Research on synthesis and properties of early strength polycarboxylate superplasticizers with different lengths of side chain

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Abstract. A series of early-strength polycarboxylate superplasticizers with different lengths of side chain were synthesized by methyl allyl polyoxyethylene ether (HPEG) as macromonomers with different molecular weights. The structural parameters of polycarboxylate superplasticizers were calculated by gel permeation chromatography method. The performance of the synthesized samples were characterized by hydration heat, X-ray powder diffraction and concrete test. The results show that the longer the side chain be, the better the early strength effect be, when the side chain length is greater than 67.64, the early strength of the synthesized polycarboxylate superplasticizers are better than that of a foreign multinational enterprise.

1. Introduction
The properties of polycarboxylate superplasticizer are closely related to its molecular structure. Polycarboxylate superplasticizer with different functions can be prepared by designing the molecular structure, meeting the actual needs of national construction engineering. At present, many scholars have studied the molecular structure of polycarboxylate superplasticizer from different levels and angles [1-5]. The molecular structure parameters of polycarboxylate superplasticizer mainly include the following aspects: main chain length, side chain length, side chain density, main chain charge density, molecular weight, etc.. The length of side chain is an important structural parameter of the polycarboxylate superplasticizer, and the length of side chain has a great influence on the properties of polycarboxylate superplasticizer, especially the early-strength performance.

In this study, in order to study the effect of different side chain lengths on the early-strength properties of polycarboxylate superplasticizers, a group of early-strength polycarboxylate superplasticizers with different side chain lengths, similar main chain polymerization degrees and the same side chain density were prepared. The performance of polycarboxylate superplasticizers were studied through a series of characterization methods.

2. Experimental

2.1. Materials

2.1.1. The main synthetic experimental raw materials. Methyl allyl polyoxyethylene ether with different molecular weight (HPEG, industrial grade), acrylic acid (AA, industrial grade), hydrogen peroxide (H_{2}O_{2}, industrial grade), vitamin C (Vc, industrial grade), thioglycolic acid (TGA, industrial grade), sodium hydroxide solution(30% aqueous solution, industrial grade).
2.1.2. **Main performance test raw materials for experiment.** Cement (C, Minfu brand, P.O 52.5R); Sand(S, river sand with fineness modulus of 2.6-2.9 and mud content less than 1%); Gravel(G1, grain size of 10-20mm ; G2, grain size of 16mm-31.5mm); Fly ash(F, Level II), Slag powder (K, S95);

2.2. **Copolymerization**
Add measured deionized water and methyl allyl polyoxyethylene ether with different molecular weight into a four-necked flask which equipped with a thermometer, a teflon stirring slurry, and a peristaltic pump. When the macromonomer is completely dissolved, add hydrogen peroxide and part of acrylic acid in one time, and after a few minutes, the aqueous solution of vitamin C (solution A), the remaining aqueous solution of acrylic acid (solution B) and the aqueous solution of thioglycolic acid (solution C) were respectively dropped in the flask for 3 and 4 hours. After the addition of the solutions A, B and C, continue stirring for 1 h, and then the 30 wt% of sodium hydroxide (NaOH) was used to set the pH to 6.0-7.0. Finally, A series of early-strength polycarboxylate superplasticizers with different lengths of side chain were obtained

2.3. **Performance test method**

2.3.1. **GPC analysis.** Molecular weight was performed by gel permeation chromatography (GPC) using Ultrahydrogel Liner Column and Ultrahydrogel 120 Column made by Waters. The elution solvent used was 0.1 M of NaNO₃ aqueous solution.

2.3.2. **X-Ray diffraction.** The cement paste mixed with polycarboxylate superplasticizer were cured to the required age, and then crushed, some internal small pieces were taken, and the hydration of the samples was terminated by soaking with absolute ethanol, and then dried at 55°C in vacuum. After drying, the samples were milled to go through a 200 mesh sieve, and X-ray diffractometer (XD-R1, Shimadzu, Japan) was carried out to analysis the samples.

2.3.3. **Hydration heat determination.** The hydration heat determination of cement slurry mixed with polycarboxylate superplasticizer is conducted in accordance with GB/T 12959-2008 " Determination Method for Cement Hydration Heat ".

2.3.4. **Concrete test.** The concrete test is conducted in accordance with GB/T50080-2016 "Standard Test Methods for Performance of Common Concrete Mixtures" and GB/T 50081-2002 “Standard Test Methods for mechanical properties of Common Concrete”. The concrete mix ratio is shown in table 1:

| Sample  | Mn  | Mw   | Mp   | Mw/Mn | Conversion rate /% |
|---------|-----|------|------|-------|--------------------|
| HPEG-1  | 723 | 2402 | 2534 | 3.32  | 100                |
| HPEG -2 | 1115| 3048 | 3627 | 2.73  | 100                |

2.3.5. **Setting time measurement.** The setting time of concrete is conducted in accordance with GB 8076-2008 "Concrete admixture".

3. **Experimental results and discussion**

3.1. **Macromonomer selection**
In this study, four HPEG macromonomers with different molecular weight were selected for synthesis research. By GPC analysis, molecular weight information of macromonomers could be obtained.
The GPC test of macromonomers was carried out. As shown in Table 2, the weight-average molecular weights (Mw) of the selected HPEG-1, HPEG-2, HPEG-3 and HPEG-4 were 2402, 3048, 4632 and 6086, respectively, and the conversion rate of all macromonomers was 100%.

### 3.2. Synthesis of polycarboxylate superplasticizers

In the experiment, the fixed acid ether ratio n (COO⁻): n (PEG) was 4.28, the amount of initiator was unchanged, and a series of polycarboxylate superplasticizers with the same side chain density, similar main chain polymerization degree and different side chain length were synthesized by adjusting the dosage of thioglycolic acid and using HPEG-1, HPEG-2, HPEG-3 and HPEG-4 as macromonomers, respectively. The corresponding synthetic samples numbers for PCS-1, PCS-2, PCS-3 and PCS-4.

| Sample | Macromonomer | Mn | Mw | Mp | Mw/Mn | Conversion rate (%) |
|--------|--------------|----|----|----|--------|---------------------|
| PCS-1  | HPEG-2402    | 27951 | 42547 | 38744 | 1.52  | 90.80               |
| PCS-2  | HPEG-3048    | 30249 | 51566 | 44598 | 1.70  | 88.59               |
| PCS-3  | HPEG-4632    | 43986 | 77352 | 49901 | 1.76  | 87.04               |
| PCS-4  | HPEG-6086    | 47273 | 100541 | 63551 | 2.13  | 85.70               |

GPC test was performed on the synthesized samples. As shown in Table 3, as the molecular weight of the macromonomer HPEG was increased, the molecular weight of the synthetic polycarboxylate superplasticizer was also increased. Among them, the average weight molecular weight (Mw) of HPEG-1 was 2402, the weight-average molecular weight of the synthesized polycarboxylate superplasticizer PCS-1 was 42547, and the average weight molecular weight of HPEG-4 was 6086, the weight-average molecular weight of the synthesized polycarboxylate superplasticizer PCS-4 was as high as 100541. And with the increase of molecular weight of macromonomer HPEG, the conversion rate of polycarboxylate superplasticizer also decreased.

### 3.3. Structural parameter calculation

The synthetic acid-ether ratio of the polymer is known, and the degree of polymerization of the main chain can be calculated from the weight-average molecular weight of the polymer and the theoretical molecular weight of the structural unit. For example, PCS-1 sample, Mw is 42547, acid-ether ratio n (COO⁻): n (HPEG) is 4.28, namely each structural unit contains 1 HPEG molecule and 4.28 acrylic molecules, and the theoretical molecular weight of the structural unit is 6394. Then, the degree of polymerization can be calculated to be 15.70 by the formula (1).

\[
\text{Main chain polymerization} = \frac{\text{Mw}}{\text{M}} = 15.70
\]

Where,
Mw: The weight-average molecular weight of PCS;  
M: The theoretical molecular weight of the structural unit.

The side chain density of PCS can be calculated according to formula (2):

\[
\text{Side chain density} = \frac{n[\text{HPEG}]}{n[\text{AA}]+n[\text{HPEG}]} \times 100\%
\]

Where,
\(n[\text{HPEG}]\): The amount of substance of HPEG;  
\(n[\text{AA}]\): The amount of substance of acrylic acid.

In this study, the side chain length of PCS was defined according to the degree of polymerization of HPEG macromonomer, and was calculated according to formula (3):

\[
\text{Side chain length} = \frac{\text{Mw}[\text{HPEG}\text{-72}]}{44}
\]
Table 4. Molecular structure parameters of synthetic polycarboxylate superplasticizers

| Sample | Structural unit theoretical molecular weight | Side chain density /% | Main chain polymerization | Side chain length |
|--------|---------------------------------------------|-----------------------|---------------------------|------------------|
| PCS-1  | 2710                                        | 19                    | 15.70                     | 52.95            |
| PCS-2  | 3356                                        | 19                    | 15.36                     | 67.64            |
| PCS-3  | 4940                                        | 19                    | 15.66                     | 103.64           |
| PCS-4  | 6394                                        | 19                    | 15.72                     | 136.68           |

table 4 shows the calculated molecular structure parameters of synthetic polycarboxylate superplasticizers. As can be seen from table 3, under the condition that the acid-ether ratio is fixed unchanged, polycarboxylate superplasticizers with the same side chain density, similar main chain polymerization degree and different side chain length can be obtained by adjusting the dosage of thioglycolic acid.

3.4. Effect of hydration heat test

The hydration and exothermic properties of polycarboxylate superplasticizers PCS-1~PCS-4 with different side chain lengths was tested. The hydration heat test results of cement mixed with different polycarboxylate superplasticizers are shown in figure 1, and the dosage is 0.1%.

![Figure 1. Hydration heat release curve](image)

It can be seen from figure 1 that as the length of the side chain increases, the accelerated reaction period of the cement hydration is advanced, and the height of the main exothermic peak rises. Among them, PCS-4 has the highest main exothermic peak, and the highest temperature peak time T is 13.2 hours, which is the shortest time. Therefore, when the length of the side chain is 136.68, the polycarboxylate superplasticizer has a better effect of early strength.

3.5. Effect of XRD test

In order to further investigate the effect of side chain length on the early strength of polycarboxylate superplasticizer, crystal analysis and semi-quantitative analysis were carried out on the cement stone which mixed with PCS-1 (Mw[HPEG]=2402), PCS-4 (Mw[HPEG]=6086) and a blank samples by XRD test, and then, the early hydration of cement paste which mixed with polycarboxylate superplasticizers with different side chain lengths were studied. The results of XRD analysis of cement slurry after hydration for 3 days are shown in figure 2.
Figure 2. XRD spectrum of cement slurry after hydration for 3 days

It can be seen from figure 2 that, compared with the blank cement sample un-mixed with polycarboxylate superplasticizer, the strength of Ca(OH)$_2$, C$_3$S, C$_2$S and CaCO$_3$ diffraction peaks of the cement samples mixed with polycarboxylate superplasticizers with different side chain length all changed, indicating that the polycarboxylate superplasticizer affected the generation of early hydration products of cement. With the increase of the length of the side chain, the diffraction peak strength of Ca(OH)$_2$ increases, while the diffraction peak strength of C$_3$S and C$_2$S decreases slightly, indicating that the polycarboxylate superplasticizer with longer side chain length promotes the early hydration of C$_3$S and C$_2$S, and produces more hydration products C-S-H. Therefore, the longer the side chain, the better the early strength effect of the synthesized polycarboxylate superplasticizer.

### 3.6. Effect of concrete test

At room temperature, the concrete comparison experiment of synthetic samples (PCS-1～PCS-4) and a foreign multinational enterprise early strength polycarboxylate superplasticizer (PCS-0) were carried out. The concrete mix ratio is shown in table 1. The slump of concrete is 70±20mm by adjusting the dosage of polycarboxylate superplasticizer, and the concrete setting time and early compressive strength are investigated. The test results are shown in table 5:

| Sample | Side chain length | Concrete slump /mm | Initial setting time /min | Compressive strength /MPa |
|--------|-------------------|---------------------|---------------------------|--------------------------|
|        |                   |                     |                           | 1d      | 3d      | 7d      |
| PCS-0  | -                 | 70                  | 275                       | 28.7    | 43.9    | 55.6    |
| PCS-1  | 52.95             | 70                  | 285                       | 28.0    | 43.6    | 54.8    |
| PCS-2  | 67.64             | 75                  | 270                       | 28.6    | 44.0    | 55.5    |
| PCS-3  | 103.64            | 80                  | 265                       | 28.9    | 45.3    | 56.2    |
| PCS-4  | 136.68            | 70                  | 260                       | 29.7    | 46.1    | 57.8    |

It can be seen from table 5 that the initial setting time of concrete mixed with polycarboxylate superplasticizer decreases with the increase of the side chain length of polycarboxylate superplasticizer, and the early compressive strength increases with the increase of the side chain length, indicating that within a certain range, the increase of the length of the side chain is helpful to accelerate the early hydration rate of cement dispersion system, accelerate the formation of C-S-H gel and ettringite crystal, and improve the early strength of cement concrete. When the length of the side
chain is 136.68, the initial setting time of concrete is the shortest and the early strength value is the highest. Compared with PCS-0, when the side chain length is greater than 67.64, the initial setting time of concrete is shorter, the early compressive strength value is higher, and the early strength performance is better than PCS-0.

4. Conclusions

(1) In this study, four HPEG macromonomers of different molecular weight were selected for synthesis research, and a series of early-strong polycarboxylate superplasticizers with different side chain lengths were synthesized by adjusting the amount of thioglycolic acid.

(2) The structural parameters of the synthetic polycarboxylate superplasticizers were calculated with GPC data. The calculated results showed that, with the acid-ether ratio unchanged, polycarboxylate superplasticizers with the same side chain density, similar main chain polymerization degree and different side chain length can be obtained by adjusting the dosage of thioglycolic acid.

(3) The hydration heat test results show that with the increase of the length of the side chain, the accelerated reaction period of cement hydration is advanced, and the height of the main exothermic peak rises.

(4) The results of XRD analysis of cement slurry after hydration for 3 days show that the polycarboxylate superplasticizer with longer side chain length promotes the early hydration of C₃S and C₂S, and produces more hydration products C-S-H.

(5) The concrete test results show that within a certain range, as the length of the side chain increases, the initial setting time of the concrete decreases, and the early compressive strength increases. When the side chain length is greater than 67.64, the early strength of the synthesized polycarboxylate superplasticizer is better than that of a multinational enterprise.

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