

# Preparation of Polycarboxylate-based Superplasticizer and Its Effects on Zeta Potential and Rheological Property of Cement Paste

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**Abstract:** A series of polycarboxylate-based superplasticizers (PCs) with different structures were synthesized and the effects of chemical structure on zeta potential and rheological property of cement paste were studied. Residual monomers in each sample of PCs were quantitatively determined. The property of the polymers in cement was tested by micro-electrophoresis apparatus and R/S rheometer. Results showed that the zeta potential and its rheological properties are related with the side-chain length and density of PCs. The PCs having shorter side chain and lower side chain density exhibit higher anionic charge density, thus resulting in higher zeta potential. The effect of side chain density on zeta potential is more notable compared with that of side-chain length, and thus affecting the initial shear yield stress and apparent viscosity of the cement paste. In addition, although increasing the side chain length will result in reduction of the anionic charge density, the steric hindrance effect is obvious, which can effectively improve the dispersion of the cement particles, and reduce the viscosity and shear yield stress of slurry.

**Key words:** comb polymer; polycarboxylate-based superplasticizers; zeta potential; cement dispersant; rheological property

## 1 Introduction

Polycarboxylate-based superplasticizers (PCs) are commonly used as cement dispersants in the construction industry. These comb polymers can disperse cement particles effectively and avoid particle aggregation and hence improve the rheological properties of concrete. Generally, the dispersion of PCs is affected by their structural parameters such as charge density, side-chain length and composition of functional groups<sup>[1-3]</sup>.

The fundamental dispersion behavior of PCs has been investigated by many researchers. In 1978, the electrostatic repulsive force induced by superplasticizer

was confirmed by Daimon and Roy<sup>[4]</sup>. It has been shown that the addition of sulfonated naphthalene-formaldehyde (SNF) condensate increases the surface potential of cement particles, causing electrostatic repulsive force between cement particles. Based on this concept, Sakai and Daimon<sup>[5]</sup> studied the zeta potential of diluted suspensions of cement mixed with PCs and SNF respectively, it was found that the zeta potential of cement particle mixed with SNF was over about  $-20$  mV, while PCs was  $-0.3$  to  $-5$  mV, but slurry mixed with PCs showed better fluidity. In 1997, Yoshioka *et al.*<sup>[6]</sup> calculated the interparticle forces and proposed a steric hindrance mechanism generated by PCs side chains. In the same year, Uchikawa *et al.*<sup>[7]</sup> using atomic force microscopy and zeta potential measurement proved that the dispersion mechanism of PCs is given priority to steric hindrance force. Additionally, nearly ten years later, the surface chemistry behavior<sup>[8-10]</sup>, existence form<sup>[11,12]</sup>, and functions of functional group of PCs were also studied respectively<sup>[13,14]</sup>.

In order to further understand the constitutive relationship of PCs, ester based PCs were used as model compounds for studying. In this research, a

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**Table 1 Chemical composition and mineral composition of the silicate base cement/wt%**

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> Oeq	f-CaO	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
22.79	4.26	2.89	66.19	1.85	0.42	0.65	0.63	59.65	20.33	6.42	8.78

series of PCs with different molecular structures were synthesized and the effects of side chain length and density of PCs on the zeta potential and rheological properties of cement paste were investigated and the dispersion mechanism of PCs was discussed. This investigation generated should help develop relationships of structure-performances and will provide a foundation for choosing or designing the high efficient cement dispersants to achieve workable concrete.

## 2 Experimental

### 2.1 Preparation of PCs samples

Currently, the molecular structures of PCs can be divided into two main categories according to bond connection between main chain and side chain. One category is the ester based, the other is the ether based. In this work, the ester based PCs were adopted as the model compounds for studying. These comb polymers were synthesized by using radical polymerization techniques. The synthetic process was carried out in two steps. The first step involves the synthesis of the methoxy polyethylene glycol methacrylate macromonomer (MPEG-MAA), which was obtained by esterification of methacrylic acid (MAA) and  $\alpha$ -methoxy- $\omega$ -hydroxy- poly(ethylene glycol) (MPEG). For improving the conversion rate of esterification, P-toluene sulfonic acid (5% mass of MPEG and MAA) was used as a catalyst and hydroquinone (0.3% mass of MPEG and MAA) was used as an polymerization inhibitor, the esterification product was separated and purified by saturated NaCl-ethyl acetate system according to Ref.[15]. In the second step, copolymer was obtained by polymerizing of MAA and MPEG-MAA in aqueous solution. Ammonia persulfate (APS) and sodium methallylsulfonate (MAS) were used as the initiator and chain transfer agent respectively. Dosage of initiator was one-hundredth part of the mass quantity of monomers. The mixture was reacted at 85 °C under nitrogen atmosphere for 4 h.

Residual monomers in each sample of PCs were quantitatively determined by reversed-phase high performance liquid chromatography (RP-LC) using Agilent-1100 chromatography system (Agilent Co., USA) equipped with SinoChrom ODS-BP (C18) column (4.6×200 mm, 5  $\mu$ m) and UV detector

(wavelength was 205 nm), as previously reported by Lei<sup>[16]</sup>. The molecular weight were determined by Sepax Nanofilm SEC - 150 gel permeation chromatography (GPC) column produced by Sepax Technologies company, and the solution of 0.05 mol·L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub> was used as eluent, and the flow rate was 0.8 mL/min. Calibration was carried out with polyacrylic acid standards giving an optimum linear function. The molecular main chain with the average degree of polymerization (AMP) was calculated according to average molecular weight (Mn) and copolymer composition.

### 2.2 Zeta potential and rheological property of cement paste

Zeta potential was determined by micro-electrophoresis apparatus (JS94J, Shanghai Zhongchen Corp). 2.5 g of cement was added to the solution containing different concentrations of PCs with a liquid / solid ratio of 100. After mixing for 5 min, the mixture was separated by the centrifuge. Then the supernatant was added into electrophoresis pool and analyzed by zeta potential analyzer.

Shear stress values as well as apparent viscosity of cement paste were measured by using R/S SST2000 soft solid tester with a vane geometry spindle (Brookfield engineering laboratories, INC, USA). The cement pastes were prepared at 25 °C with a water to cement (*W/C*) ratio of 0.29. The PCs were added to the mixing water in different amounts. After mixing 5 min, the cement mixture was transferred into the container for measuring.

Cement for experiment was supplied by China United Cement Corporation, which met the requirements of GB8076 standard. The specific surface area of particle was 343 m<sup>2</sup>/kg, the size  $d_{50}$  was 19.82  $\mu$ m. The phase and chemical composition of the Portland cement used are given in Table 1.

## 3 Results and discussion

### 3.1 Structural features of PCs samples

#### 3.1.1 Molecular structure model

The molecular structure of the designed PCs in this study is presented in Fig.1. The molar ratio of each functional group and the amount of residual monomers are shown in Table 2 and Table 3 respectively.

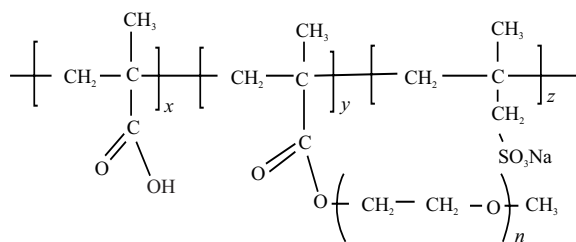


Fig.1 Molecular model of PCs with controlled density ( $x/y$ ) and length ( $n$ ) of the side chains

Side chain length refers to the number of ethylene oxide units per mole of MPEG. The MPEG is evaluated by the NMR spectroscopy for  $^1\text{H}$ . Side chain density of PCs refers to the molar ratios of MPEG-MAA to total molar amounts of MAA and MPEG-MAA. The proportion of starting materials and unreacted monomers were quantitatively determined by RP-LC as mentioned before. Based on the measurement the molar ratio of PEO side chain was calculated. As shown in Table 3, the conversion rate of total monomers are more than 98.5%, indicating that monomers are almost all take part in the polymerization. Due to the characteristics of free radical polymerization there was a good correlation between final compositions and expected one.

Residual monomers in each sample of PCs are shown in Table 3. Under the synthesis conditions, monomer conversion rate was measured  $\geq 98.5\%$  by Bromine addition-redox titration method. Under this condition, the raw material monomers have been

involved in the polymerization reaction. Further, the residual amounts of the three monomers were measured by high performance liquid chromatography respectively. MAA and (MPEG-MAA) monomer residues were found to be  $0.5 \times 10^{-3}$  mmol per gram of PCs or less. It should be noticed that MAS, it not only acted as the chain transfer agent, but also was found to participate in the polymerization reaction. Due to the fact that only very small amount of MAS was involved in the polymerization reaction, and along with the amount of residual monomer showing before, it is indicated that the composition of the polymer is consist with the design.

### 3.1.2 Anionic charge density of the PCs

Anionic charge density of PCs was calculated according to the literature<sup>[17]</sup>:

$$\frac{\text{Theoretical anionic charge density} = \mu\text{mol COO}^-}{\text{g/polymer}} = \frac{X}{M_{\text{MAA}} \cdot X + M_{(\text{MPEG-MAA})} \cdot Y}$$

where  $X$  is the molar amount of MAA,  $Y$  is the molar amount of the MPEG-MAA, the  $M_{\text{MAA}}$  and  $M_{\text{MPEG-MAA}}$  each represents the molar mass of MAA and  $M_{\text{PEG-MAA}}$ . The calculation results are shown in Table 2.

### 3.2 Effect of side chain length of PCs on zeta potential and its rheological property

The effects of different side chain length of PCs on the zeta potential and rheological property

Table 2 Molecular structural parameters of PCs

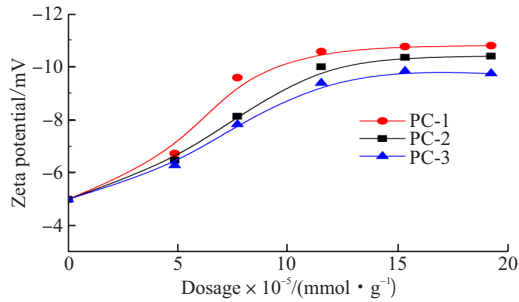
Pcs samples	$M_w$ of methoxy polyethylene glycol	Proportion of functional groups $x:y:z$	$M_n/\times 10^4$	$M_w/\times 10^5$	PDI	AMP	Charge density of anionic ( $\mu\text{eq/g}$ )
PC-1	700	3:1:0.2	9.49	8.61	9.07	37	2 923
PC-2	1 200	3:1:0.2	1.30	1.19	9.11	38	1 965
PC-3	2 200	3:1:0.2	3.03	2.41	7.95	48	1 187
PC-4	1 200	1.5:1:0.2	1.78	1.77	9.94	37	1 073
PC-5	1 200	4.5:1:0.2	1.17	0.90	7.69	39	2 719
PC-6	1 200	6:1:0.2	9.41	4.93	5.24	39	3 363

Note:  $M_n$  is the number average molecular weight;  $M_w$  is the weight average molecular weight; PDI =  $M_w/M_n$  (polydispersity index); AMP is the average degree of polymerization of the main chain

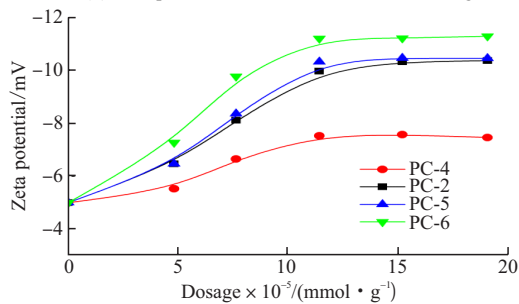
Table 3 Residual monomers in each sample of PCs

PCs samples	Total monomer $/\times 10^{-3} \text{ mmol}\cdot\text{g}^{-1}$ (Titration)	Total monomer conversion rate/%	Amount of residual monomer measured by Chromatogram $/\times 10^{-3} \text{ mmol}\cdot\text{g}^{-1}$			Total monomer $/\times 10^{-3} \text{ mmol}\cdot\text{g}^{-1}$ (Chromatography)
			MAA	(MPEG-MAA)	MAS	
PC-1	1.16	99.1	0.28	0.22	0.69	1.19
PC-2	1.15	98.7	0.29	0.16	0.73	1.18
PC-3	1.11	98.5	0.21	0.19	0.74	1.14
PC-4	1.19	98.8	0.16	0.24	0.81	1.21
PC-5	1.24	98.6	0.31	0.37	0.61	1.29
PC-6	0.80	98.8	0.15	0.07	0.60	0.82

of the cement paste are shown in Fig.3 (a) and Fig.4, respectively. Fig.3 (a) shows that, with increasing the dosage of PCs, the zeta potential of the cement particles increases obviously and then becomes stable, irrespective of the length of side chain. The minimum dosage of PCs is  $11.5 \times 10^{-5} \text{ mmol} \cdot \text{g}^{-1}$  as the zeta potential is close to flatten potential.

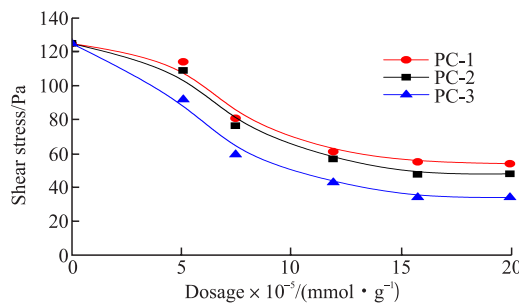


(a) Zeta potential of different side chain length

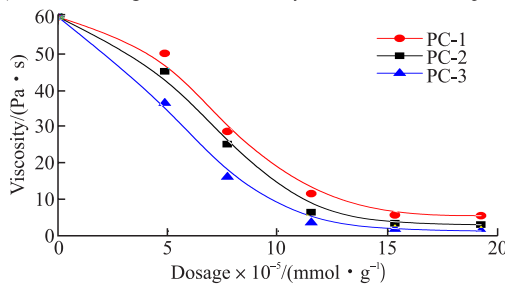


(b) Zeta potential of different side chain density

Fig.3 Effect of chemical structure of PCs on zeta potential of cement paste



(a) Side chain length of PCs on shear yield stress of cement paste



(b) Side chain length of PCs on viscosity of cement paste

Fig.4 Effect of side chain length of PCs on rheological property of cement paste at  $20 \text{ s}^{-1}$

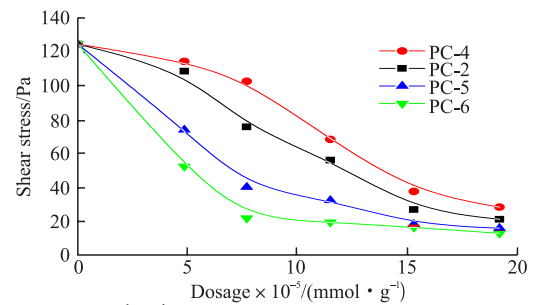
In addition, the shorter the side-chain of the PCs, the greater the amplitude of zeta potential will be. The order of increasing magnitude of zeta potential is  $\text{PC-3} > \text{PC-2} > \text{PC-1}$ . The stable zeta potential of cement

particles is  $-12.6 \text{ mV}$  after addition of PC-1, which is almost twice as much as the zeta potential without PCs. The anionic charge density of PCs with short side chain (Table 1) has great contribution to zeta potential and can increase its adsorption capacity. These results agree with the research of Ran *et al*<sup>[17]</sup>.

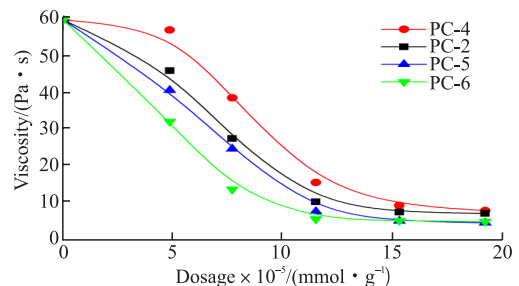
Influence of side chain length of PCs on rheological property of cement paste is shown in Figs.4(a) and (b). With increasing dosage of PCs, the shear yield stress and viscosity decrease rapidly first and then gradually tend to equilibrium. The minimum dosage of PCs is about  $15.3 \times 10^{-5} \text{ mmol} \cdot \text{g}^{-1}$ . The longer the side chain of PCs, the greater the magnitude of shearing stress and viscosity of the cement paste will reduce. The order of the reduced amplitude of the shear yield stress and viscosity is  $\text{PC-3} > \text{PC-2} > \text{PC-1}$ . This is opposite to the trend of changes of the zeta potential.

The above experimental results demonstrate that the dispersion ability of PCs depends mainly on the long side chain steric hindrance of the cement paste. The longer the side chain of PCs, the greater the steric hindrance effect is, and the more easily cement particles is dispersed in the slurry.

### 3.3 Effect of side chain density on the zeta potential and rheological property of cement paste



(a) Side chain density of PCs on shear yield stress of cement paste



(b) Side chain density of PCs on viscosity of cement paste

Fig.5 Effect of side chain density of PCs on rheological property of cement paste at  $20 \text{ s}^{-1}$

The Zeta potential and rheological properties of cement paste mixed with PCs having different side chain densities are shown in Fig.3(b) and Fig.5. It is



observed from Fig.3(b) that the zeta potential increases rapidly with increasing dosage of PCs and the order of zeta potentials magnitude is PC-4<PC-2<PC-5<PC-6. It is clear that the magnitude is much larger than that in Fig.3(a). This suggests that anionic charge density may play an important role in determining the zeta potential. The lower the side chain density of PCs, the higher the anionic charge density is. Therefore, the effect of side chain density on zeta potential is much more significant than side chain length.

Fig.5 shows that with increasing dosage of PCs, the shear yield stress and viscosity decrease rapidly first and then become leveled off. The two curves of PC-5 and PC-6 with lower side chain density show the same trend corresponding to the shear yield stress and viscosity of cement paste. The slope of the two curves is sharp below  $7.5 \times 10^{-5} \text{ mmol} \cdot \text{g}^{-1}$ , and then reaches the saturation point at higher dosages ( $>7.5 \times 10^{-5} \text{ mmol} \cdot \text{g}^{-1}$ ). While the two curves of PC-4 and PC-2 with higher side-chain density show different trends, which fall slowly at first and then rapidly decrease and finally become leveled off. The declined extent of shear yield stress and paste viscosity is PC-4<PC-2<PC-5<PC-6, but they tend to be similar in the end. The results indicate that PCs with lower side chain density exhibit higher anionic charge density and show higher initial dispersion ability at low dosage.

## 4 Conclusions

The zeta potential and its rheological properties of cement paste have an important relationship with the side chain length and side chain density of PCs. It was found that PCs with shorter side chain and lower side chain density exhibit higher anionic charge density, thus resulting in higher zeta potential. In addition, the effects of side chain density are more notable on zeta potential compared with side chain length, thus affecting the initial shear yield stress and apparent viscosity of the slurry; Although increasing the side chain length will result in reducing the anionic charge density, the steric hindrance force is more obvious, which can effectively improve the dispersion of the cement particles, and reduce the viscosity and shear yield stress of slurry.

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