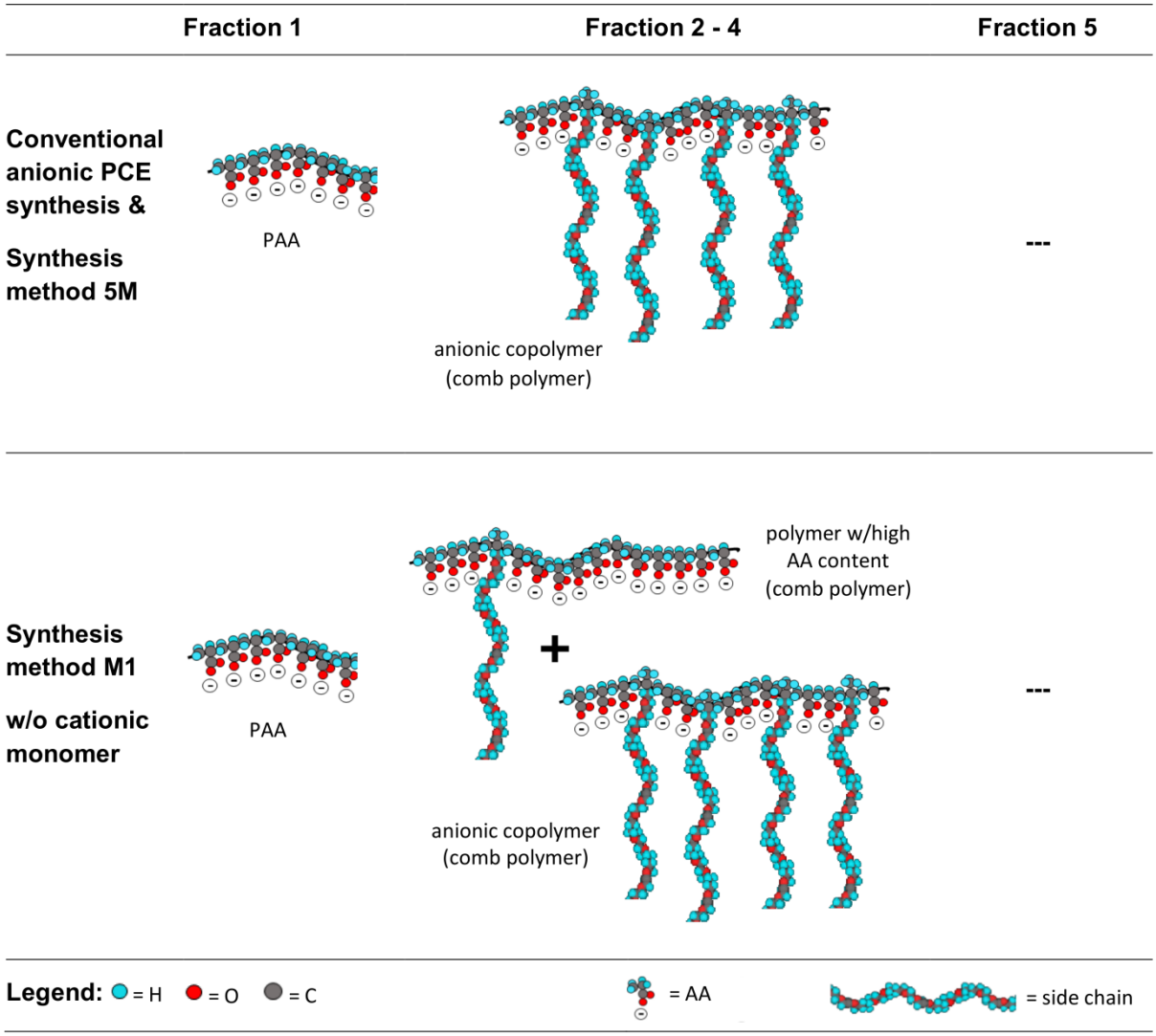


Figure 40. Polymer fractions present in the anionic PCEs prepared according to the conventional synthesis method "C" as well as to processes "5M" and "M1".

5.2.3 Anionic character and dispersing effectiveness of the PCE samples

5.2.3.1 Ionic charge amounts of the synthesized polymers

In addition to the analysis of the SEC spectra, each polymer solution was characterized by anionic charge amount measurements in different media. Therefore, the charge of all prepared zwitterionic and strictly anionic PCE samples with 4.5 mol of AA and 1 mol of macromonomer were determined in deionized water, 0.1 M NaOH and synthetic cement pore solution (SCPS) to specify the ionic character in different environments. Furthermore, their theoretical anionic charge amount was calculated based on the monomer quantities used in the synthesis (see **Section 4.2.5**). **Figure 41** represents the ionic charge amounts.

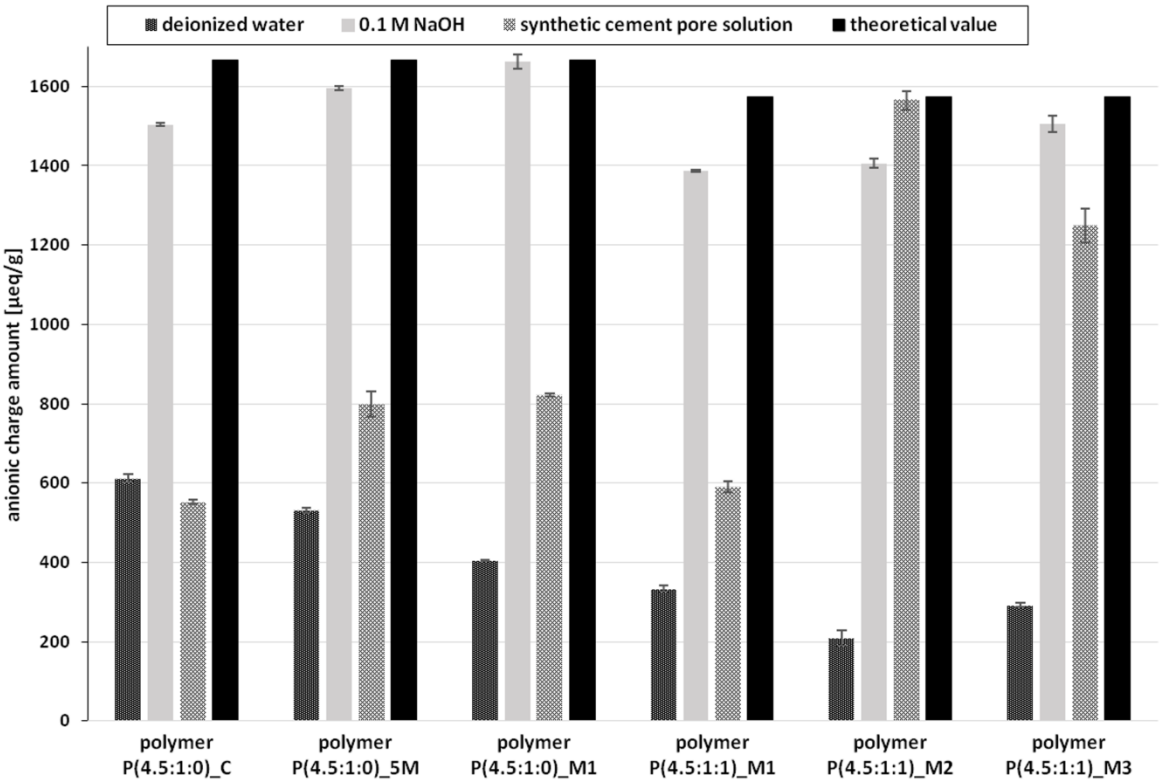


Figure 41. Anionic charge amounts of the anionic polymers P(4.5:1:0)_C, P(4.5:1:0)_5M and P(4.5:1:0)_M1 and the zwitterionic polymers P(4.5:1:1) synthesized according to methods M1, M2, and M3, measured in different solvents.

All PCE samples as prepared produced a pH value of ~ 4 in deionized water. It was found that the strictly anionic PCEs P(4.5:1:0)_C, P(4.5:1:0)_5M and P(4.5:1:0)_M1 possessed higher anionic charge amounts here (~ 400 - 600 µeq/g) compared to the zwitterionic superplasticizers P(4.5:1:1)_M1, P(4.5:1:1)_M2 and P(4.5:1:1)_M3 (~ 200 - 300 µeq/g) which contain cationic monomer. This confirmed the successful formation of cationic polymer. However, to validate that a zwitterionic polymer was actually present and not just a cationic homopolymer, the ionic charge of a mixture of poly-TMAEMC and the anionic PCE P(4.5:1:0)_M1 was determined. On the basis of the charge shielding effect of the macromonomer in the zwitterionic polymer, a higher reduction of the anionic charge was expected in this mixture than in an amphoteric polymer. Indeed, the anionic charge of the prepared mixture was clearly lower (~ 83 µeq/g) than was the case for the zwitterionic polymer P(4.5:1:1)_M1 (~ 334 µeq/g), which proved successful incorporation of cationic monomer TMAEMC into a main polymer fraction.

Due to the highly alkaline conditions in 0.1 M NaOH (pH ≥ 12), all carboxylic groups in the superplasticizers were fully deprotonated resulting in the strongest measured anionic charges of the

polymers of ~ 1400 - 1600 µeq/g. It is worth noting that here the difference between the strictly anionic PCEs and the zwitterionic polymer solutions was smaller than in deionized water. Through extensive compensation of the cationic functionalities through OH^- ions, which are present in the alkaline medium, the impact of the cationic groups on the overall charge of the polymer was reduced.

In the synthetic cement pore solution, the effect of an alkaline medium (pH ≥ 12) in the presence of ions like Ca^{2+} can be studied. In theory, it was expected that a complex was formed between the carboxylic groups and the Ca^{2+} ions which leads to a charge neutralization and consequently to a lower anionic charge amount. Additionally, zwitterionic polymers should be less affected because their cationic functionality would not complexate Ca^{2+}. However, two different groups have emerged as are shown in **Figure 41**: The anionic charge amount of the polymers P(4.5:1:0)_M1 and P(4.5:1:1)_M1 as well as of the polymers P(4.5:1:0)_C and P(4.5:1:0)_5M was significantly reduced. In contrast, the zwitterionic samples P(4.5:1:1)_M2 and P(4.5:1:1)_M3 did not show such a strong reduction in charge. This observation proved that distinctly different polymer samples with their own characteristics were formed depending on the synthesis method. This fact will be addressed in the following sections.

5.2.4 Summary of Section 5.2

This study investigated the impact of the synthesis method on the dispersing effectiveness of strictly anionic or zwitterionic isoprenol ether-based polycarboxylate superplasticizers (52IPEG PCEs). All anionic and zwitterionic PCE samples were based on 4.5 mol of AA and 1 mol of 52IPEG macromonomer. For the zwitterionic polymers, additionally 1 mol of cationic TMAEMC was introduced. The PCEs prepared according to **Section 5.1** (synthesis method “C”, “M1”, and “M2”) as well as two additional superplasticizers were used. Therefore, an even shorter (5 minutes) and faster polymerization method than “M1” was applied for anionic PCEs (“5M” method) and an even more controlled, two-step-polymerization (“M3”) was applied for zwitterionic PCEs, in which the macromonomer and the cationic monomer were polymerized first followed by the acrylic acid and the obtained reaction mixture.

A very general prediction of the formed polymer fractions in each polymer sample was hypothesized. The considerations were based on (1) the chosen synthesis method, (2) the used monomers as well

as (3) the analyzed SEC spectra of the PCEs. It became very clear that the actual composition of a PCE superplasticizer was strongly influenced by the synthesis method.

Anionic charge measurements proved successful formation of polymers for all synthesis methods. As expected for those polymers including cationic monomer (TMAEMC), a lower anionic charge was determined in deionized water, which confirmed the presence of a cationic polymer. For the polymers synthesized according to method “M2” and “M3” (samples include TMAEMC), a significantly lower anionic charge reduction was observed in synthetic cement pore solution.

5.3 Impact of different synthesis methods on the dispersing effectiveness in cement and the clay and sulfate tolerance

Parts of **Section 5.3** were published in the publication “Impact of different synthesis methods on the dispersing effectiveness of isoprenol ether-based zwitterionic and anionic polycarboxylate (PCE) superplasticizers” by C. Chomyn and J. Plank in the journal “Cement and Concrete Research” [154].

To gain more insight on the effectiveness of the synthesized superplasticizers with 4.5 mol of AA which were tested in **Section 5.2**, the dosage-dependent dispersing effect in cement as well as the dispersing effectiveness in presence of clay and sulfate ions was studied in detail. **Sections 5.3.1** to **5.3.4** (results, figures and tables) closely follow the paper published by C. Chomyn and J. Plank [154].

5.3.1 Dosage-dependent dispersing effectiveness in cement of the polymers from different synthesis methods

When determining the dosage-dependent dispersing effectiveness, three different performance groups were clearly identified in **Figure 42**. The zwitterionic polymer solutions P(4.5:1:1)_M2 and P(4.5:1:1)_M3 (= group 1) exhibited almost the same dosage-dependent dispersing effects. However, they clearly fell behind all other PCEs regarding their effectiveness. The conventional anionic polymer P(4.5:1:0)_C as well as the polymers P(4.5:1:0)_M1 and P(4.5:1:1)_M1 can be considered as the second group. Especially at dosages > 0.05 % bwoc they performed better than group 1. The third group is formed by the purified anionic polymer P(4.5:1:0)_5M which stands out in its dispersing effectiveness.

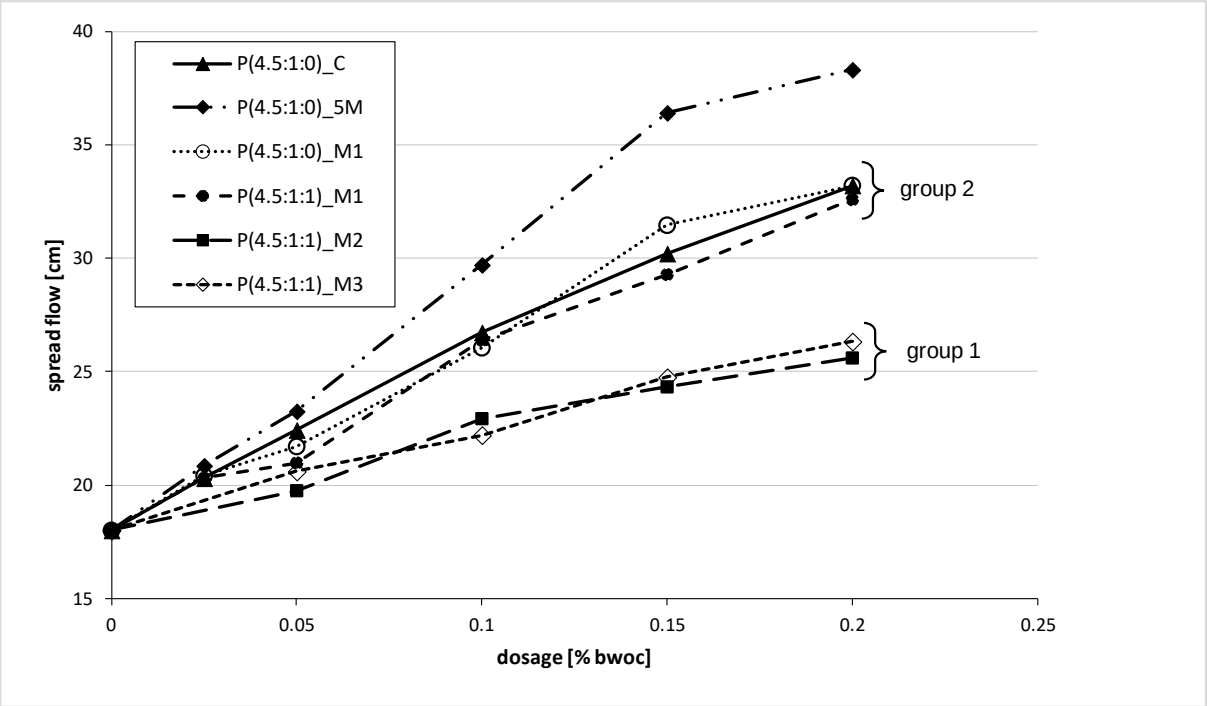


Figure 42. Comparison of the dispersing effectiveness of anionic and zwitterionic polymers prepared with 4.5 mol of AA using different synthesis methods.

5.3.2 Clay tolerance of the polymers from different synthesis methods

Clays are increasingly present in cement as they are introduced into the system through contaminated aggregates like sand or gravel. Regrettably, they often reduce the dispersing effect of PCE superplasticizers due to intercalating PCEs in between their anionic alumosilicate sheets [104]. The most detrimental clay for dispersing effectiveness of PCEs is montmorillonite [156]. To capture its effect on the polymers containing 4.5 mol of AA, “mini slump” tests with blended cement containing 1.0, 2.0, 3.0, and 5.0 % bwoc of montmorillonite clay were performed. The achieved spread flows were compared to those obtained without clay as is shown in **Figure 43**, using the dosage determined before in pure cement paste to give a spread flow of 26 cm (see **Table 20**).

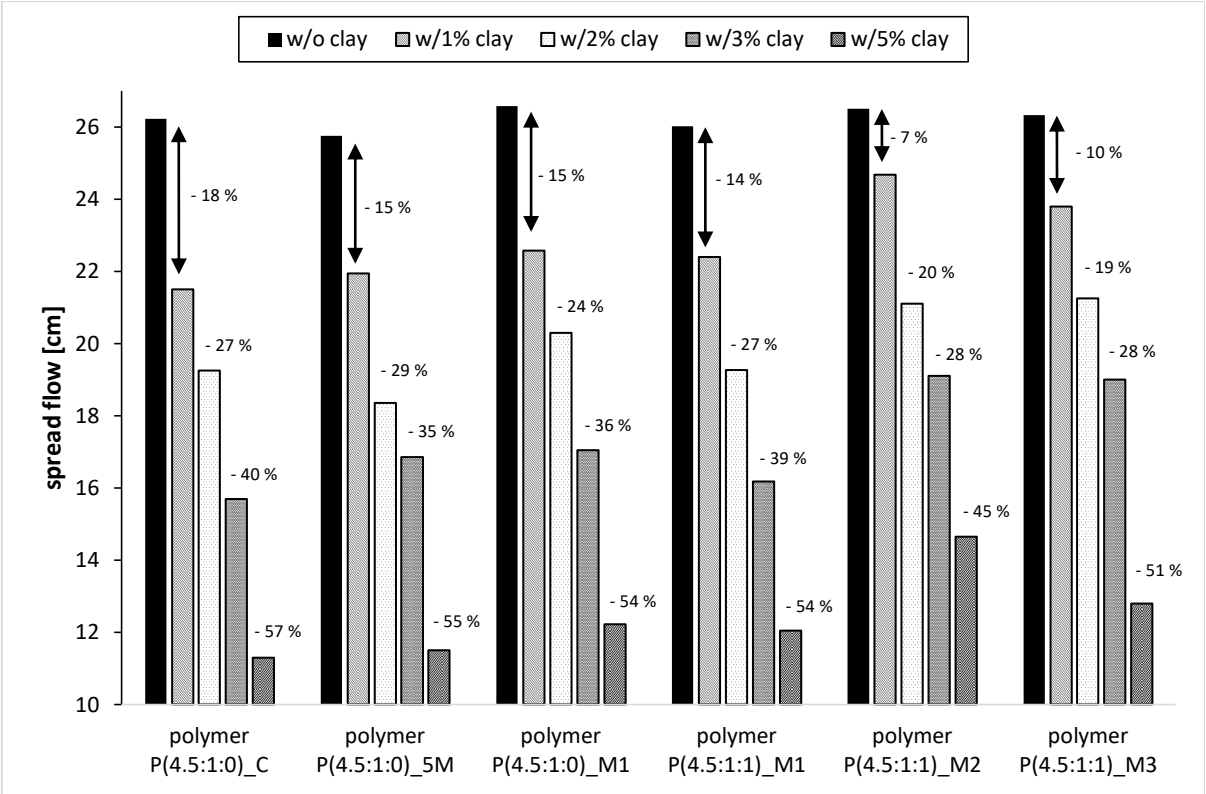


Figure 43. Spread flow of pastes prepared from pristine cement or cement/clay blends when admixed with polymers containing 4.5 mol of AA.

It was found that the dispersing ability of the zwitterionic polymers P(4.5:1:1)_M2 and P(4.5:1:1)_M3 was much less reduced in presence of clay than for all other polymers. At all rates of clay addition, they showed a higher tolerance. Especially for the “M2” polymer, it is possible that this advantageous behavior is attributed to its rather high molecular weight which prevents the PCE from intercalating into the montmorillonite structure [157]. To exclude that the improved clay tolerance is only based on the higher dosage required (~ 0.20 % bwoc instead of ~ 0.10 % bwoc) used for P(4.5:1:1)_M2 and P(4.5:1:1)_M3 (see **Table 20**) to reach 26 cm, the “mini slump” tests containing 1 – 5 % bwoc of montmorillonite clay were repeated with a fixed dosage of 0.22 % bwoc for all polymers. The spread flows are shown in **Figure 44**.

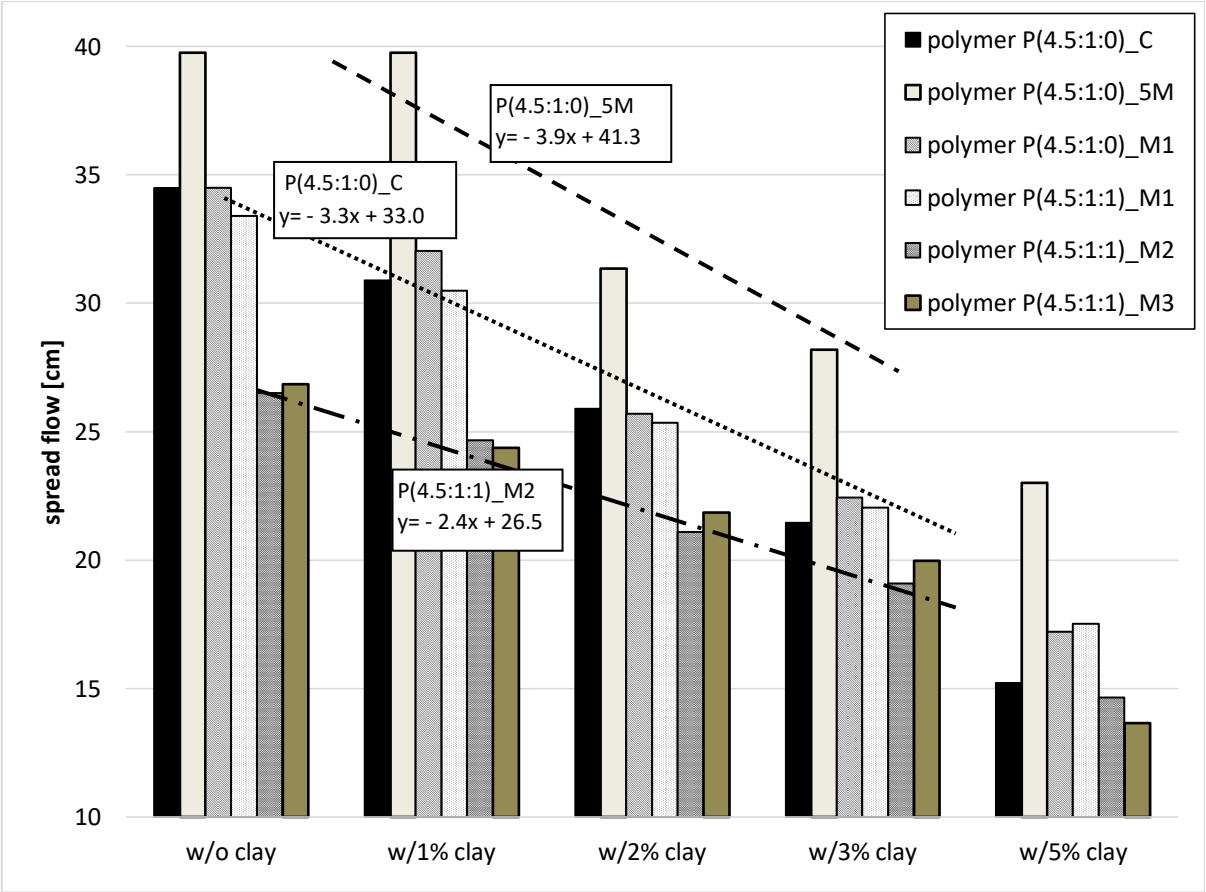


Figure 44. Spread flow of pastes prepared from cement containing 0 - 5 % bwoc of montmorillonite clay at constant polymer dosages of 0.22 % bwoc.

At the constant dosage of 0.22 % bwoc, the polymers prepared according to method “M2” and “M3” were still more clay-tolerant than all other polymers P(4.5:1:0)_M1, P(4.5:1:1)_M1, P(4.5:1:1)_5M and P(4.5:1:1)_C. As described in the dosage-dependent tests to determine the dispersing effectiveness (see **Figure 43**), the polymers can be divided into the same three groups as before. Again, the spread flow in presence of clay for the “M2” and “M3” polymers decreased at the lowest rate (-2.4 cm spread flow / 1 % added clay), while the polymer P(4.5:1:0)_5M (third group) exhibited the strongest decrease (-3.9 cm spread flow / 1 % added clay). For this polymer, the dosage of 0.22 % bwoc caused such a high dispersing effect that bleeding of the cement paste occurred. This was the reason for excluding the value “w/o clay” in the straight line in **Figure 44** to determine the decrease of the dispersing effectiveness in presence of clay. A slope of -3.3 (% clay / cm spread flow) can be assigned as a slightly lower decrease of the spread flow for the polymers P(4.5:1:0)_C, P(4.5:1:0)_M1 and P(4.5:1:1)_M1 of group 2 compared to the polymer P(4.5:1:0)_5M.

The zwitterionic polymer solutions prepared according to synthesis methods “M2” and “M3” clearly exhibited a higher clay tolerance than the zwitterionic polymer synthesized according to method “M1” or all other strictly anionic polymers. Among the anionic PCEs, P(4.5:1:0)_5M showed the lowest performance in presence of clay. This revealed that not only the zwitterionic character, but also the synthesis method of a polymer is responsible for the susceptibility to clay impurities in cement paste. The higher anionic charge in SCPS (see **Section 5.2.3.1**) for the “M2” and “M3” polymer solutions is likely to be the reason for a better protection against intercalation between the anionic alumosilicate sheets of the montmorillonite clay [104].

5.3.3 Sulfate tolerance of polymers from different synthesis methods

Sulfate ions which can be excessively present in cements (so called “over-sulfated” cements), influence the dispersing performance of PCE superplasticizers. The effect was already investigated by several groups [74,75,158]. In most cases, these ions are known to induce higher superplasticizer dosages due to the competitive adsorption between themselves and the PCE. Such a decreased dispersing ability of PCEs in the presence of SO_4^{2-} ions is called “sulfate effect” [158]. However, in the presence of SO_4^{2-} ions, specific strongly anionic PCEs can also increase their dispersing effect due to concomitant adsorption of sulfate and PCE. Habbaba et al. [159] assumed a synergistic effect between the SO_4^{2-} ions and the strongly anionic PCE in a $CaCO_3$ paste, leading to a stronger electrostatic repulsion between the $CaCO_3$ particles and therefore to a better dispersing performance in presence of sulfate ions. According to them, this effect also occurs in cement-based systems [159].

To gain insight into the dispersing ability in the presence of sulfate ions, the dispersing performance of all synthesized PCEs containing 4.5 mol of AA was determined via “mini slump” test in presence of 1 - 3 % bwoc of Na_2SO_4 in the mixing water (see **Figure 45**). As in the tests with clay (see **Section 5.3.2**), polymer dosages required to reach a spread flow of 26 cm in the pristine cement paste were used.

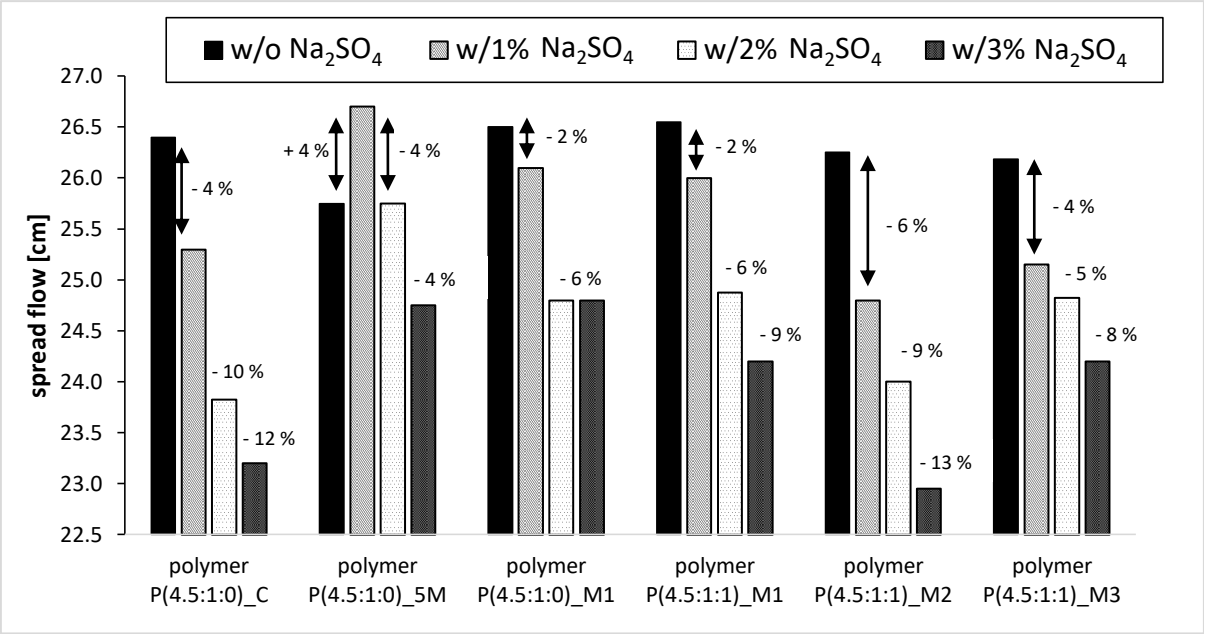


Figure 45. Spread flow of cement pastes treated with 0 - 3 % bwoc of Na_2SO_4, dispersed with zwitterionic and anionic polymers.

It was observed that the strictly anionic polymer P(4.5:1:1)_5M synthesized through a very quick polymerization method showed the highest robustness against sulfate ions. To be more precise, at a dosage of 1 % bwoc Na_2SO_4 in the mixing water, the dispersing effectiveness was even increased. By adding 2 % bwoc Na_2SO_4, the same dispersing performance as in the unpolluted cement paste was obtained, while only 4 % of the spread flow was lost when adding 3 % bwoc Na_2SO_4. The polymers prepared according to synthesis method “M1” P(4.5:1:1)_M1 as well as the anionic reference P(4.5:1:0)_M1 also showed a high sulfate tolerance at low dosages of 1 % bwoc Na_2SO_4. However, they suffered from an observable reduction at higher sulfate additions. The amphoteric polymers P(4.5:1:1)_M2 and P(4.5:1:1)_M3 and the anionic reference polymer P(4.5:1:1)_C already lost a considerable part of their dispersing ability at low amounts (1 % bwoc) of Na_2SO_4. Of these three PCEs, P(4.5:1:1)_M3 performed slightly better than the others.

5.3.4 Summary of Section 5.3

This study investigated the impact of the synthesis method on the dispersing effectiveness of strictly anionic or zwitterionic isoprenol ether-based polycarboxylate superplasticizers (52IPEG PCEs), especially in presence of montmorillonite clay or sulfate ions. Similar to **Section 5.2**, the PCE samples

prepared according to synthesis method “C”, “M1”, “M2”, “M3” and “5M” with a feeding ratio of 4.5 mol of AA and 1 mol of 52IPEG macromonomer were tested.

Analyzing the dosage-dependent dispersing effect, it became clear that the anionic “5M” polymer performed best. The highest dispersing performance for the same dosages was received here. Although dialysis may provide a small benefit for this PCE, the dispersing ability was well above that of the others. A considerably lower dispersing ability could be found for the polymers “M2” and “M3”. For those PCEs, the composition of the polymer fractions seemed to be decisive for their properties. Moreover, for the “M2” sample, the high molecular weight of the polymer fractions might diminish the dispersing effectiveness. This was however not the case for the “M3” polymer solution. Almost no difference was observed between the polymers from method M1 (anionic and zwitterionic) and the conventional PCE. They performed in a medium range.

Impurities of montmorillonite clay least affected the dispersing performance of the “M2” and “M3” polymers. The remaining samples showed a similarly low clay tolerance. Most stable against sulfate ions was the polymer “5M”. It performed even better in the presence of 1 % Na_2SO_4 than without any addition (reference value). The zwitterionic and the anionic polymers synthesized by method “M1” also dispersed the cement paste well when sulfate ions were present. They exceeded the conventional and the zwitterionic “M2” and “M3” samples.

Table 21. Properties and advantages of the tested PCEs.

Polymer solution	Charge character & initiator system	Amount of main polymer fractions	M_w for main polymer fraction(s)	advantage
P(4.5:1:0)_C Conventional	anionic APS	1	~ 69,000 Da (peak 2)	---
P(4.5:1:0)_5M 5 Minute method	anionic redox	1	~ 64,000 Da (peak 2)	Sulfate tolerance up to ~ 2 % bwoc Na_2SO_4
P(4.5:1:0)_M1 Method M1	anionic redox	3	~ 3,500 Da (peak 4) ~ 35,000 Da (peak 3) ~ 200,000 Da (peak 2)	Sulfate tolerance up to ~ 1 % bwoc Na_2SO_4
P(4.5:1:1)_M1 Method M1	zwitterionic redox	3	~ 4,400 Da (peak 4) ~ 28,500 Da (peak 3) ~ 150,000 Da (peak 2)	Sulfate tolerance up to ~ 1 % bwoc Na_2SO_4
P(4.5:1:1)_M2 Method M2	zwitterionic redox	3	~ 26,500 Da (peak 4) ~ 67,000 Da (peak 3) ~ 430,000 Da (peak 2)	Best clay tolerance
P(4.5:1:1)_M3 Method M3	zwitterionic redox	3	~ 4,000 Da (peak 4) ~ 27,000 Da (peak 3) ~ 210,000 Da (peak 2)	Best clay tolerance

As presented in **Table 21**, polymers with cationic portions seemed to be most clay tolerant (“M2” and “M3”). However, it was not only the polymer composition which was responsible for the properties of the PCE. The zwitterionic “M1” polymer was not as good in clay tolerance as expected, but showed a certain sulfate tolerance instead. This advantage could also be achieved by the anionic polymer synthesized with process “M1”. Moreover, the amount of main polymer fractions in one PCE sample was not decisive for the dispersing performance or a special feature: The conventional polymer as well as the zwitterionic and anionic polymers synthesized with “M1” performed equally well at increasing dosage. These comparisons led to the following conclusions:

1. The amount of main polymer fractions is not decisive for the dispersing effectiveness of PCE superplasticizers.
2. The molecular weight of the polymer fraction(s) of a PCE superplasticizer does not necessarily play a role in the dispersing performance. However, very high molecular weights can decrease the dispersing performance.
3. The cationic monomer TMAEMC does not guarantee clay tolerance of the PCE superplasticizer.
4. The same synthesis method for an anionic and zwitterionic polymer led to PCEs with similar properties.

5.4 In-depth evaluation of time-saving polymerization processes for isoprenol ether-based polycarboxylate (PCE) superplasticizers

Some of the data in **Section 5.4** concerning the polymers 23P(6:1:0)_C and 52P(6:1:0)_C as well as the basic principle of the synthesis methods “30M” and “5M” were published in the bachelor study “Synthesis and Characterization of different IPEG-PCE polymers” from Lai Hsiao Yu [155] who was supervisied by C. Chomyn and J. Plank.

In **Sections 5.1** to **5.3**, it was found that different synthesis methods lead to PCEs with an excellent dispersing effectiveness and unique properties. With respect to power consumption and costs during the polymerization process, especially the synthesis methods “M1” and “5M” are highlighted (see **Sections 5.1** to **5.3**) in which a redox initiator system allowed the low reaction temperature of 30 °C and polymerization times of only 15 or even 5 minutes.

For this reason, this section is dedicated to the detailed investigation of short-polymerization time synthesis processes. Therefore, two different IPEG macromonomers with 52 and 23 EO units were utilized. Anionic PCEs with a low molar ratio of AA:MM = 2:1 were chosen to perform slump retaining tests. The “5M” process (5-Minute method) as described in **Section 5.2.1.2** and a 30-Minute synthesis method (“30M”) were established to capture the influence of the polymerization time on the dispersing performance of the resulting PCEs. The “5M” synthesis method is identical to the first 5 minutes of the “30M” synthesis and can therefore be understood as an interrupted “30M” process. As a reference (“C”), polymers with a molar ratio of AA:MM with 2:1 and 6:1 were synthesized according to the conventional synthesis process.

By tracking the polymer formation during the reaction process via SEC measurements, the main differences obtained for the different PCEs could be assessed. Testing the dispersing performance in cement paste and mortar with different w/c values and in presence of montmorillonite clay or sulfate ions proved the quality of the superplasticizers.

5.4.1 Polymer synthesis

5.4.1.1 Synthesis of 23P(2:1:0)_30M and 52P(2:1:0)_30M

In the following section, the synthesis procedure for the anionic polymer 23P(2:1:0)_30M is specified. The “30M” process only differs from the “M1” method already described in reaction time and batch size (see **Section 5.1.2.1**).

As a preparation for the polymerization process, a clear solution was produced by stirring 7.21 g of AA (100.06 mmol), 55.0 g of 23IPEG (50.0 mmol), 1.50 g of NaH_2PO_2 (17.05 mmol), 0.15 g of $FeSO_4 \cdot 7\ H_2O$ (0.54 mmol) and 60 mL (**120 mL*) of deionized water in a 1 L five-neck round-bottomed flask for ~ 10 min. Afterwards, the solution was purged with N_2 and heated to a temperature of 30 °C. To start the reaction, two solutions (solution A = 3.70 g of 30 wt.-% (32.63 mmol) H_2O_2 and 10 mL (**20 mL*) of deionized water and solution B = 1.60 g of Rongalit® (12.87 mmol) and 10 mL (**20 mL*) of deionized water) were dropped at the same time with peristaltic pumps in the flask over **30 minutes**. To compensate the heat release of the reaction, the flask was cooled by a water bath in order to keep the temperature below 38 °C. After solutions A and B had been completely added, 1 hour of stirring at 30 °C finished the reaction. After cooling to room temperature, the pH value was adjusted to 7 with 30 wt.-% NaOH and the polymer mixture obtained was dialyzed for 48 hours (MWCO = 10,000 Da). The reaction product was a yellow/orange, viscous polymer solution with a solid content of 30 wt.-%.

The polymer sample 52P(2:1:0)_30M was synthesized in the same way except that the water amounts were changed (*values in bracket**). The amounts of the monomers required for each individual PCE are given in **Table 23**.

5.4.1.2 Synthesis of 23P(2:1:0)_5M and 52P(2:1:0)_5M

This synthesis method optimized the "30M" process by reducing the polymerization time. The same procedure was used as for the “30M” polymerization except that the **reaction was stopped after five minutes** by interrupting the feeding of the initiator and cooling the reaction mixture immediately in ice for 5 minutes and then for 1 hour at 7 °C. Directly afterwards, the polymer solution was dialyzed for 48 hours (MWCO = 10,000 Da) to prevent still unreacted AA from further polymerizing as well as to get rid of excess AA. Subsequently, the polymer solution was neutralized with 30 wt.-% NaOH.

For 52P(2:1:0)_5M, the same water amounts (values in brackets) were used as for 52P(2:1:0)_30M (see **Section 5.4.1.1**). All amounts of chemicals required for the synthesis are listed in **Table 23**.

The “5M” process used here is the same as described in **Section 5.2.1.2**, only the batch size, the time of dialysis, and the amounts of chemicals used differ.

5.4.1.3 Synthesis of 23P(2 or 6:1:0)_C and 52P(2 or 6:1:0)_C

The conventional reference polymers 23P(2 or 6:1:0)_C and 52P(2 or 6:1:0)_C were synthesized in the same manner as described in **Section 5.1.1.1**. The chemical and water amounts which were used for these polymers are listed in **Tables 22** and **23**. In addition, the polymers received were neutralized with 30 wt.-% NaOH and dialyzed for 48 hours (MWCO = 10,000 Da).

Table 22. Water amounts [mL] used in the synthesis of the conventional reference polymers.

Superplasticizer	Water amount in the solution filled in the five-neck round-bottomed flask [mL]	Water amount in solution A [mL]	Water amount in solution B [mL]
23P(2:1:0)_C	120	50	60
23P(6:1:0)_C	50	20	30
52P(2:1:0)_C	120	60	60
52P(6:1:0)_C	140	60	90

Table 23. Designation, composition and solution properties of synthesized polymers.

Polymer	Molar ratio AA:IPEG	Monomer quantities [g]						Solid content [%]
		AA	IPEG	NaH_2PO_2/ SMAS	$FeSO_4 \cdot 7\ H_2O$	30 wt.% H_2O_2	Rongalit®/ APS	
23P(2:1:0)_C	2:1	12.97	100.0	5.14	---	---	4.20	33.48
23P(2:1:0)_30M	2:1	7.21	55.0	1.50	0.15	3.7	1.60	29.60
23P(2:1:0)_5M	2:1	7.21	55.0	1.50	0.15	3.7	1.60	20.30
23P(6:1:0)_C	6:1	12.97	33.3	4.00	---	---	3.26	18.01
52P(2:1:0)_C	2:1	7.21	120.0	2.86	---	---	2.33	35.00
52P(2:1:0)_30M	2:1	7.21	120.0	3.00	0.30	7.2	3.20	26.57
52P(2:1:0)_5M	2:1	7.21	120.0	3.00	0.30	7.2	3.20	20.68
52P(6:1:0)_C	6:1	19.44	108.0	11.20	---	---	8.91	23.97

5.4.2 SEC analysis of the anionic PCEs

All synthesized superplasticizers were characterized by their molecular properties via SEC measurements. **Figure 46** represents the obtained spectra and **Table 24** the molecular parameters.

As usual, fraction 1 exhibited a negligible amount of poly(acrylic acid) and fraction 5 showed unreacted macromonomer while peak 6 represented salt and water from the eluent in all SEC spectra.

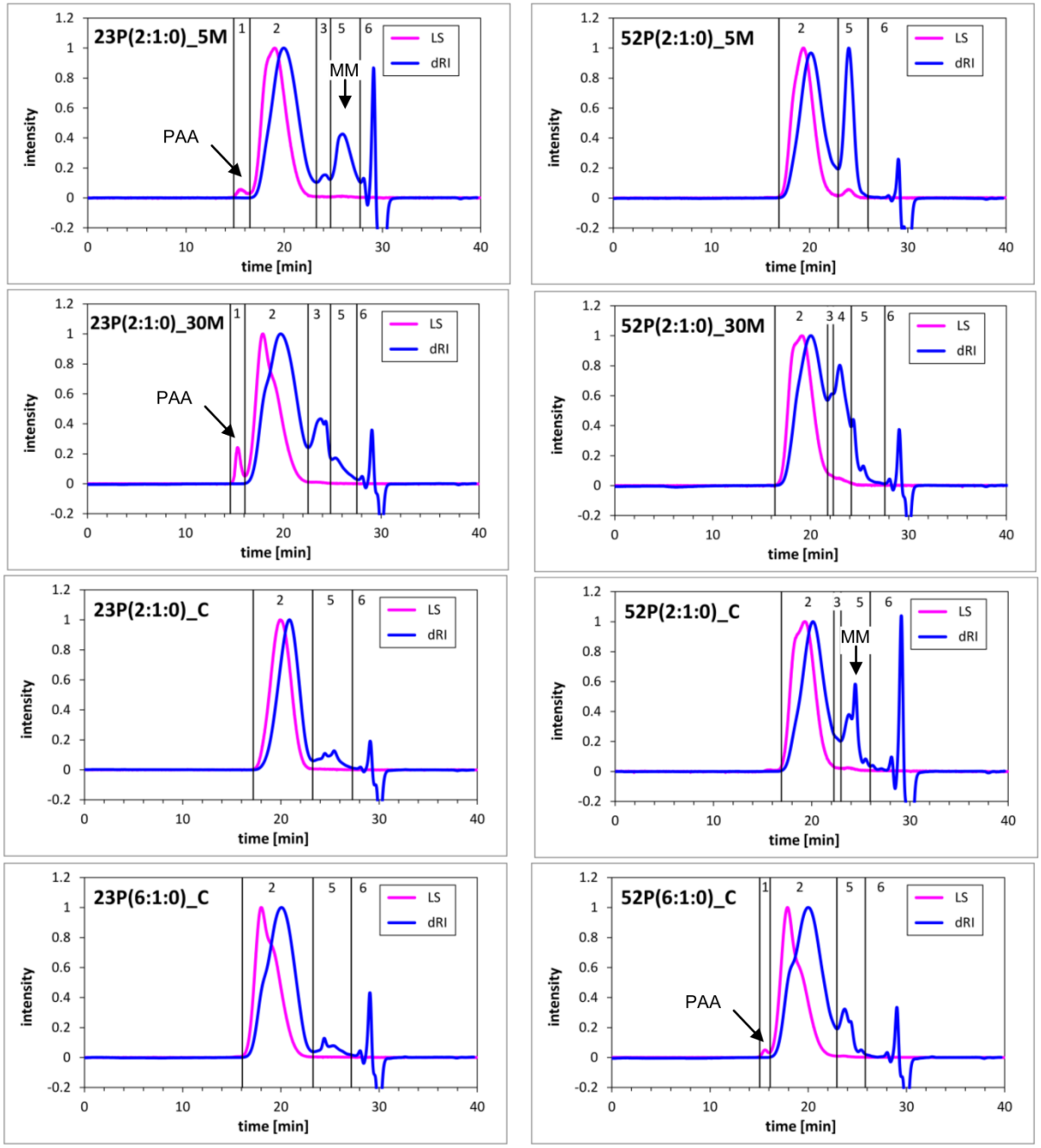


Figure 46. SEC spectra of the IPEG polymers with 23 and 52 EO units synthesized by different processes.

Table 24. Molecular parameters and macromonomer conversion for the synthesized polymers.

Polymer sample	PDI [M_w/M_n]	M_w [g mol^{-1}]					MM conversion [%]
	(Peak 2 - 4)	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	(Peak 1 - 3)
23P(2:1:0)_5M	3.2 (*2.2)	---[+]	52,010	3,421	---	1,744	80.5
23P(2:1:0)_30M	3.7	4,288,000	74,030	2,498	---	1,936	94.0
23P(2:1:0)_C	1.9	---	31,350	---	---	1,692	89.9
23P(6:1:0)_C	2.7	---	67,900	---	---	4,042	93.7
52P(2:1:0)_5M	2.2	---	45,240	---	---	2,829	70.2
52P(2:1:0)_30M	4.1	---	51,760	6,301	3,361	2,490	92.6
52P(2:1:0)_C	3.0 (*2.0)	---	58,650	6,660		3,716	80.0
52P(6:1:0)_C	3.1	2,495,000	77,830	---		3,742	88.4

* PDI of Peak 2
[+] M_w was not determinable by SEC measurement (insufficient amount)

As expected and in accordance with **Section 5.1.1.2**, the conventional PCEs consisted of only one rather uniform main polymer fraction (peak 2) except for 52P(2:1:0)_C which showed a small amount of an additional fraction (~ 4 %; peak 3). This intermediate fraction might have occurred because of the lower macromonomer conversion for this polymer. For the conventional PCE with 23 EO units and a higher AA content (6 mol), a slightly larger molecular weight distribution (PDI ~ 2.7 instead of ~ 1.9) as well as a higher M_w for the polymer fraction (M_w ~ 68,000 g mol^{-1} instead of 31,000 g mol^{-1}) was observed. Furthermore, relatively high macromonomer conversions of 80 to 94 % were received for all conventional PCEs. In general, slightly lower macromonomer conversions appeared for the sterically more hindered IPEG macromonomer with 52 EO units independent of the chosen synthesis method.

As already seen in the "M1" polymers (see **Section 5.1.2.2**), a mixture of polymer fractions (main polymer fractions; peak 2 - 4) instead of one polymer fraction was formed during the reaction process of the "30M" PCEs, which considerably increased the PDI to ~ 3.9. Moreover, a high similarity between the "M1" and the "30M" polymer samples was noticed, which confirmed that a difference of 15 minutes in reaction time only showed a minor effect in the polymerization. The molecular weights of the main polymer fractions were higher (63,000 g mol^{-1}) than for the conventional references with the same AA amount while the macromonomer conversions were in the same range (~ 93 %).

The "5M" polymers were rather uniform as already observed for the polymer P(4.5:1:0)_5M in **Section 5.2.1.3** and for the anionic conventional reference superplasticizers. Although the macromonomer conversions (~ 70 to 81 %) were lower than for the references and for 23P(2:1:0)_5M

an additional polymer fraction (peak 3) occurred, a high accordance with the conventional PCEs was observed. Even the PDIs of the main polymer fraction (peak 2) of ~ 2.2 and the molecular weights of ~ 48,500 g mol $^{-1}$ were in a comparable range with each other.

Very surprising is the high similarity between the conventional and the "5M" PCEs when considering their different synthesis methods – especially the strongly varying reaction times. At the same time, the difference between the "30M" and "5M" PCEs is unexpected as the only difference in the two synthesis methods was the shorter polymerization time. To clarify this observation, the polymer formation over time was examined more closely.

5.4.3 Polymer formation over time

In order to gain insight into the formation of different polymer fractions over time during the synthesis process, samples of the reaction mixture (synthesized according to **Section 5.4.1**) were taken at predetermined intervals and SEC measurements were carried out. The amount of non-polymerized macromonomer as well as the amount of polymer formed at every interval was determined from the SEC spectra obtained and plotted in a diagram as can be seen in **Figures 47** - **50**. This approach allowed to observe at which time the polymerization process had been completed. Furthermore, the formation of different polymer fractions over time could be observed in the polymer solutions.

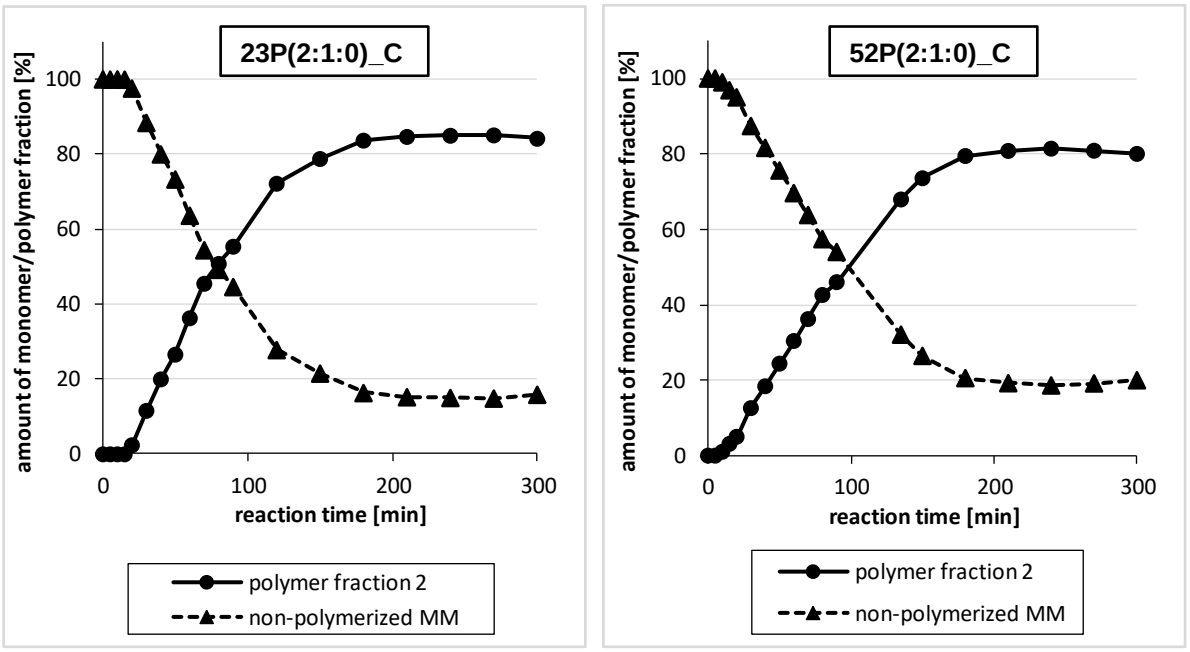


Figure 47. Polymer formation over time for 23P(2:1:0)_C (left) and 52P(2:1:0)_C (right).

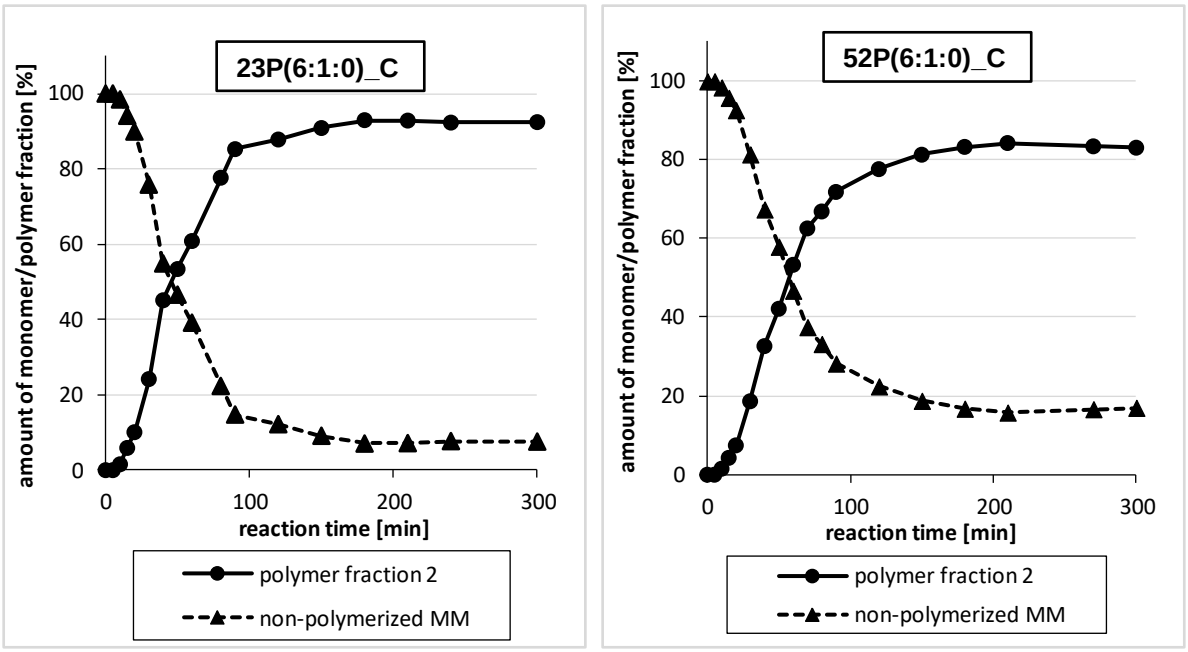


Figure 48. Polymer formation over time for 23P(6:1:0)_C (left) and 52P(6:1:0)_C (right) [155].

Independent of the EO units (23 or 52) contained in the IPEG macromonomer and the amount of the acrylic acid (2 or 6 mol), for the conventional, well-controlled PCE synthesis method, only one main polymer fraction (fraction 2, see SEC in **Figure 46**) occurred as represented in **Figures 47** and **48** except for 52P(2:1:0)_C (see **Figure 47**, right side) which showed a small amount of fraction 3. Since the amount of this fraction was < 5 %, it was not separately marked in the diagram, but the macromonomer conversion was added to that of fraction 2.

It was very surprising that the polymerization process did not start with the addition of the initiator APS to the reaction mixture. Polymerization commenced only after a delay of ~ 20 minutes for the 23P(2:1:0)_C and ~ 10 minutes for 52P(2:1:0)_C, 23P(6:1:0)_C and 52P(6:1:0)_C. This demonstrated that without a certain amount of AA (~ 10 %) in the reaction system, polymerization of the IPEG macromonomer was not possible when initiated with APS. This behaviour may have been caused by the inhibitor which is contained in small amounts in acrylic acid and the macromonomer to prohibit spontaneous homopolymerization during storage and must first be overcome for a polymerization reaction to be initiated. Once started however, the polymerization process for the PCEs with 2 mol of AA proceeded continuously and uniformly over a period of ~ 2 hours until a macromonomer conversion of ~ 70 % was reached. For those PCEs with 6 mol of AA, this process was faster (~ 90 min) and especially for 23P(6:1:0)_C, the conversion was already about 80 %. After this ideal progression, only a small amount of macromonomer remained to polymerize (~ 10 %) and after

180 minutes, when no more initiator was added to the system, no more reaction was observed. These observations showed that the polymerization process cannot be further improved when stirring the reaction mixture after the initiator addition was completed for theses systems.

As already discussed in **Section 5.1.2.2**, the rather uncontrolled reaction conditions for the “M1” polymers or for the “30M” samples led to the formation of several main polymer fractions. For both IPEG macromonomers, the polymer fraction 2 was immediately formed within only 5 minutes and represented the fraction with the highest portion in the main polymer (see **Figure 49**).

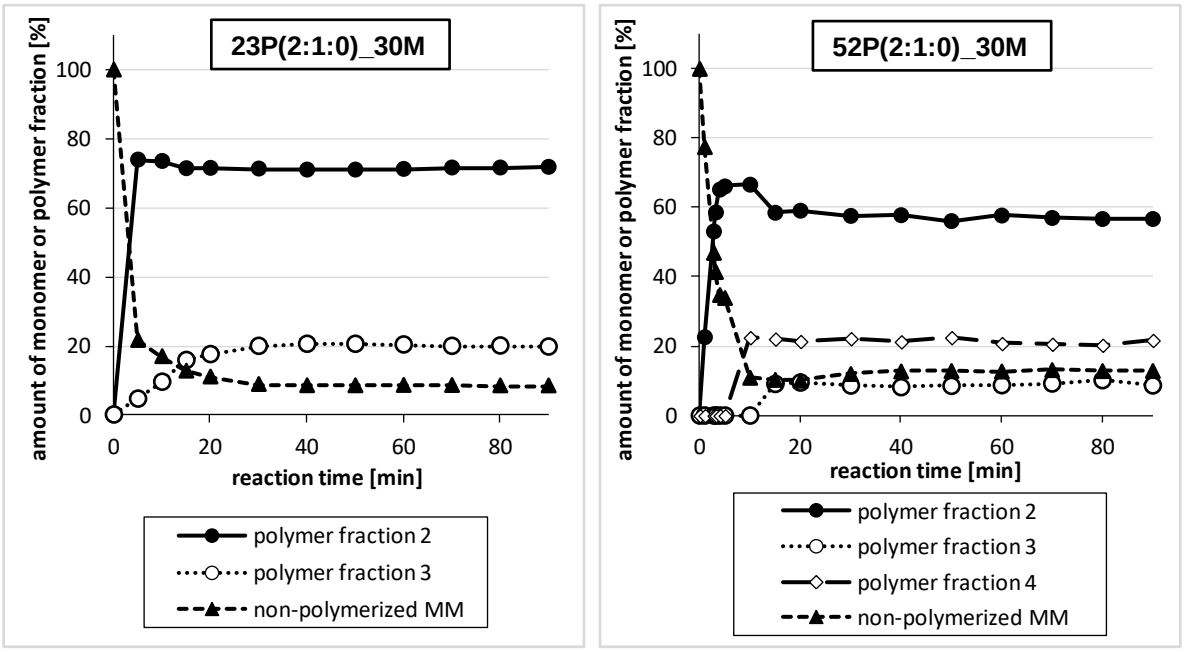


Figure 49. Polymer formation over time for 23P(2:1:0)_30M (left) and 52P(2:1:0)_30M (right).

For 23P(2:1:0)_30M, polymer fraction 3 increased between the reaction start and 30 minutes, while for 52P(2:1:0)_30M this fraction was abruptly formed at ~ 15 minutes. For 52P(2:1:0)_30M, the additional fraction 4 entirely developed after 5 to 10 minutes. Since all further main polymer fractions (fraction 3 and 4) only formed after 5 minutes, it was clear that the “5M” PCEs mainly consist of polymer fraction 2 and exhibit a relatively uniform polymer.

In addition, for 52P(2:1:0)_30M, the amount of fraction 2 seemed to be reduced after 10 minutes, which is not possible and does not correspond to reality. This anomaly was caused by the simultaneous formation of the polymer fraction 3 (see **Figure 49**, right side). As both fractions overlap in the SEC spectrum and the applied software did not allow peak deconvolution (see **Section 4.2.3**), parts of polymer fraction 2 were cut off in the evaluation, which resulted in a smaller amount of

polymerized macromonomer for fraction 2. However, this decrease can be neglected due to the decrease being minor which proved that polymer fraction 2 did not change after 5 minutes.

After a reaction time of 15 minutes, no further change was observed for polymer fraction 3 either. This early end of the polymerization reaction explains the high similarity to the “M1” polymer samples, where the synthesis time was only 15 minutes because no change occurred afterwards.

As a summary, the polymerization reaction was extremely fast in the “30M” synthesis method. The main macromonomer conversion (~ 70 %) was already completed after 5 minutes. Additional main polymer fractions only occurred afterwards in minor quantities. Moreover, no time delay was observed at the beginning of the reaction which can be attributed to the instant presence of AA in the reaction system. Similar to the conventional superplasticizers at the latest, no polymer fraction was formed after termination of the initiator addition. Additionally, the stirring time of 1 hour at 30 °C could also be omitted with respect to macromonomer conversion during the synthesis. Based on these findings, the redox initiator system was classified as a much stronger initiator system than the peroxide based system.

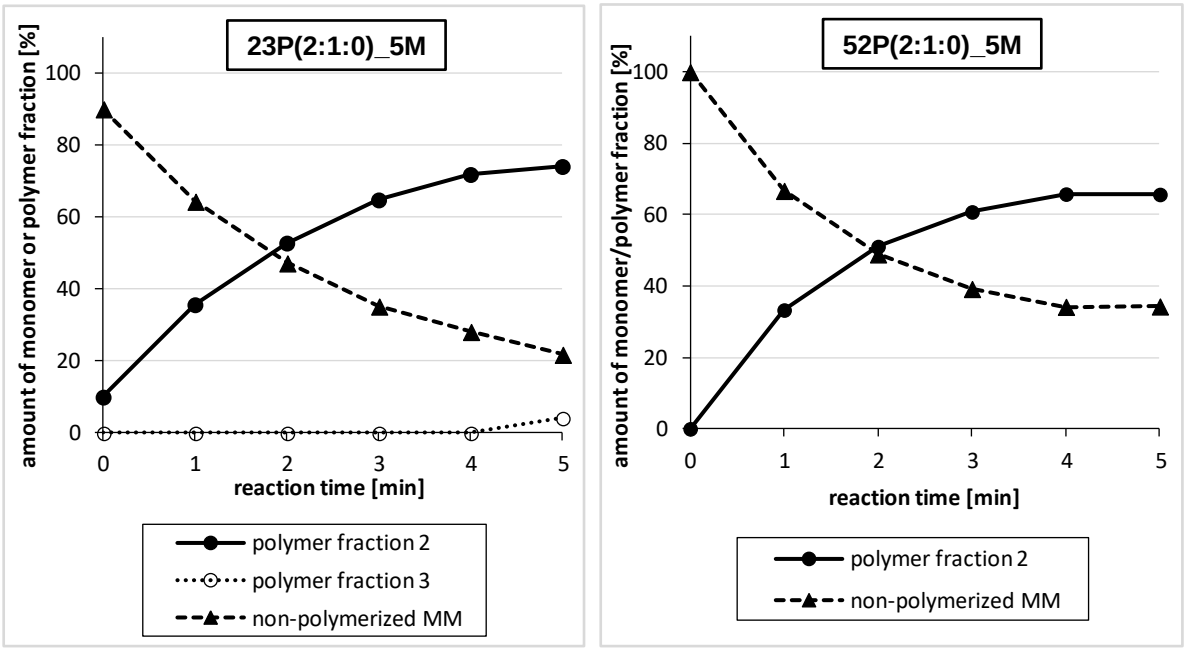


Figure 50. Polymer formation over time for 23P(2:1:0)_5M (left) and 52P(2:1:0)_5M (right).

Figure 50 presents the polymer formation for the “5M” polymers. Due to the same reaction conditions and the same initiator system (redox) as used for the “30M” polymer samples, the same quick polymerization process was observed. For 23P(2:1:0)_5M, the reaction process was so strong at the

very beginning that a macromonomer conversion of ~ 10 % was already achieved after a few seconds. A second polymer fraction (fraction 3) additionally started to form between 4 and 5 minutes in this sample. In this synthesis process, the macromonomer conversion was steadily increasing which led to maximum efficiency in comparison to the other synthesis processes.

5.4.4 Anionic charge amount of polymers

For further comparison between the different IPEG PCEs, their anionic charge amount was determined in deionized water (pH = 7), 0.1 M NaOH (pH ≥ 12) and synthetic cement pore solution (pH ≥ 12). **Table 25** shows the values for each PCE found in different media as well as the calculated values based on the amount of monomers used (see **Section 4.2.5**).

Table 25. Anionic charge amount of the synthesized IPEG PCEs.

PCE Sample	DI water [µeq/g]	0.1 M NaOH [µeq/g]	SCPS [µeq/g]	Calculated value [µeq/g]
23P(2:1:0)_5M	535 ± 18	1,944 ± 87	267 ± 18	1,608
23P(2:1:0)_30M	1,485 ± 6	2,035 ± 7	704 ± 16	1,608
23P(2:1:0)_C	1,185 ± 14	1,580 ± 49	288 ± 6	1,608
23P(6:1:0)_C	3,195 ± 29	3,621 ± 110	2,717 ± 71	3,917
52P(2:1:0)_5M	447 ± 9	1,130 ± 3	272 ± 12	793
52P(2:1:0)_30M	783 ± 7	1,076 ± 26	300 ± 15	793
52P(2:1:0)_C	605 ± 1	1,128 ± 39	251 ± 2	793
52P(6:1:0)_C	1,482 ± 28	2,021 ± 72	871 ± 41	2,136

As expected and already discussed in **Section 5.2.3.1**, the anionic charge amount was weakest in the synthetic cement pore solution, while the strongest anionic charges became apparent in 0.1 M NaOH, independent of the synthesis method or the amount of AA in the reaction system. Especially for the samples in 0.1 M NaOH, a stronger anionic charge was experimentally determined than the theoretical, calculated values suggested. These differences can originate from the incomplete macromonomer conversions in the polymers which led to a higher AA:MM ratio in the polymer fractions than originally calculated, and therefore to a higher determined anionic charge amount. However, the samples prepared with the 52IPEG macromonomer were less anionic than their counterparts with shorter side chains (IPEG with 23 EO units). Expectedly, the conventional polymers containing 6 mol of AA were considerably more negative than the samples with only 2 mol of AA. It

was interesting that only minor differences between the samples made of the same chemicals, but prepared by different methods were observed. This proved that differences in the dispersing effectiveness or other properties may not result from different anionic charge amounts.

5.4.5 Influence of different synthesis methods on the dispersing effectiveness of "5M" and "30M" PCEs

To prove the effectiveness of the obtained superplasticizers, "mini slump" tests were performed at different w/c values in cement (w/c ratio = 0.62, 0.45 and 0.3) as well as in mortar (w/c ratio = 0.4 and 0.5). The dosages to reach a spread flow of 26 cm (cement paste) or a slump flow of 18 cm (mortar) are listed in **Tables 26** and **27**. Furthermore, their slump retaining behaviors were tested (see **Section 5.4.6**).

Table 26. Dosages [% bwoc] required to reach a spread flow of 26 cm in cement paste at different w/c values in CEM I 52.5 R.

Superplasticizer	w/c = 0.62	w/c = 0.45	w/c = 0.30
23P(2:1:0)_5M	0.08	0.17	0.31
23P(2:1:0)_30M	0.08	0.19	0.35
23P(2:1:0)_C	0.06	0.29	---*
23P(6:1:0)_C	0.13	0.44	---
52P(2:1:0)_5M	0.10	0.20	0.37
52P(2:1:0)_30M	0.10	0.25	0.44
52P(2:1:0)_C	0.08	0.32	---*
52P(6:1:0)_C	0.09	0.27	0.60

* When 1.0 % bwoc dosage of a polymer was insufficient to reach 26 cm spread flow, the "mini slump" tests were discontinued

Table 26 lists the required dosages of the PCE samples to reach 26 cm in the "mini slump" tests. The dosages to reach this value at a w/c ratio of 0.62 were very similar for all tested PCEs (0.06 - 0.10 % bwoc) except for 23P(6:1:0)_C which required a slightly higher dosage (0.13 % bwoc). It was noteworthy that the dosages for the "30M" and "5M" PCEs were all the same although the macromonomer conversion of the "5M" polymers was much lower.

With a decreasing amount of water in the tests (w/c ratio = 0.45), the conventional PCEs were disadvantaged compared to the "30M" and "5M" PCEs. With the same amount of acrylic acid (2 mol of

AA), approximately 50 % more dosage was required for the same spread flow. This trend became even more pronounced at a decreasing amount of water (w/c ratio = 0.30). Here, the conventional PCEs did not longer show any dispersing effectiveness or needed a high dosage (0.6 % bwoc) while the “30M” and “5M” PCEs required dosages of only 0.31 - 0.44 % bwoc. This was very surprising considering the significantly lower macromonomer conversion for the “5M” PCEs. With respect to these results it was most interesting that the macromonomer conversion as the sole reason for the high dispersing ability can be excluded. Instead, a very uniform polymer still exhibiting a high amount of non-reacted macromonomer was best at low w/c values.

In a next step, the dispersing effectiveness of the synthesized samples was tested in standard mortar (see **Table 27**).

Table 27. Dosages [% bwoc] required to reach a slump flow of 18 cm in mortar at different w/c values**.**

Superplasticizer	w/c = 0.50	w/c = 0.40
23P(2:1:0)_5M	0.02	0.22
23P(2:1:0)_30M	0.05	0.22
23P(2:1:0)_C	0.02	0.22
23P(6:1:0)_C	0.08	1.00
52P(2:1:0)_5M	0.04	0.22
52P(2:1:0)_30M	0.08	0.22
52P(2:1:0)_C	0.02	0.20
52P(6:1:0)_C	0.09	0.43

At a w/c ratio of 0.5, the “30M” PCEs required slightly higher dosages than the “5M” and conventional (2 mol AA) PCEs. It was assumed that the intermediate fractions in the “30M” polymer solutions had a negative impact on the dispersing effect in this particle-rich system exhibiting large surface. However, all IPEG PCEs with 2 mol of AA showed the same dispersing ability (~ 0.22 % bwoc dosage for 18 cm) at low water content (w/c ratio = 0.4), independent of the side chain lengths. Apparently, the mortar system was so solids loaded that differences of the PCEs in the microstructure as well as in the side chain length no longer played a role. Decisive for the slump flow was only the amount of macromonomer and AA. The strongly anionic charged PCEs 23P(6:1:0)_C and 52P(6:1:0)_C clearly required the highest dosage to disperse the mortar paste, no matter which w/c ratio was applied.

5.4.6 Slump retaining behaviour at low w/c values

As already mentioned in **Section 3.3.1.5**, PCE superplasticizers containing a low amount of anionic charge (here acrylic acid) can retain dispersing effectiveness over time because not all of the PCE has adsorbed on the cement particles directly after the mixing process. Therefore, the residual free polymer is available for adsorption at later times and can still disperse the system for a certain time period.

5.4.6.1 Slump retaining behavior at low w/c value (0.3) in cement paste

The slump retaining behavior at a low w/c value of 0.3 and a fixed superplasticizer dosage of 0.5 % bwoc was investigated in CEM I 52.5 R and is visualized in **Figures 51** and **52**.

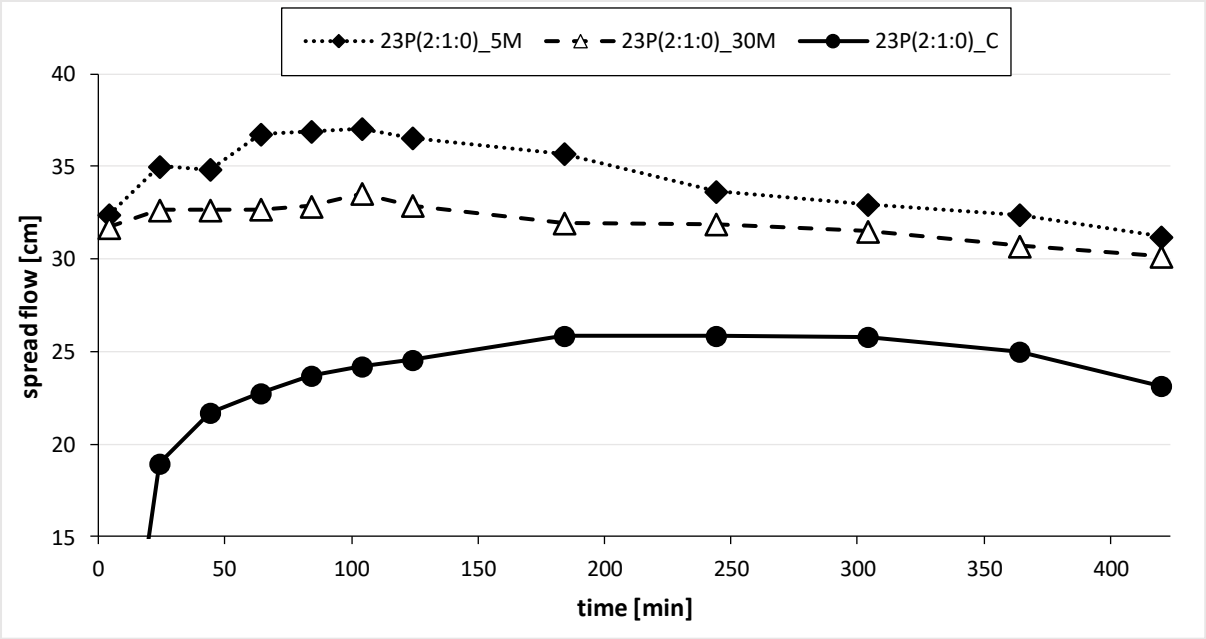


Figure 51. Slump loss behavior of cement pastes (CEM I 52.5 R, w/c ratio = 0.3) containing 23P(2:1:0)_C, 23P(2:1:0)_30M or 23P(2:1:0)_5M at a fixed polymer dosage of 0.5 % bwoc.

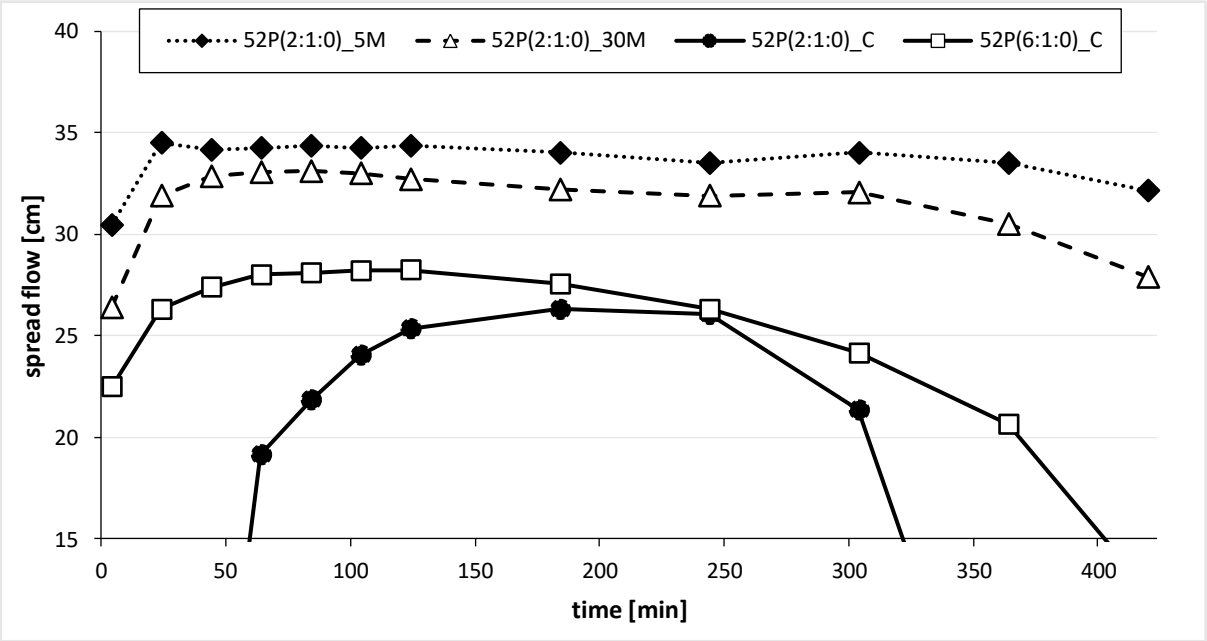


Figure 52. Slump loss behavior of cement pastes (CEM I 52.5 R, w/c ratio = 0.3) containing 52P(2:1:0)_C, 52P(2:1:0)_30M, 52P(2:1:0)_5M or 52P(6:1:0)_C at a fixed polymer dosage of 0.5 % bwoc.

Under these difficult testing conditions, the conventional polymers 23P(2:1:0)_C and 52P(2:1:0)_C did not ensure a flowable cement paste directly after the mixing procedure. A considerable dispersing effect was not obtained until ~ 20 to 60 minutes after mixing. For 23P(2:1:0)_C, the spread flow was stable over 6 hours while only 4 hours were achieved by 52P(2:1:0)_C. In contrast, the “30M” and “5M” samples (for IPEG with 52 and 23 EO units) exhibited a tremendous dispersing effect directly after the mixing procedure (cement paste flow of ~ 31 cm after 4 minutes) at the same dosage. A continuous spread flow over a period of 7 hours was obtained. The “5M” polymers even exceeded the “30M” polymer samples regarding their dispersing performance over time. However, it has to be mentioned that bleeding was also observed in the “5M” and “30M” systems. This behavior was already indicated by the extremely high spread flow (> 30 cm) of these PCEs and was especially observed in the first 3 hours. The dispersing performance for the reference 23P(6:1:0)_C was not sufficient to disperse the cement slurry at all. 52P(6:1:0)_C achieved a spread flow of ~ 26 cm, but its slump retention was only stable over 2 hours.

5.4.6.2 Slump retaining behavior at low w/c value (0.4) in mortar

To prove the slump retaining behavior in a system closer to the application (not only cement), mortar tests with CEM I 52.5 R at a low w/c value of 0.4 and a fixed superplasticizer dosage of 0.43 % bwoc were applied. This was the highest dosage for all PCEs, except for 23P(6:1:0)_C, tested to reach a slump flow of 18 cm in this system (see **Table 27**). The slump loss behaviors obtained are presented in **Figures 53** and **54**.

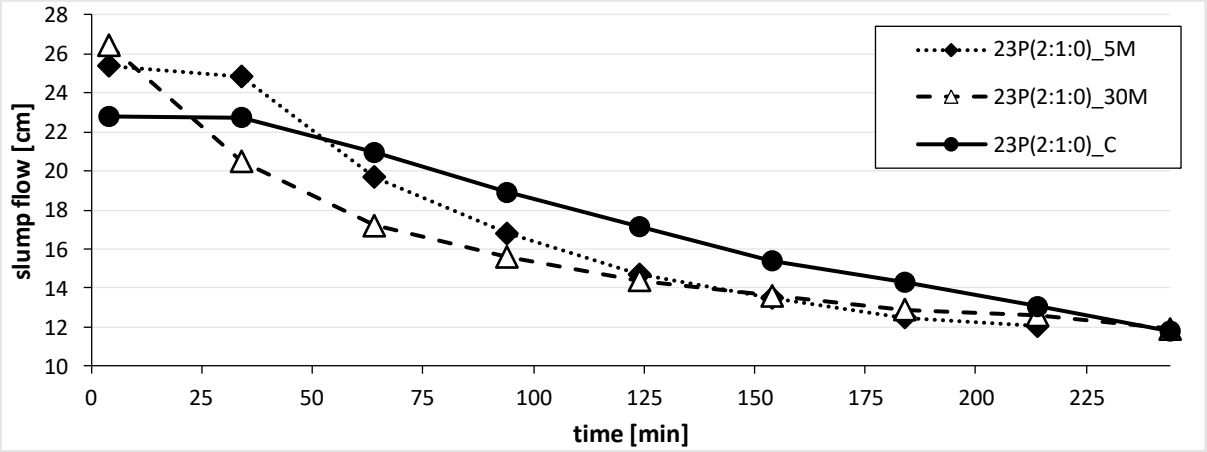


Figure 53. Slump loss behavior of mortar (CEM I 52.5 R, w/c ratio = 0.4) containing 23P(2:1:0)_C, 23P(2:1:0)_30M or 23P(2:1:0)_5M at a fixed polymer dosage of 0.43 % bwoc.

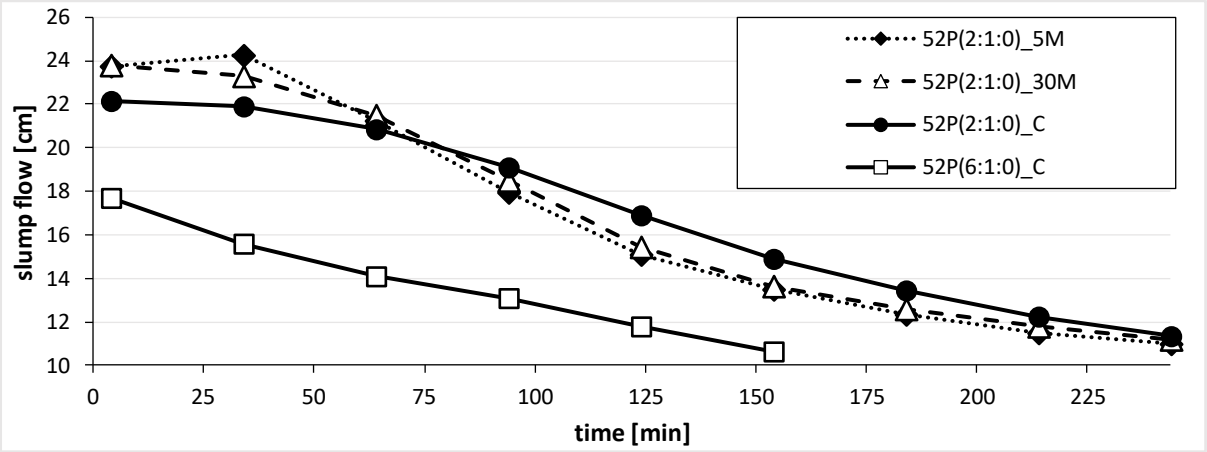


Figure 54. Slump loss behavior of mortar (CEM I 52.5 R, w/c ratio = 0.4) containing 52P(2:1:0)_C, 52P(2:1:0)_30M, 52P(2:1:0)_5M or 52P(6:1:0)_C at a fixed polymer dosage of 0.43 % bwoc.

Interestingly, the high slump retaining effect of the “30M” and “5M” PCEs in cement paste was not observed in mortar, however this effect is well known as it is much harder to achieve long slump

retention in mixes containing aggregates. Actually, a similar or slightly improved dispersing effect directly after the mixing procedure (4 min) was obtained for the “30M” and “5M” samples, but the slump loss of the mortar over time was stronger than for the anionic references 23P(2:1:0)_C and 52P(2:1:0)_C. Generally, the slump retaining behavior for all PCE samples tested in mortar (CEM I 52.5 R and a w/c ratio = 0.3) was very low or even non-existent, as stable slump flows for 2 to 3 hours and even longer are common in concrete. In this study, a stable slump flow of half an hour at the most was received. Whether this low efficiency was caused by the chosen system (mortar instead of concrete) or by the PCE samples themselves cannot be conclusively clarified here. Nevertheless, further differences between the tested samples were identified. The strongly anionic references 23P(6:1:0)_C and 52P(6:1:0)_C only showed a very poor dispersing effect in this system and therefore were ignored in the following tests.

5.4.7 Clay tolerance

To clarify whether the “30M” and “5M” PCEs were suitable for cement containing clay impurities as well, spread flow and slump flow tests were repeated with a cement which comprised 1 % bwoc of montmorillonite clay.

5.4.7.1 Clay tolerance in cement paste

Figures 55 and **56** show the decrease of the spread flow for all tested superplasticizers in % compared to the reference value of 26 cm reached without any clay impurities. The dosages used for each PCE were the same as those given in **Table 26.**

At a high w/c value of 0.62, the strongly negative reference polymers 23P(6:1:0)_C and 52P(6:1:0)_C were more clay tolerant (~ 13 % reduction) than all less charged PCEs. Consequently, all PCEs with only 2 mol of AA suffered a loss of ~ 19 %, independent of the synthesis method. In contrast, the conventional low anionic samples 23P(2:1:0)_C and 52P(2:1:0)_C showed the smallest decrease of only ~ 10 % at a w/c ratio of 0.45, while especially the “30M” and “5M” PCEs with 23 EO units were strongly affected by montmorillonite clay (~ 30 %). Furthermore, the strongly negative reference polymers 23P(6:1:0)_C and 52P(6:1:0)_C performed poorly under those conditions (~ 20 - 35 % reduction). At a w/c ratio of 0.3, the conventional PCEs 23P(2:1:0)_C, 52P(2:1:0)_C and 23P(6:1:0)_C

were not able to disperse the cement slurry any more. Thus, no data (d.n.a. = data not available) were received for the clay tolerance. However, the decrease for the “5M” and “30M” PCEs with 23 EO units was about 25 - 35 %. For the long side chain lengths (52 EO units), the tested PCEs showed a decrease of ~ 16 % in the spread flow independent of the synthesis method.

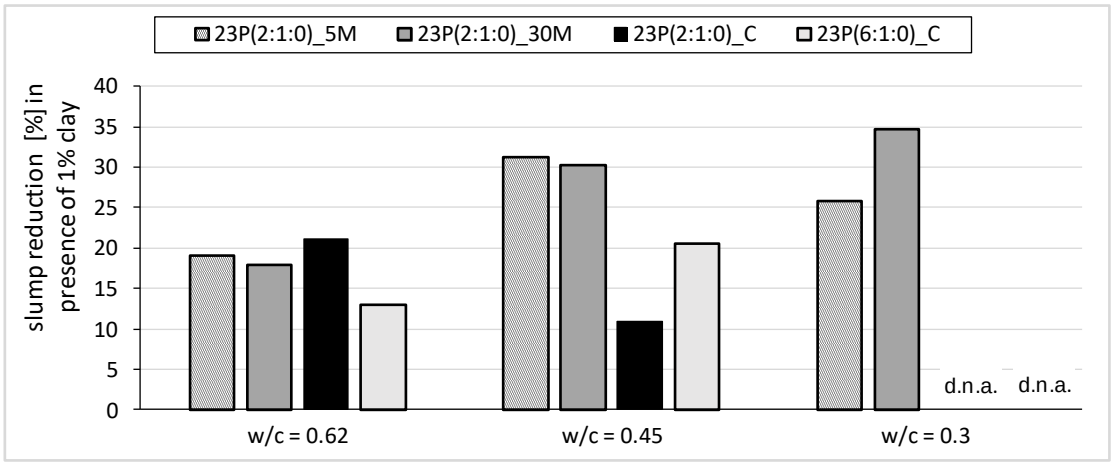


Figure 55. Decrease of spread flow [%] in CEM I 52.5 R in presence of 1 % montmorillonite clay for PCEs with 23 EO units at different w/c values; polymer dosages used for 26 cm spread flow; d.n.a. = data not available.

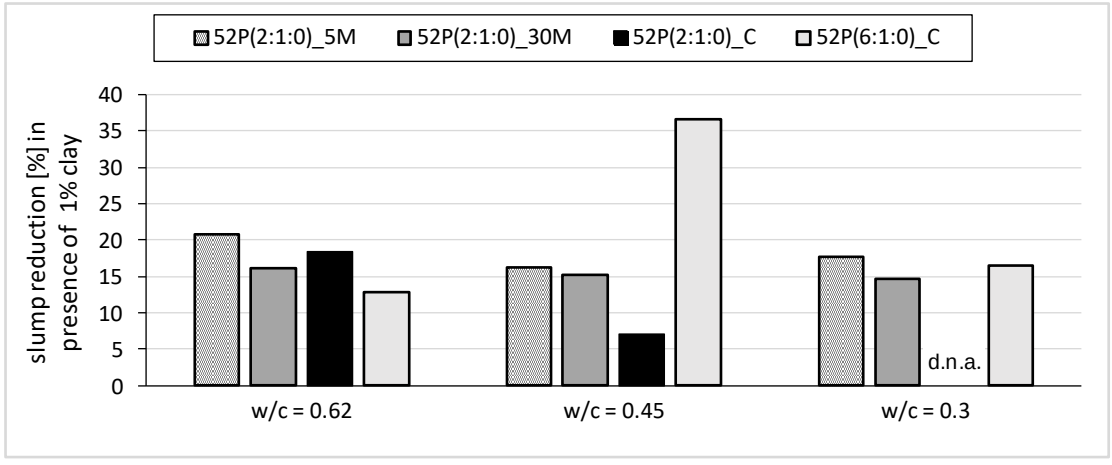


Figure 56. Decrease of spread flow [%] in CEM I 52.5 R in presence of 1 % montmorillonite clay for PCEs with 52 EO units at different w/c values; polymer dosages used for 26 cm spread flow; d.n.a. = data not available.

These observations led to the following conclusion: With a high amount of water in the cement slurry, a strongly anionic character can prevent the PCE from being intercalated into the montmorillonite structure. With a decreasing distance (w/c ratio = 0.45) between cement and clay particles, other

properties of the PCEs (e.g. microstructure) played an increasing role. However, when the water demand was very low (w/c ratio = 0.3), only steric factors like the side chain length were decisive for the clay tolerance, independent of the anionic charge or synthesis method of the PCEs used.

5.4.7.2 Clay tolerance in mortar

As can be seen in **Figures 57** and **58**, similar to cement paste, the strongly negative PCEs 23P(6:1:0)_C and 52P(6:1:0)_C showed better tolerance against clay and lost the least dispersing effectiveness at a w/c ratio of 0.5. Furthermore, in mortar this benefit remained for 52P(6:1:0)_C at all w/c values. For 23P(6:1:0)_C, no statement can be made for the clay tolerance at a w/c ratio of 0.4 because no slump flow of 18 cm without clay could be obtained for this polymer.

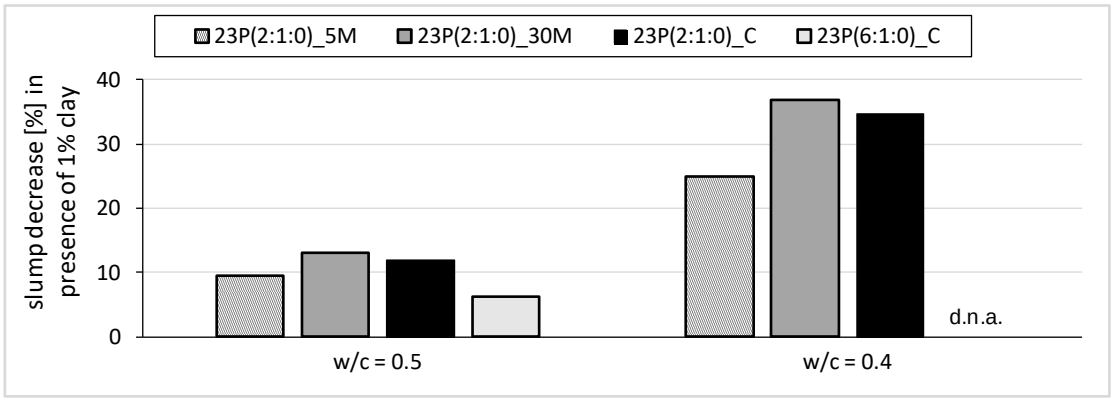


Figure 57. Decrease [%] of slump flow (CEM I 52.5 R) in presence of 1 % montmorillonite clay for PCEs with 23 EO units at different w/c values; polymer dosage used for 18 cm slump flow; d.n.a. = data not available.

Concerning the weakly anionic PCEs with only 2 mol of AA, the “5M” PCEs were most clay tolerant at high w/c values. As seen before in cement paste at low w/c values, primarily steric reasons (length of side chain) were decisive for the clay tolerance.

The following general results can be formulated: In cement paste and mortar with a high water content (w/c ratio = 0.62 or 0.5), strongly anionic polymers were most stable against clay intercalation. With a decreasing water amount (w/c ratio = 0.45), the synthesis method and the resulting polymer formation and polymer microstructure of the PCEs also played a role. At low w/c values, only the steric effect i.e. the side chain length was responsible for the clay tolerance.

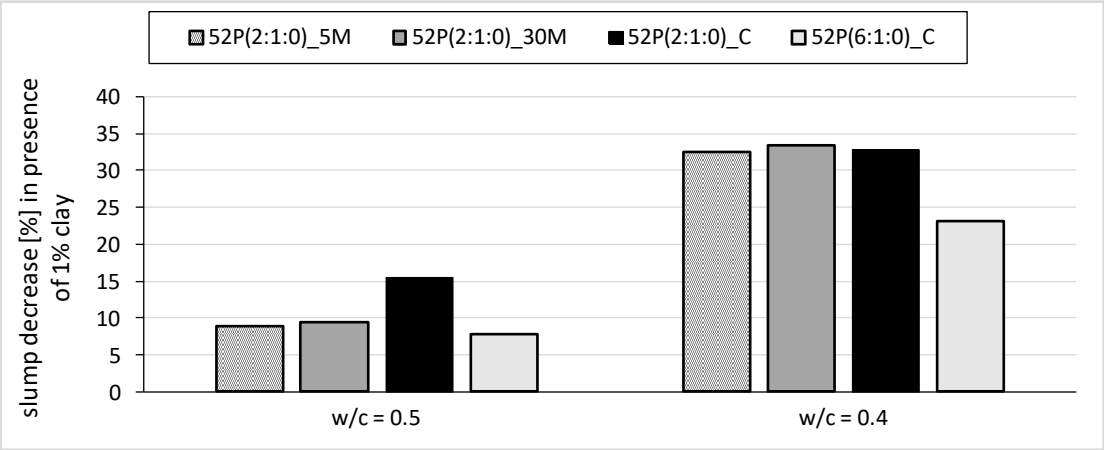


Figure 58. Decrease [%] of slump flow (CEM I 52.5 R) in presence of 1 % montmorillonite clay for PCEs with 52 EO units at different w/c values; polymer dosage used for 18 cm slump flow.

5.4.8 Sulfate tolerance

To gain an understanding to what degree the synthesis method influences the sulfate tolerance of the PCEs, “mini slump” tests were prepared with 1 % Na_2SO_4 added to the mixing water. The results are displayed in **Figures 59** and **60**. Since the decrease of the spread flow in presence of SO_4^{2-} ions was based on a competitive adsorption between the PCE and sulfate ions [74,75,158], the polymers with strongly negative charge amounts were expected to be most stable because of their stronger adsorption ability [159].

5.4.8.1 Sulfate tolerance in cement paste

Figures 59 and **60** show all changes in the spread flow in % when adding 1 % bwoc Na_2SO_4 to the mixing water. The polymer dosage required to obtain a spread flow of 26 cm without any additional impurities like clay or sulfate was used. As already explained in **Section 5.4.5**, no values for 23P(2:1:0)_C, 23P(6:1:0)_C and 52P(2:1:0)_C at a w/c ratio of 0.3 were received (d.n.a.).

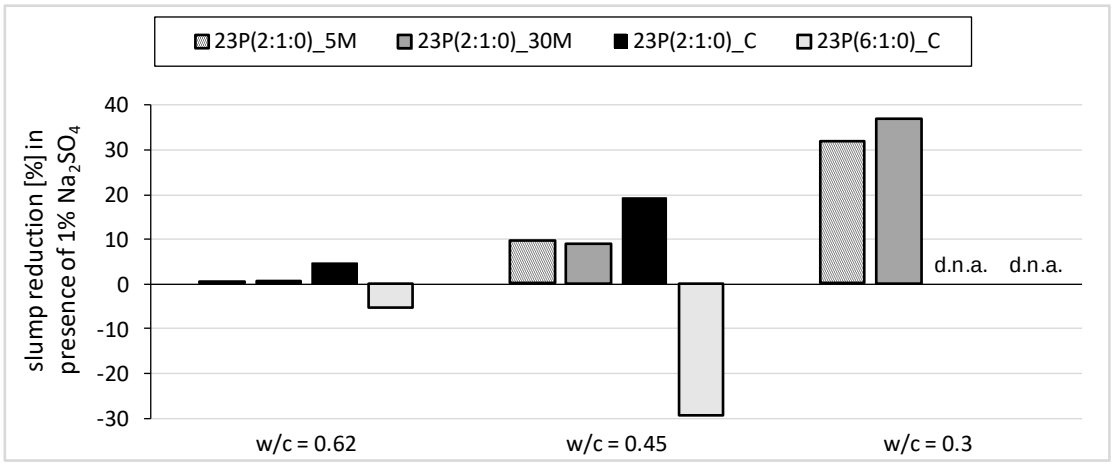


Figure 59. Decrease (+) and increase (-) in [%] from 26 cm spread flow (CEM I 52.5 R) in presence of 1 % Na_2SO_4 for PCEs with 23 EO units at different w/c values; polymer dosages used for 26 cm spread flow; d.n.a. = data not available.

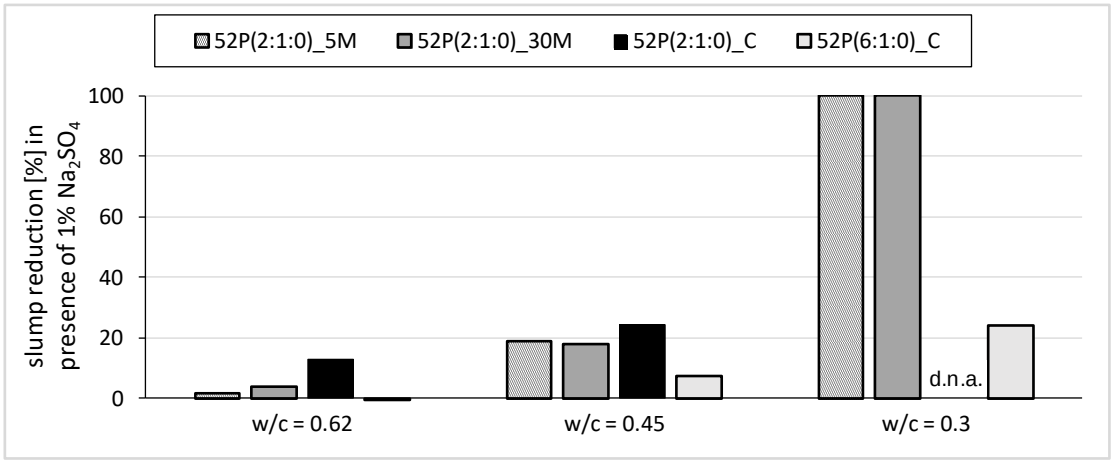


Figure 60. Decrease (+) and increase (-) in [%] from 26 cm spread flow (CEM I 52.5 R) in presence of 1 % Na_2SO_4 for PCEs with 52 EO units at different w/c values; polymer dosages used for 26 cm spread flow; d.n.a. = data not available.

As hypothesized, the highly anionic PCEs 23P(6:1:0)_C and 52P(6:1:0)_C exhibited the lowest decrease of the spread flow in presence of 1 % Na_2SO_4 in all tested w/c values. Even an increase for 23P(6:1:0)_C was observed. For weakly anionic PCEs (2 mol of AA), the “30M” and “5M” polymers were more sulfate tolerant than the conventional ones. For PCEs with a long side chain length (52 EO units), the conventional sample 52P(6:1:0)_C remained most tolerant against sulfate even at a low w/c ratio of 0.3, while the “30M” and “5M” PCEs lost almost their complete dispersing performance which resulted in a stirrable, but non-flowable cement paste (= slump loss of 100 %).

5.4.8.2 Sulfate tolerance in mortar

The decrease and increase from 18 cm slump flow in % in the presence of 1 % Na_2SO_4 are given in **Figures 61** and **62**. Independent of the w/c ratio used, the strongly anionic PCEs 23P(6:1:0)_C and 52P(6:1:0)_C performed best in the presence of sulfate ions, followed by the "30M" and "5M" samples, as already observed in the cement paste.

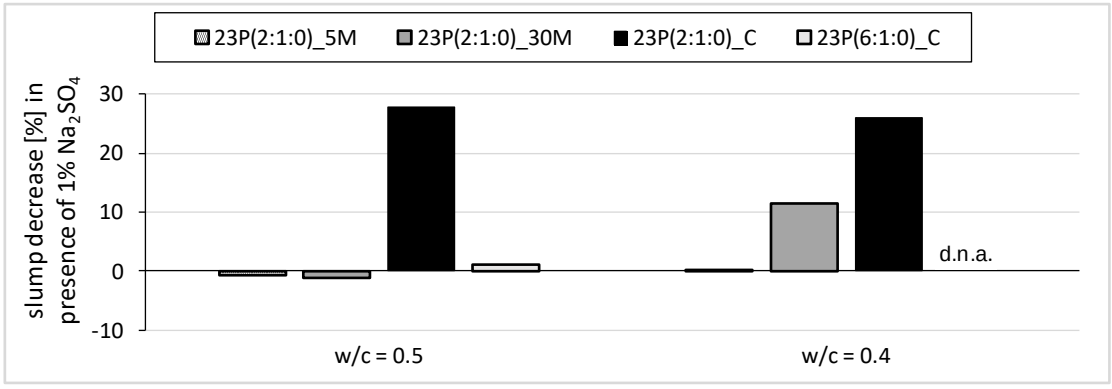


Figure 61. Decrease (+) and increase (-) in [%] from 18 cm slump flow (CEM I 52.5 R) in presence of 1 % Na_2SO_4 for PCEs with 23 EO units at different w/c values; polymer dosages used for 18 cm slump flow; d.n.a. = data not available.

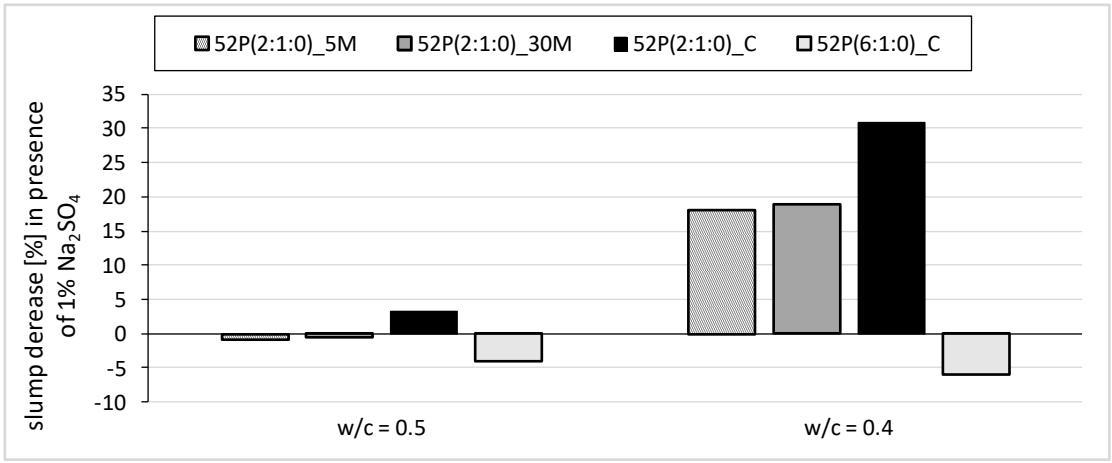


Figure 62. Decrease (+) and increase (-) in [%] from 18 cm slump flow (CEM I 52.5 R) in presence of 1 % Na_2SO_4 for PCEs with 52 EO units at different w/c values; polymer dosages used for 18 cm slump flow.

To summarize, it can be noted that both in cement paste and in mortar, the PCEs synthesized through the "30M" or "5M" method clearly had a higher sulfate tolerance than their conventional counterparts. Only the conventional PCEs which had a significantly higher anionic charge (52P(6:1:0)_C and 23P(6:1:0)_C) were even more stable in their dispersing performance in the presence of sulfate ions.

5.4.9 Summary of Section 5.4

In this study, the composition and effectiveness of isoprenol ether-based PCEs with 23 and 52 EO units per side chain and a molar ratio of AA:MM = 2:1 synthesized through the quick polymerization processes “5M” was investigated in detail. An additional synthesis process with a polymerization time of 30 minutes (“30M”) was established to examine the influence of the polymerization time on the dispersing performance of the resulting PCEs. Here, the first 5 minutes of the polymerization were similar to the “5M” process, whereby the “5M” synthesis can be classified as an interrupted “30M” synthesis. A redox catalyst system comprising Fe^{2+}, Rongalit®, and H_2O_2 was utilized for both methods. Furthermore, all monomers were placed together in the reaction flask and polymerization was started by adding the initiator over time.

When tracking the polymer formation over time by means of SEC measurements, it was discovered that, in case of the redox initiator system, the polymerization reaction immediately started when adding the initiator. For the “30M” synthesis process, further polymer fractions were formed after ~ 5 minutes which resulted in a polymer mixture for these PCEs. Since the polymerization process was stopped exactly at this point of time for the “5M” PCEs, only one polymer fraction was primarily generated as was also the case for the conventional PCEs. However, when adding the initiator APS and the monomer AA to the IPEG macromonomer for the conventional superplasticizers, the polymerization reaction only started after 10 - 20 minutes. Independent of the selected initiator system (APS or redox), the polymerization reaction for the IPEG macromonomer discontinued whenever the initiator solution was completely added to the reaction mixture. This clarified that subsequent stirring had no effect on the increase of the macromonomer conversion.

When comparing the dispersing effectiveness of the PCEs via “mini slump” tests it was observed that the “30M” and “5M” PCEs required significantly lower dosages at low w/c values of 0.45 or 0.3 to reach a spread flow of 26 cm in cement paste (CEM I 52.5 R) than the conventional ones. Similar dosages were necessary in mortar. Furthermore, “30M” and “5M” PCEs showed an improved slump retaining behavior in cement paste (PCE dosage 0.5 % bwoc; w/c ratio = 0.3) compared to the conventional PCEs. In mortar, this benefit could not be observed; here, a stronger slump loss was received over time as compared to the conventional PCEs. However, such discrepancies between cement paste and mortar tests are well known.

The property of clay tolerance of the PCEs strongly depended on the side chain length of the IPEG macromonomer and not primarily on the synthesis method of the PCE. Although slightly different dispersing abilities could be observed, there was no uniform trend. Basically, all PCEs holding 52 EO units were more clay tolerant than those with 23 EO units. Additionally, the “30M” and “5M” PCEs were more sulfate tolerant in both cement paste and in mortar than the conventional ones with the same AA:MM ratio (= 2:1).

In summary, interrupting a rather uncontrolled “batch” polymerization at the right time can lead to a relatively uniform polymer (“5M” PCEs). A uniform polymer is also common for conventional PCEs even if their polymerization time is much longer than the 5 minutes required for the “5M” PCEs. In spite of lower macromonomer conversions for “5M” PCEs caused by an interrupted polymerization process, their dispersing performance in cement systems of low w/c values outperforms the performance of conventional PCEs, while in mortar, they behave similarly. Furthermore, a significantly better slump retaining behavior was observed for “5M” and “30M” PCEs in cement paste. However, this advantage could not be achieved in mortar. The “5M” polymers and “30M” polymer samples exhibited excellent sulfate tolerance in cement paste and mortar. When clay impurities were present, a slightly stronger decrease was found in the dispersing performance than for the conventional PCEs. Thus, the “5M” PCE is a serious alternative to the conventionally synthesized PCE superplasticizer: while the polymerization time is significantly shortened, no real disadvantages in the dispersing performance in absence or presence of clay and sulfate ions have to be accepted. Instead, significantly better dispersing effects can even be achieved. However, it has to be mentioned that the whole “5M” PCE synthesis method required the interruption of the polymerization reaction by strong cooling and by dialysis, which makes this process unfeasible for industrial application. Therefore, further studies should be carried out to simplify the process of interrupting the polymerization process after 5 minutes without cooling and dialysis, for instance by adding inhibitors to the reaction mixture.

5.5 Impact of different pH values on the dispersing effectiveness of polycarboxylate (PCE) superplasticizers

Parts of **Section 5.5** were published in “Impact of Different pH-Values of Polycarboxylate (PCE) Superplasticizer Solutions on their Dispersing Effectiveness” by C. Chomyn and J. Plank in the journal “Construction and Building Materials” [160].

In the previous sections, the optimization of the synthesis method as well as the effect of these improvements on the dispersing performance and properties of the PCEs was investigated. Now, the focus lay on the influence of the pH value of the superplasticizer solution on its dispersing capabilities. All (anionic) PCE solutions usually have an acidic pH value as soon as the synthesis procedure has been completed because they always contain carboxylic acids such as acrylic acid or maleic acid to provide an anionic charge which is required for the dispersing mechanism (see **Section 3.3.1.4**). In order to avoid accidents and to simplify the storage of the PCE solutions, the superplasticizer solutions are generally neutralized. To clarify whether neutralization influences the dispersing performance of PCEs, three different kinds (APEG, IPEG, and HPEG) with a pH value of 1.5 and 7.0 were tested and compared in cements with different compositions. Moreover, the reason for the differing dispersing effectiveness of the PCEs with a pH value of 1.5 or 7.0 was investigated by means of adsorption measurements and ettringite crystallization in the presence of those PCEs. **Sections 5.5.1 - 5.5.6** (results, figures and tables) closely follow the paper prepared by C. Chomyn and J. Plank. [160].

5.5.1 Polymer synthesis

To gain insight into the different behaviors of the various PCE types and the influence of the anionic character of the sample, IPEG macromonomer with 52 EO units and HPEG macromonomer with 50 EO units polymerized with 2, 6, and 10 mol of AA were investigated as well as an APEG PCE with 34 EO units. Their synthesis procedure is described in the following sections.

5.5.1.1 Synthesis of HPEG and IPEG PCEs

In the following research, only PCEs produced via the conventional synthesis method were tested. The synthesis procedure for the HPEG PCEs (50HP(2, 6 or 10:1:0)_C) was identical to that of the

IPEG PCEs (52P(2, 6 or 10:1:0)_C) and was described in **Section 5.1.1.1**. Only for 52P(10:1:0)_C and 50HP(10:1:0)_C, 68 mL of water instead of 48 mL of deionized water were used. The pH value was adjusted to 1.5 or 7.0 (in the following abbreviated with 7) using HCl solution or 30 wt.-% NaOH. For 52P(10:1:0)_C and 50HP(10:1:0)_C, the pH value already was 1.5 after the synthesis. **Table 28** lists the amounts of the initiator (APS) and the chain transfer agent while **Table 29** displays the amount of monomers used for the synthesis of the IPEG and HPEG PCEs.

Table 28. Amounts of APS and sodium methallyl sulfonate used in the synthesis of IPEG and HPEG PCEs.

Polymer designation	Amount of APS	Amount of sodium methallyl sulfonate
52P(2:1:0)_C	0.70 g (3.07 mmol)	0.86 g (5.44 mmol)
52P(6:1:0)_C	2.97 g (13.02 mmol)	3.73 g (23.58 mmol)
52P(10:1:0)_C	4.66 g (20.42 mmol)	6.33 g (40.02 mmol)
50HP(2:1:0)_C	0.70 g (3.07 mmol)	0.86 g (5.44 mmol)
50HP(6:1:0)_C	1.63 g (7.14 mmol)	2.00 g (12.65 mmol)
50HP(10:1:0)_C	4.66 g (20.42 mmol)	6.33 g (40.02 mmol)

Table 29. Denomination, composition, and solution properties of the synthesized anionic comb polymers.

Polymer denomination	Synthesis method	Molar ratio macromonomer:acid	Monomer quantities		Solid content of PCE solution [wt.-%]
			AA or MA	APEG or IPEG or HPEG	
34AP(1:1:0)_C	bulk	1:1 [1:1]	6.86 g (0.07 mol)	105.0 (0.070 mol)	39.5
52P(2:1:0)_C	aqueous solution	1:2 [0.83:2]	2.16 g (0.03 mol)	36.0 (0.015 mol)	28.2
52P(6:1:0)_C	aqueous solution	1:6 [0.87:6]	6.48 g (0.09 mol)	36.0 (0.015 mol)	32.2
52P(10:1:0)_C	aqueous solution	1:10 [0.83:10]	10.81 g (0.15 mol)	36.0 (0.015 mol)	32.4
50HP(2:1:0)_C	aqueous solution	1:2 [0.77:2]	2.16 g (0.03 mol)	34.5 (0.015 mol)	28.1
50HP(6:1:0)_C	aqueous solution	1:6 [0.91:6]	6.48 g (0.09 mol)	34.5 (0.015 mol)	31.3
50HP(10:1:0)_C	aqueous solution	1:10 [0.82:10]	10.81 g (0.15 mol)	34.5 (0.015 mol)	32.8

[ ] molar ratios actually present in the polymers calculated from SEC measurements; for APEG PCEs, the ratio is always 1:1

5.5.1.2 Synthesis of APEG PCE (34AP(1:1:0)_C)

The APEG PCE was synthesized in bulk according to a well-established procedure [15]. There, the initiator system benzoyl peroxide and the APEG macromonomer with 34 EO units were utilized. The

synthesis was run without a chain transfer agent because degradative chain transfers take place in this reaction (see **Section 3.3.3.2.1.2**) [111-113,161]. In the following, the synthesis procedure for 34AP(1:1:0)_C is described.

105.0 g (70.0 mmol) of 34APEG macromonomer and 6.86 g (70.0 mmol) maleic anhydride (MA) were molten at 70 °C in a 500 mL five-neck round-bottomed flask. Next, the reaction mixture was purged with N_2 and 0.283 g (0.876 mmol) of 75 wt.-% benzoyl peroxide was added to the reaction mixture. Afterwards, an amount of 0.063 g (0.195 mmol) of 75 wt.-% benzoyl peroxide was inserted every 10 minutes over a period of **90 minutes**. When the initiator addition was complete, the mixture was first stirred for 2 hours at 70 °C and then for 30 minutes at 90 °C. After this, 175 mL of deionized water were immediately added to the mixture which led to a slightly yellow, viscous PCE solution (39.5 % solid content) with a pH value of 2.3. The pH value was adjusted to 1.5 or 7.0 (in the following abbreviated with 7) using HCl solution or 30 wt.-% NaOH.

5.5.2 SEC analysis of the synthesized PCEs

All synthesized superplasticizers were characterized by means of SEC measurements. **Figure 63** displays the spectra obtained and **Table 30** lists the molecular properties of the PCEs.

Table 30. Molar mass (M_w), polydispersity index (PDI) and macromonomer conversion for the synthesized PCEs.

Polymer sample	M_w [g mol^{-1}]			PDI [M_w/M_n]	MM conversion [%]
	Peak 1	Peak 2	Peak 3	(Peak 2)	(Peak 1 - 2)
34AP(1:1:0)_C	---	30,430	1,803	2.6	76.7
52P(10:1:0)_C	---*	35,690	2,759	2.6	82.5
50HP(10:1:0)_C	493,100	28,360	1,334	2.7	82.1
52P(2:1:0)_C	---	48,930	2,667	2.2	81.9
52P(6:1:0)_C	---	42,850	1,716	2.8	87.3
50HP(2:1:0)_C	---	31,880	2,366	2.0	75.6
50HP(6:1:0)_C	---	64,960	2,661	2.6	91.5

*M_w was not determinable by SEC measurement (insufficient amount)

Independent of the type of PCE or the amount of acid in the superplasticizers, high macromonomer conversions of ~ 80 % were received which made all samples comparable. Moreover, only one main polymer fraction occurred for each PCE with a molecular weight of ~ 28,000 - 65,000 g mol $^{-1}$. For the

molecular weight distribution of the main polymer fraction, a PDI of ~ 2.6 was found which represents a rather uniform polymer. Only the IPEG and HPEG PCE with 2 mol of AA showed an even more uniform distribution (PDI ~ 2.0). Due to the high amount of acrylic acid in the polymers 52P(10:1:0)_C and 50HP(10:1:0)_C (10 mol of AA), a minor amount of very high molecular poly(acrylic acid) (see peak 1) occurred. The amount of this fraction was so small that it was only visible in the light scattering signal which allowed this fraction to be neglected.

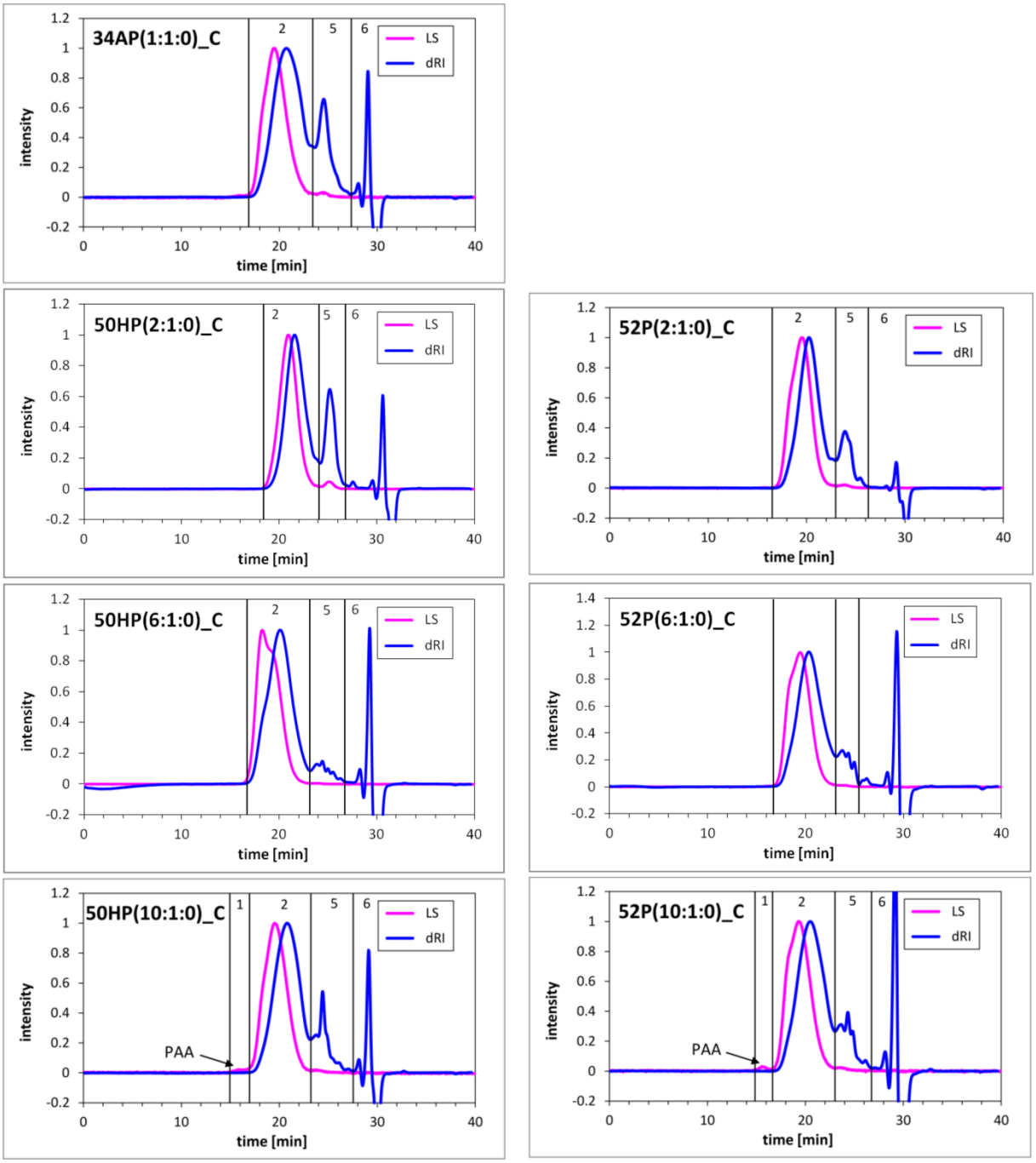


Figure 63. SEC spectra for the synthesized PCEs.

5.5.3 Dispersing performance of PCEs depending on their pH value

5.5.3.1 Dispersing performance in CEM I 52.5 R

To clarify the impact of different pH values of PCE solutions on the dispersing effectiveness, “mini slump” tests were carried out with PCE solutions of pH = 1.5 and 7 in CEM I 52.5 R at two w/c ratios of 0.62 and 0.35. Since it was not possible to disperse the cement slurry with less than 1 % bwoc of the polymers 52P(2:1:0)_C and 50HP(2:1:0)_C at a w/c ratio of 0.35, no data is presented for these polymers. Whenever a difference between the acidic and neutralized sample of only 0.01 % bwoc dosage was detected, the dispersing performance was defined as being the same because these minor differences were within the margin of error.

In **Figure 64**, the results for 34AP(1:1:0)_C are presented. In spite of the different pH values of the PCE solution, no different dispersing performances were observed here.

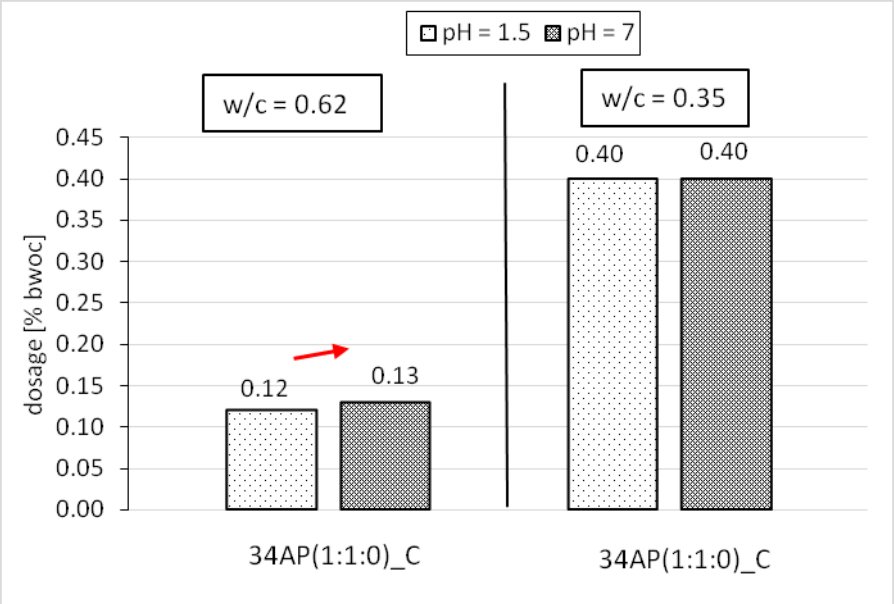


Figure 64. Dosages (± 0.01% bwoc) of 34AP(1:1:0)_C with pH = 1.5 or 7 required to reach a spread flow of 26 cm in CEM I 52.5 R; w/c ratio = 0.62 or 0.35.

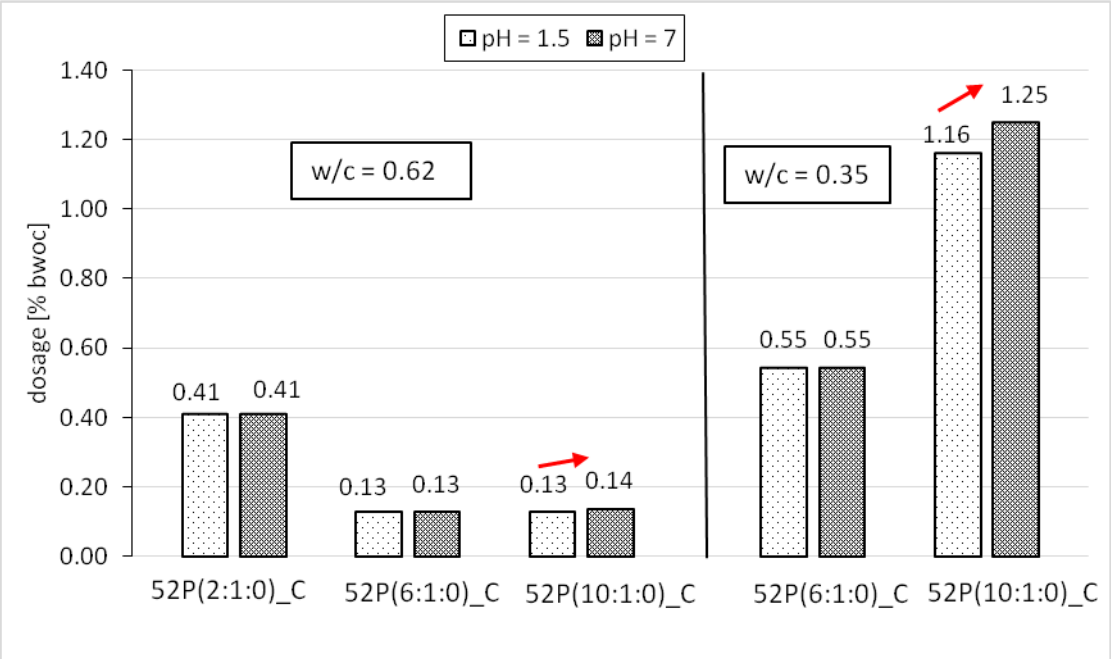


Figure 65. Dosages (± 0.01% bwoc) of IPEG PCEs with pH = 1.5 or 7 required to reach a spread flow of 26 cm in CEM I 52.5 R; w/c ratio = 0.62 or 0.35.

Also for the IPEG PCEs (see **Figure 65**), no impact of the pH value could be determined for the spread flow in cement paste with the high w/c ratio of 0.62. However, for the lower w/c ratio of 0.35, the strongly negative polymer 52P(10:1:0)_C showed a slight difference between the acidic and neutralized PCE solution of 0.09 % bwoc. Here, the acidic PCE performed somewhat better than the neutralized one.

Similar to the IPEG superplasticizers, the acidic solution of strongly negative HPEG PCE 50HP(10:1:0)_C also accomplished a better dispersion than the neutralized version (see **Figure 66**). However, a slight difference (0.02 % bwoc) was detected for this polymer already at a high w/c ratio of 0.62. A much larger effect was observed at a w/c ratio of 0.35, where the acidic solution required a 0.31 % bwoc lower dosage than the neutralized sample to achieve the same dispersing effect. Moreover, the HPEG PCE with 6 mol of AA (50HP(6:1:0)_C) also displayed a small dispersing difference (0.02 % bwoc) between the acidic and the neutralized polymer solution in cement paste at a low w/c ratio of 0.35.

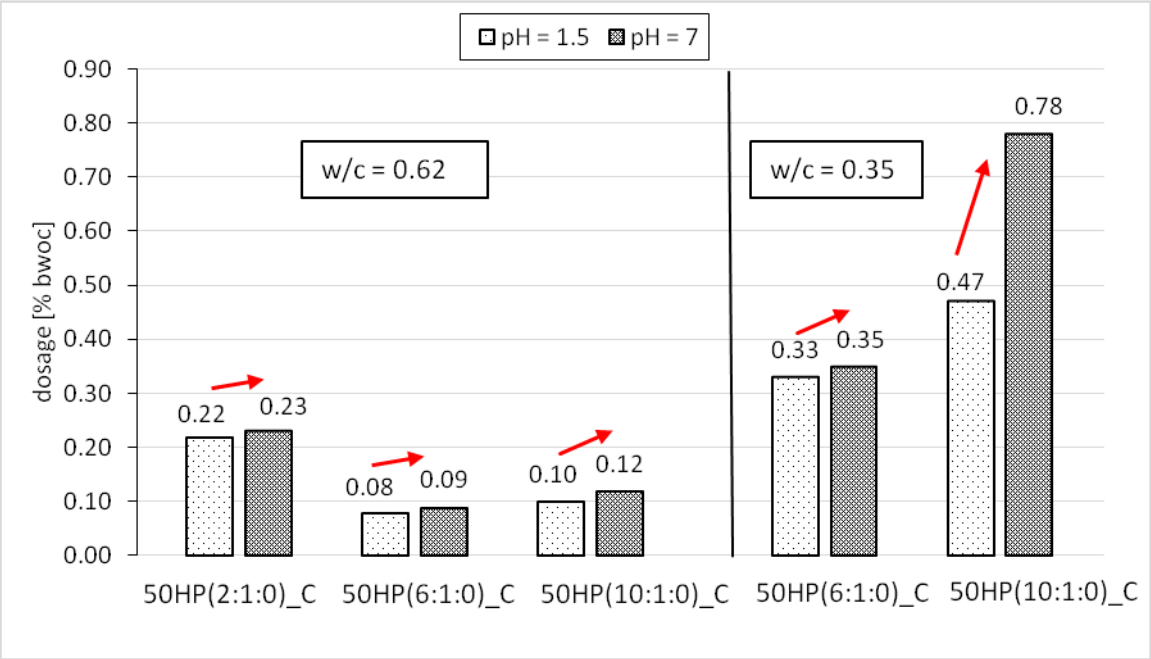


Figure 66. Dosage (± 0.01% bwoc) of HPEG PCEs with pH = 1.5 or 7 required to reach a spread flow of 26 cm in CEM I 52.5 R; w/c ratio = 0.62 or 0.35.

These “mini slump” tests demonstrated that a difference in the dispersing performance between acidic or neutralized PCE solutions especially occurred for the strongly anionic PCEs. In general, the acidic PCE solution performed better than the neutralized form. Furthermore, it showed that this effect was more distinctive for HPEG PCEs than for IPEG PCEs which can be solely attributed to the macromonomer used.

5.5.3.2 Dispersing performance in API Class G oil well cement and CEM I 42.5 R

To clarify whether different cement compositions influence the difference in the dispersing performance between acidic and neutralized PCE solutions, the “mini slump” tests were repeated in an API Class G oil well cement and a third ordinary Portland cement CEM I 42.5 R. The strongly anionic PCEs 52P(10:1:0)_C and 50HP(10:1:0)_C which clearly revealed a pH dependency, and the weakly charged 34AP(1:1:0)_C were tested here. The API Class G cement is characteristic for its low C_3A content (no orthorhombic C_3A (C_3A_o)) and therefore a C_3A_o / SO_4^{2-} ratio of ~ 0. Furthermore, its hydration reaction is very slow. In contrast, the CEM I 42.5 R possessed a high C_3A_o / SO_4^{2-} ratio of 1.17 (reference CEM I 52.5 R: C_3A_o / SO_4^{2-} = 0.93).

As can be seen in **Figure 67**, no differences in the dispersing performance of both IPEG and HPEG PCEs regarding the pH value of the superplasticizer solutions were observed in the API Class G cement. Even a low w/c value (0.3) did not lead to a difference in the observed performance. Additionally, the low PCE dosages required to reach a spread flow of 26 cm were expected due to the slow hydration of this cement type in addition to its large particle size and low C_3A content.

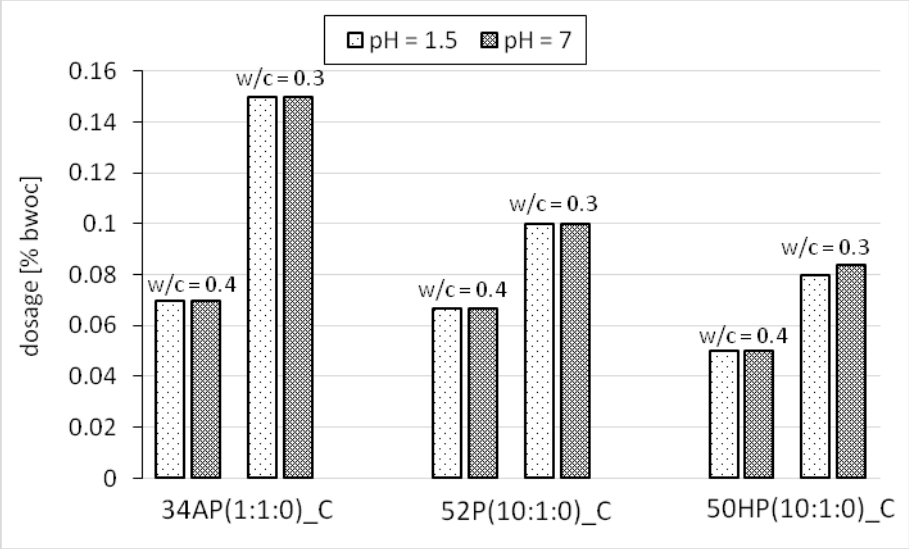


Figure 67. Dosage (± 0.01% bwoc) of PCEs with pH = 1.5 or 7 required to reach a spread flow of 26 cm in API Class G cement; w/c ratio = 0.4 or 0.3.

Completely different results were received in the “mini slump” tests carried out with CEM I 42.5 R at a w/c ratio of 0.5. While the neutralized polymers 52P(10:1:0)_C and 50HP(10:1:0)_C did not reach 26 cm with 1 % bwoc dosage, the acidic counterparts required dosages of only 0.15 % bwoc for 52P(10:1:0)_C and 0.12 % bwoc for 50HP(10:1:0)_C. This represented the strongest dispersing difference for all cements tested. However, like in all other tests performed before, again no difference was observed for 34AP(1:1:0)_C. Here, both the acidic and neutralized PCE solutions required a dosage of 0.18 % bwoc.

This cement screening proved that different dispersing capabilities induced by acidic or neutralized PCE solutions are strongly dependent on the cement composition. The difference in performance increased with a higher C_3A_o / SO_4^{2-} ratio. Only for the weakly anionic PCE 34AP(1:1:0), no pH-dependent effect occurred in any system. This confirms the assumption that the anionic charge amount was the determining factor whether a difference in the dispersing effectiveness for acidic or neutralized PCE solutions occurs.

5.5.4 Anionic charge amounts of the polymers

To determine the difference in the anionic character of the tested PCEs, the anionic charge amount was measured for the acidic and neutralized PCE solutions in deionized water and 0.1 M NaOH as is shown in **Figure 68**. When comparing the acidic with the neutralized PCE, a reduced anionic charge amount for the acidic polymer was obtained in deionized water which was due to a higher amount of protonated carboxylic groups. This difference did not occur in 0.1 M NaOH (pH ~ 12) due to the almost complete deprotonation of the carboxylic groups for all PCEs, independent of the original pH value due to the high excess of alkaline solvent. As expected, both polymers 52P(10:1:0)_C and 50HP(10:1:0)_C with 10 mol of AA especially in 0.1 M NaOH showed a significantly higher anionic charge amount (3,200 µeq/g) than for 34AP(1:1:0)_C (1,100 µeq/g). Therefore, the designation of "strongly anionic" and "weakly anionic" PCEs was confirmed experimentally.

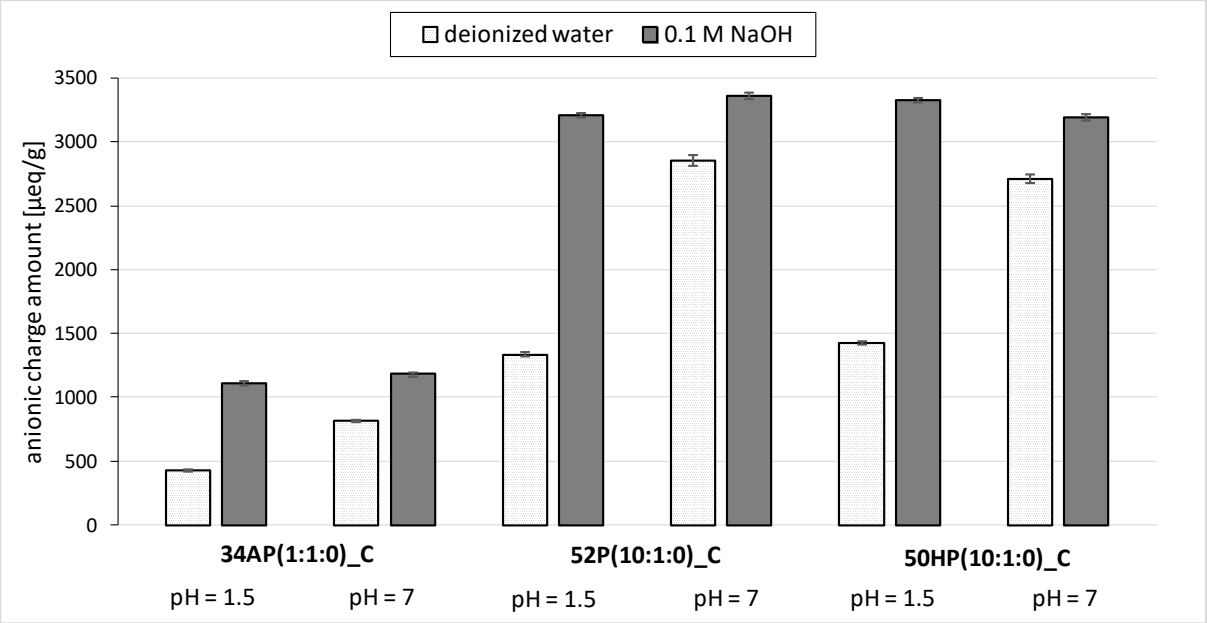


Figure 68. Anionic charge amounts of the PCEs 34AP(1:1:0)_C, 52P(10:1:0)_C and 50HP(10:1:0)_C with pH = 1.5 or 7 in deionized water and 0.1 M NaOH.

5.5.5 The origin of pH dependent dispersing performance of PCEs

Further investigations using the strongly anionic PCEs 52P(10:1:0)_C and 50HP(10:1:0)_C (strongest pH dependency) and the weakly charged 34AP(1:1:0)_C were conducted to explain the reason for the pH-dependent dispersing performance of PCE superplasticizers.

The previous experiments had demonstrated that acidic, highly anionic PCE solutions performed better than their neutralized counterparts. Furthermore, it showed that this behavior did not apply to weakly anionic polymers. This effect was strengthened when the cement contained a high amount of C_3A_o and SO_4^{2-} ions. This dependency on the cement composition suggests that different interactions between the acidic or neutralized polymer solution and the cement hydration process might be responsible for the effect. In order to determine in which cement hydration phase the effect occurs, "mini slump" tests with delayed PCE addition to the paste were carried out.

5.5.5.1 Dispersing performance with delayed PCE addition in CEM I 52.5 R

For delayed PCE addition in the "mini slump" tests, the superplasticizer solutions (pH 1.5 or 7) were not predissolved in the mixing water, but directly added to the cement paste after the mixing procedure has been completed (see **Section 4.2.6**). A fixed PCE dosage of 0.35 % bwoc and a w/c ratio of 0.35 were chosen for the CEM I 52.5 R.

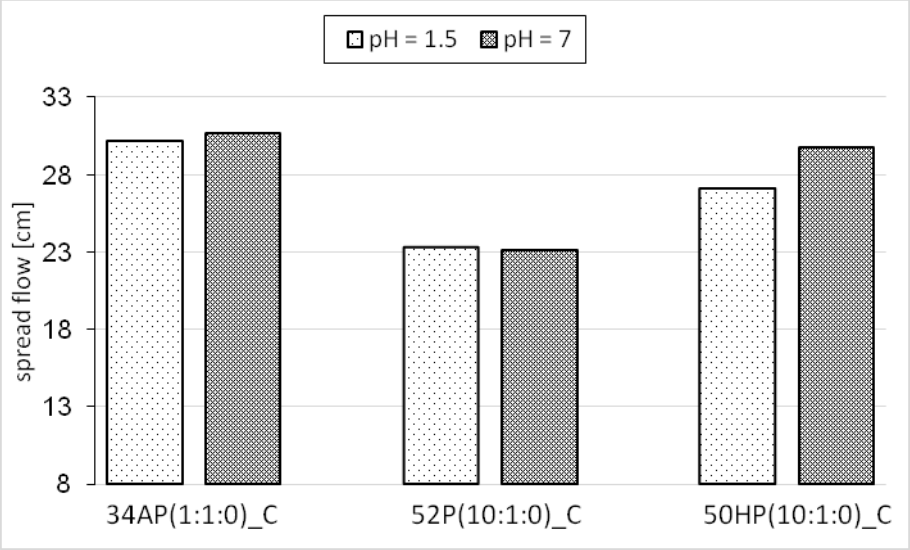


Figure 69. Spread flow of CEM I 52.5 R (w/c ratio = 0.35) with a PCE dosage of 0.35 % bwoc using delayed PCE addition.

As is shown in **Figure 69**, no dispersing difference between the acidic and neutralized PCE solutions was observed, similar to the results obtained in API Class G cement. For 50HP(10:1:0)_C, a slightly improved dispersing effectiveness was obtained for the neutral PCE solution which might have been due to inaccuracy.

Not adding the PCE until the cement has come in contact with water and has started to hydrate is sufficient to prevent a different dispersing effectiveness. This result proved that the difference in the dispersing ability between acidic or neutralized PCEs is caused by different interactions between the respective PCE solution and the very early processes taking place during cement hydration.

5.5.5.2 Influence of PCEs with pH = 1.5 or 7 on ettringite formation

As already known from literature (see **Section 3.2.1**), ettringite crystals are the first products of cement hydration formation (within milliseconds). Besides, their morphology is very strongly influenced by PCEs (see **Section 3.2.2**).

Based on literature and the previous results, it was assumed that acidic and neutralized PCE solutions affect ettringite crystallization in a variety of ways which led to the pH-dependent dispersing performances. This hypothesis was validated by experiments with synthetic ettringite in the presence of PCE solutions (pH 1.5 and 7). In accordance with Struble [153], synthetic ettringite formation was induced by combining an aluminum sulfate solution with a saturated calcium hydroxide solution. To introduce PCEs to this system, the superplasticizer solutions and a magnetic stir bar were already in the vessel in which the ettringite was precipitated (see **Section 4.2.8**).

5.5.5.2.1 Precipitation times of ettringite crystals in presence of PCE

As a first step, the precipitation times for ettringite crystals in the presence of the PCEs 52P(10:1:0)_C, 50HP(10:1:0)_C, and 34AP(1:1:0)_C were visually observed and listed in **Table 31**. The precipitation time was defined as the time after which the initially clear solution of $Ca(OH)_2$, $Al_2(SO_4)_3$ and PCE has become turbid.

Table 31. Precipitation times of the ettringite crystals in the presence of different PCEs.

Dosage of PCE	**34AP(1:1:0)_C**		**52P(10:1:0)_C**		**50HP(10:1:0)_C**	
	pH = 1.5	**pH = 7**	**pH = 1.5**	**pH = 7**	**pH = 1.5**	**pH = 7**
w/o PCE (reference)	10 sec		10 sec		10 sec	
0.025 g PCE	20 sec	20 sec	90 sec	60 sec	120 sec	80 sec
0.05 g PCE	40 sec	30 sec	34 min	14 min	---	20 min
0.075 g PCE	90 sec	50 sec	---	3.5 h	---	60 min

To better understand the definition of the precipitation time, photos of the precipitation vessels were taken over time including the reference without any PCE solution (**Figure 70**) and the acidic or neutralized polymer 34AP(1:1:0)_C (see **Figures 71** - **73**). For the reference without PCE, the ettringite precipitation started almost immediately after mixing the starting components together, as can be seen in **Figure 70**. After 10 seconds, the solution had already become turbid.

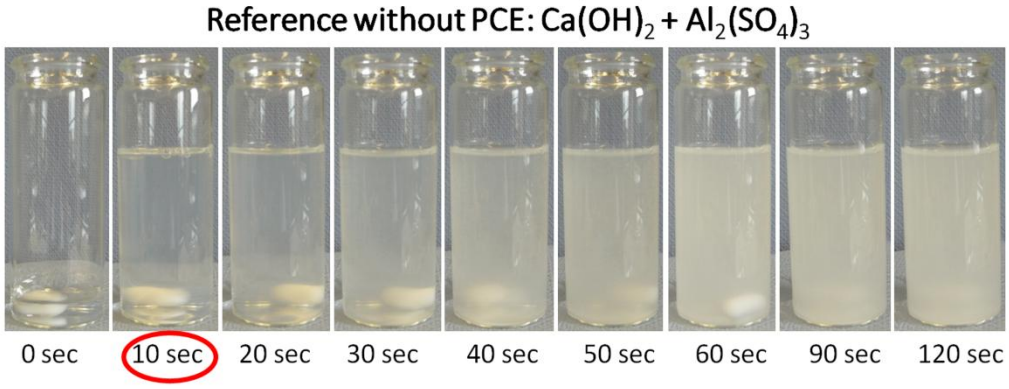


Figure 70. Visual determination of the precipitation time of ettringite without PCE.

When adding PCE to the system, the precipitation was always delayed. Generally, the acidic PCE solution had a greater influence on the precipitation process (more delay) than the neutralized counterpart, as can be observed in **Figures 71** - **73**.

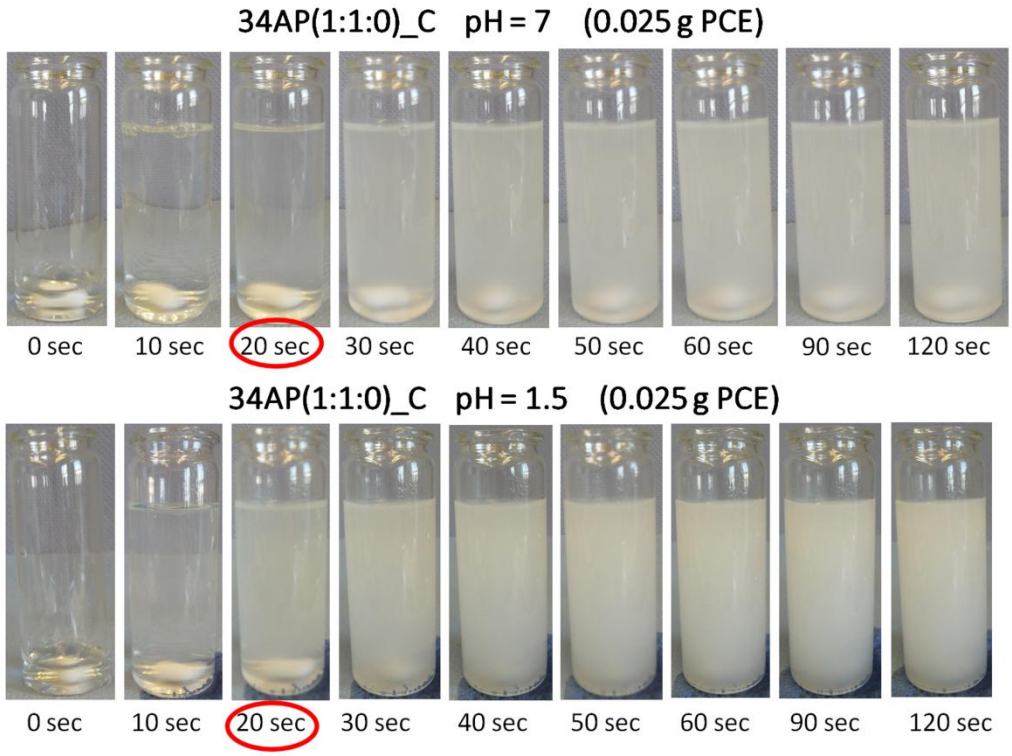


Figure 71. Visual determination of the precipitation time of ettringite in the presence of 0.025 g (= 3.5 % of the theor. maximum ettringite amount) 34AP(1:1:0)_C.

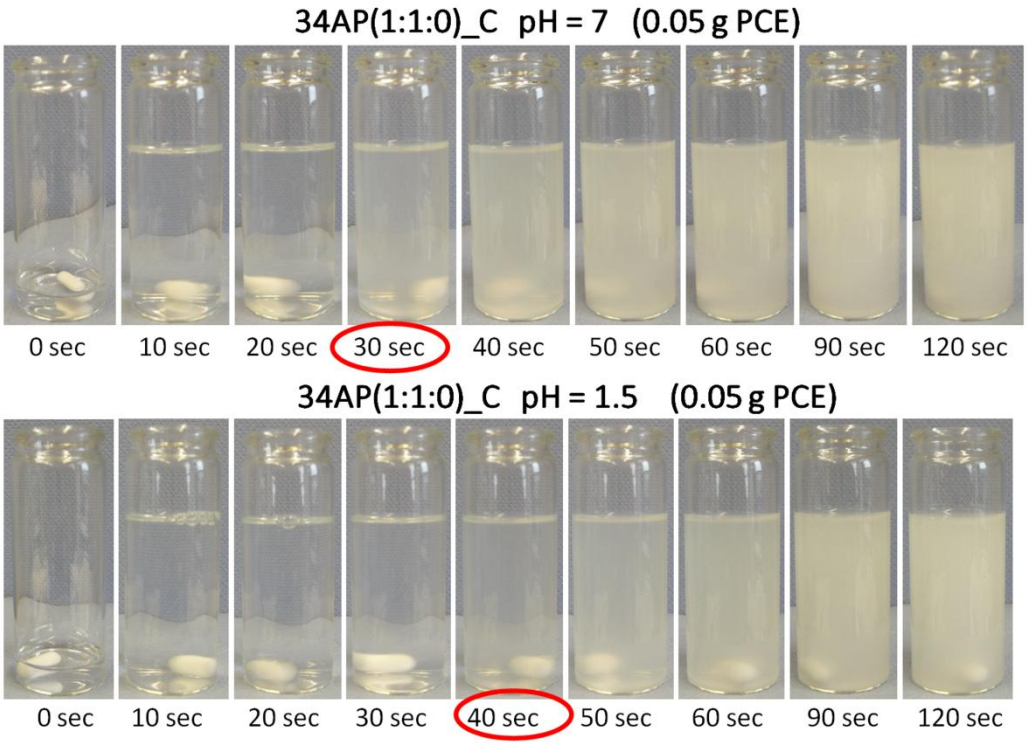


Figure 72. Visual determination of the precipitation time of ettringite in the presence of 0.05 g (= 6.9 % of the theor. maximum ettringite amount) 34AP(1:1:0)_C.

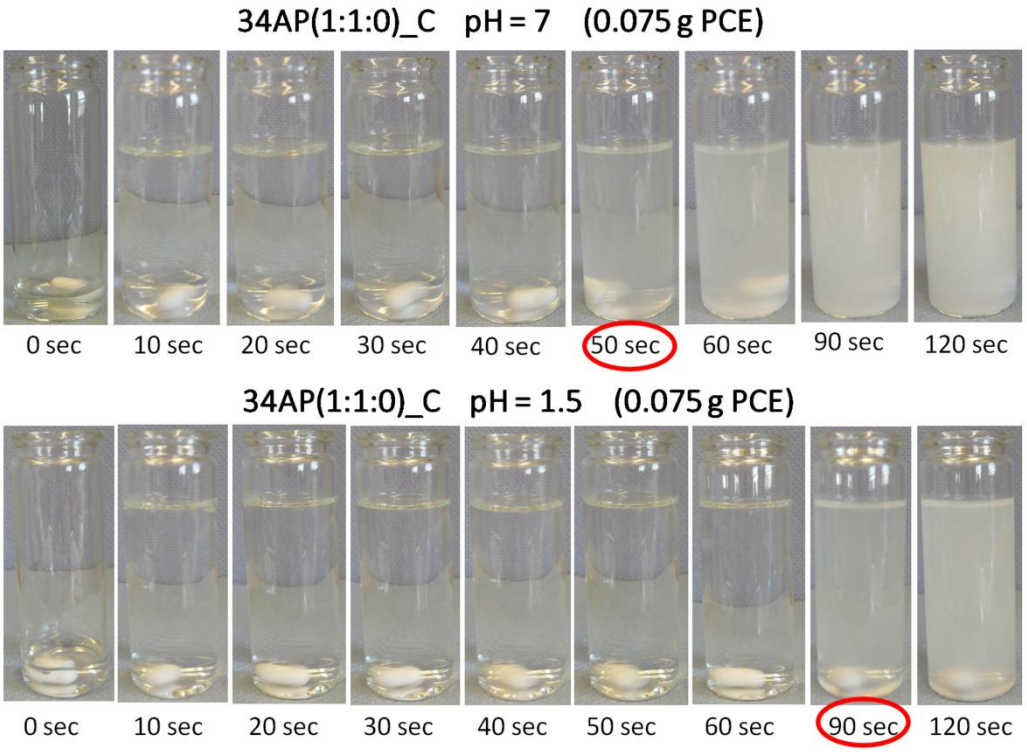


Figure 73. Visual determination of the precipitation time of ettringite in the presence of 0.075 g (= 10.4 % of the theor. maximum ettringite amount) 34AP(1:1:0)_C.

Moreover, higher amounts of PCE further increased the time required for precipitation. The type of PCE and its anionic charge amount also influenced this process: while the weakly anionic 34AP(1:1:0)_C caused the smallest time delays (20 - 90 seconds), strongly anionic PCEs like 52P(10:1:0)_C and 50HP(10:1:0)_C showed a much stronger retardation (minutes or hours) or even completely prevented the precipitation. This was in accordance with previous findings from Meier et al. [55]. In addition, the HPEG PCE showed even greater delays than the IPEG PCE.

5.5.5.2.2 Amount and composition of precipitated ettringite crystals

The amount of the precipitated ettringite crystals for every PCE sample was determined (see **Section 4.2.13**) and is listed in **Table 32**.

Table 32. Amounts of precipitated ettringite crystals in the presence of PCEs.

Dosage of PCE	34AP(1:1:0)_C		52P(10:1:0)_C		50HP(10:1:0)_C	
	pH = 1.5	pH = 7	pH = 1.5	pH = 7	pH = 1.5	pH = 7
0.025 g PCE	75.3 mg	83.2 mg	46.2 mg	70.7 mg	38.1 mg	68.7 mg
0.05 g PCE	53.3 mg	67.9 mg	15.1 mg	50.4 mg	---	39.6 mg
0.075 g PCE	39.6 mg	59.0 mg	---	24.2 mg	---	27.2 mg

(--- = no crystallization observed)

In the presence of acidic PCE solutions, the amount of ettringite crystals was always smaller than the amount from the neutralized counterpart. Moreover, at increased PCE dosages a decreasing amount of ettringite was obtained. Additionally, the later the precipitation occured (see **Table 31**), the fewer ettringite crystals were formed. Consequently, the highest amounts of ettringite crystals in the presence of PCEs were found for 34AP(1:1:0)_C, while the lowest amounts were obtained from the HPEG PCE. In the absence of PCE, an amount of 85 mg of ettringite was formed. Although this was the highest amount of precipitated ettringite in the employed system, it was very small compared to the theoretical (calculated) amount of 0.72 g of ettringite. Presumably, this was caused by the closed system, in which the free ion concentration decreased with an increasing precipitation of ettringite. Therefore, the driving force for the precipitation quickly dropped which resulted in only small amounts of ettringite.

X-ray diffractions confirmed the formation of ettringite. In **Figure 74**, the diffractograms for precipitated ettringite formed in the presence of 0.05 g 34AP(1:1:0)_C, 52P(10:1:0)_C, and 50HP(10:1:0)_C are presented.

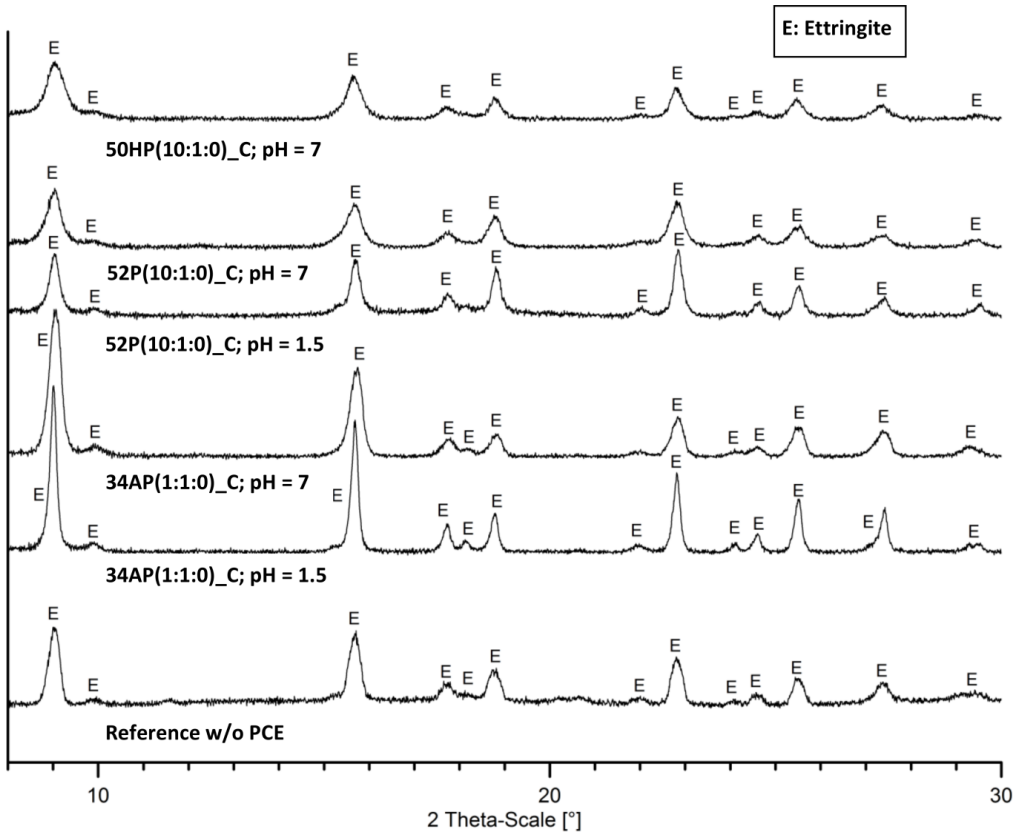


Figure 74. X-ray diffractograms of ettringite crystals obtained from combined $Ca(OH)_2/Al_2(SO_4)_3$ solutions after 24 hours of crystallization in the absence and presence of 34AP(1:1:0)_C, 52P(10:1:0)_C, and 50HP(10:1:0)_C with pH = 1.5 or 7 at a dosage of 0.05 g.

5.5.5.2.3 SEM images of the precipitated ettringite crystals

In addition to X-ray diffraction, the precipitated powder was analyzed by scanning electron microscopic imaging (SEM). The images obtained for each precipitated ettringite sample in the absence and presence of different PCEs and various PCE dosages are shown in **Figures 75 - 77**. According to literature [55], ettringite crystals have a needle-like shape which was confirmed for the precipitated reference (w/o PCE) as expected (see **Figure 75, top**). A high similarity was observed for the samples prepared in the presence of 34AP(1:1:0)_C. Although the crystals became shorter and thinner with an increasing PCE concentration, the needle shape could be clearly identified (see **Figure 75**). At the maximum dosage of PCE added (0.075 g), Ca^{2+} salts such as $CaCO_3$ or portlandite were also detected.

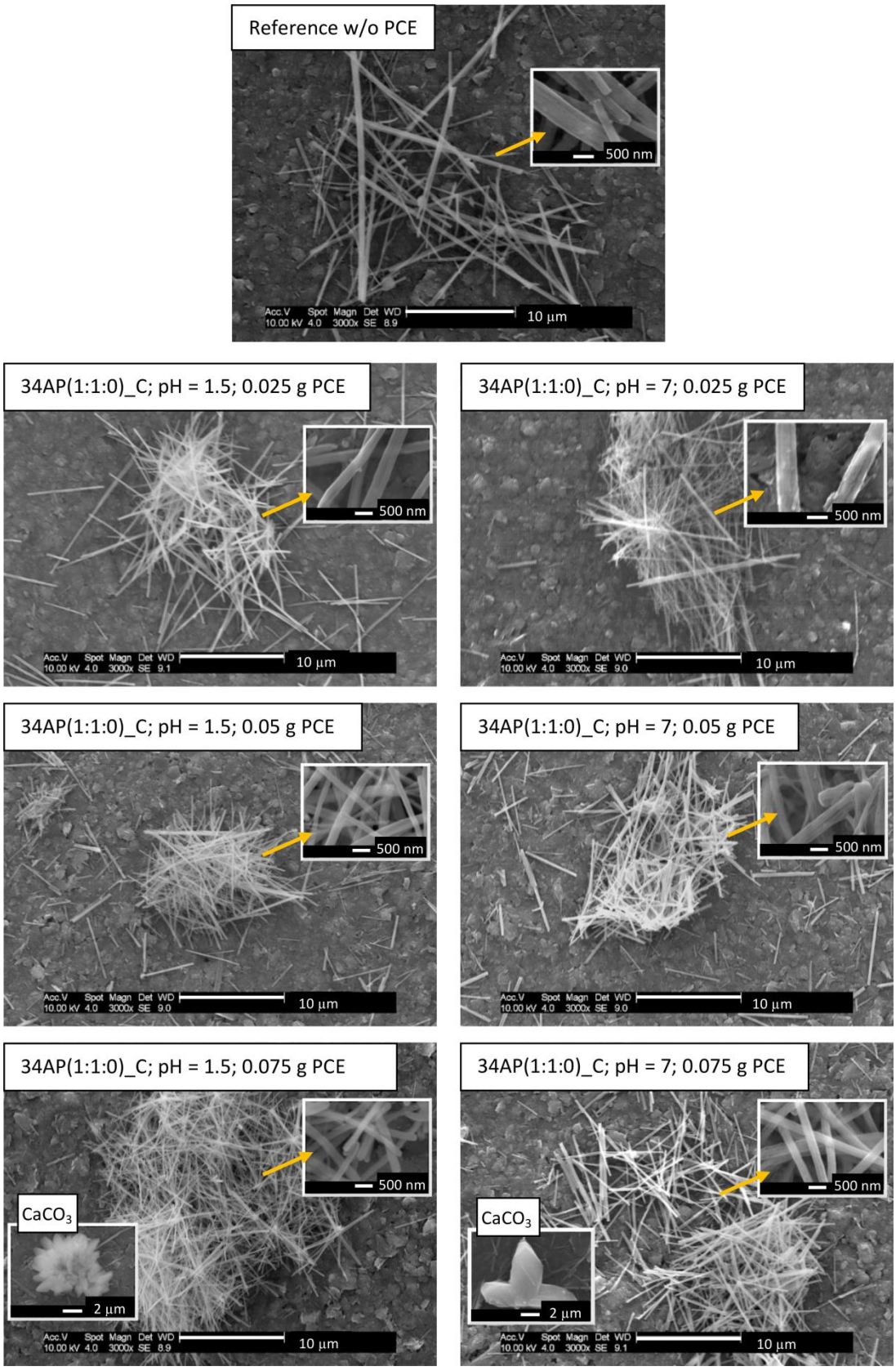


Figure 75. SEM images of ettringite crystals (needles) obtained from combined $Ca(OH)_2/Al_2(SO_4)_3$ solutions after 24 hours of crystallization in the absence and presence of 34AP(1:1:0)_C with pH = 1.5 or 7 and different dosages.

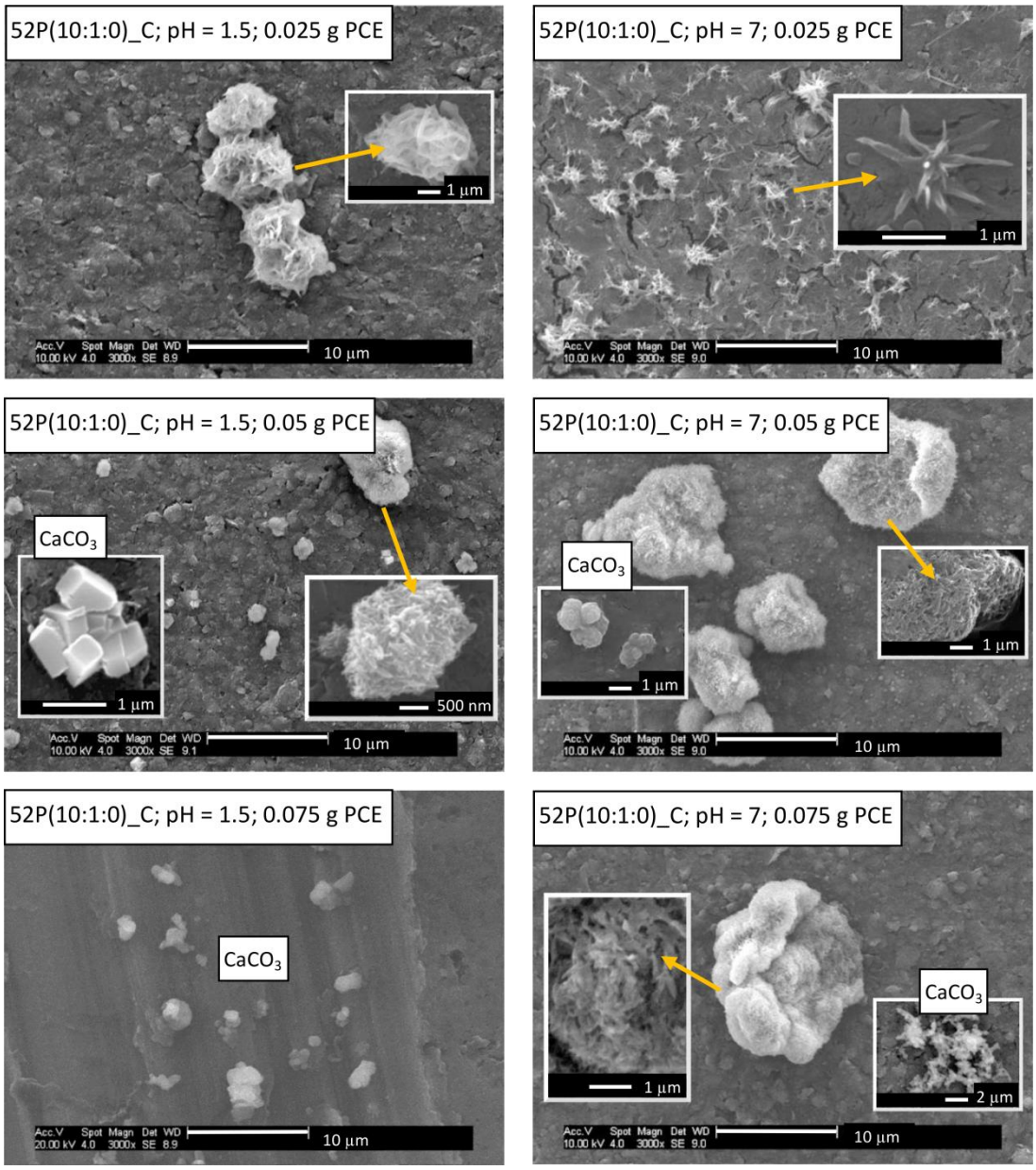


Figure 76. SEM images of ettringite crystals (needles) obtained from combined $Ca(OH)_2/Al_2(SO_4)_3$ solutions after 24 hours of crystallization in the presence of 52P(10:1:0)_C with pH = 1.5 or 7 and different dosages.

For 52P(10:1:0)_C and 50HP(10:1:0)_C, significantly smaller needles were formed (~ 1/10), as can be seen in **Figures 76** and **77**. Needles could still be identified at low PCE dosages. However, with an increasing PCE amount, they were extremely small and agglomerated more strongly into clusters. Furthermore, the Ca^{2+} salts (presumably $CaCO_3$) were found already at lower PCE dosages (0.05 g) than was the case for the APEG PCE (0.075 g). Only $CaCO_3$ was observed in the samples in which no precipitate was obtained (acidic 52P(10:1:0)_C with 0.075 g and 50HP(10:1:0)_C with 0.05 g or 0.075 g).

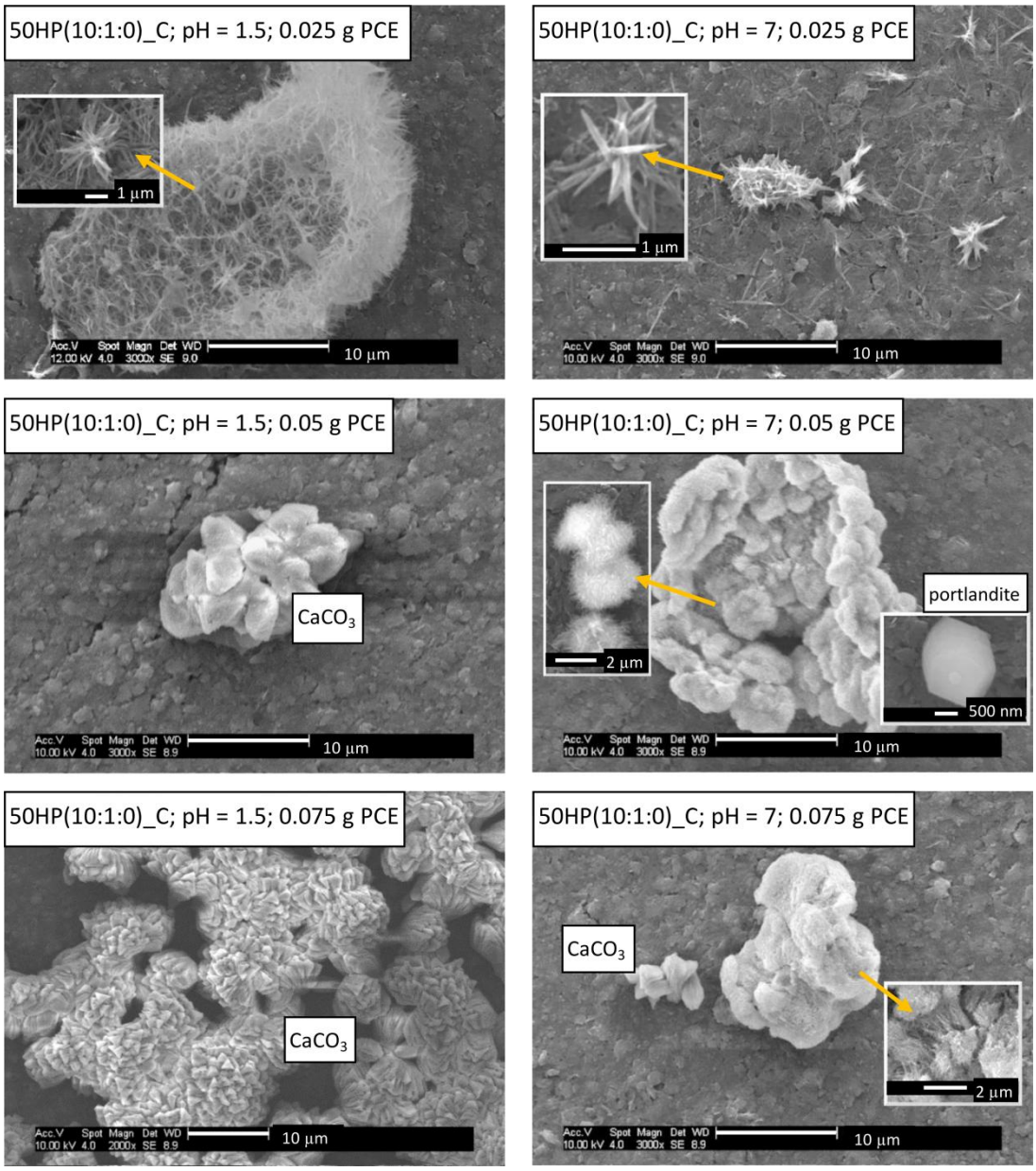


Figure 77. SEM images of ettringite crystals (needles) obtained from combined $Ca(OH)_2/Al_2(SO_4)_3$ solutions after 24 hours of crystallization in the presence of 50HP(10:1:0)_C with pH = 1.5 or 7 and different dosages.

Table 33 gives an overview of the crystals observed in each sample. Apparently, an increasing amount of PCE in the system led to lower amounts of ettringite crystals and therefore to a higher amount of Ca^{2+} salts in acetone.

Table 33. Composition of precipitated crystals in the presence of PCEs.

Dosage of PCE	34AP(1:1:0)_C		52P(10:1:0)_C		50HP(10:1:0)_C	
	pH = 1.5	pH = 7	pH = 1.5	pH = 7	pH = 1.5	pH = 7
0.025 g PCE	ettringite	ettringite	ettringite	ettringite	ettringite	ettringite
0.05 g PCE	ettringite	ettringite	ettringite + $CaCO_3$	ettringite + $CaCO_3$	no ettringite formed	ettringite + $CaCO_3$
0.075 g PCE	ettringite + $CaCO_3$	ettringite + $CaCO_3$	no ettringite formed	ettringite + $CaCO_3$	no ettringite formed	ettringite + $CaCO_3$

5.5.5.2.4 Size of the precipitated ettringite crystals

DLS and SEM measurements were applied to determine the size of the ettringite crystals (see **Sections 4.2.9** and **4.2.10**). The values obtained in these measurements are listed in **Table 34**.

Table 34. Particle size [nm] of the precipitates formed in the presence of PCEs with pH = 1.5 or 7 and at different dosages. For SEM, the upper number indicates the length and the lower number the width of the ettringite needle.

Dosage of PCE	Method	Particle size [nm]					
		34AP(1:1:0)_C		52P(10:1:0)_C		50HP(10:1:0)_C	
		pH = 1.5	pH = 7	pH = 1.5	pH = 7	pH = 1.5	pH = 7
0.025 g PCE	DLS	1,103 ± 54	1,651 ± 85	256 ± 27	540 ± 2	204 ± 35	504 ± 47
	SEM	10,179 ± 2,918 335 ± 130	10,088 ± 4,654 324 ± 115	881 ± 394 141 ± 34	899 ± 378 150 ± 69	1,314 ± 414 127 ± 40	1,107 ± 456 239 ± 136
0.05 g PCE	DLS	902 ± 82	1,131 ± 76	161 ± 8	239 ± 21	8 ± 1	174 ± 9
	SEM	5,437 ± 2,196 221± 73	6,577 ± 2,384 273 ± 89	667 ± 427 104 ± 34	479 ± 153 94 ± 31	no ettringite formed	400 ± 176 69 ± 20
0.075 g PCE	DLS	742 ± 36	895 ± 39	59 ± 19	87 ± 23	10 ± 0	131 ± 16
	SEM	3,208 ± 1,245 164 ± 70	5,144 ± 2,249 203 ± 66	no ettringite formed	433 ± 94 111 ± 33	no ettringite formed	389 ± 142 83 ± 16

Remarkable was the big difference between the obtained absolute values depending on the method. For DLS, they were significantly smaller than for SEM which might be attributable to two factors: while DLS measurements are based on the model of ideal spherical particles, the needle shape of the ettringite crystals can be taken into account in the SEM analysis. Furthermore, both ettringite and $CaCO_3$ crystals were detected in the DLS measurements, while only ettringite crystals were evaluated in the SEM images. However, both methods showed that with an increasing PCE amount in the system, the precipitated ettringite crystals became smaller. It was additionally striking that the ettringite

crystals were much larger in presence of the APEG PCE (meso-sized, up to 10,000 nm) than they were for the IPEG and HPEG PCE (nano sized, ≤ 1,300 nm). The size of the reference particles (w/o PCE) was 12,786 ± 6,689 nm. This confirmed that both strongly anionic PCEs were much more efficient “modifying agents” than the weakly negative APEG PCE. According to DLS measurements, acidic PCEs led to the formation of smaller crystals than neutral PCEs. In SEM analysis, this could only be observed when using APEG PCE, but not for the IPEG or HPEG PCEs. Since the particle size was so small in the latter case, inaccuracies did not allow the observation of the effect.

To determine the degree of the “modifying agent” of each PCE tested, the aspect ratios (length/width) of the ettringite crystals formed were calculated and are presented in **Figure 78**. As expected, the APEG PCE had the lowest influence on the ratio, while the IPEG and HPEG PCEs caused a large reduction. No differences were observed between acidic or neutralized PCE solutions. However, with an increasing PCE amount in the system, the aspect ratio decreased. No ratio was specified for samples in which no ettringite crystals were precipitated.

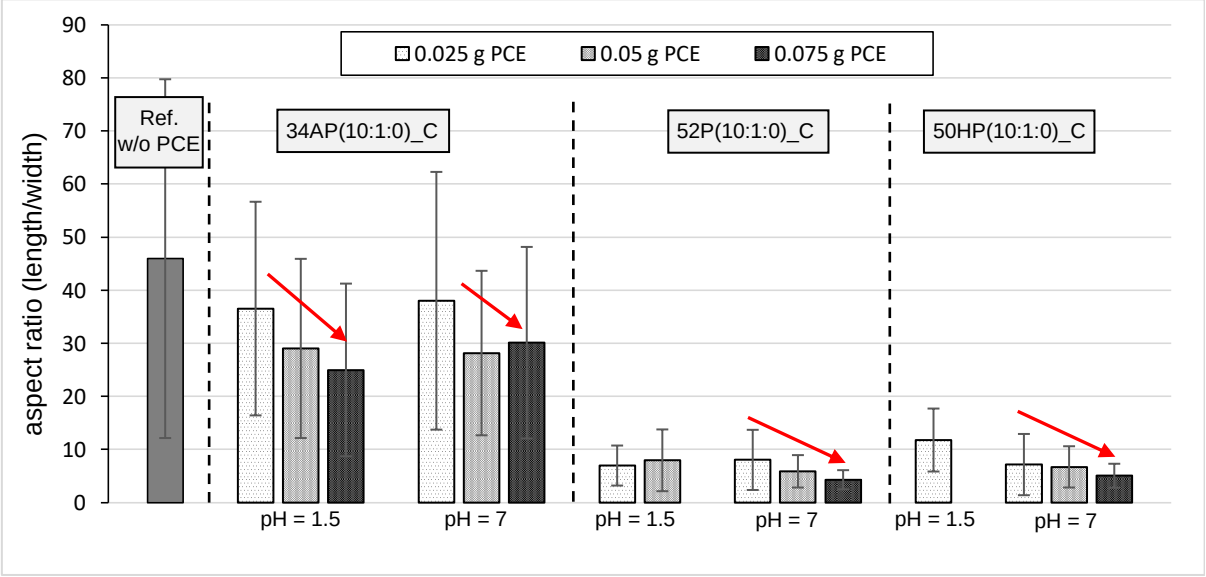


Figure 78. Aspect ratio of ettringite crystals obtained from combined $Ca(OH)_2/Al_2(SO_4)_3$ solutions after 24 hours of crystallization in the presence of various PCEs with pH = 1.5 or 7 and different dosages, as determined by means of SEM imaging.

5.5.5.3 Influence of the pH value of the PCE solution on the cement paste

To confirm that nano ettringite was formed in different amounts in the presence of acidic or neutralized PCE solutions in an actual system like cement paste, tests were performed to extract the ettringite from the cement slurry. According to Lange's method [53], nano ettringite was separated as a white, gel-like top layer when centrifuging "mini slump" pastes including PCE. Therefore, "mini slump" pastes were prepared with the respective PCE dosage required to reach 26 cm spread flow. To determine the dependence on the cement composition, tests were performed involving the same three cements which were already used for dispersing effectiveness tests (CEM I 52.5 R and 42.5 R as well as API Class G cement). The results obtained are shown in **Figures 79** - **81**.

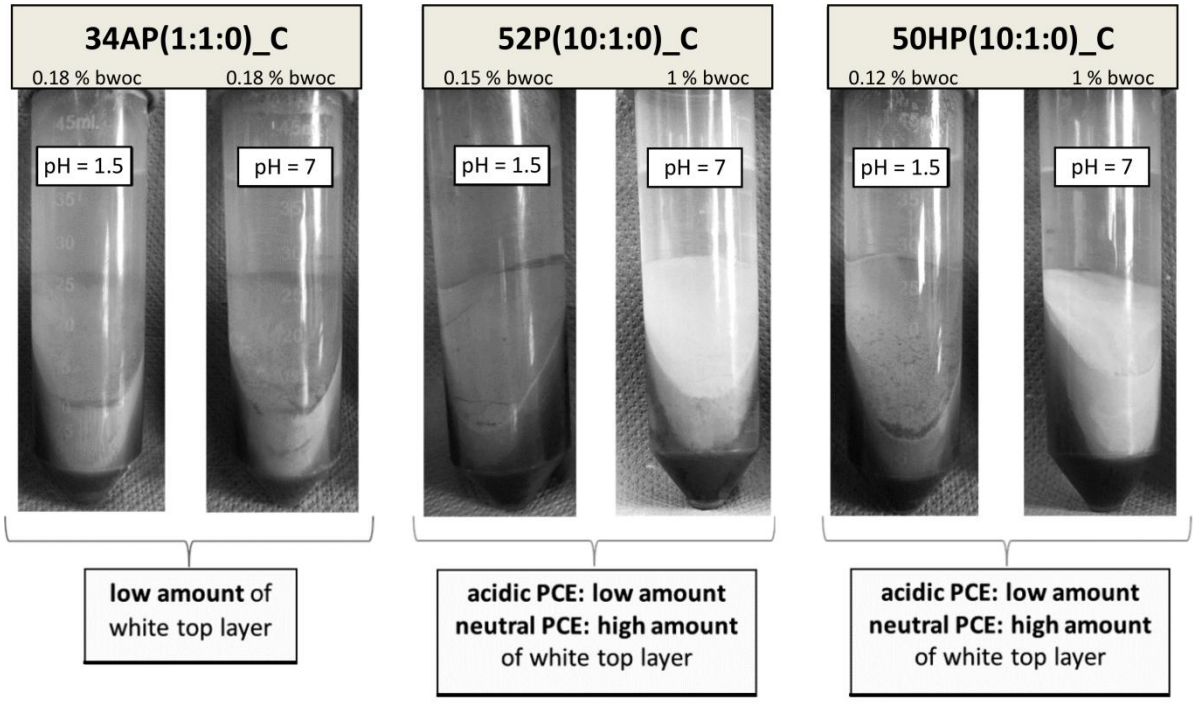


Figure 79. Comparison of the amounts of ettringite gel deposited as top layer after the centrifugation of the cement paste (CEM I 42.5 R, w/c ratio = 0.5) in the presence of PCE (dosage for 26 cm spread flow).

In accordance with the tests performed with synthetic ettringite (see **Section 5.5.5.2**), the neutralized polymers 52P(10:1:0)_C and 50HP(10:1:0)_C led to a significant amount of nano ettringite (white top layer) in CEM I 42.5 R and 52.5 R (see **Figures 79** and **80**), while the acidic counterparts as well as both samples (pH =1.5 and 7) of 34AP(1:1:0)_C led to no or only a thin white layer in these cements.

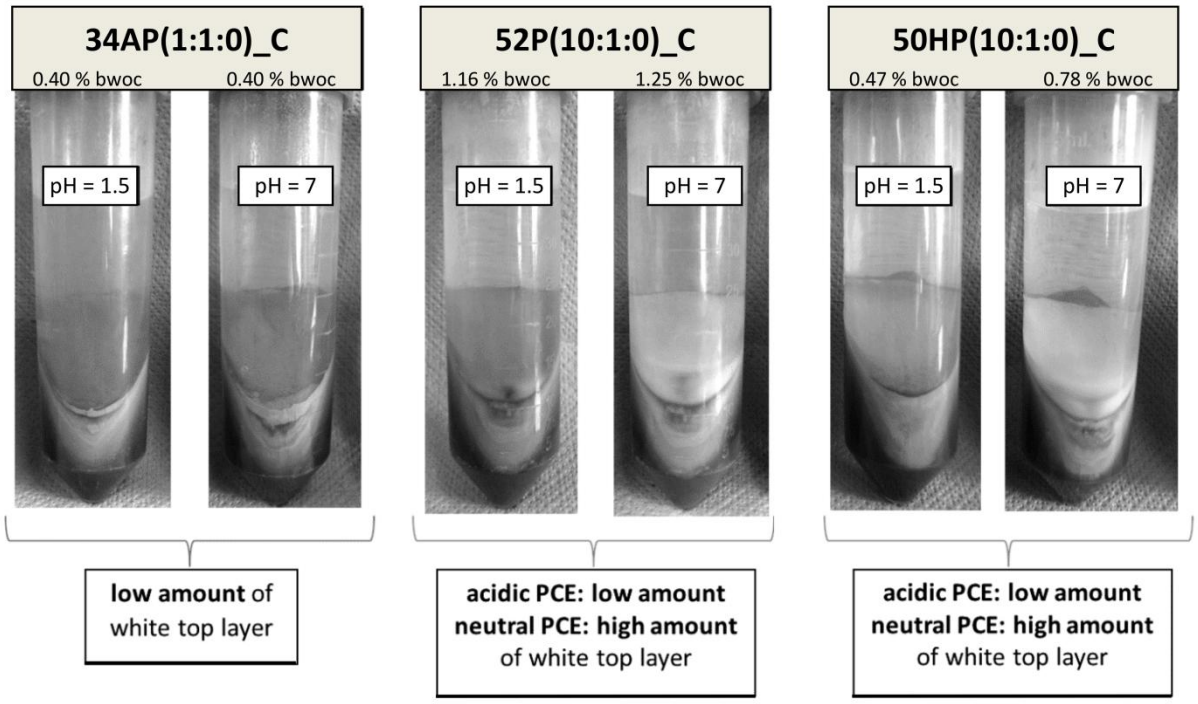


Figure 80. Comparison of the amounts of ettringite gel deposited as top layer after the centrifugation of the cement paste (CEM I 52.5 R, w/c ratio = 0.35) in the presence of PCE (dosage for 26 cm spread flow).

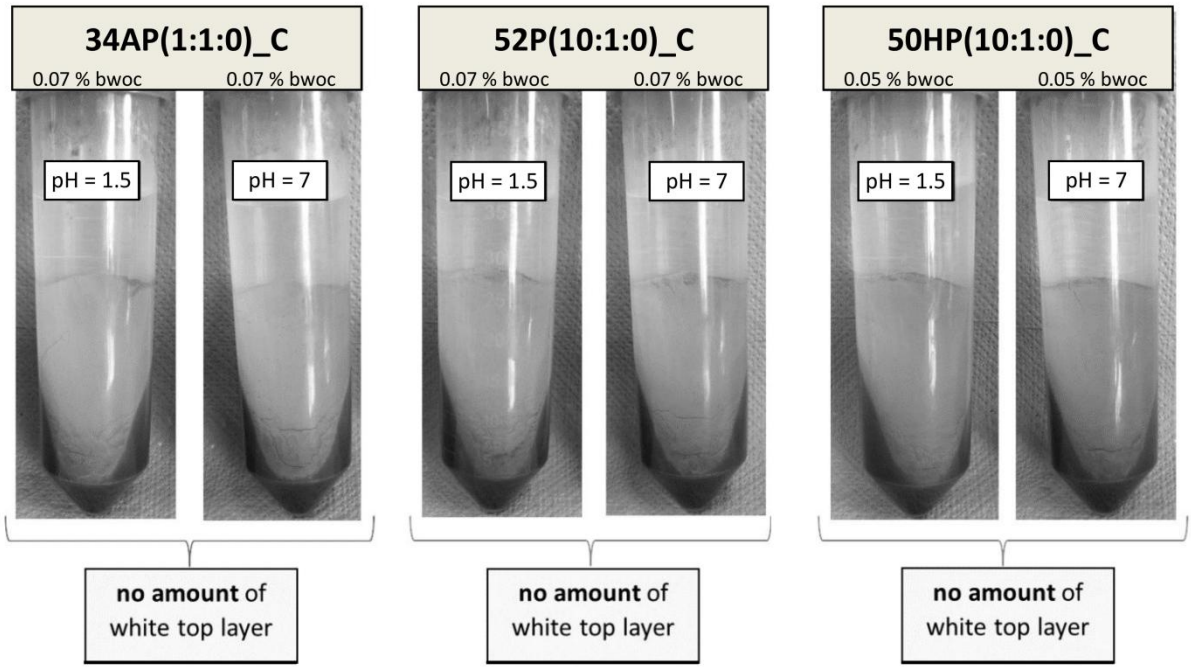


Figure 81. Comparison of the amounts of ettringite gel deposited as top layer after the centrifugation of the cement paste (API Class G cement, w/c ratio = 0.4) in the presence of PCE (dosage for 26 cm spread flow).

Contrary to the results obtained for CEM I 42.5 R and 52.5 R, no white top layer could be extracted for any of the samples when using API Class G cement (see **Figure 81**).

To summarize, there is a direct relation between the amounts of nano ettringite formed in the ettringite gel tests and the dispersing effectiveness of each acidic or neutralized PCE in the “mini slump” tests (see **Section 5.5.3.1**): The dispersing strength of the PCE was lower when more nano ettringite had formed. The reason for this behavior might be the larger surface areas of the nano ettringite, for which additional amounts (a higher dosage) of PCEs are required to saturate them and thus prevent agglomeration.

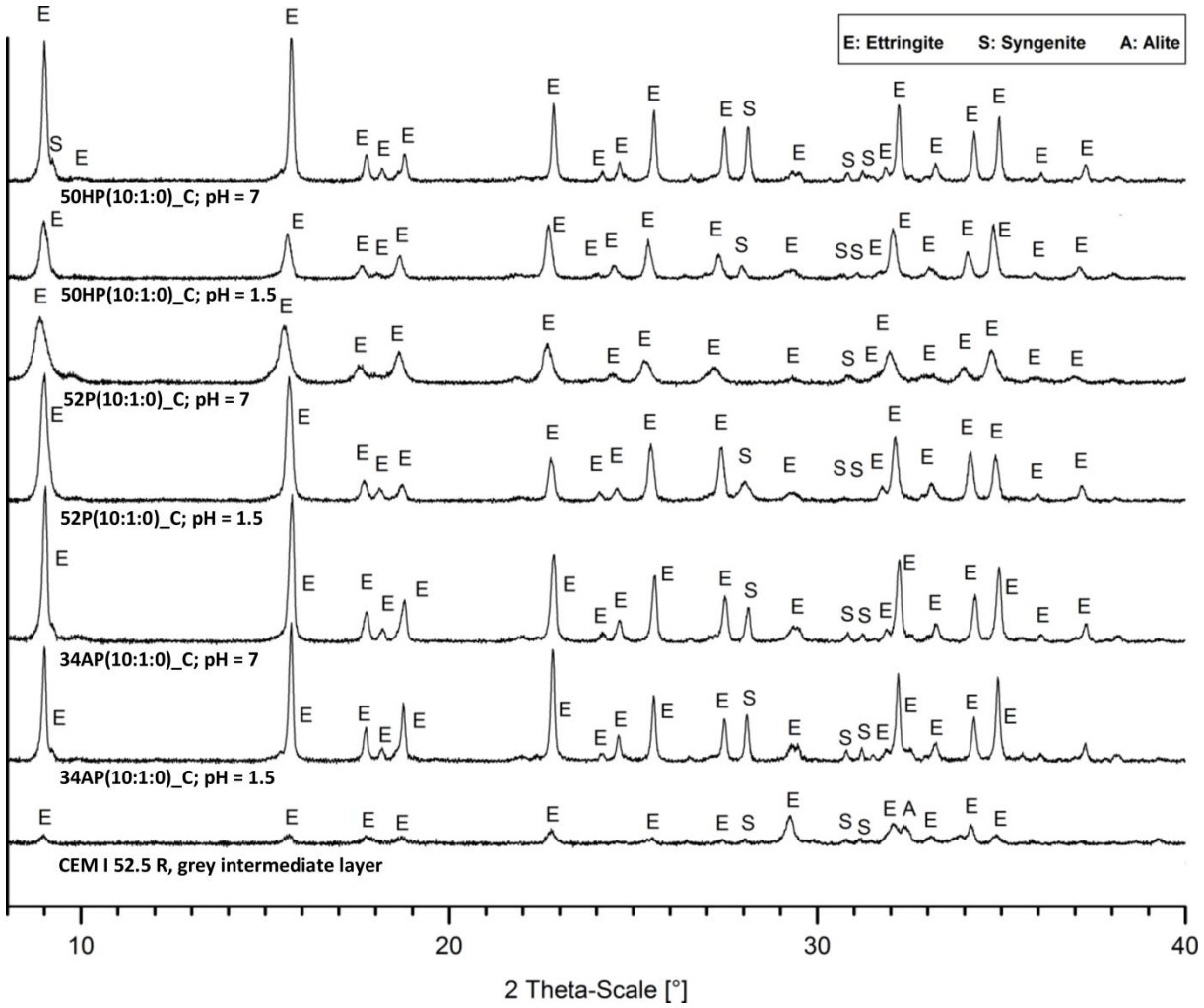


Figure 82. X-ray diffractograms of the white top layer of centrifuged cement pastes (CEM I 52.5 R, w/c ratio = 0.35) containing 34AP(1:1:0)_C, 52P(10:1:0)_C, and 50HP(10:1:0)_C with pH = 1.5 or 7 at the dosage to reach a spread flow of 26 cm and of the grey intermediate layer.

According to XRD analysis (see **Figure 82**), the white top layer extracted in the tests consisted of ettringite including small impurities of syngenite. Additionaly, a grey layer was formed for each sample between the dark cement paste and, if present, the white ettringite layer. This was a mixture of ettringite and alite.

5.5.5.4 Influence of the pH value of the PCE on the adsorption behavior on cement

In **Section 5.5.5.2**, it was clarified that acidic PCE solutions influenced the ettringite formation to a higher extent than their neutralized counterpart. Therefore, the amount of nano ettringite crystals which were formed in the presence of the acidic PCE solution was smaller than in the case of the neutralized polymer. For the neutralized PCE solution, this resulted in a higher amount of nano ettringite crystals formed and therefore in more surface area, which in turn should lead to a higher adsorption of the superplasticizer. To confirm this assumption, adsorption measurements according to the standard and a short-time (s.t.) procedure were carried out in a CEM I 52.5 R with a w/c ratio of 0.35. The values determined are presented in **Figures 83** - **85**.

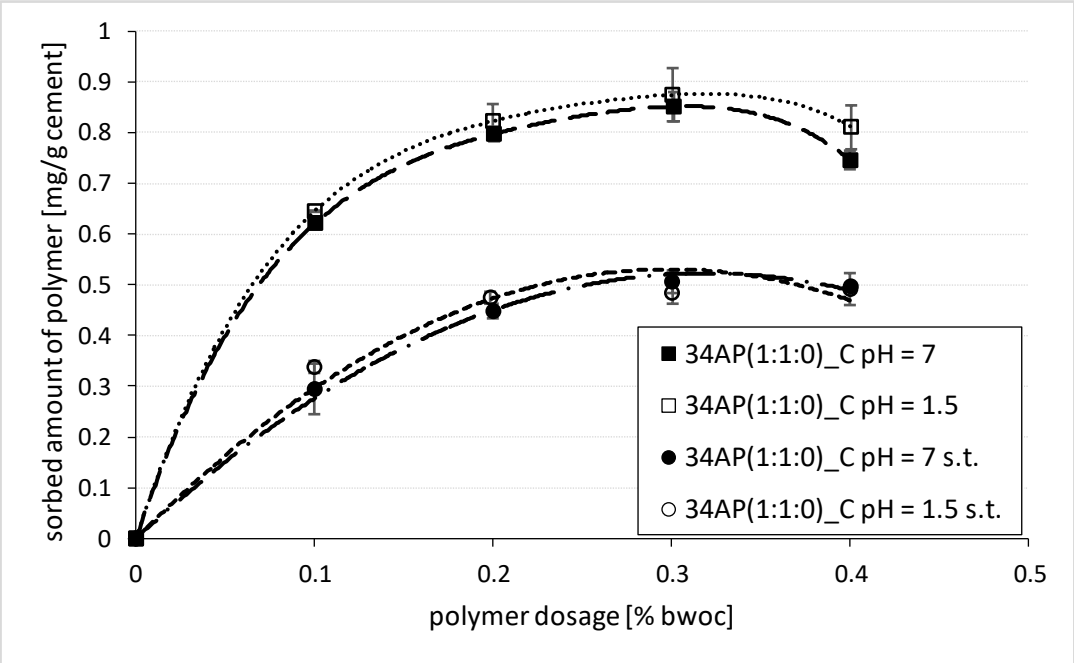


Figure 83. Sorption isotherms for 34AP(1:1:0)_C on CEM I 52.5 R at w/c = 0.35 according to the standard method and the short-time method (s.t.).

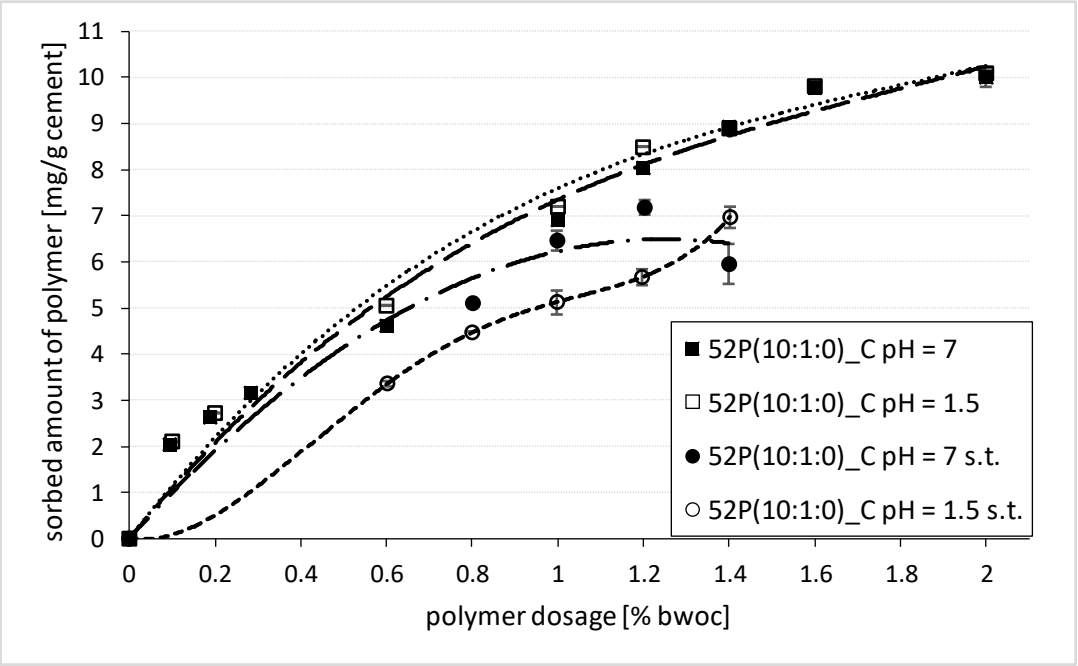


Figure 84. Sorption isotherms for 52P(10:1:0)_C on CEM I 52.5 R at w/c = 0.35 according to the standard method and the short-time method (s.t.).

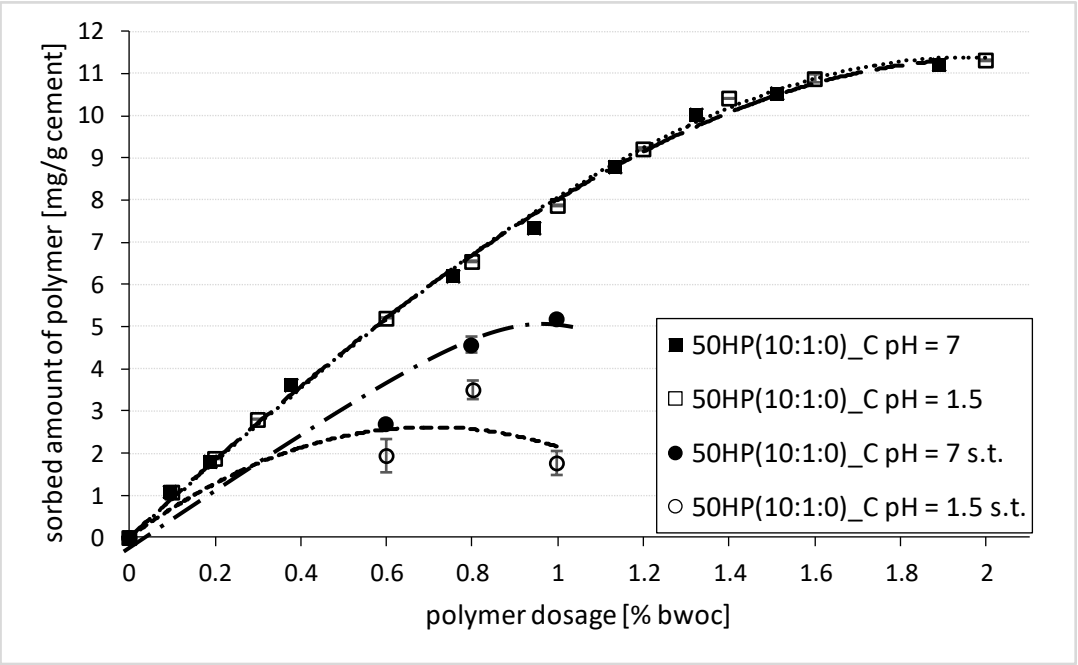


Figure 85. Sorption isotherms for 50HP(10:1:0)_C on CEM I 52.5 R at w/c = 0.35 according to the standard method and the short-time method (s.t.).

When performing tests using the standard procedure, no difference in the adsorption amounts for acidic or neutralized PCE solutions was observed. As expected, the strongly anionic PCEs (52P(10:1:0)_C and 50HP(10:1:0)_C) showed a much higher maximum adsorption amount (~ 10 mg/g cement) than the weakly negative APEG PCE (~ 0.9 mg/g cement). To evaluate only the early cement hydration products by means of the measurement, an adapted procedure with less time delay was used. In this short time (s.t.) preparation method, only 20 seconds instead of 2 minutes of mixing were employed. As a result, the adsorption amounts for all tested PCE solutions were lower than in the standard procedure which was expected. Moreover, a higher adsorption for neutralized IPEG and HPEG PCEs than for the acidic solutions was determined as was again expected. However, for 34AP(1:1:0)_C, this was not the case. This was not surprising due to the minor influence of this PCE on ettringite formation (see **Section 5.5.5.3**) and its slow and low adsorption rate as well as the large meso-sized ettringite crystals (= no increased surface area).

These measurements proved that higher amounts of nano ettringite formed in the presence of strongly anionic neutralized PCEs also lead to a higher adsorbed amount of these PCEs due to increased adsorption surfaces. This results in a higher PCE consumption and therefore an increased dosage is required for the same dispersing effect than is obtained for the acidic PCE. Whenever the same amount of ettringite was formed (for weakly anionic PCEs or in API Class G cement), the same amount of neutralized and acidic PCE was required to achieve the same dispersing effect.

5.5.6 Summary of Section 5.5

This research aimed at studying the pH-dependent (pH = 1.5 or 7) dispersing effectiveness of anionic PCE superplasticizers. To clarify for which kinds of PCE a different dispersing effectiveness occurred, “mini slump” tests were performed with a 34APEG PCE (1 mol of maleic anhydride and 1 mol of 34APEG) as well as with 52IPEG and 50HPEG PCEs with 2, 6, or 10 mol of acrylic acid and 1 mol of macromonomer. In cements with high C_3A_o / SO_4^{2-} ratios (CEM I 42.5 R and 52.5 R), especially the acidic strongly anionic PCEs (52P(10:1:0)_C, 50HP(10:1:0)_C) required lower dosages than their neutralized counterparts to reach a spread flow of 26 cm. Meanwhile, no difference was found for the weakly anionic 34APEG PCE. Moreover, 50HPEG PCE showed a stronger influence on the dispersing strength than 52IPEG PCE regarding the pH value.

However, when adding the PCE solution to the “mini slump” tests at a delayed point of time, no difference in the dispersing ability was observed between the acidic or neutralized PCE any more. Therefore, interactions of the PCE solutions with the early cement hydration processes such as the ettringite formation were believed to be responsible for the pH-dependent dispersing performance. This hypothesis could be verified by precipitating synthetic ettringite in absence and presence of 34AP(1:1:0)_C, 52P(10:1:0)_C, and 50HP(10:1:0)_C PCE solutions (pH = 1.5 and 7) to evaluate the impact of the superplasticizers on the ettringite formation. It was found that all PCEs led to a delayed ettringite precipitation, which was stronger with increasing PCE dosages. Additionally, the acidic PCE caused a greater delay than the neutralized counterpart, which led to smaller ettringite amounts. Furthermore, the strongly anionic PCEs (52P(10:1:0)_C, 50HP(10:1:0)_C) had a stronger impact and further delayed precipitation or even completely prevented it. The extraction of nano ettringite from cement pastes confirmed these findings. When strongly acidic anionic PCEs were present, almost no nano ettringite was formed, while crystals were observed for the neutralized counterparts. Independent of the pH value of the PCE solution, rarely any nano ettringite was obtained for 34APEG.

SEM images of the precipitated synthetic ettringite needles revealed that the strongly anionic PCEs reduced the crystal size extremely from the µm to nm range, while the weakly anionic 34APEG PCE hardly influenced the crystal size.

The performance of short-time adsorption measurements for acidic and neutralized PCEs on cement paste indicated that the neutralized strongly anionic PCEs adsorbed more strongly than their acidic counterparts. This confirmed the different amounts of nano ettringite previously found in the extraction tests because a larger amount of nano ettringite possesses more surface area for PCE adsorption. For the 34APEG PCE, the same adsorbed amounts were determined, which also verified the results when extracting nano ettringite from cement paste.

To summarize, strongly acidic anionic PCEs delayed the early ettringite formation in cement paste to a higher extent than their neutralized counterpart which resulted in a larger quantity of nano ettringite for the neutralized PCE. This was not the case for weakly anionic PCEs as their influence on early ettringite formation was significantly lower. However, high amounts of nano ettringite resulted in additional surfaces which can agglomerate as well as create further adsorption sites for PCE molecules. Therefore, higher dosages of neutralized strongly anionic PCEs were necessary to obtain the same spread flow as for the acidic PCE.

6 Summary and outlook

This research work aimed at studying the influence of variations in the synthesis process of anionic and zwitterionic isoprenol ether-based polycarboxylate superplasticizers (IPEG PCEs) on their composition as well as on their dispersing performance in cement. All syntheses were exclusively based on the “free radical copolymerization” process. For the well-established standard procedure, the initiator was ammonium persulfate while for the modified procedures, a redox initiator system consisting of an Fe(II)-salt, Rongalit® and H_2O_2 was used. Changes in the synthesis methods were accomplished by varying the addition process of the monomers or parts of the initiator system during the polymerization. Therefore, a very uncontrolled, easy, and short-time synthesis method (M1) was established for stricty anionic and zwitterionic PCEs as well as a slightly more controlled method (M2) for zwitterionic PCEs.

It was observed that all synthesis methods initiated with the redox system led to polymer mixtures which had several polymer fractions of different molecular weights. This occurred for all polymerization methods tested, independent of whether a cationic monomer (TMAEMC) was additionally used or how the monomers and the initiator were added to the reaction. In contrast, the conventional industrial synthesis method of PCEs produced only one main polymer fraction. This reveals that the polymer composition is strongly determined by the synthesis method chosen.

The dispersing effectiveness of the superplasticizers obtained was screened via “mini slump” tests. Here, all synthesized PCEs with a molar ratio of acrylic acid:macromonomer = 4.5:1 required the lowest dosage to reach a spread flow of 26 cm. Except for the polymers from the “M2” synthesis method which had significantly higher molecular weights, very similar dispersing abilities were found for the conventional PCEs and the strictly anionic or zwitterionic multi-component PCEs (“M1”). Therefore, it was proved that PCEs consisting of several polymer fractions do not necessarily show a reduced dispersing strength. As a consequence, the synthesis method “M1” is a suitable alternative to the conventional synthesis as it requires a much shorter synthesis time and a lower reaction temperature (30 °C).

In the **second part** of this thesis (**Sections 5.2** and **5.3**), some of the synthesized PCEs were further investigated. The PCEs which showed the best dispersing effectiveness in cement for each synthesis process (molar ratio of acrylic acid : macromonomer = 4.5:1) were chosen for tests to determine the clay and sulfate tolerance. In addition to the synthesis methods “M1” and “M2”, two more processes were established. The so-called “5M” method, an even shorter (5 minutes) and faster method concerning the polymerization process than “M1” (15 minutes) was developed for anionic PCEs, and a more controlled, two-step polymerization (“M3”) was applied for zwitterionic PCEs in which the macromonomer and the cationic monomer were polymerized first, followed by polymerization of the obtained reaction mixture and acrylic acid.

Measuring the anionic charge amount of the PCEs proved successful polymer formation. Lower anionic charge amounts in deionized water for all zwitterionic superplasticizers revealed the formation of the cationic polymer. The zwitterionic “M2” and “M3” polymers displayed a lower reduction of the anionic charge when measuring in a synthetic cement pore solution compared to the other PCEs which indicates the different properties of these PCEs.

The determination of the dosage-dependent dispersing effectiveness in cement paste (CEM I 52.5 R, w/c ratio = 0.62) suggested that the strictly anionic PCE “5M” outperforms the anionic and zwitterionic “M1” polymer samples as well as the conventional reference polymer. The necessary dialysis in the “5M” synthesis process may greatly benefit the resulting polymer, however no data were generated for the polymer solution as obtained (= without dialysis). Also, the zwitterionic “M2” and “M3” polymers are clearly outperformed by all other superplasticizers regarding their dispersing ability.

Moreover, it was observed that the dispersing performance of the zwitterionic “M2” and “M3” polymers were least affected by the presence of montmorillonite clay. Tests using the same PCE dosage for all superplasticizers confirmed that this property was not simply due to the higher dosages required for these PCEs, but based on their polymer mixture composition.

Sulfate ions had the least negative effect on the dispersing performance of the “5M” polymer. Here, even a slight improvement in the presence of 1 % bwoc Na_2SO_4 was observed. The strictly anionic and zwitterionic polymer samples prepared by method “M1” showed only a slight decrease in their dispersing performance when Na_2SO_4 was present and easily outperformed the conventional and the zwitterionic “M2” PCEs.

Table 35 displays all PCEs tested and their characteristic properties.

Table 35. Characteristic properties of the PCEs tested.

Polymer solution	Synthesis process (Reaction time)	Initiator system	Charge character	Advantage
P(4.5:1:0)_C	Conventional (3 h + 2 h)	APS	anionic	---
P(4.5:1:0)_5M	5 minute PCE (5 min)*	redox	anionic	Sulfate tolerance up to ~ 2 % bwoc Na_2SO_4
P(4.5:1:0)	Method M1 (15 min + 1h)	redox	anionic	Sulfate tolerance up to ~ 1 % bwoc Na_2SO_4
P(4.5:1:1)_M1	Method M1 (15 min + 1 h)	redox	zwitterionic	Sulfate tolerance up to ~ 1 % bwoc Na_2SO_4
P(4.5:1:1)_M2	Method M2 (1 h + 1 h)	redox	zwitterionic	Best clay tolerance
P(4.5:1:1)_M3	Method M3 (2x15 min + 2x 1 h)	redox	zwitterionic	Best clay tolerance

*additional reaction termination and dialysis required

The quintessence of these tests can be formulated as follows. The properties of a PCE strongly depend on the synthesis method and therefore also on its polymer composition. It cannot easily be predicted which PCE composition leads to which property as is shown by the following example: Generally, PCE polymers with cationic portions (“M2” and “M3” synthesis method) appeared more clay tolerant than strictly anionic PCEs. However, this was not the case for the zwitterionic “M1” polymer which therefore does not allow for a generalized statement such as “zwitterionic PCEs are more tolerant against clay than anionic PCEs”.

From the results obtained, the following generalizations can be made:

1. The amount of its main polymer fraction is not decisive for the dispersing effectiveness of a PCE superplasticizer.
2. In this study, the molecular weight of the polymer fraction(s) of a PCE superplasticizer does not necessarily play a role on its dispersing performance.
3. The cationic monomer TMAEMC does not guarantee clay tolerance of the PCE superplasticizer.
4. The same synthesis method for an anionic and zwitterionic polymer samples led to PCEs with similar properties.

The **third part** of this dissertation (**Section 5.4**) focused on the “5M” synthesis method for anionic PCEs due to its short polymerization process (5 minutes) and because it leads to PCE polymers with an excellent dispersing performance. To capture the impact of the reaction time on the dispersing performance and the properties of these PCEs, additionally superplasticizers with a polymerization time of 30 minutes were prepared (“30M”), with the “5M” synthesis method being identical to the first 5 minutes of the “30M” synthesis. Therefore, the “5M” process can be understood as an interrupted “30M” process. Two different side chain lengths (23 and 52 ethylene glycol units) of isoprenol ether-based polycarboxylate superplasticizers (IPEG PCEs) were utilized for each synthesis method while the molar ratio of acrylic acid : macromonomer always remained at 2:1.

Following the polymer formation over time by means of SEC measurements showed that the polymerization process for the “5M” and “30M” PCEs started almost immediately when adding the redox initiator to the reaction mixture, while the synthesis of the conventional PCEs was delayed for about 10 to 20 minutes when adding ammonium persulfate. As discussed in **Section 5.1** of this thesis, only one main polymer fraction occurred for the conventional PCEs, while mixtures of different polymers were formed after ~ 5 minutes reaction time in the “30M” method. This ensured a relatively uniform polymer for the “5M” synthesis method because its polymerization process was interrupted before several different fractions have been formed. Independent of the initiator system used, polymerization stopped whenever no further initiator was added to the reaction mixture, which makes stirring after this process unnecessary with respect to macromonomer conversion. However, further investigations would be interesting on whether side effects occur such as the continued presence of reactive initiator molecules when subsequent stirring is omitted, and the resulting consequences for the PCE quality.

“Mini slump” tests showed that “30M” and “5M” PCEs required significantly lower dosages than the conventional PCEs at low w/c values of 0.45 or 0.30 to reach a spread flow of 26 cm in cement paste. Extended slump flow for these PCEs was achieved when using a constant superplasticizer dosage of 0.50 % bwoc at a w/c ratio of 0.3. Furthermore, the PCEs with 23 EO units required a 0.02 - 0.05 % bwoc lower dosage to reach the same spread flow than the PCEs with 52 EO units. In mortar, no difference in the dispersing performance was observed between the conventional and the PCEs made via short-time processes. When testing the dispersing performance in mortar over time, a slightly improved dispersing effect was however observed for the “5M” and “30M” PCEs directly after the

mixing procedure, but the dispersing performance decreased faster than for the conventional PCEs. In general, a very poor slump retaining behavior (almost none) in mortar was identified for all superplasticizers. Here, tests in concrete would be helpful to determine the retaining behavior in a realistic system in order to characterize them further. Moreover, surprisingly, the superplasticizers possessing shorter side chains lost their dispersing performance over time slightly faster than those with longer side chains.

In this section, the clay tolerance in cement paste strongly depended on the side chain length of the macromonomer and not on the synthesis method of the superplasticizer – the PCEs with only 23 EO units were less clay-tolerant than those containing 52 EO units, especially at low w/c ratios of 0.45 or 0.30. In mortar however, these differences disappeared, but no PCE could be classified as best. In contrast to clay tolerance, the sulfate tolerance strongly depended on the synthesis method. Here, the “30M” and “5M” PCEs were more sulfate-tolerant in cement paste and in mortar than the conventional PCEs. Additionally, the 23IPEG PCEs showed a lower reduction in the dispersing performance than the 52IPEG PCEs.

The tests performed showed that by interrupting a rather uncontrolled “batch” polymerization at the proper time, a uniform polymer (“5M” PCEs), as is common for conventional PCEs, could be obtained. Its dispersing properties are very similar to those of the conventional PCEs and even outperform them in cements pastes mixed at low w/c values. Furthermore, the “5M” polymers exhibited an improved sulfate tolerance in mortar and cement paste. These properties as well as the short polymerization time (5 minutes) and the lower reaction temperature makes the “5M” PCEs quite interesting. The disadvantages of the “5M” PCEs are currently the necessary interruption of the polymerization process after 5 minutes and the required cooling and subsequent dialysis which are not easy to carry out for an industrial product. Therefore, further attempts should be made to terminate the reaction with the help of polymerization inhibitors.

Additionally, the following conclusions were drawn from the short-time synthesis studies on PCEs containing 2 mol of AA:

1. The macromonomer conversion for any synthesis method does not improve by stirring the polymer reaction mixture when the addition of the initiator has already been completed.
2. The polymerization process in the redox-initiated synthesis procedures immediately started when adding the initiator while the conventional (APS) synthesis started after a time delay.

3. The minor macromonomer conversion for the “5M” PCEs obtained when interrupting the polymerization process of the “30M” polymer solutions did not lead to a decreased, but to an increased dispersing performance, especially at low w/c values. However, this applies to the dialysed product “5M”.
4. Clay tolerance in cement and mortar is hardly influenced by the synthesis methods “5M”, “30M” or conventional “C”.
5. “5M” and “30M” PCEs were more sulphate tolerant than conventional PCEs with the same ratio of acrylic acid : macromonomer.

Figure 86 illustrates the relationships between the PCE superplasticizers tested in **Sections 5.1** to **5.4**.

As can be seen here, in the first section (5.1), the well-established conventional synthesis method "C" for anionic PCEs was used to develop the much more uncontrolled and shorter synthesis process "M1" for anionic and zwitterionic PCEs. This resulted in the synthesis method "M2" for zwitterionic PCEs which was further modified in the second section (5.2) to the synthesis process "M3". In addition, the synthesis method "M1" for anionic PCEs was further shortened in the second section (5.2), which led to the "5M" synthesis while in the third section (5.4), the reaction time of the "M1" method was increased resulting in the "30M" method.

While the first section (5.1) focused on the composition of the PCEs depending on their synthesis method and the amount of AA contained in the PCE, the second section (5.2 and 5.3) examined the dispersing performance of PCEs in more detail. Since all polymers showed the best dispersing effect regardless of their synthesis method with 4.5 mol of AA and 1 mol of MM, they were used for further tests (clay and sulfate tolerance). Due to the good dispersing effectiveness of the "5M" PCEs, these superplasticizers were examined in more detail in the third section (5.4). For this purpose, the formation of polymer fractions during the synthesis process was tracked via SEC measurements and the clay and sulfate tolerance was proven in cement and mortar.

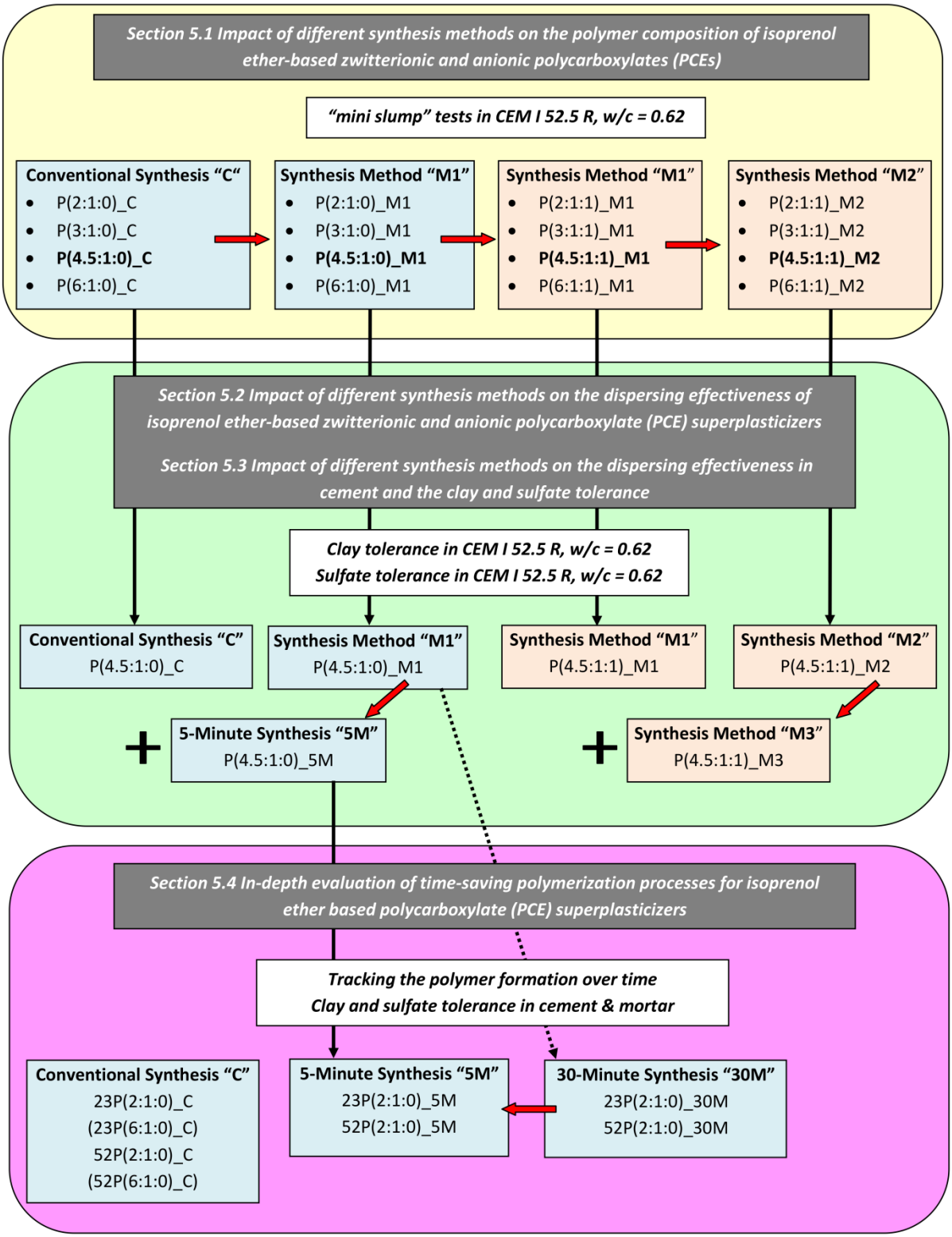


Figure 86. Overview of the synthesis methods used and the relationships between the synthesized PCEs in **Sections 5.1** to **5.4**.

In the **last part** of this thesis (**Section 5.5**), the influence of the pH value of a superplasticizer solution on its dispersing performance in cement was investigated. Therefore, “mini slump” tests for APEG, IPEG, and HPEG PCE solutions with a pH value of 1.5 and 7.0 were performed in order to determine the differences. In the standard cement (CEM I 52.5 R), no difference was found for the APEG PCE, while for strongly anionic 52IPEG and 50HPEG PCEs (10 mol of acrylic acid), the acidic PCE solutions performed better than itheir neutralized counterpart. Especially in a cement with a high C_3A_o / SO_4^{2-} ratio of 1.17 (CEM I 42.5 R), the dispersing performances differed extremely, while for a cement with very low C_3A_o / SO_4^{2-} ratio of almost 0 (API Class G), the effect was not observed at all.

When using a time-delayed PCE addition in the “mini slump” tests with the standard cement, the acidic and neutralized PCEs showed the same dispersing performance. This implied that the effect was linked to processes occurring at very early cement hydration, possibly caused by different interactions between the PCE solutions (pH = 1.5 or 7.0) and ettringite formation.

Precipitation studies with synthetic ettringite in the presence of acidic and neutralized PCEs showed that acidic PCEs delayed ettringite formation to a greater extent than neutralized PCEs. Furthermore, only a minor amount of precipitated ettringite was found in the presence of acidic PCE solutions. Moreover, the strongly anionic IPEG and HPEG PCEs had a much greater impact on the system than the weakly anionic APEG PCE. Therefore, nano ettringite was formed instead of meso ettringite. SEM images of the precipitated ettringite needles confirmed these findings and allowed to determine the crystal size of the ettringite.

Centrifugation tests with cement paste prepared according to the “mini slump” tests allowed to extract nano ettringite which was present in the cement slurry. As already observed in the precipitation tests with synthetic ettringite, a lower amount of nano ettringite was formed than for the neutralized counterpart in the presence of the acidic PCE solution in CEM I 52.5 R and 42.5 R, respectively. For the acidic and neutralized APEG PCE, the same low amount of nano ettringite was obtained in both samples. However, in API Class G cement (very slow hydrating cement), no difference was observed for all samples. This supported the assumption that a different influence of acidic and neutralized PCE on the ettringite formation caused the different dispersing performances. Higher amounts of nano ettringite led to additional surfaces which have to be covered by more PCEs. Therefore, the adsorbed amount of neutralized polymer should be higher in cement pastes where ettringite is formed during the early hydration due to higher nano ettringite amounts than in presence of acidic PCE.

Therefore, the required dosage for neutralized PCEs to obtain the same spread flow as acidic PCEs should also be increased.

To prove this hypothesis, early adsorption measurements were conducted. As assumed, it was found that the neutralized strongly anionic IPEG and HPEG PCEs adsorb in higher amounts than their acidic counterparts. The weakly anionic APEG PCE adsorbs in acidic or neutralized form in the same amount which corresponds with the observations of equal dispersing performances for acidic and neutralized APEG PCEs.

To summarize, the following findings were made:

1. Differences in the dispersing effectiveness between acidic and neutralized PCE solutions only occur for strongly anionic PCEs (approximately ≥ 6 mol of acrylic acid).
2. The macromonomer also has an impact on the extent of the effect; in this study, the 50HPEG PCE showed a stronger effect than the 52IPEG PCE.
3. The origin for a differing dispersing effectiveness depending on the pH value of the PCE lies in the different extent of the influence of the acidic and neutralized PCE solution on early nano ettringite formation in cement paste; acidic PCE has a stronger impact than neutralized PCE.
4. During ettringite precipitation, strongly anionic PCEs change the morphology of ettringite crystals and lead to nano ettringite of decreasing aspect ratio whereas weakly anionic PCEs influence the precipitation of ettringite crystals much less (still meso size).
5. Compared to the neutralized PCE solution, the acidic PCE solution delays the precipitation of synthetic ettringite to a higher degree and reduces the amount formed more strongly.
6. A higher amount of nano ettringite which can be formed in the presence of neutralized PCE provides more positively charged surfaces which need to be covered by PCEs, thus resulting in higher amounts of adsorbed PCE for the same dispersing effect.

Theoretically, higher dispersing performances can be achieved by simply keeping the PCE solution of a strongly anionic PCE superplasticizer acidic. However, this represents a significant risk for users (pH ~ 1.5 - 3) and involves difficult storage conditions (high quality steel tanks) due to the low pH value and therefore are a reason for the industry to avoid this option. Besides, studies would be of interest which focus on the impact of differently formed amounts of nano ettringite for acidic and

neutralized PCE solutions in the early cement hydration. Does this difference also play a role for other additives or admixtures, and can these differences still be observed during late hydration processes?

Figure 87 shows the most important results obtained from the different research fields in this work.

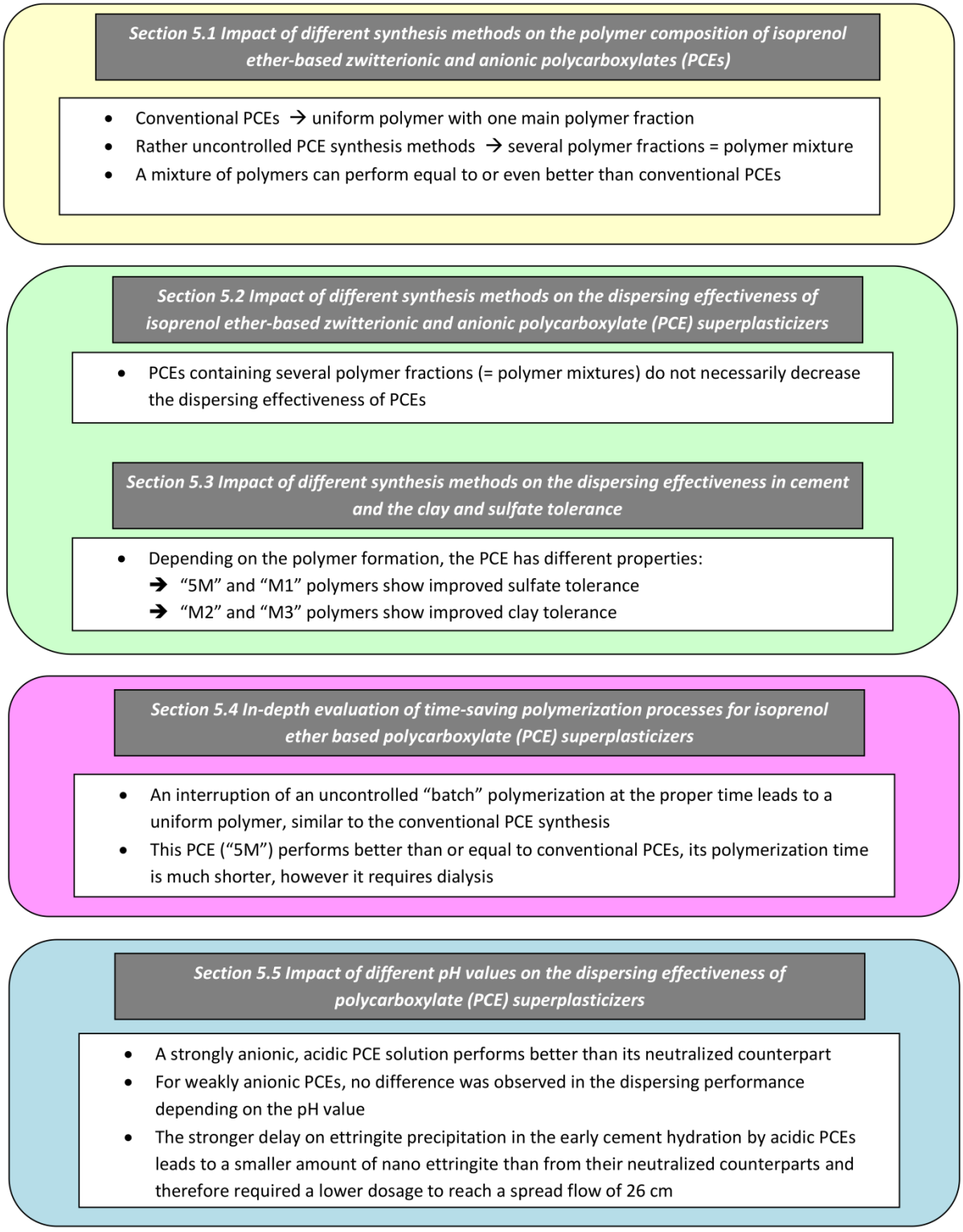


Figure 87. Overview of the most important results obtained in this thesis.

7 Zusammenfassung und Ausblick

Das Ziel dieser Arbeit war, den Einfluss von Veränderungen im Syntheseprozess von Isoprenolether-basierten Polycarboxylat-Fließmitteln (IPEG-PCEs) auf ihre Zusammensetzung sowie auf ihre Fließwirkung in Zement zu untersuchen. Dabei basierten alle Synthesen ausschließlich auf dem Mechanismus der „freien radikalischen Copolymerisation“, wobei für die herkömmliche Standardprozedur der Initiator Ammoniumpersulfat und für die abgeänderten Prozesse ein Redox-Initiatorsystem bestehend aus Fe(II)-Salz, Rongalit® und H_2O_2 verwendet wurden. Änderungen in den Synthesemethoden wurden durch Modifikationen des Zugabeprozesses von Monomeren oder Teilen des Initiatorsystems während der Reaktion umgesetzt. Dazu wurde eine sehr unkontrollierte, einfache und schnell durchführbare Synthesemethode („M1“) für rein anionische und zwitterionische PCEs sowie eine etwas stärker kontrollierte Synthese („M2“) für zwitterionische PCEs entwickelt.

Es konnte beobachtet werden, dass alle Synthesemethoden, die mit einem Redox-System initiiert wurden, zu Polymergemischen führten, welche mehrere Polymerfraktionen mit unterschiedlichen Molekulargewichten aufwiesen. Dies trat bei allen getesteten Polymerisationsmethoden auf, unabhängig davon, ob zusätzlich kationisches Monomer (TMAEMC) verwendet wurde oder wie die Monomere und der Initiator zur Reaktion zugegeben wurden. Im Gegensatz dazu entstand bei der konventionellen, industriellen Synthesemethode von PCEs nur eine Haupt-Polymerfraktion. Dies zeigt, dass die Polymerzusammensetzung stark von der gewählten Synthesemethode abhängt.

Die Dispergierwirkung der erhaltenen Fließmittel wurde mittels „Mini Slump“ Test geprüft. Alle synthetisierten PCEs mit einem molaren Verhältnis von Acrylsäure : Makromonomer = 4,5:1 benötigten die geringste Dosierung für ein Ausbreitmaß von 26 cm. Bis auf für das Polymer von Syntheseverfahren „M2“, welches ein deutlich höheres Molekulargewicht aufwies, wurden sehr ähnliche Dispergiereffekte für das konventionelle PCE im Vergleich zu den rein anionischen oder zwitterionischen Polymergemischen („M1“) gefunden. Damit konnte bewiesen werden, dass PCEs, welche aus mehreren Polymerfraktionen bestehen, nicht zwangsläufig eine geringere Dispergierwirkung aufweisen. Die Synthesemethode „M1“ stellt somit eine Alternative zur konventionellen Synthese dar, da hierfür eine deutlich geringere Synthesedauer und eine niedrigere Reaktionstemperatur (30 °C) benötigt werden.

Im zweiten Teil dieser Arbeit (**Kapitel 5.2** und **5.3**) wurden weitere Untersuchungen für einige der synthetisierten PCEs durchgeführt. Die PCEs mit der besten Dispergierwirkung in Zement eines jeden Syntheseprozesses (Molverhältnis von Acrylsäure : Makromonomer = 4,5:1) wurden für Tests, welche die Ton- und Sulfat-Beständigkeit beschreiben, ausgewählt. Zusätzlich zu den Synthesemethoden „M1“ und „M2“ wurden zwei weitere Prozesse getestet. Dazu wurde für anionische PCEs die so genannte „5M“ Methode, eine noch kürzere (5 Minuten) und schnellere Methode als „M1“, sowie für zwitterionische PCEs die stärker kontrollierte 2-Stufen-Reaktion („M3“) eingeführt, in der zuerst das Makromonomer und das kationische Monomer und danach die Acrylsäure mit dem zuvor entstandenem Reaktionsgemisch polymerisiert wurden.

Messungen der anionischen Ladungsmenge der PCEs bestätigten die erfolgreiche Bildung von Polymeren, wobei niedrigere anionische Ladungsmengen für alle zwitterionischen Fließmittel in deionisiertem Wasser auf die Bildung von kationischem Polymer schließen ließen. Zudem zeigten die zwitterionischen „M2“ und „M3“ Polymere deutlich weniger Rückgang der anionischen Ladung in synthetischer Zementporenlösung als alle anderen getesteten PCEs, was andere Eigenschaften dieser PCEs vermuten lässt.

Dosierungsabhängiges Dispergierverhalten in Zement (CEM I 52,5 R, w/z = 0,62) zeigte, dass das rein anionische „5M“ PCE die anionische und zwitterionische „M1“ Polymermischung und das konventionelle Referenzpolymer in seiner Wirkung übertraf. Die notwendige Dialyse im „5M“ Syntheseprozess ist für dieses Polymer jedoch sehr nachteilig; nichtsdestotrotz ist seine Wirkung erheblich besser. Dennoch unterliegen die zwitterionischen „M2“ und „M3“ Polymere deutlich allen anderen Fließmitteln in ihrer Dispergierwirkung.

Darüber hinaus konnte beobachtet werden, dass die Dispergierwirkung der zwitterionischen „M2“ und „M3“ Polymere in Gegenwart von Montmorillonit-Ton am wenigsten beeinflusst wurden. Tests, in denen die gleiche Dosierung für alle Fließmittel verwendet wurde, bestätigten, dass diese Eigenschaft nicht einfach nur der benötigten höheren Dosierung dieser PCEs zuzuschreiben war, sondern dass dies auf der Zusammensetzung der Polymermischungen gründete.

Sulfationen hatten den geringsten negativen Effekt auf die Dispergierwirkung des „5M“ Polymers. Hier konnte sogar eine leichte Verbesserung in Gegenwart von 1 % bwoc Na_2SO_4 beobachtet werden. Nur ein geringer Rückgang in Anwesenheit von Na_2SO_4 in der Dispergierwirkung wurde für die

ausschließlich anionischen und zwitterionischen Polymermischungen, welche nach der Methode „M1“ synthetisiert wurden, festgestellt. Somit übertrafen diese leicht das konventionelle und das zwitterionische „M2“ PCE.

Die **Tabelle 36** zeigt alle getesteten PCEs und deren zugehörige besondere Eigenschaften.

Table 36. Besondere Eigenschaften der getesteten PCEs.

Polymer	Synthesemethode	Initiator-system	Ladungs-charakter	Vorteil, besondere Eigenschaft
P(4,5:1:0)_C	konventionell	APS	anionisch	---
P(4,5:1:0)_5M	5 Minuten Methode	Redox	anionisch	sulfattolerant bis ~ 2 % bwoc Na_2SO_4
P(4,5:1:0)	Methode M1	Redox	anionisch	sulfattolerant bis ~ 1 % bwoc Na_2SO_4
P(4,5:1:1)_M1	Methode M1	Redox	zwitterionisch	sulfattolerant bis ~ 1 % bwoc Na_2SO_4
P(4,5:1:1)_M2	Methode M2	Redox	zwitterionisch	beste Tontoleranz
P(4,5:1:1)_M3	Methode M3	Redox	zwitterionisch	beste Tontoleranz

Die Quintessenz dieser Tests kann folgendermaßen zusammengefasst werden: Abhängig von der Synthesemethode eines PCEs und damit der Polymerzusammensetzung können dessen Eigenschaften stark beeinflusst werden. Eine Vorhersage über die Eigenschaften eines PCEs anhand dessen Zusammensetzung kann jedoch nicht einfach getroffen werden, wie folgendes Beispiel zeigt: Allgemein scheinen PCE-Polymermischungen mit kationischen Anteilen („M2“ und „M3“ Synthesemethode) tontoleranter als rein anionische PCEs zu sein. Dies trifft jedoch nicht für die zwitterionische „M1“ - Polymermischung zu, was eine verallgemeinerte Aussage wie z.B. „zwitterionische PCEs sind tontoleranter als anionische PCEs“ nicht zulässt.

Durch die gewonnenen Ergebnisse können folgende allgemeingültige Aussagen getroffen werden:

1. Der Anteil an der Haupt-Polymerfraktion in einem PCE ist nicht ausschlaggebend für dessen Dispergierwirkung.
2. In den hier untersuchten PCEs spielt das Molekulargewicht der Polymerfraktion(en) eines PCE Fließmittels nicht zwingend eine Rolle für die Dispergierwirkung.
3. Der Einbau des kationischen Monomers TMAEMC garantiert nicht die Tontoleranz eines PCE Fließmittels.
4. Die gleiche Synthesevorschrift für eine anionische und zwitterionische Polymermischung führt zu PCEs mit ähnlichen Eigenschaften.

Der dritte Teil dieser Dissertation (**Kapitel 5.4**) beschäftigt sich mit der „5M“ Synthesevorschrift, welche einen kurzen Polymerisationsprozess (5 Minuten) aufweist und daraus resultierende PCE-Polymere mit exzellenter Dispergierwirkung hervorbringt. Um die Rolle der Reaktionszeit der PCEs auf deren Dispergierwirkung und Eigenschaften zu erfassen, wurden zusätzlich Fließmittel mit einer Reaktionszeit von 30 Minuten („30M“) hergestellt, wobei die „5M“ Synthesemethode identisch zu den ersten 5 Minuten der „30M“ Synthese ist. Damit kann der „5M“ Prozess als unterbrochener „30M“ Prozess angesehen werden. Für jeden Syntheseprozess wurden dabei zwei verschieden lange Seitenketten (23 und 52 Ethylenglykol-Einheiten) von isoprenolether-basierten Polycarboxylat-Fließmitteln (IPEG-PCEs) eingesetzt. Das Molverhältnis von Acrylsäure zu Makromonomer betrug stets 2:1.

Durch das Überprüfen der Bildung von Polymeren über die Zeit mit SEC Messungen konnte gezeigt werden, dass der Polymerisationsprozess für die „5M“ und „30M“ PCEs nahezu sofort startet, wenn der Redox-Initiator zum Reaktionsgemisch gegeben wird, während für die Synthese der konventionellen PCEs eine Verzögerung nach Zugabe des Initiators Ammoniumpersulfat von ca. 10 - 20 Minuten eintritt. Wie bereits in **Kapitel 5.1** dieser Arbeit diskutiert, wurde für die konventionellen PCEs nur eine Hauptpolymerfraktion erhalten, während für die „30M“ Vorschrift ab ca. 5 Minuten Reaktionszeit eine Polymermischung entstand. Dies hat ein relativ einheitliches Polymer für die „5M“ Synthesemethode zur Folge, da dessen Polymerisationsprozess vor der Bildung mehrerer Fraktionen abgebrochen wird. Unabhängig vom eingesetzten Initiatorsystem endete die Polymerisation, wenn kein weiterer Initiator zur Reaktionsmischung gegeben wurde. Im Hinblick auf den Makromonomer-Umsatz ist Rühren nach diesem Prozess somit überflüssig. Interessant wären allerdings weiterführende Untersuchungen, ob das Weglassen des nachträglichen Rührens Nebeneffekte, wie z.B. ein Verbleib reaktiver Initiatormoleküle in der Reaktionsmischung, mit sich bringt.

In „Mini Slump“ Tests benötigten die 30M“ und „5M“ PCEs eine deutlich geringere Dosierung als die konventionellen PCEs, um ein Ausbreitmaß von 26 cm in Zement bei niedrigen w/z-Werten von 0,45 und 0,3 zu erreichen. Dies führte zu einer besseren Dispergierwirkung über die Zeit für diese PCEs, wenn gleichbleibende Fließmitteldosierungen von 0,50 % bwoc und ein w/z von 0,3 verwendet wurden. Darüber hinaus benötigten die PCEs mit 23 EO Einheiten 0,02 - 0,05 % bwoc weniger

Dosierung für dasselbe Ausbreitmaß als die PCEs mit 52 EO Einheiten. Im Mörtel wurde kein Unterschied in der Dispergierwirkung zwischen den konventionellen und den Kurzzeit-PCEs entdeckt.

Bei Tests zum zeitlichen Verlauf der Dispergierwirkung in Mörtel wurde eine minimal verbesserte Wirkung direkt nach dem Anmischen für die „5M“ und „30M“ PCEs erzielt, allerdings war die Abnahme der Dispergierwirkung über die Zeit stärker als bei den konventionellen PCEs. Insgesamt wurde für alle Fließmittel eine nur sehr geringe (nahezu keine) Konsistenzerhaltung über die Zeit im Mörtel erreicht. Hier wären Tests im Beton hilfreich, um den zeitlichen Verlauf der Fließwirkung in einem realistischen System zu testen und die PCEs dann richtig einordnen zu können. Darüber hinaus verloren überraschenderweise Fließmittel mit kurzer Seitenkette im zeitlichen Verlauf etwas schneller die Fließwirkung als die mit langer Seitenkettenlänge.

Die Tontoleranz im Zement hing stark von der Seitenkettenlänge des Makromonomers und nicht von der Synthesemethode des Fließmittels ab – die PCEs mit nur 23 EO Einheiten waren besonders bei niedrigen w/z Werten von 0,45 oder 0,30 weniger tontolerant als die mit 52 EO Einheiten. Im Mörtel traten diese Unterschiede nicht mehr auf, allerdings konnte sich kein PCE als das Beste herauskristallisieren. Im Gegensatz zur Tontoleranz hing die Sulfattoleranz stark von der Synthesemethode ab. Hier zeigten die „30M“ und „5M“ PCEs mehr Sulfattoleranz im Zement und im Mörtel als die konventionellen PCEs. Darüber hinaus wurde die Fließwirkung des 23IPEG-PCEs weniger vermindert als die der 52IPEG-PCEs.

Die durchgeführten Tests zeigten, dass durch eine Unterbrechung einer ziemlich unkontrollierten „batch“ Polymerisation (alle Monomere zu Beginn im Reaktionskolben) zum richtigen Zeitpunkt ein einheitliches Polymer („5M“ PCE) gebildet werden kann, wie es normalerweise bei der konventionellen Synthese von PCEs erhalten wird. Die Fließfähigkeit ist sehr ähnlich zu der der konventionellen PCEs und übertrifft diese sogar in Zementpasten mit niedrigem w/z-Wert. Des Weiteren zeigen die „5M“ Polymere eine bessere Sulfattoleranz in Mörtel und Zementschlämmen. Sowohl diese Eigenschaften als auch die kurze Polymerisationszeit (5 Minuten) und die niedrigere Reaktionstemperatur (30 °C) lassen das „5M“-PCE im Vergleich zum konventionell synthetisierten PCE-Fließmittel (3 h, 60 °C) interessant erscheinen. Die Nachteile des „5M“ PCEs sind jedoch die Durchführung der Polymerisationsunterbrechung nach 5 Minuten sowie das erforderliche Kühlen und die anschließende Dialyse, was in industriellen Prozessen nicht einfach umzusetzen ist. Daher sollten weitere

Untersuchungen zum Abbruch der Reaktion unter Zuhilfenahme von Polymerisations-Inhibitoren unternommen werden.

Zudem können folgende Schlussfolgerungen über die Kurzzeit-Synthese gezogen werden:

1. Der Makromonomerumsatz einer Synthese kann nicht verbessert werden, indem die Polymer-Reaktionsmischung nach erfolgter Zugabe des Initiators weiter gerührt wird.
2. Der Polymerisationsprozess mit einem Redox-Initiatorsystem beginnt sofort, wenn der Initiator zugegeben wird, während die konventionelle Synthese unter Einsatz eines Peroxid-Initiators mit einer Zeitverzögerung beginnt.
3. Der geringere Makromonomerumsatz für die „5M" PCEs, der durch die Unterbrechung des Polymerisationsprozesses der „30M" Polymermischung entsteht, führt nicht zu einem verringerten Dispergiereffekt, sondern zu einer verbesserten Leistung bei niedrigen w/z-Werten. Dabei ist zu beachten, dass dies für das dialysierte Produkt „5M" gilt.
4. Die Tontoleranz in Zement und Mörtel wird kaum durch die verschiedenen Synthesemethoden „5M", „30M" und konventionell („C") beeinflusst.
5. „5M" und „30M" PCEs sind deutlich sulfattoleranter als konventionelle PCEs mit dem gleichen Molverhältnis von Acrylsäure : Macromonomer (= 2:1).

Im **letzten Abschnitt** dieser Arbeit wurde der Einfluss des pH-Werts einer Fließmittellösung auf deren Dispergierwirkung in Zement untersucht. Dazu wurden „Mini Slump" Tests für APEG-, IPEG-, und HPEG- PCE-Lösungen mit einem pH-Wert von 1,5 und 7,0 durchgeführt, um Unterschiede sichtbar zu machen. Im Standardzement (CEM I 52,5 R) zeigte sich für das APEG-PCE kein Unterschied, während bei den stark anionischen 52IPEG- und 50HPEG-PCEs (10 Mol Acrylsäure) die saure PCE-Lösung besser wirkte als die neutralisierte. Besonders in einem Zement mit hohem C_3A_o / SO_4^{2-} Verhältnis von 1,17 (CEM I 42,5 R) trat der Unterschied extrem stark hervor, während für den Zement mit einem sehr niedrigen C_3A_o / SO_4^{2-} Verhältnis von nahezu 0 (API Class G) dieser Effekt nicht auftrat.

Eine zeitverzögerte Zugabe von PCE beim „Mini Slump" Test mit einem Standard-Zement verhinderte unterschiedlich starke Verflüssigungswirkungen für saure und neutrale PCEs, was bewies, dass der Unterschied der Dispergierwirkung von Produkten bzw. Prozessen der sehr frühen Zementhydratation

abhängt. Damit könnte der Effekt von einer unterschiedlich starken Wechselwirkung der PCE-Lösungen (pH = 1,5 oder 7,0) mit dem sich bildenden Ettringit in der Zementschlämme stammen.

Studien zur Ausfällung von synthetischem Ettringit in Gegenwart von sauren oder neutralen PCEs zeigten, dass saures PCE die Ettringitbildung stärker verzögert als neutralisiertes PCE. Darüberhinaus war die Menge an gefälltem Ettringit geringer in Anwesenheit von saurer PCE-Lösung. Des Weiteren übten die stark anionischen IPEG- und HPEG-PCEs einen deutlich stärkeren Einfluss auf das System aus als das schwach anionische APEG-PCE. Es entstand nano-Ettringit anstatt meso-Ettringit. REM-Bilder der gefällten Ettringit-Nadeln bestätigten diese Beobachtungen. Zusätzlich konnte damit die Kristallgröße der Ettringitnadeln bestimmt werden.

Die Zentrifugation von Zementschlämmen, die analog zu den „Mini Slump" Tests hergestellt wurden, ermöglichte die Extraktion von nano-Ettringit, welches in der Zementschlämme gebildet wird. Wie bereits in den Fällungsexperimenten mit synthetischem Ettringit beobachtet, bildete sich in CEM I 42,5 R und 52,5 R und in Gegenwart von saurer PCE-Lösung weniger nano-Ettringit als für die neutralisierte Lösung. In Falle des sauren und neutralisierten APEG-PCEs wurden nur sehr geringe Mengen an nano-Ettringit für beide Proben erhalten. Darüberhinaus konnte in API Class G Zement (sehr langsam hydratisierender Zement) kein Unterschied bei allen PCE-Proben festgestellt werden. Dies unterstützte die Annahme, dass der unterschiedlich starke Einfluss von sauren und neutralisierten PCEs auf die Ettringitbildung auch die unterschiedliche Fließwirkung der PCEs verursacht. Größere Mengen an nano-Ettringit führen zu zusätzlichen Oberflächen, welche mit zusätzlichem PCE bedeckt werden müssen. Dadurch sollte die adsorbierte Menge an neutralisiertem Polymer in Zementschlämmen, die Ettringit in der frühen Hydratation bilden, aufgrund größerer nano-Ettringitmengen höher sein als in Gegenwart von saurem PCE. Die dadurch benötigten Dosierungen für neutralisierte PCEs sollten also erhöht sein, um das gleiche Ausbreitmaß wie für saures PCE zu erhalten.

Um diese Theorie zu beweisen, wurden 'frühe' (d.h. 20 Sekunden nach Anmischbeginn anstatt 2 Minuten) Adsorptionsmessungen durchgeführt. Es zeigte sich, dass – wie bereits angenommen – neutralisierte, stark anionische IPEG- und HPEG-PCEs in größeren Mengen als ihre sauren PCE-Lösungen adsorbierten. Nur das stets schwach anionische APEG-PCE adsorbierte in saurer oder neutralisierter Form in gleicher Weise, was die Beobachtungen der gleichen Dispergierfähigkeit für das saure und neutrale APEG-PCE unterstützt.

Zusammenfassend ließen sich folgende Erkenntnisse gewinnen:

1. Unterschiede in der Fließwirkung zwischen sauren und neutralisierten PCE-Lösungen traten nur für stark anionische PCEs auf (ca. ≥ 6 Mol Acrylsäure).
2. Das Makromonomer beeinflusst ebenfalls den Effekt; in dieser Studie war der Effekt für das 50HPEG-PCE stärker als für das 52IPEG-PCE.
3. Ursache für die verschiedenen Fließwirkungen abhängig vom pH-Wert des PCEs ist der unterschiedlich starke Einfluss von saurem und neutralem PCE auf die frühe nano-Ettringitbildung in der Zementschlämme; saures PCE hat einen stärkeren Einfluss als neutralisiertes PCE.
4. Stark anionische PCEs verändern während der Fällung und Kristallisation die Morphologie von Ettringit-Kristallen und führen zu nano-Ettringit (geringeres Aspekt-Verhältnis), während schwach anionische PCEs die Fällung von Ettringit-Kristallen deutlich weniger stark beeinflussen (noch meso-Ettringit).
5. Saure PCE-Lösungen verzögern, verglichen mit neutralisierter PCE-Lösung, die Fällung von synthetischem Ettringit in stärkerem Ausmaß und verringern die gebildete Menge erheblich.
6. Eine größere Menge an nano-Ettringit bedingt mehr positive Oberflächen, welche durch PCEs bedeckt werden müssen und erfordert größere Mengen an adsorbiertem PCE zur Dispergierung.

Theoretisch können bessere Dispergierwirkungen für stark anionische PCEs einfach durch das Weglassen der Neutralisation erzielt werden. Durch den niedrigen pH-Wert (pH ~ 1,5 - 3) ergeben sich jedoch erhebliche Gefahren für Anwender und schwierigere Lagerbedingungen (z.B. Erfordernis von korrosionsbeständigen Lagertanks), was ein Grund sein könnte, dieses Verfahren nicht in der Industrie anzuwenden. Allerdings wären Studien, die den Einfluss von unterschiedlich gebildeten Mengen nano-Ettringit in der frühen Hydratation für saure und neutralisierte PCE-Lösungen untersuchen, durchaus interessant. Spielt dieser Unterschied auch eine Rolle für andere Additive? Und können Unterschiede immer noch in der späten Hydratation beobachtet werden?

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9 Appendix

9.1 General reaction scheme for the PCEs synthesized in Section 5.1

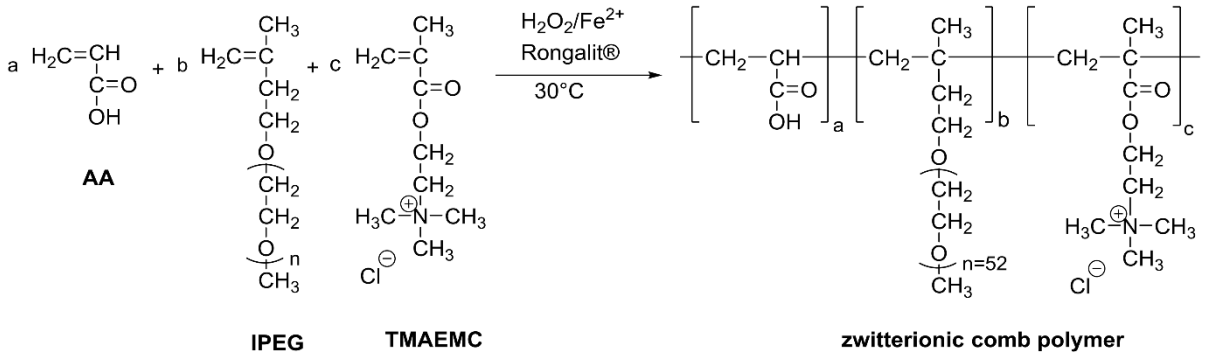


Figure 88. Preparation and general composition of the synthesized (zwitterionic) comb polymers [154].

9.2 Prestudy for SEC evaluation

In order to correctly assign the peaks obtained in the SEC spectra (see **Section 5.1.2.2**), additional SECs were recorded (see **Figure 89**).

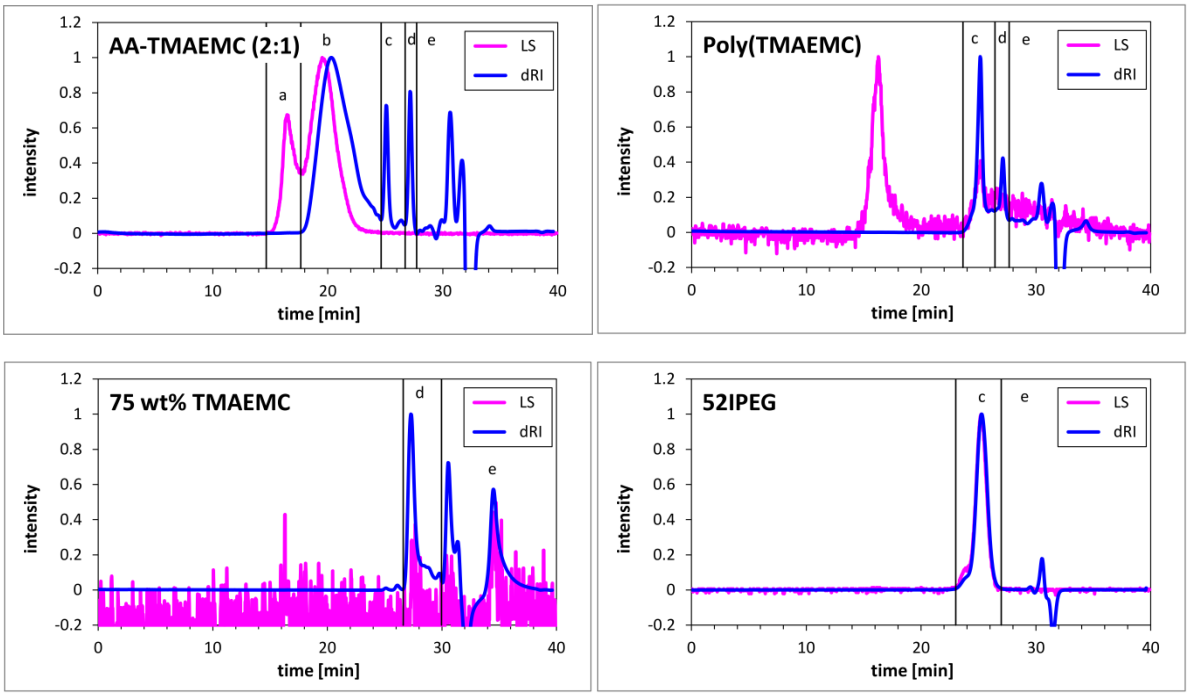


Figure 89. SEC spectra of (1) AA-TMAEMC (2:1) polymer, (2) Homopolymer of TMAEMC (Poly(TMAEMC)), (3) 75 wt.-% TMAEMC and (4) 52IPEG.

Table 37 lists the composition of the obtained polymer fractions, **Table 38** the molecular parameters. The synthesis method for the polymer consisting of acrylic acid and TMAEMC as well as for poly(TMAEMC) was according to method "M1" (see **Section 5.1.2.1**). **Table 39** gives the amounts of chemicals used for the preparation of the polymers.

Table 37. Composition of the polymer fractions.

Peak	Composition of the polymer fraction
Peak a	Poly acrylic acid
Peak b	Copolymer from Acrylic acid (AA) and TMAEMC
Peak c	Poly(TMAEMC) or unreacted 52IPEG macromonomer
Peak d	Unreacted TMAEMC
Peak e	Salt and eluent

Table 38. Molecular parameters and macromonomer conversion for (1) AA-TMAEMC (2:1) polymer, (2) homopolymer of TMAEMC (Poly(TMAEMC)), (3) 75 wt.-% TMAEMC and (4) 52IPEG.

Polymer solution	M_w [g mol^{-1}]				MM conversion [%]
	Peak a	Peak b	Peak c	Peak d	(Peak a-c)
AA-TMAEMC (2:1)	17,750,000	58,110	2,877	3,470	92
Poly(TMAEMC)	---	---	969	971	62
75 wt.-% TMAEMC	---	---	111	---	---
52IPEG	---	---	2,525	---	---

Table 39. Amounts of chemicals used in the synthesis of the polymer AA-TMAEMC (2:1) and poly(TMAEMC).

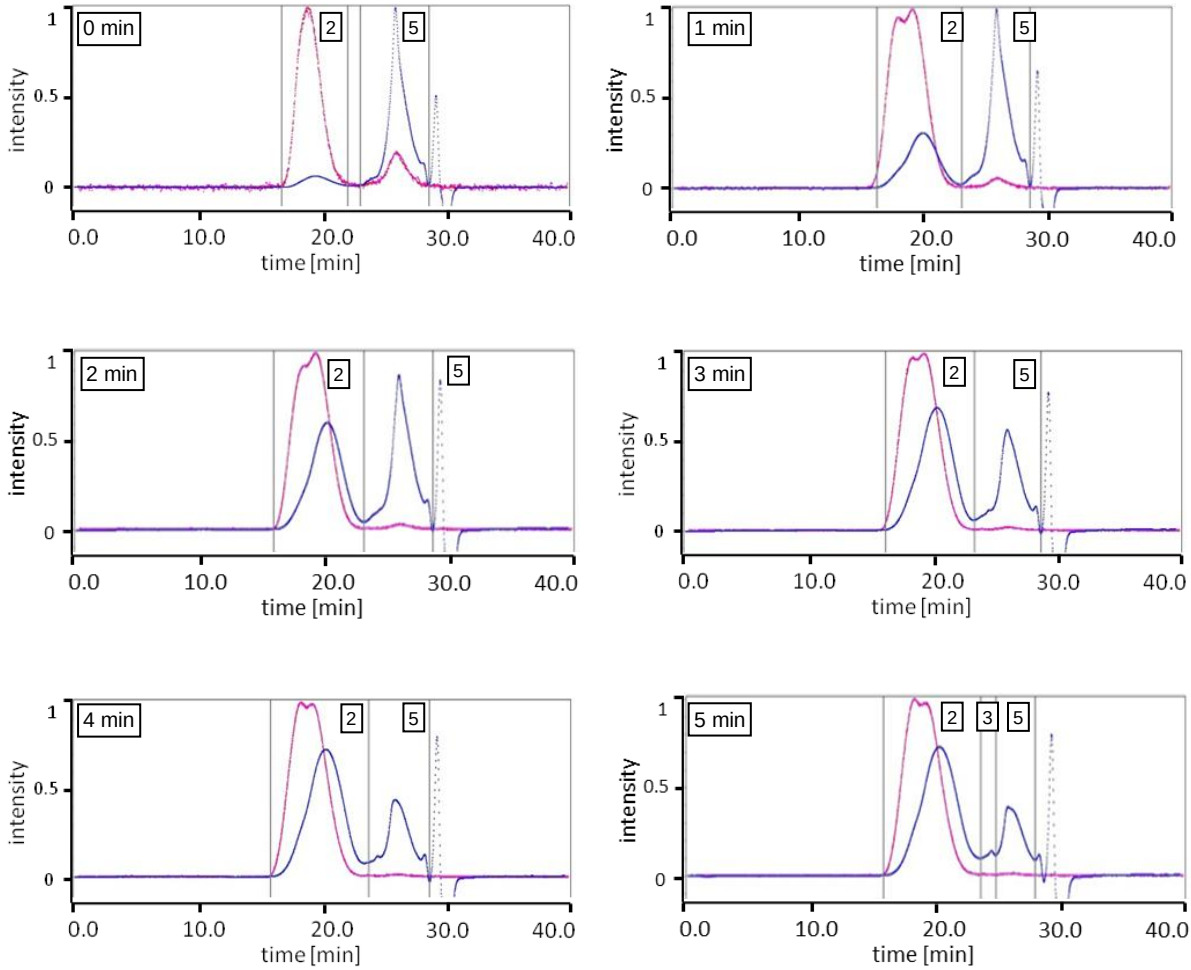
Chemical	AA-TMAEMC (2:1)	Poly(TMAEMC)
75 wt.-% TMAEMC	6.88 g	2.6 g
Acrylic acid	3.60 g	---
NaH_2PO_2	0.38 g	0.38 g
$FeSO_4 \cdot 7\ H_2O$	0.04 g	0.04 g
solution A	0.90 g of 30 wt.-% H_2O_2 and 4.50 mL of deionized water	1.50 g of 30 wt.-% H_2O_2 and 5.00 mL of deionized water
solution B	0.80 g of Rongalit® and 5 mL of deionized water	0.80 g of Rongalit® and 10 mL of deionized water
H_2O in reaction vessel	17 mL	20 mL

9.3 SEC spectra for determination of the polymer formation over time

9.3.1 SEC data for 23P(2:1:0)_5M

Table 40. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 23P(2:1:0)_5M, depending on the reaction time.

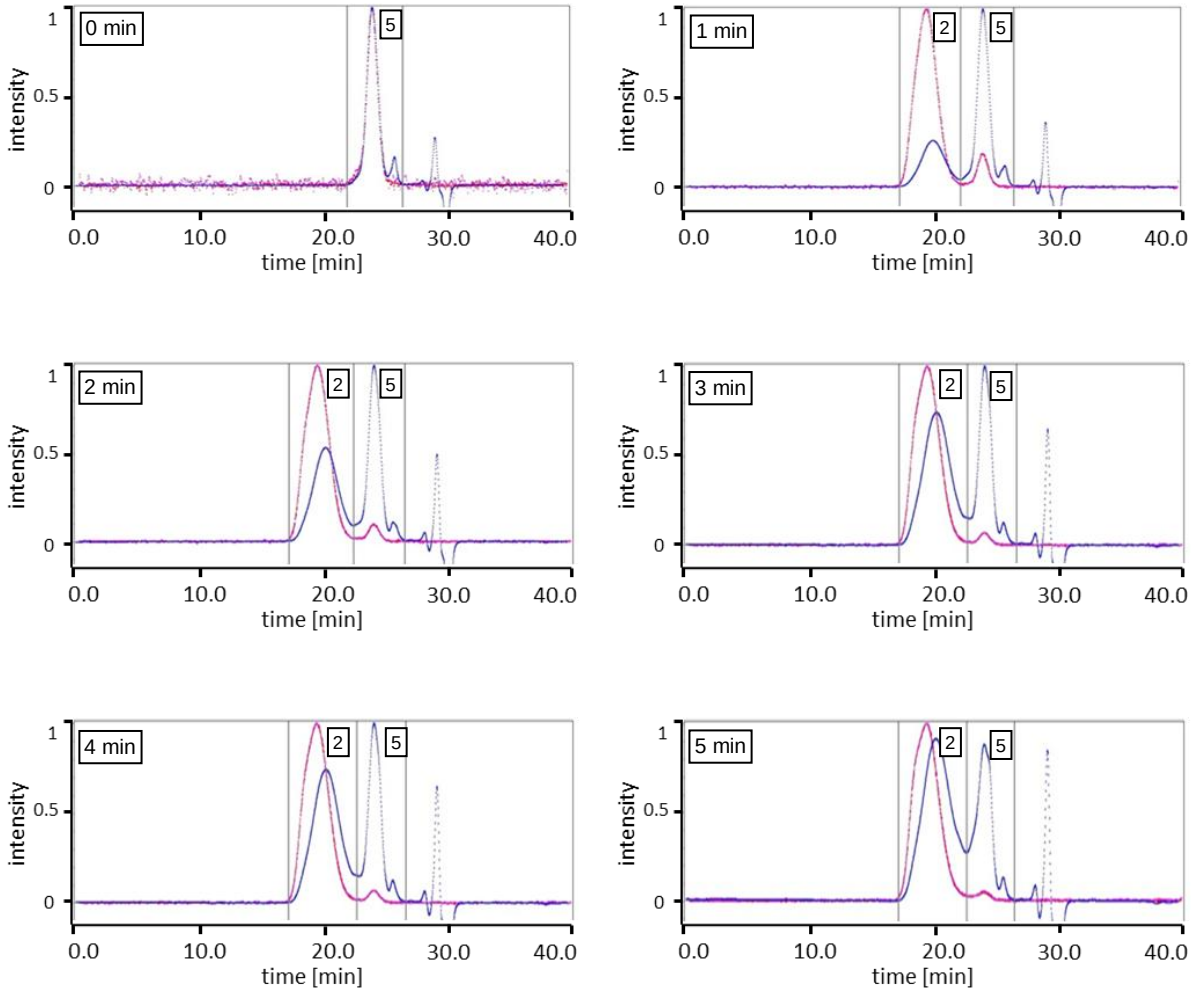
time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	60,460	---	---	1,123
1	---	63,550	---	---	1,153
2	---	60,170	---	---	1,203
3	---	60,140	---	---	1,313
4	---	59,470	---	---	1,181
5	---	60,220	2,262	---	1,239



9.3.2 SEC data for 52P(2:1:0)_5M

Table 41. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 52P(2:1:0)_5M, depending on the reaction time.

time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	---	---	---	2,638
1	---	51,020	---	---	2,735
2	---	49,680	---	---	2,725
3	---	48,730	---	---	2,580
4	---	48,060	---	---	2,539
5	---	48,960	---	---	2,738

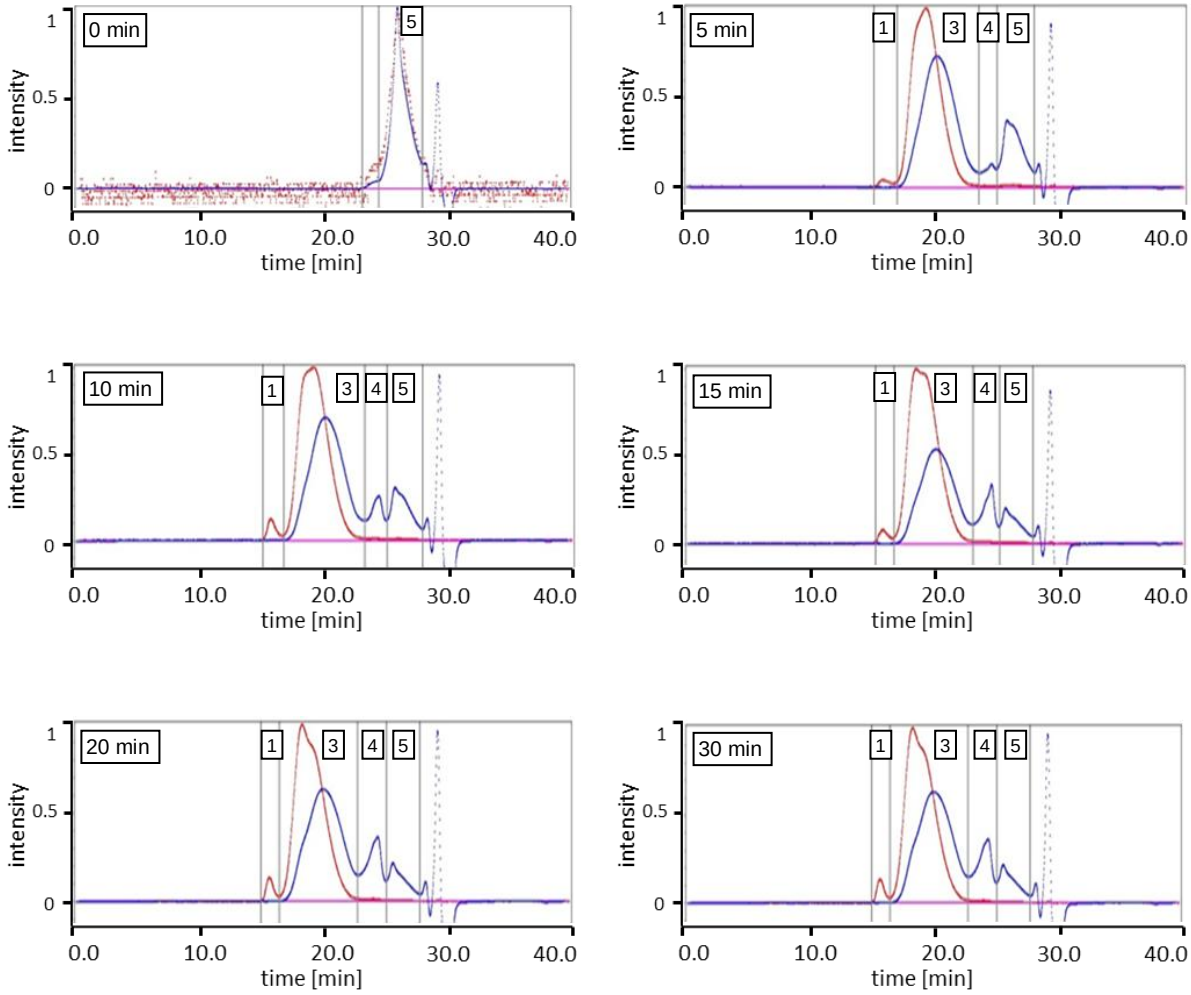


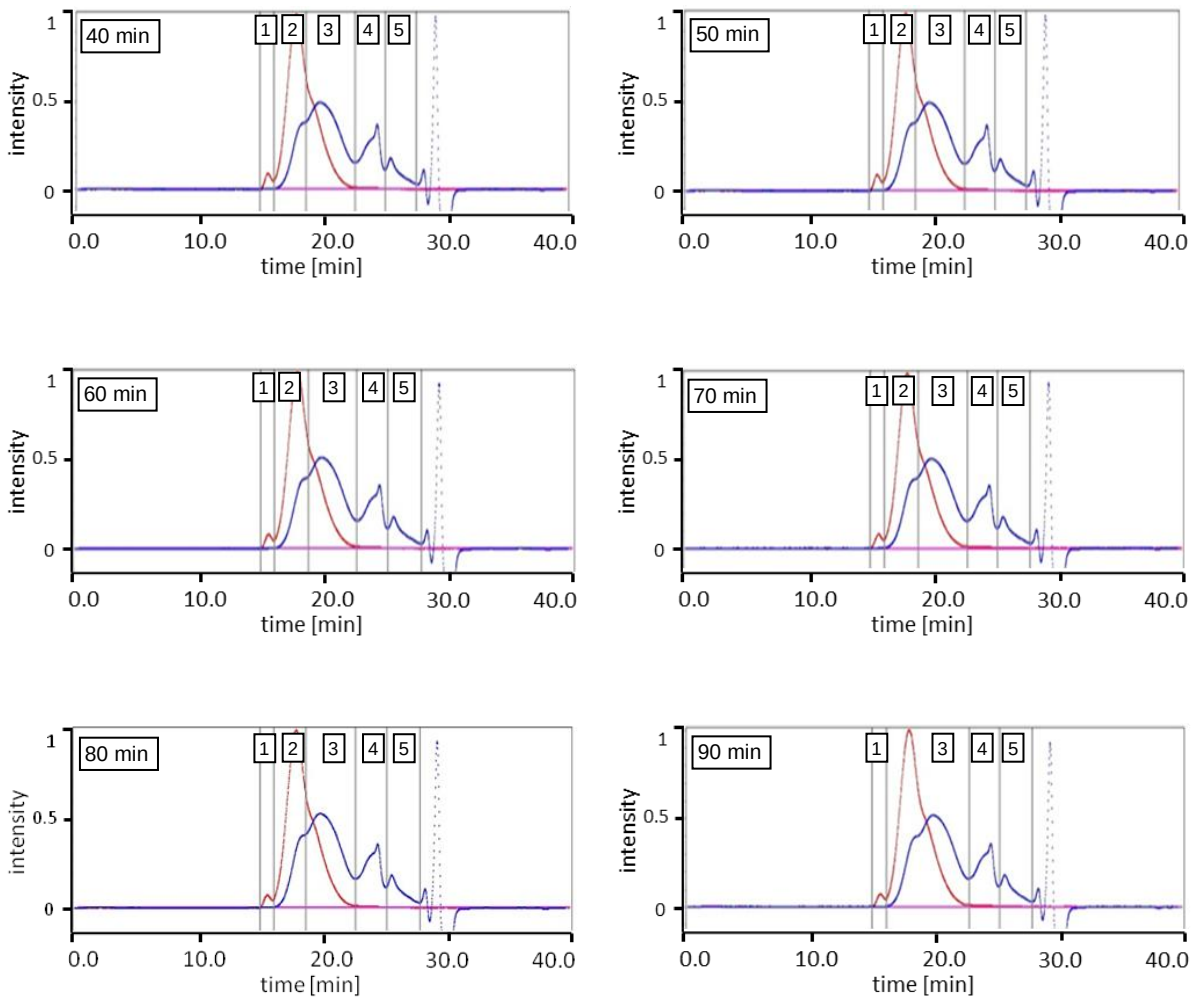
9.3.3 SEC data for 23P(2:1:0)_30M

Table 42. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 23P(2:1:0)_30M, depending on the reaction time.

time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	---	---	---	1,087
5	794,100	---	50,760	3,380	1,783
10	---*	---	53,900	2,450	1,664
15	---*	---	57,460	1,889	1,548
20	1,834,000	---	62,470	2,343	1,989
30	---*	---	84,550	2,122	1,515
40	2,739,000	254,500	43,810	2,221	1,760
50	3,101,000	254,900	44,230	2,286	1,564
60	---*	252,000	43,180	2,437	1,787
70	2,653,000	250,500	42,590	2,219	1,521
80	2,673,000	258,400	44,370	2,200	1,367
90	2,665,000	---	94,520	2,367	1,795

*M_w was not measurable by SEC measurement (insufficient amount)



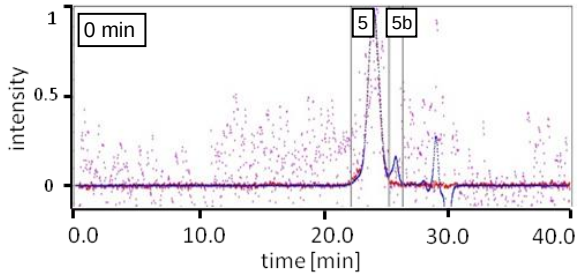


9.3.4 SEC data for 52P(2:1:0)_30M

Table 43. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 52P(2:1:0)_30M, depending on the reaction time; peak 5b is a side fraction of peak 5.

time [min]	peak 1	peak 2	peak 3	peak 4	peak 5	peak 5b
0	---	---	---	---	2,652	---
1	---	44,000	---	---	2,664	777
2.8	---	46,930	---	---	2,589	1,223
3.2	---	47,740	---	---	2,727	1,602
4	---	47,050	---	---	2,634	1,482
5	---	47,220	---	---	2,509	1,340
10	---	48,560	---	3,186	1,918	2,329
15	---	56,060	6,281	3,079	1,181	3,115
20	---*	57,670	6,281	3,312	1,569	2,630
30	544,500	59,860	6,678	3,461	1,470	3,067
40	187,200	59,920	6,327	3,385	1,619	3,232
50	---	57,740	3,797	1,412**	72,630**	200,800**
60	---	58,170	4,878	2,262	479**	---
70	---	58,230	5,083	2,488	665**	---
80	---*	63,670	10,400**	5,265	3,533**	9,223**
90	---*	60,910	6,824	3,619	1,779	3,839

*M_w was not measurable by SEC measurement (insufficient amount)
**Deviating and non realistic values (measurement errors)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5b
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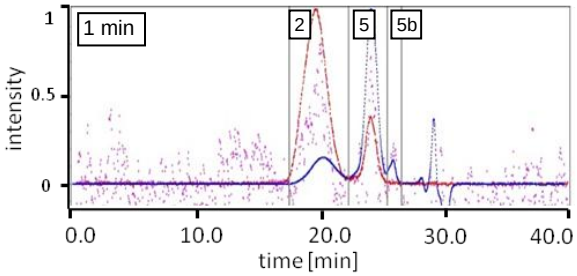
time [min]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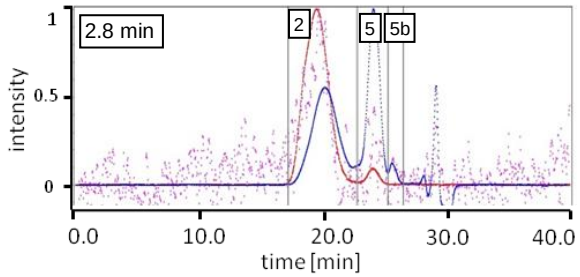
5
5b
intensity
time [min]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5
5b
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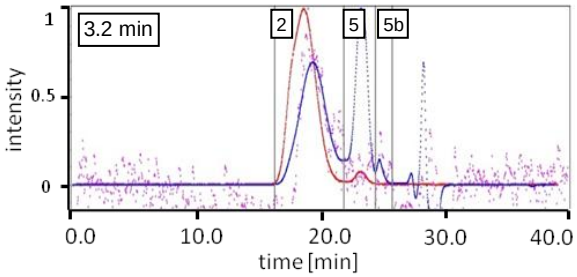
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5b
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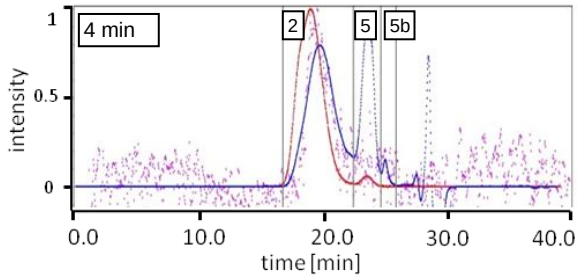
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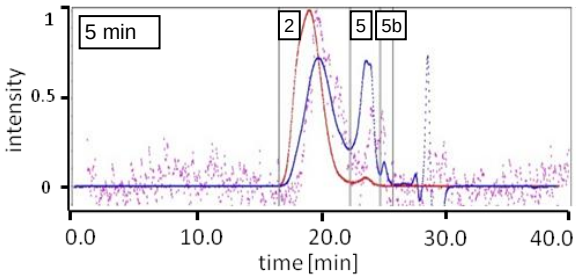
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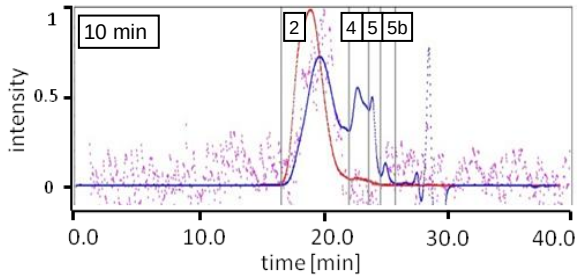
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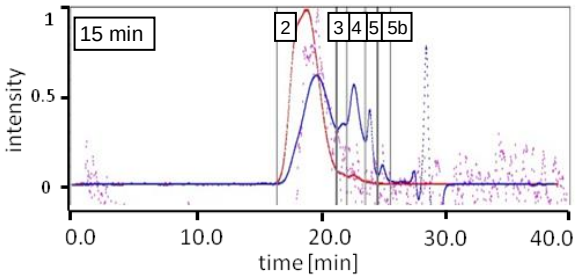
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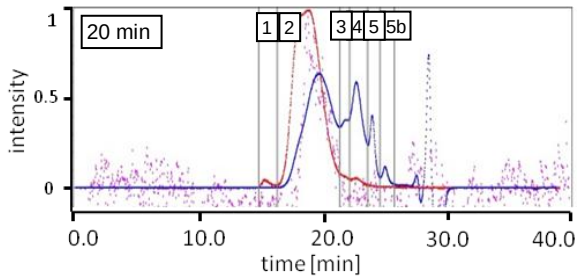
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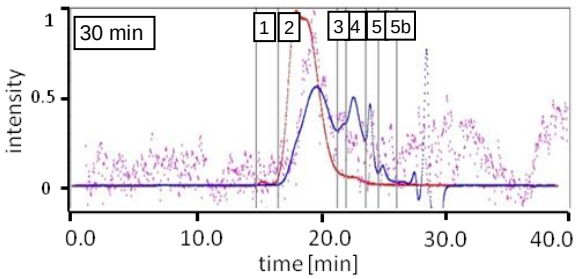
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intensity
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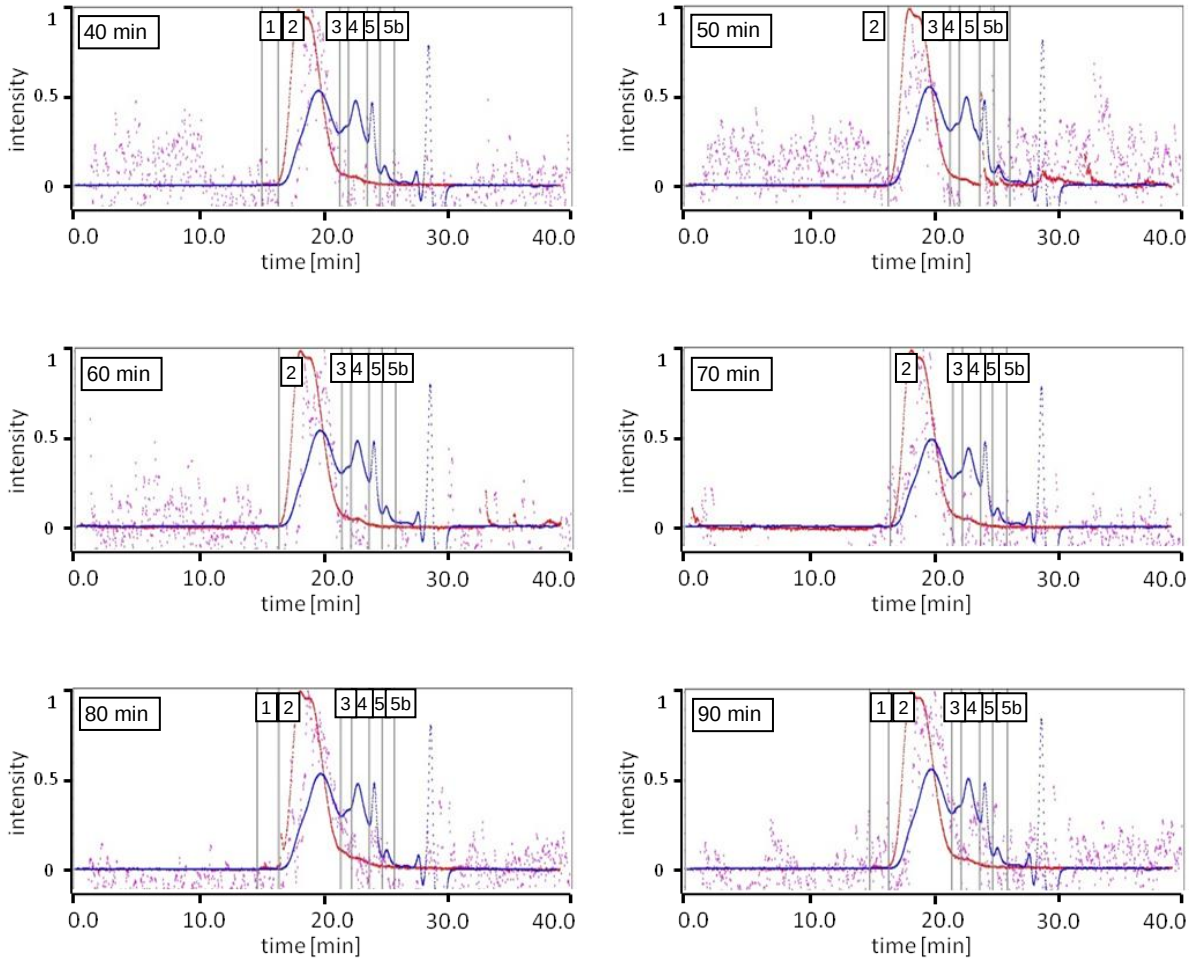
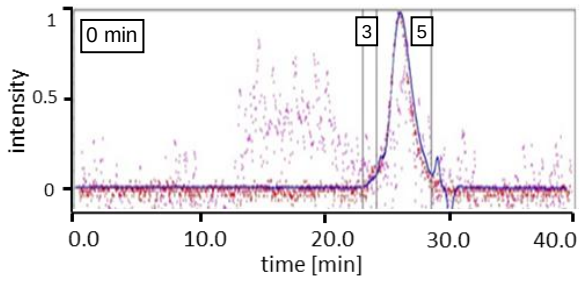


9.3.5 SEC data for 23P(2:1:0)_C

Table 44. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 23P(2:1:0)_C depending on the reaction time.

time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	---	3,143	---	1,207
5	---	---	2,199	---	1,182
10	---	---	2,449	---	1,129
15	---	---	2,523	---	1,155
20	---	34,520	2,546	---	1,160
30	---	34,520	2,050	---	1,122
40	---	32,470	3,201	---	1,205
50	---	30,370	2,369	---	1,152
60	---	28,140	2,490	---	1,151
70	---	26,850	2,751	---	1,204
80	---	26,040	2,745	---	1,218
90	---	25,850	3,094	---	1,315
120	---	24,860	2,571	---	1,192
150	---*	25,920	2,231	---	9,961**
180	---*	27,440	2,664	---	1,498
210	367,800	29,470	27,370**	---	1,417
240	---*	30,130	2,400	---	9,220**
270	---*	30,430	2,438	---	1,064
300	---*	30,900	2,654	---	1,560

*M_w was not measurable by SEC measurement (insufficient amount); **Deviating and non realistic values (measurement errors)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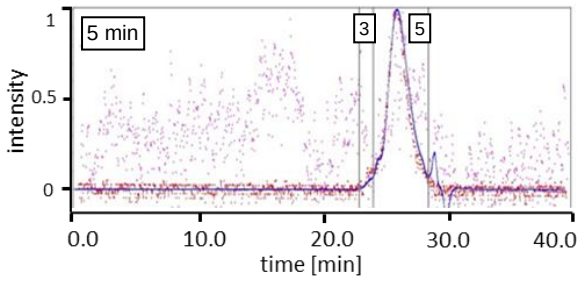
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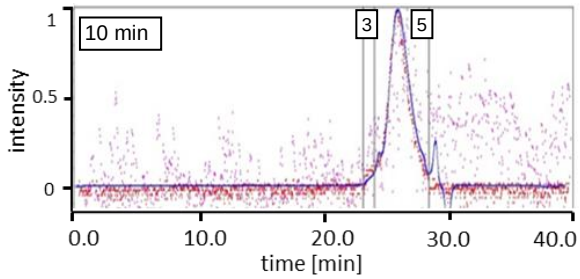
time [min]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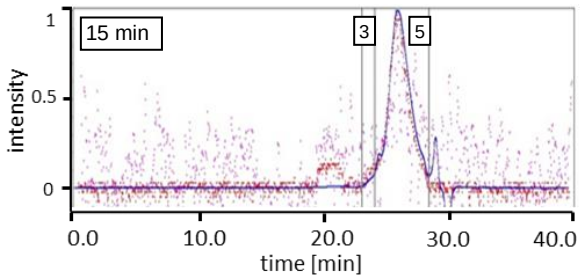
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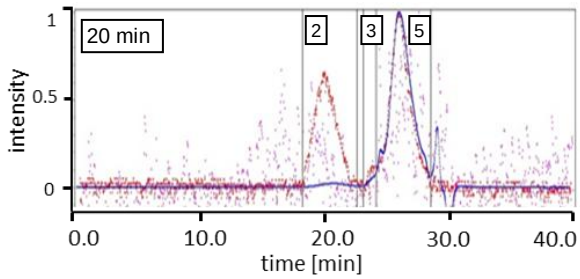
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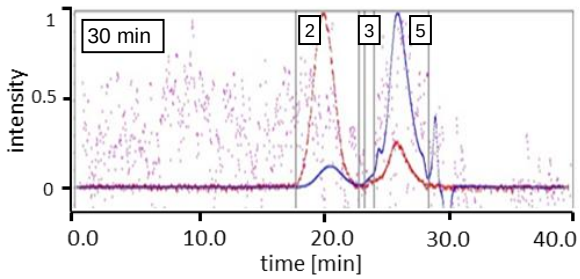
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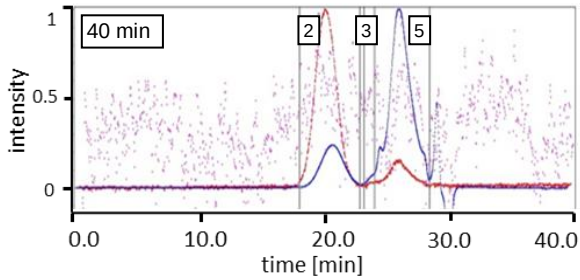
time [min]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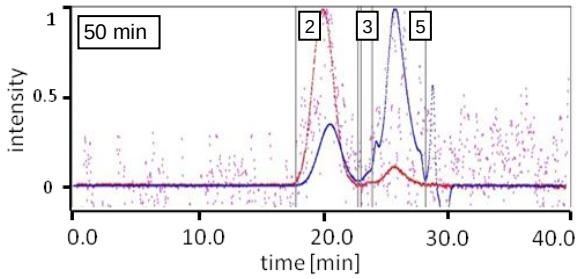
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intensity
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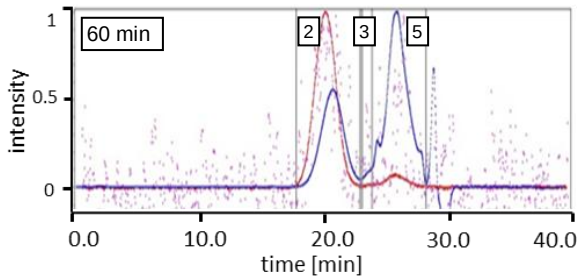
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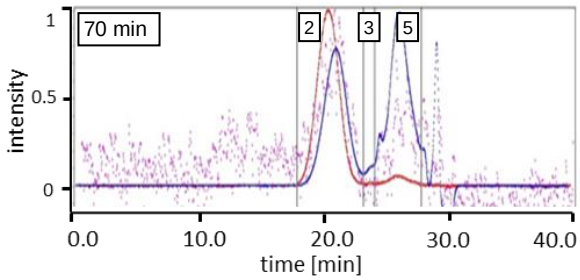
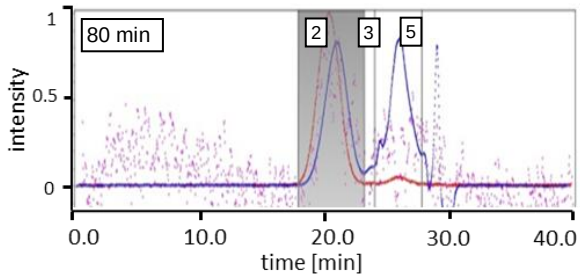
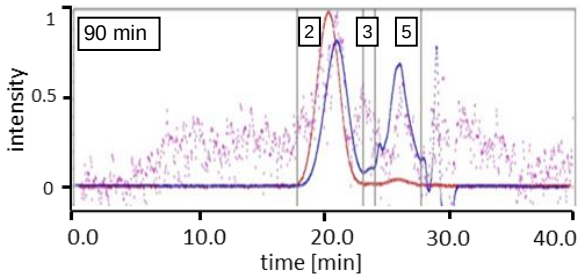
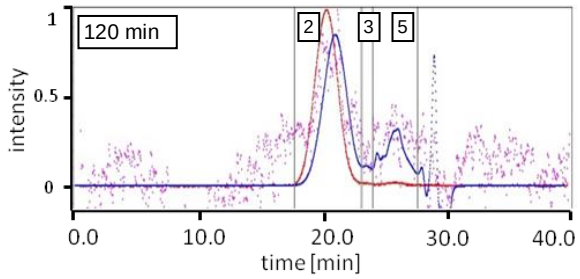
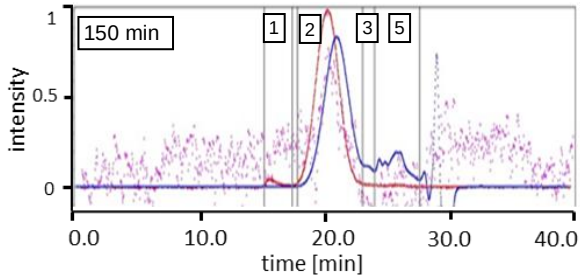
intensity
time [min]

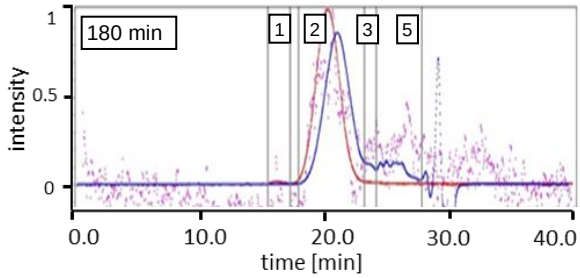

70 min
2
3
5
intensity
time [min]

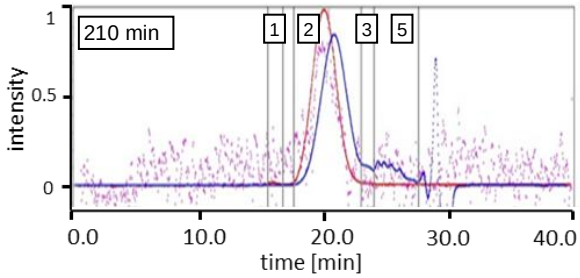

80 min
2
3
5
intensity
time [min]

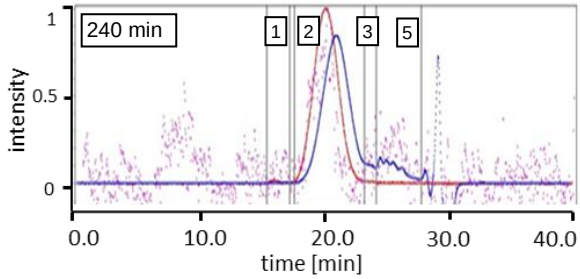

90 min
2
3
5
intensity
time [min]

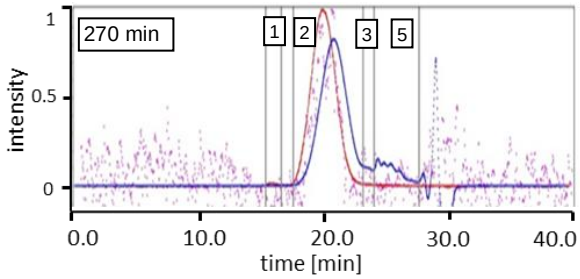

120 min
2
3
5
intensity
time [min]

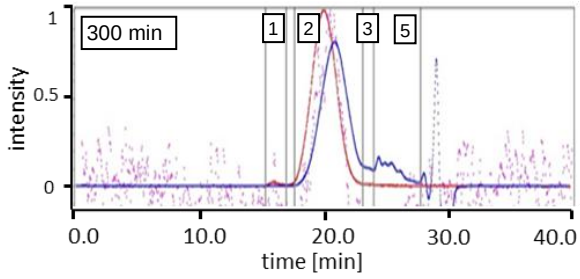

150 min
1
2
3
5
intensity
time [min]


180 min
1
2
3
5
intensity
time [min]


210 min
1
2
3
5
intensity
time [min]


240 min
1
2
3
5
intensity
time [min]

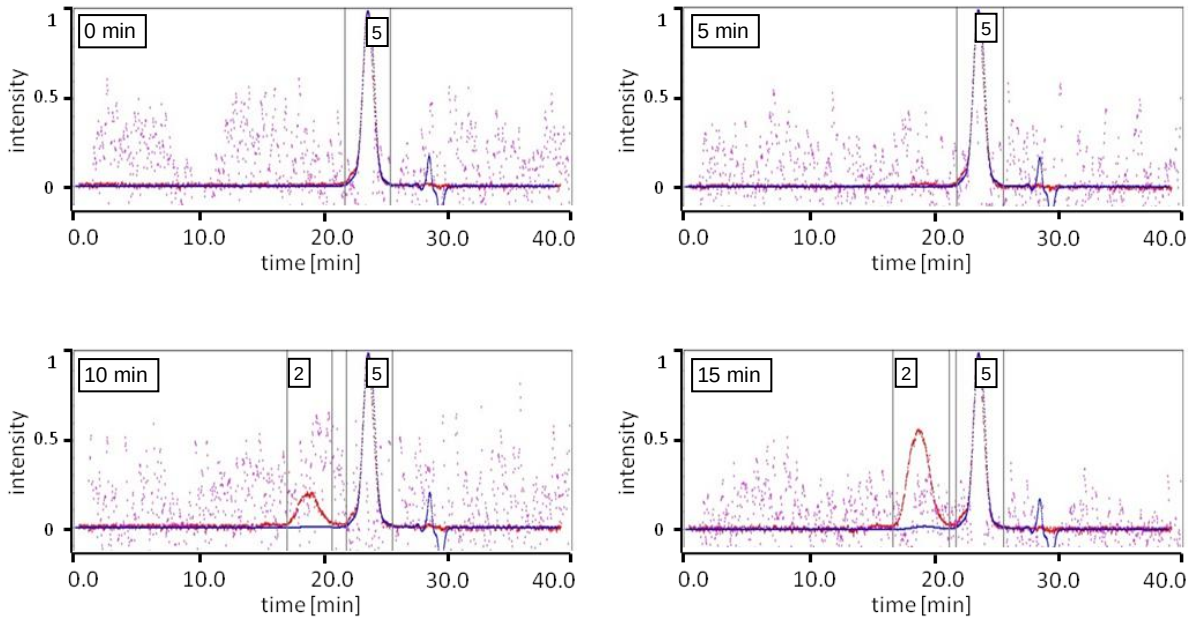

270 min
1
2
3
5
intensity
time [min]

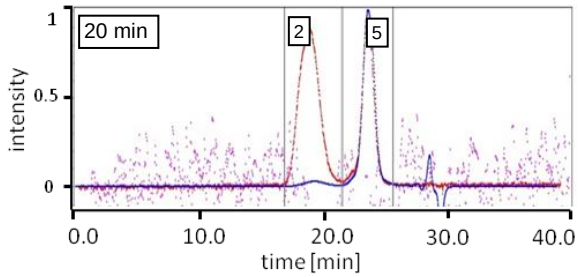

300 min
1
2
3
5
intensity
time [min]

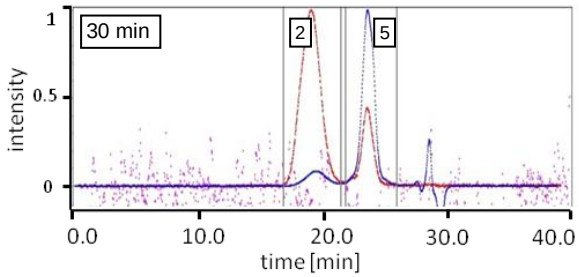
9.3.6 SEC data for 52P(2:1:0)_C

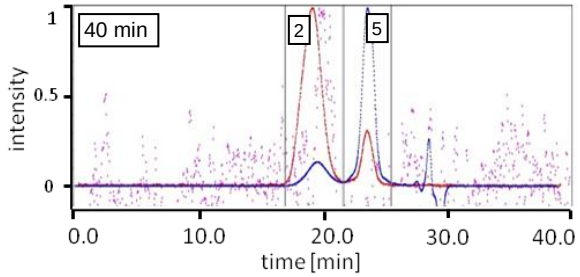
Table 45. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 52P(2:1:0)_C, depending on the reaction time.

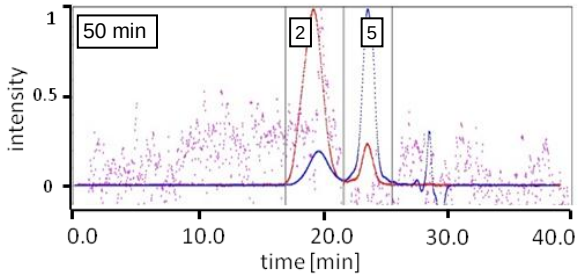
time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	---	---	---	2,761
5	---	---	---	---	2,697
10	---	88,200	---	---	2,704
15	---	82,780	---	---	2,709
20	---	79,190	---	---	2,746
30	---	68,570	---	---	2,657
40	---	63,170	---	---	2,748
50	---	58,560	---	---	2,757
60	---	54,350	---	---	2,692
70	---	51,160	---	---	2,625
80	---	48,920	---	---	2,718
90	---	47,810	---	---	2,656
135	---	45,310	4,235	---	2,409
150	---	45,990	4,297	---	2,405
180	---	48,390	4,088	---	2,193
210	---	50,950	3,998	---	1,968
240	---	54,430	4,261	---	1,997
270	---	56,770	5,024	---	2,786
300	507,000	58,650	6,660	---	3,716

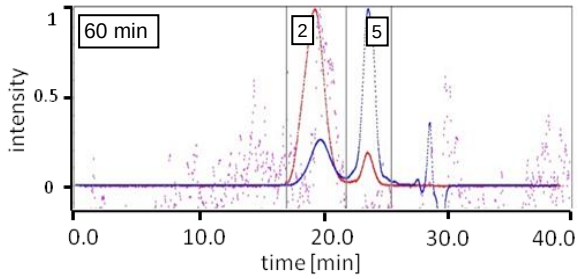


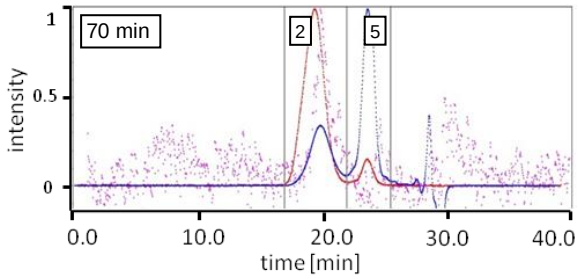

20 min
2
5
intensity
time [min]

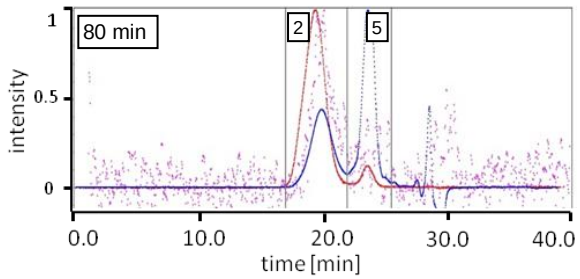

30 min
2
5
intensity
time [min]

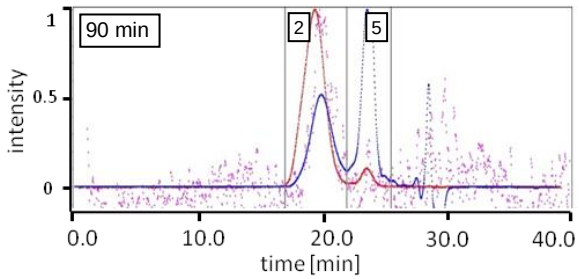

40 min
2
5
intensity
time [min]

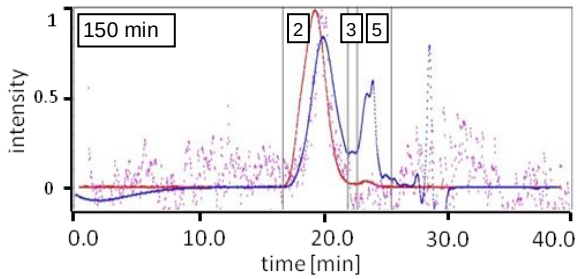

50 min
2
5
intensity
time [min]

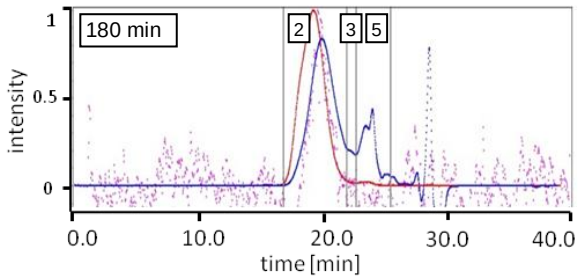

60 min
2
5
intensity
time [min]

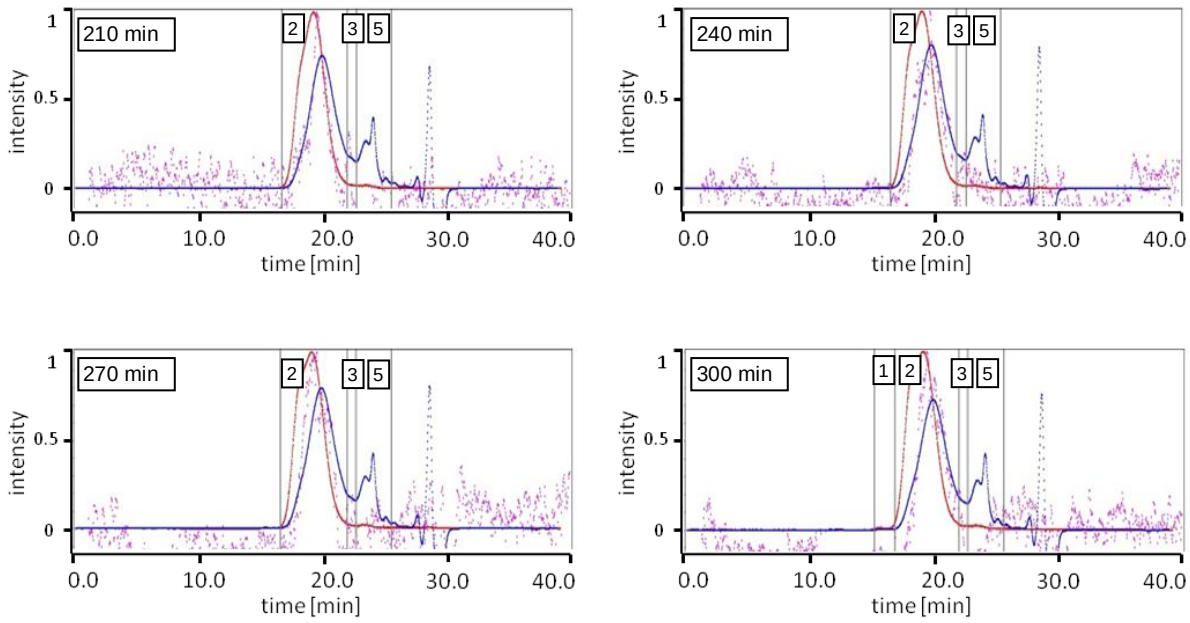

70 min
2
5
intensity
time [min]


80 min
2
5
intensity
time [min]


90 min
2
5
intensity
time [min]


150 min
2
3
5
intensity
time [min]


180 min
2
3
5
intensity
time [min]

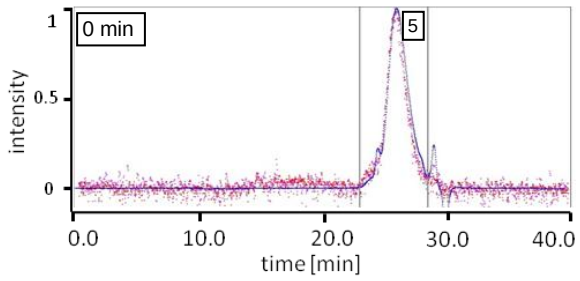


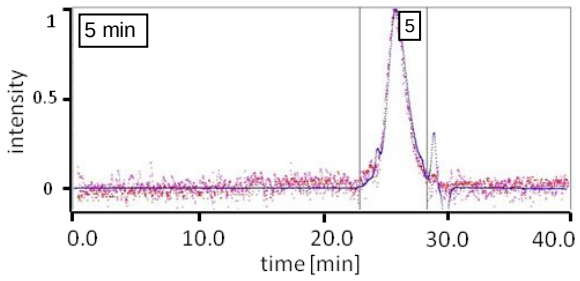
9.3.7 SEC data for 23P(6:1:0)_C

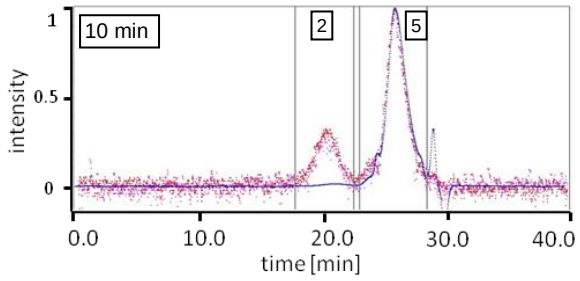
Table 46. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 23P(6:1:0)_C, depending on the reaction time.

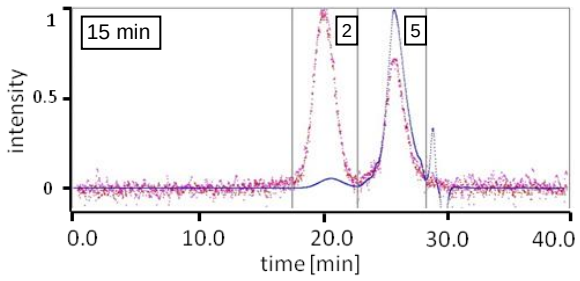
time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	---	---	---	---	1,143
5	---	---	---	---	1,126
10	---	28,080	---	---	1,126
15	---	27,940	---	---	1,099
20	---	27,300	---	---	1,078
30	---	24,550	---	---	1,022
40	---	22,620	---	---	1,106
50	---	22,300	---	---	1,104
60	---	22,140	---	---	1,196
70	---	23,260	---	---	1,445
80	---	22,970	---	---	1,491
90	---	23,720	---	---	1,169
120	---*	30,330	---	---	1,804
150	760,300	39,950	---	---	2,249
180	---*	52,650	---	---	2,189
210	1,705,000	63,550	---	---	3,319
240	1,134,000	72,750	---	---	2,326
270	---*	84,460	---	---	691**
300	---*	91,880	---	---	3,214

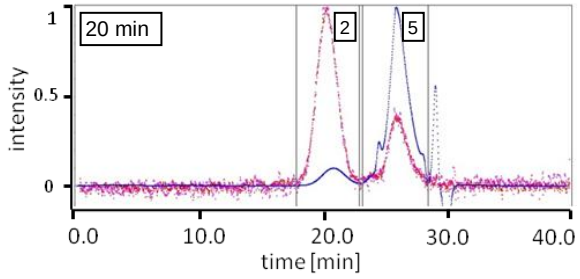
*M_w was not measurable by SEC measurement (insufficient amount)
**Deviating and non realistic values (measurement errors)

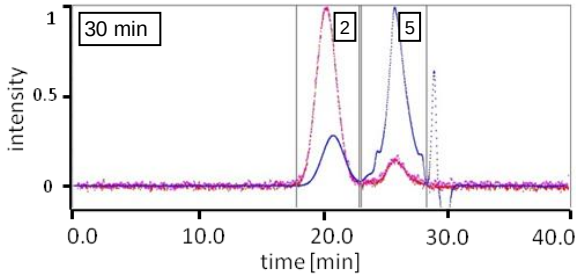

0 min
5
intensity
time [min]

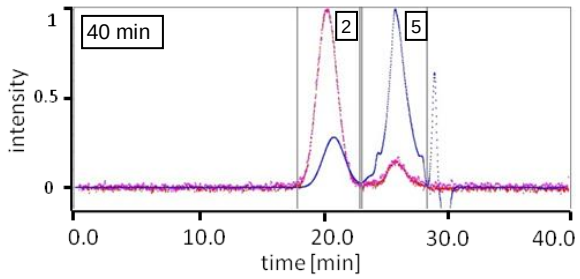

5 min
5
intensity
time [min]

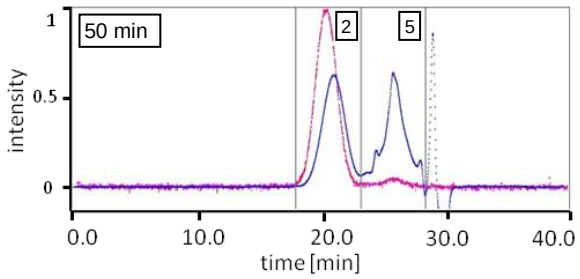

10 min
2
5
intensity
time [min]

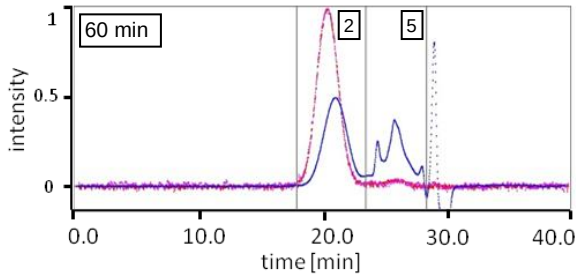

15 min
2
5
intensity
time [min]

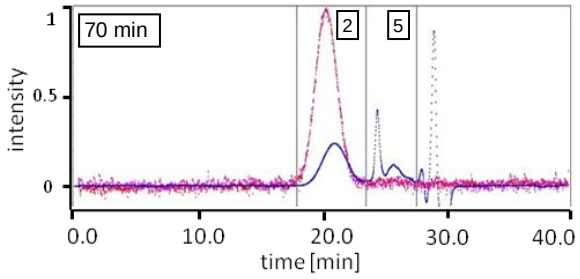

20 min
2
5
intensity
time [min]

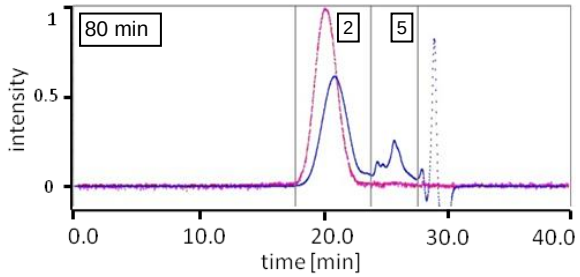

30 min
2
5
intensity
time [min]

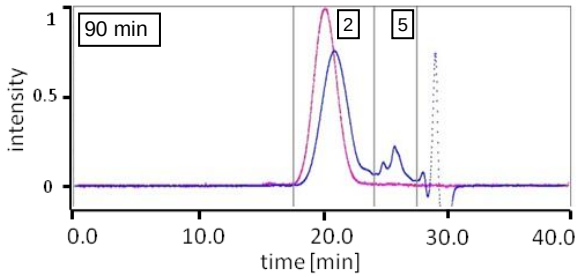

40 min
2
5
intensity
time [min]

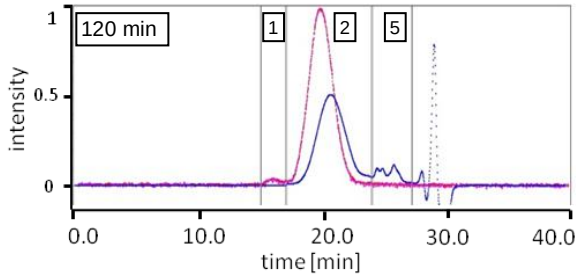

50 min
2
5
intensity
time [min]

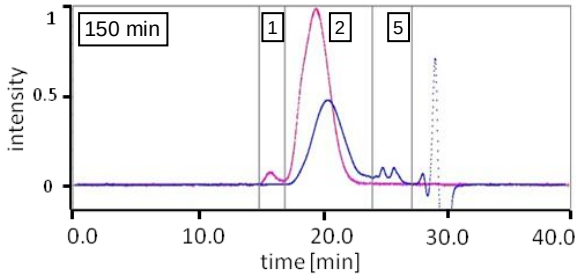

60 min
2
5
intensity
time [min]

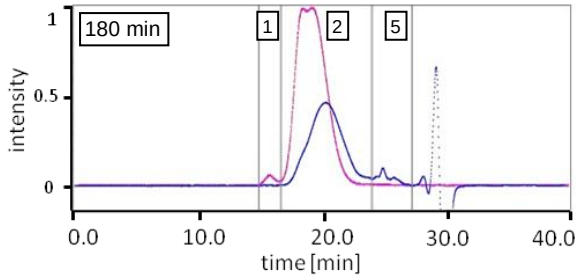

70 min
2
5
intensity
time [min]

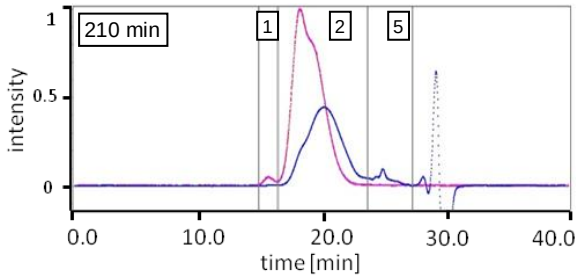

80 min
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]

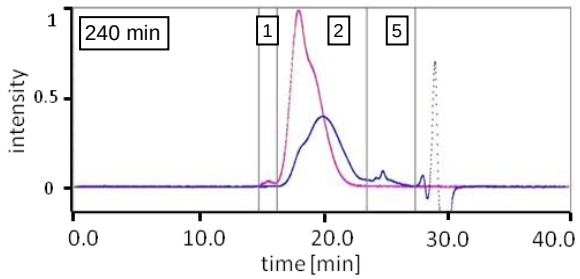

90 min
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]

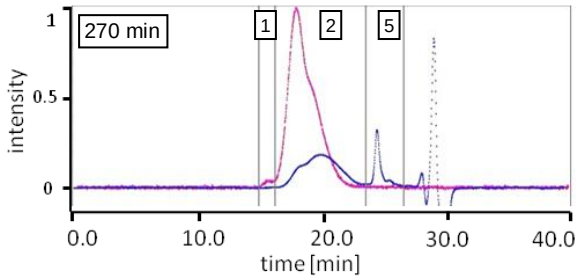

120 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]

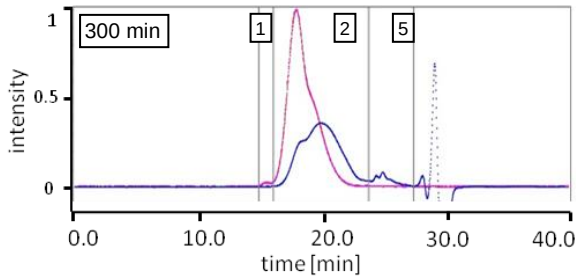

150 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


180 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


210 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


240 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


270 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]

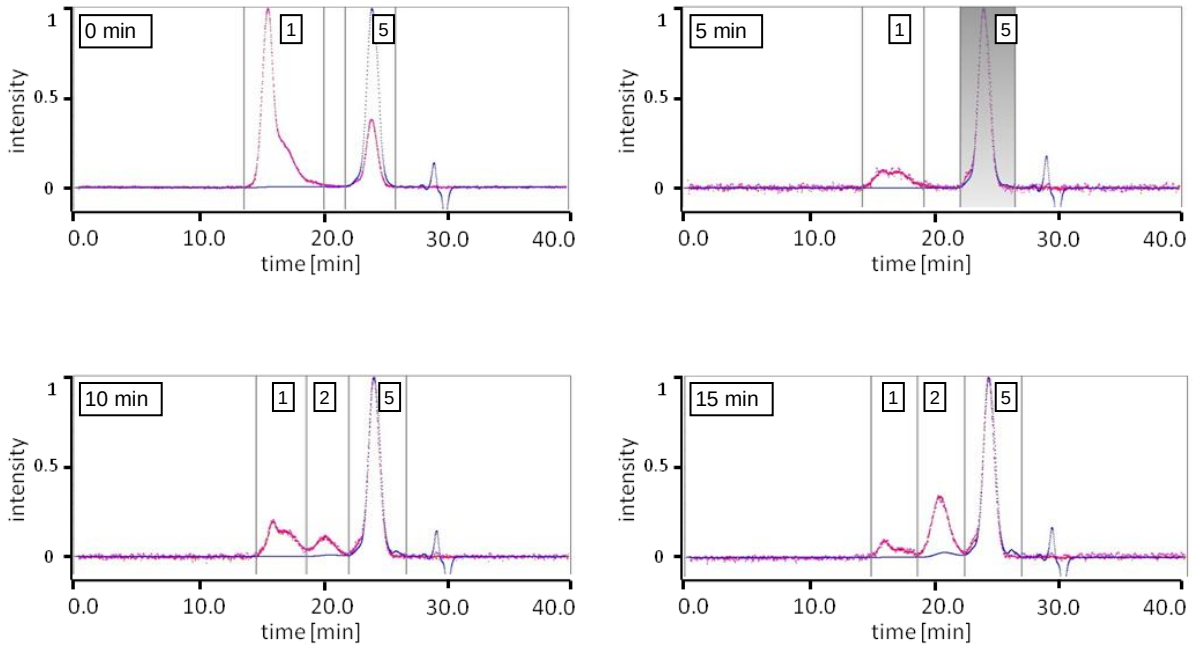

300 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]

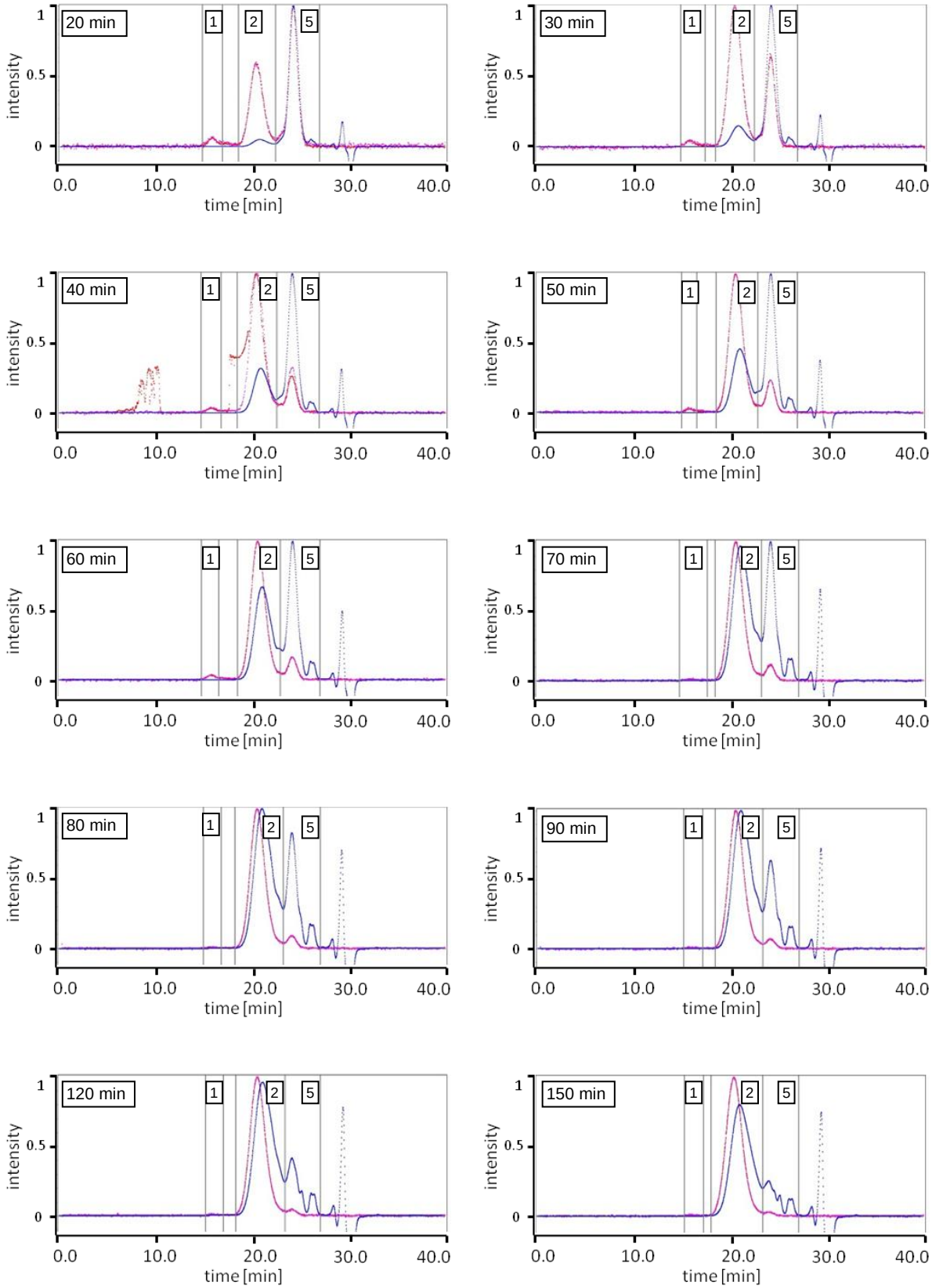
9.3.8 SEC data for 52P(6:1:0)_C

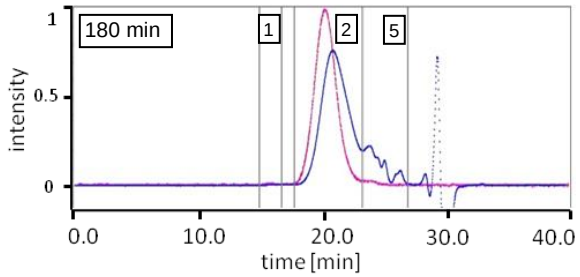
Table 47. Molecular weight M_w [g mol^{-1}] of the polymer fractions in 52P(6:1:0)_C, depending on the reaction time.

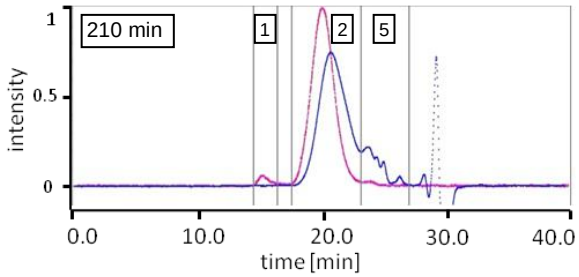
time [min]	peak 1	peak 2	peak 3	peak 4	peak 5
0	1,609,000	---	---	---	2,641
5	301,600	---	---	---	2,572
10	459,900	32,600	---	---	2,563
15	330,900	30,400	---	---	2,551
20	---*	28,480	---	---	2,553
30	304,500	25,630	---	---	2,594
40	---*	26,000	---	---	3,014
50	---*	22,330	---	---	2,736
60	---*	20,890	---	---	2,687
70	---*	20,340	---	---	2,592
80	---*	20,020	---	---	2,517
90	---*	20,280	---	---	2,531
120	---*	20,770	---	---	2,298
150	167,500	22,430	---	---	2,040
180	340,900	23,900	---	---	2,080
210	---*	26,190	---	---	2,167
270	---*	27,170	---	---	2,214
300	---*	27,450	---	---	2,041

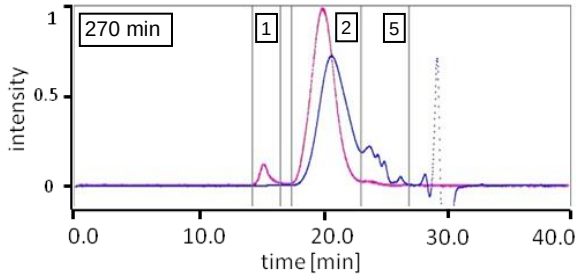
*M_w was not measurable by SEC measurement (insufficient amount)

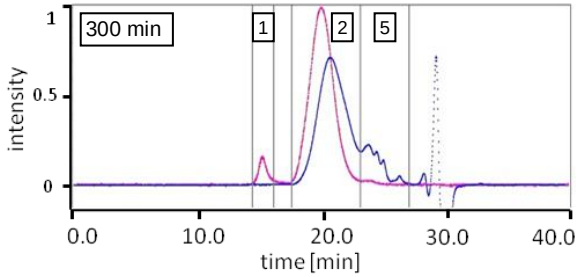



20 min
30 min
40 min
50 min
60 min
70 min
80 min
90 min
120 min
150 min
1
2
5
intensity
time [min]
0.0
10.0
20.0
30.0
40.0
0
0.5
1


180 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


210 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


270 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]


300 min
1
2
5
intensity
1
0.5
0
0.0
10.0
20.0
30.0
40.0
time [min]