# Study on the influence of polycarboxylate superplasticizer molecular weight on microstructure and application performance

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**Abstract.** Polycarboxylic acid samples were prepared using methyl allyl alcohol polyoxyethylene ether (TPEG) and acrylic acid (AA) as raw materials using an redox initiator system (ammonium persulfate sodium hypophosphate). Explored the influence of polycarboxylic acid molecular weight on microstructure and application performance. The experimental results show that as the reaction progresses, the acid ether ratio gradually increases. When the reaction time is 180 minutes, the carboxyl density is the highest. As the amount of chain transfer increases, the Mark Houwink constant a of polycarboxylate water reducer gradually increases, and its structure gradually shifts from random curling to rigid structure. At the same amount of fixed content, as the molecular weight of polycarboxylic acid decreases, the fluidity of the cement paste gradually increases, and the yield stress gradually decreases. There is a certain difference in adsorption on the surface of cement particles, but the difference is not significant.

**Keywords:** Polycarboxylic acid, molecular weight, microstructure, application performance

## 1 Introduction

Polycarboxylic acid water reducer is a polymer material that relies on steric hindrance and electrostatic repulsion to disperse particles. The differences in molecular structure lead to differences in its dispersibility and dispersion retention [1-3].

In the production process, the molecular weight and structure are adjusted by controlling the amount of chain transfer agent, reaction time, etc., in order to achieve the goal of reducing water and maintaining slump [4-5]. There are many researchers both domestically and internationally conducting research in this area, but their research focuses mainly on the effects of factors such as monomer types and reaction conditions on macroscopic properties such as slurry fluidity and concrete properties [6-8]. Some scholars have also conducted research on adsorption, hydration, and other aspects [9-10].

This article explores the effects of reaction time and chain transfer agent dosage on the structure of polycarboxylic acid water reducing agents from a microscopic

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perspective, in order to establish a connection with macroscopic performance and provide guidance and reference value for the production and application of polycarboxylic acid.

# 2 Experimental part

## 2.1 Raw materials and reagents

Methyl allyl alcohol polyoxyethylene ether (TPEG, molecular weight 2400), acrylic acid (AA), ammonium persulfate, 32% NaOH, and sodium hypophosphate are all commercially available industrial grade. Red Lion Cement P.O42.5 (R), water is tap water. As shown in Fig.1.

**Fig. 1.** TPEG(left) and cement(right)

Automatic dripping device; Electronic balance; Infrared spectrometer(IR); Gel permeation chromatography(GPC); Rheometer; Clean slurry mixer; total organic carbon(TOC). As shown in Fig.2.


**Fig. 2.** IR(left) and GPC (right)

## 2.2 Synthesis process

Add 332 g of TPEG and 41.5 g of water to four necked flask, stir the water bath to raise the temperature to 63°C, and add 2.78 g of sodium hypophosphate one-time. At the same time, start dripping liquid A (a mixture of 1.1 g of ammonium persulfate and 20 g of water) and liquid B (a mixture of 22.24 g of AA and 12.5 g of water). The dripping time for liquid A and liquid B is 210 minutes and 180 minutes, respectively. After the dripping is completed, the reaction is held for 1 hour, and 12.2 g of 32% NaOH solution and 11 g of water are uniformly added within 10 minutes.

### 2.3 Testing and Characterization

**Determination of net slurry fluidity.**

According to the method for determining the fluidity of cement paste in GB/T8077-2012 the fixed cement dosage is 300g, and the water cement ratio is 0.29.

**IR determination.**

Take a trace amount of synthesized polycarboxylic acid, add ethanol for precipitation and filtration, dry it with an infrared lamp, grind it together with potassium bromide to form a thin plate, and use an infrared spectrometer for determination and analysis.

**GPC determination.**

Weigh 0.5 g of sample, dissolve it in 10 mL of prepared mobile phase, and then fix the volume in a 50 mL volumetric flask. Test with GPC. The flow rate is set to 1.0 mL/min.

**Determination of TOC adsorption capacity.**

The remaining TOC content in the solution after adsorption of cement slurry is tested, and the difference between the two is compared to characterize the adsorption amount of water reducing agent in cement slurry.

**Determination of rheological properties of slurry.**

The initial fluidity of the fixed slurry is 200 ± 5 mm, and the rheological performance of the slurry is tested using an Anton paar RheolabQC rotary rheometer.

## 3 Results and Discussion

### 3.1 Changes in acid ether ratio at different reaction times

Starting from liquid A and liquid B, the timing of the dripping process is constant. The changes in the acid ether ratio were observed at reaction times of 30 minutes, 60 minutes, 120 minutes, 180 minutes, and 240 minutes, as shown in Figure 1.

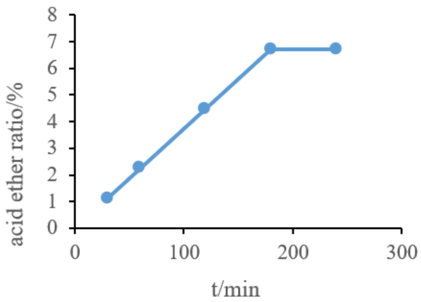


**Fig. 3.** Changes in acid ether ratio at different times

As shown in Fig.3, as the reaction progresses, the acid to ether ratio gradually increases. By 180 minutes, all the acid has been added, and the acid to ether ratio no longer changes. However, at this point, the B liquid has not been added completely, and the synthesis reaction will continue.

### 3.2 The effect of different molecular weights on functional groups

Fix other synthesis conditions, change the amount of chain transfer agent, and synthesize four samples from small to large, PCE-1, PCE-2, PCE-3, and PCE-4. Perform infrared spectroscopy tests on four samples, with a carbonyl peak of approximately 1722 $cm^{-1}$ as the test peak. Calculate the peak area ratio of carbonyl peak area to total integrated area by integrating the peak area and total integrated area of carbonyl, as shown in Figure 2.

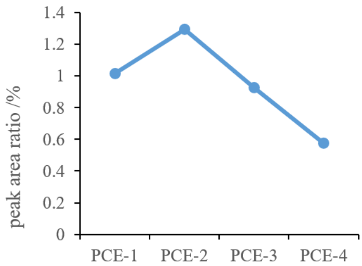


**Fig. 4.** Trend chart of peak arearatio with different molecular weights

From Fig.4, it can be seen that the proportion of peak area in PCE-2 testing is the largest, and then the proportion of peak area gradually decreases, indicating that the amount of chain transfer agent has a certain impact on the proportion of peak area to peak area in testing. When the amount of chain transfer agent is constant, the proportion of peak area in PCE-2 testing is the largest, and the structure contains the largest proportion of carbonyl groups at this time.

### 3.3 The Effect of Polycarboxylic Acid Molecular Weight on Microstructure

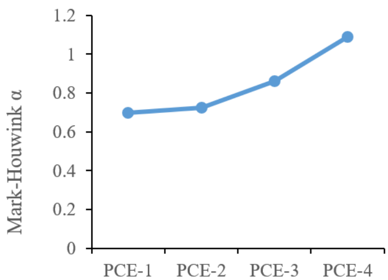


**Fig. 5.** Effect of different molecular weights on Mark Houwink α

Fig.5 shows the effect different molecular weights on the Mark Houwink constant α. When α<0.5, it is a spherical structure, when 0.5<α<0.8, it is a random curl, and when α>0.8, it is a rigid structure. As shown in Figure3, with the increase of the amount of chain transfer agent, the structure of polycarboxylic acid gradually shifts from random curling to rigid structure. This is because the longer the molecular chain, the more likely the conformation is, and the stronger the flexibility. Under the same process conditions, the larger the molecular weight of polycarboxylic acid, the higher its flexibility, and the lower its rigidity.

## 3.4 The effect of polycarboxylic acid molecular weight on the performance of clean pulp

At a fixed water cement ratio of W/C=0.29, the net slurry performance of different samples was investigated under the same amount of additives. The results are shown in Table 1.

**Table 1.** Comparison of Slurry Properties of Samples with Different Molecular Weights

| sample | Initial fluidity/mm |
|---|---|
| PCE-1 | 191 |
| PCE-2 | 197 |
| PCE-3 | 200 |
| PCE-4 | 180 |

From Table 1, it can be seen that under the same amount of fixed content, the initial fluidity of PCE-3 slurry is the highest, and it can better adsorb on the surface of cement particles. The initial dispersion performance is good, with a lower molecular weight, higher side chain density, and higher spatial hindrance, which is conducive to its better dispersion.

## 3.5 The effect of polycarboxylic acid molecular weight on rheological properties

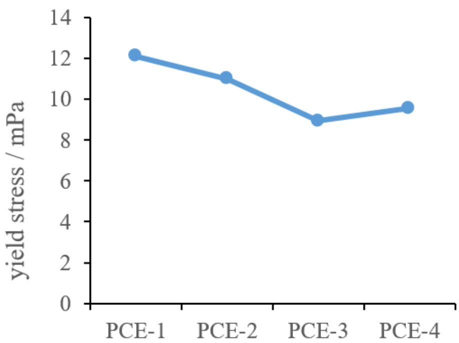


**Fig. 6.** Effect of different molecular weights on yield stress

As shown in Fig.6, with the increase of molecular weight, the yield stress increases. After the hydrophobic main chain of polycarboxylate water reducing agent is adsorbed on the surface of cement particles, the hydrophilic structures such as hydroxyl groups and ethers of the branched chains associate with water molecules through hydrogen bonds, forming a stable water film on the surface of cement particles. This water film has good lubrication effect and can effectively reduce the resistance between cement particles, making it easy for cement particles to slide and reducing the yield stress.

### 3.6 The effect of polycarboxylic acid molecular weight on adsorption capacity

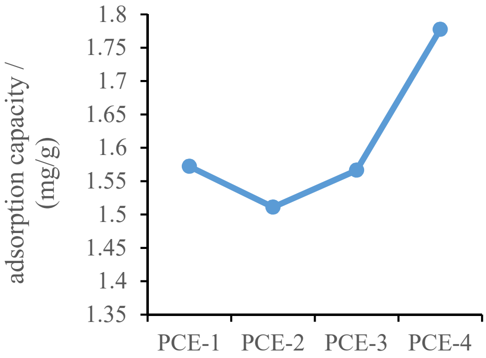


**Fig. 7.** Effect of different molecular weights on adsorption capacity

From Fig.7, it can be seen that there are certain differences in the adsorption o with different molecular weights on the surface of cement particles, but the difference is not significant. The adsorption amounts of PCE-2 and PCE-3 are relatively small, while PCE-4 has the largest adsorption amount. This is because the carboxyl content in PCE-2 and PCE-3 is relatively high, but their molecular weight is relatively small, making a small contribution to the adsorption capacity. Therefore, their adsorption capacity is smaller. PCE-4 with smaller molecular weight has smaller steric hindrance, which can better adsorb the water reducing agent on the surface of cement particles, resulting in the largest adsorption capacity.

## 4 Conclusion

The conclusions drawn from the above research are as follows:

(1) As the reaction progresses, its acid ether ratio gradually increases and the density of carboxyl groups gradually increases. When the reaction time is 180 minutes, its acid ether ratio is the highest and the density of carboxyl groups is the highest.

(2) As the amount of chain transfer increases, its α gradually increases, and the molecular structure of polycarboxylates gradually shifts from random curls to rigid structures.

(3) At the same amount of fixed content, as the molecular weight decreases, the fluidity of the slurry gradually increases, and its yield stress gradually decreases. The adsorption change on the surface of cement particles is not significant.

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